217e Diffusioosmosis of an Electrolyte Solution along a Plane Wall

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1. Introduction

Diffusioosmosis of an electrolyte solution is the electrokinetic flow involving a tangential concentration gradient of the electrolyte that interacts with a charged wall. Electrolyte solutions with a concentration gradient of order 1 M/cm along solid surfaces with a zeta 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 a velocity of order µm/s. The fluid motion caused by diffusioosmosis was analytically examined for the flow near a plane wall [1-6]. In these studies, however, the effect of lateral distributions of the counterions and co-ions on the local electric field induced by the imposed electrolyte concentration gradient in the tangential direction inside the electric double layer or the effect of the ionic convection on it caused by the diffusioosmotic flow was neglected.

In this work we present a comprehensive analysis of the diffusioosmosis of an electrolyte solution with a constant prescribed concentration gradient along a charged plane wall. No assumption is made concerning the magnitude of the electric potential or the thickness of the double layer, and both the lateral distribution of the induced tangential electric field and the effect of the electrolyte convection on it are allowed. Semi-analytical results for the fluid velocity profile and the bulk-phase diffusioosmotic velocity are obtained for various cases.

2. Analysis

We consider the diffusioosmotic flow of an infinitely thick solution of a symmetric electrolyte of valence *Z* tangential to a uniformly charged plane wall at the steady state. The applied electrolyte concentration gradient [illegible] is a constant along the tangential (*z*) direction, where [illegible] is the linear concentration (number density) distribution of the electrolyte in the bulk solution phase far from the wall (with [illegible]). It is assumed that [illegible] is only slightly nonuniform such that the variation of the electrostatic potential and ionic concentrations in the double layer adjacent to the wall with the tangential position can be neglected in comparison with their corresponding quantities at [illegible] (the midpoint along the plane wall).

The electrostatic potential distribution in the electrolyte solution near the charged plane wall, [illegible], is the well-known Gouy-Chapman result [1],

$$\bar{\psi}=2\ln\frac{1+\gamma\exp(-\kappa x)}{1-\gamma\exp(-\kappa x)}, \qquad (1)$$

where [illegible], [illegible], [illegible], [illegible] is the zeta potential of the wall, and [illegible], where [illegible] is the relative permittivity of the electrolyte solution and [illegible] is the permittivity of a vacuum.

The local concentrations [illegible] and [illegible] of the cations and anions, respectively, in the fluid undergoing diffusioosmosis along the plane wall are not uniform in both tangential [illegible] and normal [illegible] directions, and their gradients in the tangential direction can give rise to a "diffusion current" distribution. To prevent a continuous separation of the counterions and co-ions, an electric field distribution along the tangential direction arises spontaneously in the electrolyte solution to produce another electric current distribution which exactly balances the diffusion current. This induced electric field generates an electroosmotic flow of the fluid parallel to the plane wall, in addition to the chemiosmotic flow caused by the electrolyte gradient directly. Both the chemiosmotic and the electroosmotic flows also generate an electric current distribution by the ionic convection, and alternately, this secondary "convection current" again needs to be balanced by the electric current contributed from the induced electric field.

The total flux of either ionic species can be expressed as the general form

$$\mathbf{J}_\pm = -D_\pm[\nabla n_\pm \pm \frac{Ze}{kT} n_\pm(\nabla\psi - \mathbf{E})] + n_\pm \mathbf{u}, \qquad (2)$$

where $\mathbf{u} = u(y)\mathbf{e}_x$ is the fluid velocity relative to the plane wall in the direction of decreasing electrolyte concentration (i.e., $\mathbf{e}_x$ is the unit vector in the direction of $-\nabla n^\infty$), D_+ and D_- are the diffusion coefficients of the cations and anions, respectively, $\mathbf{E} = E\mathbf{e}_x$ is the macroscopic electric field induced by the concentration gradient of the electrolyte. To have no net electric current arising from the cocurrent diffusion, electric migration, and diffusioosmotic convection of the cations and anions, one must require that $J_+ = J_-$. Applying this constraint to Eq. (2), we obtain

