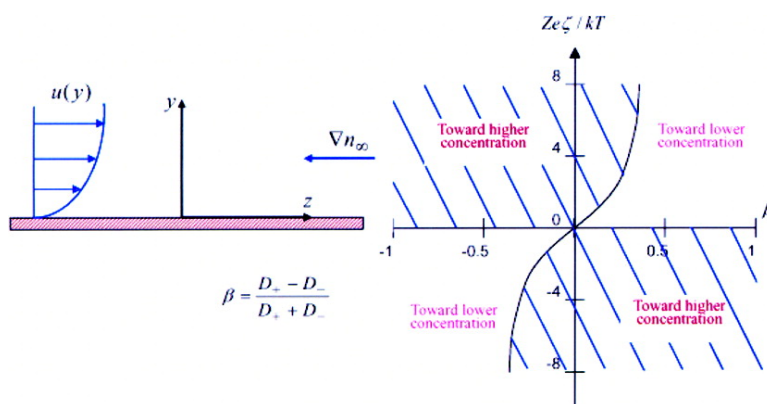


## Diffusioosmosis of Electrolyte Solutions along a Charged Plane Wall

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# Diffusioosmosis of Electrolyte Solutions along a Charged Plane Wall

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The steady diffusioosmotic flow of an electrolyte solution along a dielectric plane wall caused by an imposed tangential concentration gradient is analytically examined. The plane wall may have either a constant surface potential or a constant surface charge density of an arbitrary quantity. The electric double layer adjacent to the charged wall may have an arbitrary thickness, and its electrostatic potential distribution is determined by the Poisson–Boltzmann equation. The macroscopic electric field along the tangential direction induced by the imposed electrolyte concentration gradient is obtained as a function of the lateral position. A closed-form formula for the fluid velocity profile is derived as the solution of a modified Navier–Stokes equation. The direction of the diffusioosmotic flow relative to the concentration gradient is determined by the combination of the zeta potential of the wall and the properties of the electrolyte solution. For a given concentration gradient of an electrolyte along a plane wall, the magnitude of fluid velocity at a position in general increases with an increase in its electrokinetic distance from the wall, but there are exceptions. The effect of the lateral distribution of the induced tangential electric field in the double layer on the diffusioosmotic flow is found to be very significant and cannot be ignored.

## 1. Introduction

The electrokinetic flows of an electrolyte solution along a charged solid surface are of much fundamental and practical interest in various areas of science and engineering. Perhaps the most familiar example of electrokinetic flows is electroosmosis, which results from the interaction between an external tangential electric field and the electric double layer adjacent to the charged wall. Problems of fluid flow caused by this well-known mechanism have been studied extensively in the past.<sup>1–11</sup>

Another example of electrokinetic flows, which is termed diffusioosmosis and has caught less attention, involves a tangential concentration gradient of the electrolyte that interacts with the charged wall. Same as in the case of electroosmosis, the electrolyte–wall interaction in diffusioosmosis is electrostatic in nature and its range is the Debye screening length  $\kappa^{-1}$ . The fluid motion caused by diffusioosmosis has been analytically examined for flows near a plane wall<sup>5,12–17</sup> and inside a capillary pore.<sup>18–21</sup>

Some experimental results and interesting applications concerning diffusioosmosis are also available in the literature.<sup>22</sup> Electrolyte solutions with a concentration gradient of order 100 kmol/m<sup>4</sup> (=1 M/cm) along solid surfaces with a zeta potential of order  $kT/e$  ( $\sim 25$  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 micrometers per second.

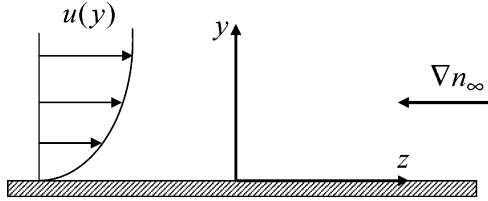
A tangential gradient of a dissociating electrolyte produces fluid flow along a charged solid surface by two mechanisms. The first involves the stresses developed by the tangential gradient of the excess pressure within the electric double layer (chemiosmotic effect), and the second is based on the macroscopic electric field that is generated because the tangential diffusive fluxes of the two electrolyte ions are not equal (electroosmotic effect). Both mechanisms were considered in previous investigations for the diffusioosmotic flow parallel to a plane wall.<sup>5,12–17</sup> In these studies, however, the effect of lateral distributions of the counterions and co-ions (or of the electrostatic potential) on the local electric field induced by the imposed electrolyte concentration gradient in the tangential direction inside the double layer, which can be very important, was neglected.

In this paper we present a comprehensive analysis of the diffusioosmosis of an electrolyte solution with a constant prescribed concentration gradient along a charged plane wall. The zeta potential or surface charge density of the wall is assumed to be uniform, but no assumption is made concerning the magnitude of the electric potential or the thickness of the double layer, and the lateral

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**Figure 1.** Geometrical sketch for the diffusi-osmotic flow tangential to a plane wall due to an applied concentration gradient of electrolyte.

distribution of the induced tangential electric field is allowed. Closed-form expressions for the fluid velocity profile and the bulk-phase diffusi-osmotic velocity are obtained in eqs 27 and 31, respectively. These results show that the effect of the deviation of the induced tangential electric field in the double layer from its bulk-phase quantity on the diffusi-osmotic velocity of the fluid is dominantly significant in most practical situations, even for the case of a very thin double layer.

## 2. Electric Potential Distribution

We consider the diffusi-osmotic flow of an infinitely thick solution of a symmetrically charged binary electrolyte of valence  $Z$  (where  $Z$  is a positive integer) tangential to a dielectric plane wall of length  $L$ , as illustrated in Figure 1, at the steady state. The discrete nature of the surface charges, which are uniformly distributed over the wall, is ignored. The applied electrolyte concentration gradient  $\nabla n^\infty$  is a constant along the tangential ( $z$ ) direction, where  $n^\infty(z)$  is the linear concentration (number density) distribution of the electrolyte in the bulk solution phase far from the wall (with  $y \rightarrow \infty$  or beyond the influence of the charged wall). It is assumed that  $n^\infty$  is only slightly nonuniform such that  $L|\nabla n^\infty|/n^\infty(z=0) \ll 1$ , where  $z=0$  is set at the midpoint along the plane wall. Thus, the variations of the electrostatic potential and ionic concentrations in the electric double layer adjacent to the wall with the tangential position can be neglected in comparison with their corresponding quantities at  $z=0$ .

For the electrolyte solution near the plane wall, let  $\psi(y)$  be the electrostatic potential at a position  $y$  relative to that in the bulk solution and  $n_+(y, z)$  and  $n_-(y, z)$  be the local concentrations of the cations and anions, respectively. Then the Poisson equation gives

$$\frac{d^2\psi}{dy^2} = -\frac{4\pi Ze}{\epsilon} [n_+(y, 0) - n_-(y, 0)] \quad (1)$$

with  $\epsilon = 4\pi\epsilon_0\epsilon_r$ , where  $\epsilon_r$  is the relative permittivity of the electrolyte solution and  $\epsilon_0$  is the permittivity of a vacuum.

The local ionic concentrations can also be related to the electrostatic potential by the Boltzmann equation,

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

Substitution of eq 2 into eq 1 leads to the well-known Poisson–Boltzmann equation,

$$\frac{d^2\psi}{dy^2} = \kappa \frac{2kT}{Ze} \sinh \frac{Ze\psi}{kT} \quad (3)$$

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

**2.1. Case of Constant Surface Potential.** For the case of constant surface potential, the boundary

conditions for  $\psi$  are

$$y=0: \psi = \zeta \quad (4a)$$

$$y \rightarrow \infty: \psi = 0 \quad (4b)$$

where the constant  $\zeta$  is the zeta potential at the shear plane of the wall adjacent to the electrolyte solution having a uniform bulk concentration  $n^\infty(z=0)$ . The effects of the Stern layer between the solid surface and the diffuse part of the electric double layer are neglected. The solution to eqs 3 and 4 is the well-known Gouy–Chapman result,<sup>5–7</sup>

$$\psi = \frac{2kT}{Ze} \ln \left[ \frac{1 + \gamma \exp(-\kappa y)}{1 - \gamma \exp(-\kappa y)} \right] \quad (5)$$

where  $\gamma = \tanh(Ze\zeta/4kT)$ .