$$E = \text{[illegible]}, \qquad (3)$$

where

$$U^* = \frac{2kT}{\eta\kappa^2}|\nabla n^\infty|, \qquad (4)$$

which is a characteristic value of the diffusioosmotic velocity,

$$\beta = \frac{D_+ - D_-}{D_+ + D_-}, \qquad (5)$$

$$\mathrm{Pe} = \frac{\text{[illegible]}}{(D_+ + D_-)|\nabla n^\infty|}, \qquad (6)$$

and η is the fluid viscosity. Evidently, the induced electric filed E given by Eq. (3) in a self-consistent way depends on the local electrostatic potential ψ and fluid velocity u.

For the steady diffusioosmotic flow along a plane wall, the momentum balance on the electrolyte solution in the x direction gives

$$\eta\frac{d^2u}{dy^2} = \frac{\partial p}{\partial x} - Ze(n_+ - n_-)E, \qquad (7)$$

where the pressure distribution

$$p = p_\infty + 2n^\infty(x)kT(\cosh\bar{\psi} - 1). \qquad (8)$$

and p_∞ is the pressure far away from the wall, which is a constant in the absence of the applied pressure gradient.

Substituting the Boltzmann distributions of n_+ and n_- and the pressure profile of Eq. (8) into Eq. (7) and then performing the integration with respect to *y* twice subject to appropriate boundary conditions, we obtain

$$\frac{u}{U^*} = \text{[illegible]}. \qquad (9)$$

After the substitution of Eq. (9) for *u* and Eq. (1) for ψ into Eq. (3), the induced electric field *E* can be numerically solved as a function of the parameters [illegible], [illegible], β, and Pe. With the known results of ψ and *E*, the diffusioosmotic velocity distribution of the electrolyte solution can be determined from Eq. (9) with the numerical integrations. The bulk-phase diffusioosmotic velocity [illegible] of the electrolyte solution at a large distance from the plane wall as a function of the relevant parameters can be obtained from the distribution *u* by taking [illegible].

3. Results and discussion

The results of the normalized diffusioosmotic velocity distribution [illegible] are plotted in Figure 1. For fixed values of the parameters [illegible], Pe, and [illegible], the value of [illegible] approaches a constant (equal to [illegible]) as [illegible]. When Pe=0 and the product of [illegible] and [illegible] is negative, [illegible] is also negative, meaning that the diffusioosmotic flow is in the direction of increasing electrolyte concentration. The magnitude of [illegible] increases monotonically with an increase in the electrokinetic distance [illegible] from the wall, with an increase in [illegible], and with an increase in [illegible], for an otherwise specified condition. When Pe=0 and [illegible] is positive, the direction of the diffusioosmotic flow depends on the combination of parameters [illegible], [illegible], and [illegible]. When the value of Pe is finite, the dependence of [illegible] on [illegible] is similar to that for the case of Pe=0 if the value of [illegible] is small, but [illegible] can be positive for any given value of [illegible] if the value of [illegible] is large. In general, the value of [illegible] increases monotonically with an increase in the value of Pe for specified values of [illegible], [illegible], and [illegible] except for the situation that the value of [illegible] is close to unity.

Maps showing the direction of the normalized diffusioosmotic velocity [illegible] of the electrolyte solution far away from the plane wall for various values of the parameters Pe, [illegible], and [illegible] are drawn in Figure 2. When Pe=0 and the product of [illegible] and [illegible] is negative (inside the second and fourth quadrants in Figure 6a), [illegible] is negative and the electrolyte solution flows toward higher concentration. When Pe=0 and the product of [illegible] and [illegible] is positive (inside the first and third quadrants in Figure 6a), the bulk-phase diffusioosmotic velocity may reverse its direction from against the concentration gradient to along with it as [illegible] increases not much from zero for the case of a small magnitude of [illegible], or as [illegible] decreases from 1 to 0 for a given value of [illegible]. When the value of Pe is finite, as indicated in Fig. 2b, the diffusioosmotic flow of the electrolyte solution in many cases (such as that with a negative value of [illegible] and a sufficiently large magnitude of [illegible]) may reverse its direction from toward higher concentration to toward lower concentration, due to the effect of the electrolyte convection. References