**2.2. Case of Constant Surface Charge Density.** If the constant surface charge density  $\sigma$ , instead of the surface potential  $\zeta$ , is known at the plane wall, the boundary condition specified by eq 4a should be replaced by the Gauss condition,

$$y=0: \frac{d\psi}{dy} = -\frac{4\pi\sigma}{\epsilon} \quad (6)$$

Now, the solution for  $\psi$  given by eq 5 is still valid, with

$$\zeta = \frac{2kT}{Ze} \sinh^{-1} \left( \frac{2\pi Ze\sigma}{\epsilon \kappa kT} \right) \quad (7)$$

**2.3. Case of Low Electric Potential.** When the surface potential  $\zeta$  is small (say,  $Ze|\zeta|/kT \leq 2$ ), eq 3 can be linearized (known as the Debye–Huckel approximation), and eqs 5 and 7 reduce to

$$\psi = \zeta \exp(-\kappa y) \quad (8)$$

and

$$\zeta = \frac{4\pi\sigma}{\epsilon \kappa} \quad (9)$$

Both eq 7 and eq 9 indicate that  $\sigma$  increases with an increase in  $\kappa$  for the case of constant surface potential and  $\zeta$  decreases with an increase in  $\kappa$  for the case of constant surface charge density.

## 3. Induced Electric Field Distribution

The ionic concentrations  $n_+$  and  $n_-$  in the fluid undergoing diffusi-osmosis along the plane wall are not uniform in both tangential ( $z$ ) and normal ( $y$ ) 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  $\mathbf{E}(y)$  along the tangential direction arises spontaneously in the electrolyte solution to produce another electric current distribution which exactly balances the diffusion current.<sup>12–17</sup> 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.

**3.1. General Analysis.** The flux of either ionic species can be expressed by the Nernst–Planck equation,

$$\mathbf{J}_\pm = -D_\pm \left[ \nabla n_\pm \pm \frac{Ze}{kT} n_\pm (\nabla\psi - \mathbf{E}) \right] \quad (10)$$

where  $D_+$  and  $D_-$  are the diffusion coefficients of the cations and anions, respectively, and the principle of superposition

for the electric potential is used. To have no net current arising from the cocurrent diffusion and electric migration of the cations and anions, one must require that  $\mathbf{J}_+ = \mathbf{J}_- = \mathbf{J}$  (the normal component of  $\mathbf{J}$  vanishes and the ionic fluxes induced by  $\nabla\psi$  in eq 10 are balanced by the normal components of the diffusive ionic fluxes as required by the Boltzmann distribution given by eq 2). Applying this constraint to eq 10, one obtains

$$\mathbf{E} = \frac{kT}{Ze} \frac{G_+ - G_-}{G_+ + G_-} \frac{\nabla n^\infty}{n^\infty(z=0)} \quad (11)$$

where

$$G_\pm = D_\pm \exp\left(\mp \frac{Ze\psi}{kT}\right) \quad (12)$$

The coefficients  $G_+$  and  $G_-$  defined by the above equation reflect the fact of an increase in the tangential diffusive flux of the counterions and a decrease in the flux of the co-ions inside the electric double layer. Evidently, the induced electric field  $\mathbf{E}$  given by eq 11 depends on the local electrostatic potential  $\psi$ .

Substitution of eqs 11 and 12 into eq 10 leads to a net flux distribution of the electrolyte,

$$\mathbf{J} = -D\nabla n^\infty \quad (13)$$

where the position-dependent net diffusivity is

$$D = \frac{2G_+G_-}{G_+ + G_-} = \frac{2D_+D_-}{D_+ + D_-} \quad (14)$$

which is always positive. Equations 11 and 13 indicate clearly that both  $\mathbf{E}$  and  $\mathbf{J}$  are collinear with and proportional to the tangentially imposed electrolyte gradient  $\nabla n^\infty$ . For the special case of an uncharged wall ( $\zeta = 0$ ), both  $\mathbf{E}$  and  $D$  at any location  $y$  are identical to their corresponding bulk-phase quantities.

When  $Ze|\psi|/kT \rightarrow \infty$ , the ratio  $(G_+ - G_-)/(G_+ + G_-)$  in eq 11 approaches the value  $-\zeta/|\zeta|$  (whose magnitude is unity) and the induced electric field  $\mathbf{E}$  becomes independent of the ionic diffusion coefficients. In this limit, the net diffusivity  $D$  given by eq 14 will vanish asymptotically as  $2G_+$  if  $\zeta > 0$  and as  $2G_-$  if  $\zeta < 0$ .

**3.2. Case of Low Electric Potential.** When the magnitude of electrostatic potential  $\psi$  is small, a Taylor expansion applies to eq 12, and eqs 11 and 14 can be expressed as

$$\mathbf{E} = \frac{kT}{Ze} \left[ \beta - (1 - \beta^2) \frac{Ze\psi}{kT} - \beta(1 - \beta^2) \left( \frac{Ze\psi}{kT} \right)^2 + O(\psi^3) \right] \frac{\nabla n^\infty}{n^\infty(z=0)} \quad (15)$$

and

$$D = \frac{2D_+D_-}{D_+ + D_-} \left[ 1 + \beta \frac{Ze\psi}{kT} - \left( \frac{1}{2} - \beta^2 \right) \left( \frac{Ze\psi}{kT} \right)^2 + O(\psi^3) \right] \quad (16)$$

where  $\beta$  is the difference between cation and anion diffusivities normalized by their sum,

$$\beta = \frac{D_+ - D_-}{D_+ + D_-} \quad (17)$$

Evidently,  $-1 \leq \beta \leq 1$ , with the upper and lower bounds occurring as  $D_-/D_+ \rightarrow 0$  and  $\infty$ , respectively.

Note that, even if the cation and anion diffusivities are identical (i.e.,  $\beta = 0$ ), the  $O(\psi)$  term in eq 15 for the induced electric field  $\mathbf{E}$  and the  $O(\psi^2)$  term in eq 16 for the net diffusivity  $D$  still exist, due to the adsorption of the counterions and depletion of the co-ions near the plane wall. For the limiting case of  $\beta = \pm 1$  (one of the ionic diffusion coefficients vanishes), the induced electric field at any location is independent of the local electrostatic potential and equals its bulk-phase quantity, as shown by either eq 11 or eq 15.

In previous studies of the diffusioosmosis of electrolyte solutions along a plane wall,<sup>5,12-17</sup> only the first term in the brackets of eq 15, which is a constant, was considered for  $\mathbf{E}$  (the bulk-phase electrostatic potential  $\psi = 0$  is taken everywhere), and, thus, the effect of the lateral distribution of the induced electric field on the fluid velocity was excluded.

#### 4. Fluid Velocity Distribution

We now consider the steady diffusioosmotic flow of a symmetric electrolyte solution along a plane wall under the influence of a constant concentration gradient  $\nabla n^\infty$  of the electrolyte prescribed tangentially. The momentum balances on the incompressible Newtonian fluid in the  $y$  and  $z$  directions give

$$\frac{\partial p}{\partial y} + Ze(n_+ - n_-) \frac{d\psi}{dy} = 0 \quad (18a)$$

$$\eta \frac{d^2 u}{dy^2} = \frac{\partial p}{\partial z} - Ze(n_+ - n_-) |\mathbf{E}| \quad (18b)$$

where  $u(y)$  is the fluid velocity profile relative to the plane wall in the direction of decreasing electrolyte concentration (i.e., direction of  $-\nabla n^\infty$ ),  $p(y, z)$  is the pressure distribution,  $\eta$  is the fluid viscosity, and  $\mathbf{E}(y)$  is the macroscopic electric field induced by the concentration gradient of the electrolyte given by eq 11.

With the assumption that  $|\mathbf{E}| \ll \kappa|\zeta|$  [or  $\beta|\nabla n^\infty|/\kappa n^\infty(z=0) \ll Ze|\zeta|/kT$ ], a scaling argument applied to the continuity equation shows  $u$  to be the only significant velocity component.<sup>14</sup> The boundary conditions for  $u$  at the no-slip wall and at infinity are

$$y = 0: \quad u = 0 \quad (19a)$$

$$y \rightarrow \infty: \quad \frac{du}{dy} = 0 \quad (19b)$$

**4.1. General Analysis.** After the substitution of eq 2 into eq 18a (based on the assumption that the equilibrium ionic distributions are not affected by the net diffusive flux  $\mathbf{J}$ , the induced electric field  $\mathbf{E}$ , and the fluid velocity  $u$ , which is warranted if  $|\nabla n^\infty|/\kappa n^\infty(z=0) \ll 1$ , the pressure distribution can be determined as

$$p = p_\infty + 2n^\infty(z)kT \left( \cosh \frac{Ze\psi}{kT} - 1 \right) \quad (20)$$

Here,  $p_\infty$  is the pressure far away from the wall, which is a constant in the absence of applied pressure gradient, and the electric potential distribution  $\psi(y)$  is given by eq 5.