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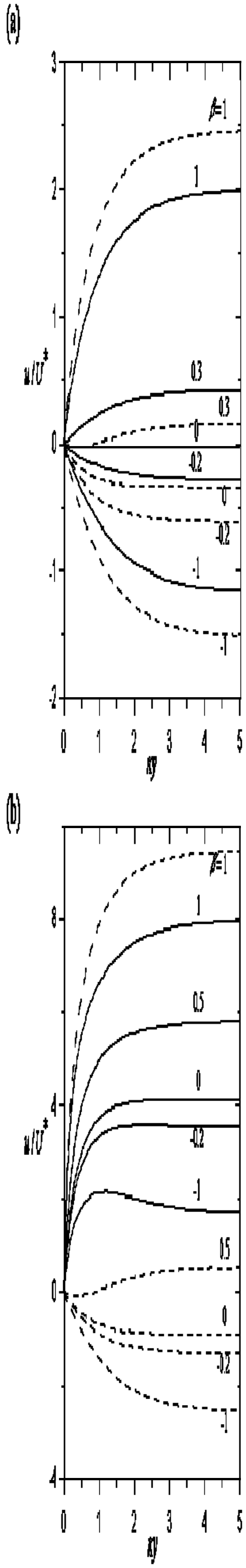
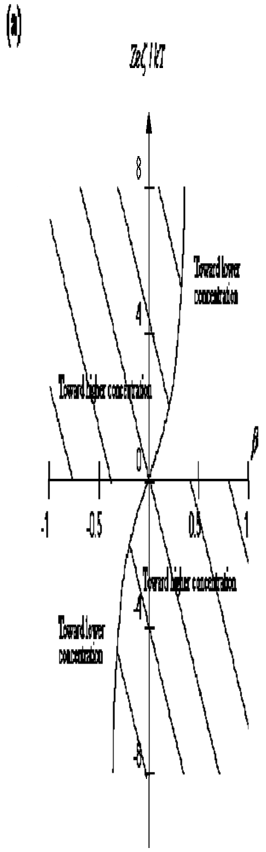


(a)
3
2
1
0
-1
-2
u/U*
β=1
1
0.3
0.3
0
-0.2
0
-0.2
-1
-1
0
1
2
3
4
5
κy
(b)
8
4
0
-4
u/U*
γ=1
1
0.5
0
-0.2
-1
0.5
0
-0.2
-1
0
1
2
3
4
5
κy

Figure 1. The normalized diffusioosmotic velocity [illegible] versus [illegible] for various values of [illegible] with Pe=1 (solid curves) and Pe=0 (dashed curves): (a) [illegible]; (b) [illegible].


(a)
Zeζ / kT
8
4
0
-4
-8
-1
-0.5
0.5
1
β
Toward lower concentration
Toward higher concentration
Toward higher concentration
Toward lower concentration

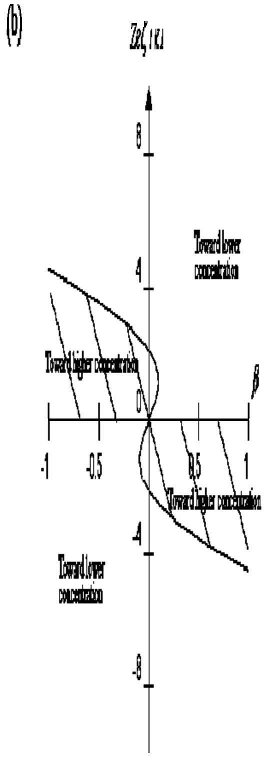

(b)
Zeζ / kT
8
4
0
-4
-8
-1
-0.5
0.5
1
β
Toward lower concentration
Toward higher concentration
Toward higher concentration
Toward lower concentration

Figure 2. Maps showing the direction of the bulk-phase diffusioosmotic velocity [illegible]: (a) Pe=0; (b) Pe=1.