Substituting the ionic concentration distributions of eq 2, the electrostatic potential distribution of eq 5, the pressure profile of eq 20, and the induced electric field

profile of eq 11 into eq 18b yields

$$\frac{d}{dx} \left[ (x^2 - 1) \frac{d(u/U^*)}{dx} \right] = \frac{4(x^2 - \omega^4)}{x^4 + \omega^4} \quad (21)$$

where

$$x = \frac{1 + \gamma \exp(-\kappa y)}{1 - \gamma \exp(-\kappa y)} \quad (22)$$

$$\omega = \left( \frac{1 + \beta}{1 - \beta} \right)^{1/4} = \left( \frac{D_+}{D_-} \right)^{1/4} \quad (23)$$

and the diffusioosmotic velocity is normalized by a characteristic value given by

$$U^* = \frac{\epsilon |\nabla n^\infty| (kT)^2}{4\pi \eta n^\infty(0) (Ze)^2} = \frac{2kT}{\eta \kappa^2} |\nabla n^\infty| \quad (24)$$

Integration of eq 21 from  $y \rightarrow \infty$  to  $y = y$  using eq 19b leads to

$$\frac{d(u/U^*)}{dx} = \frac{2}{x^2 - 1} [g(x) - g(1)] \quad (25)$$

where

$$g(x) = \frac{1}{\sqrt{2\omega}} \left[ (1 - \omega^2) \tan^{-1} \frac{\sqrt{2\omega}x}{\omega^2 - x^2} + \frac{1}{2}(1 + \omega^2) \ln \frac{x^2 - \sqrt{2\omega}x + \omega^2}{x^2 + \sqrt{2\omega}x + \omega^2} \right] \quad (26)$$

The diffusioosmotic velocity profile of the electrolyte solution parallel to the plane wall can be solved by integrating eq 25 from  $y = 0$  to  $y = y$  subject to the boundary condition in eq 19a, with the result

$$\frac{u}{U^*} = F(x) - F\left(\frac{1 + \gamma}{1 - \gamma}\right) \quad (27)$$

where

$$F(x) = \left[ \frac{1 - \omega^2}{\sqrt{2\omega}} m\pi + g(x) - g(1) \right] \ln \frac{x - 1}{x + 1} + \frac{1 + i}{2\sqrt{2\omega}} \{ (\omega^2 - i)[h_{0+}(x) - h_{1+}(x) + h_{1-}(x)] + (1 - i\omega^2)[h_{0-}(x) - h_{2+}(x) + h_{2-}(x)] \} \quad (28)$$

$$h_{0\pm}(x) = \ln \frac{\sqrt{2\omega} + (1 \pm i)}{\sqrt{2\omega} - (1 \pm i)} \ln(x^2 \pm i\omega^2) \quad (29)$$

$$h_{1\pm}(x) = \text{Li}_2 \left[ \frac{\sqrt{2\omega} + (1 - i)x}{\sqrt{2\omega} \pm (1 - i)} \right] + \text{Li}_2 \left[ \frac{\sqrt{2\omega} - (1 - i)x}{\sqrt{2\omega} \pm (1 - i)} \right] \quad (30a)$$

$$h_{2\pm}(x) = \text{Li}_2 \left[ \frac{\sqrt{2\omega} + (1 + i)x}{\sqrt{2\omega} \pm (1 + i)} \right] + \text{Li}_2 \left[ \frac{\sqrt{2\omega} - (1 + i)x}{\sqrt{2\omega} \pm (1 + i)} \right] \quad (30b)$$

$i = \sqrt{-1}$ , and  $\text{Li}_2$  is the polylogarithm function of order

2, also known as the Euler dilogarithm function.<sup>23</sup> In eq 28,  $m = 1$  if  $x \geq \omega \geq 1$  or  $x \leq \omega \leq 1$ , and  $m = 0$  otherwise.

Equations 27–30 predict that the normalized fluid velocity  $u/U^*$  is only a function of the dimensionless parameters  $\gamma$  (or  $Ze\zeta/kT$ ),  $\omega$  (or  $\beta$ ), and  $\kappa y$ . Evidently,  $u/U^* = 0$  everywhere if  $\zeta = 0$  (or  $\gamma = 0$ ). It is understood that, for a given value of  $\kappa y$ , the quantity  $u/U^*$  with specified values  $-Ze\zeta/kT$  and  $\beta$  is equal to that with the values  $Ze\zeta/kT$  and  $-\beta$ .

**4.2. Bulk Fluid Velocity.** If we consider the situation that  $\kappa y \rightarrow \infty$ , the fluid velocity at a large distance from the plane wall caused by the imposed electrolyte concentration gradient can be evaluated from eq 27. The result of this bulk-phase diffusioosmotic velocity, denoted by  $u_\infty$ , is

$$\frac{u_\infty}{U^*} = F(1) - F\left(\frac{1 + \gamma}{1 - \gamma}\right) \quad (31)$$

regardless of the thickness of the electric double layer. For the diffusioosmosis of electrolyte solutions in a straight capillary tube or slit with  $\kappa R \rightarrow \infty$ , where  $R$  is the radius of the tube or half thickness of the slit, the fluid velocity at a large distance from the capillary wall (with  $\kappa y \gg 1$ ) can also be evaluated by eq 31.

In previous studies of the diffusioosmosis of electrolyte solutions along a plane wall,<sup>5,12–17</sup> the constant bulk-phase quantity of the induced electric field  $\mathbf{E}$  given by eq 11 taking  $\psi = 0$  everywhere was used in eq 18b, and its solution gives

$$\frac{u_\infty}{U^*} = \beta \frac{Ze\zeta}{kT} + 4 \ln \cosh\left(\frac{Ze\zeta}{4kT}\right) \quad (32)$$

The difference between eq 31 and eq 32 is quite obvious, and their comparison will be graphically displayed in the next section. Note that, in eq 32, the electroosmotic contribution represented by the first term on the right-hand side and the chemiosmotic contribution denoted by the second term are decoupled as a result of the assumption of constant  $\mathbf{E}$ .

**4.3. Case of Low Electric Potential.** When the Debye–Huckel approximation is used, eqs 2 and 20 for the concentration and pressure distributions can be expressed by their Taylor expansions in  $Ze\psi/kT$ , and eqs 5 and 11 for the electrostatic potential and induced tangential electric field reduce to eqs 8 and 15. With this simplification, eqs 27, 31, and 32 become

$$\frac{u}{U^*} = \beta \frac{Ze\zeta}{kT} [1 - \exp(-\kappa y)] + \left[ \frac{1}{8} - \frac{1}{4}(1 - \beta^2) \right] \left( \frac{Ze\zeta}{kT} \right)^2 [1 - \exp(-2\kappa y)] + O(\zeta^3) \quad (33)$$

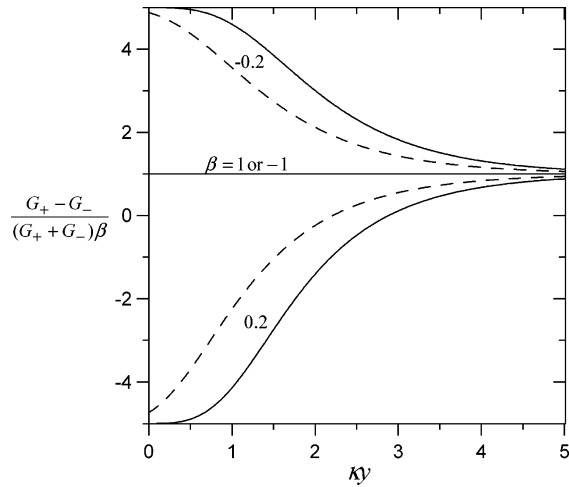
$$\frac{u_\infty}{U^*} = \beta \frac{Ze\zeta}{kT} + \left[ \frac{1}{8} - \frac{1}{4}(1 - \beta^2) \right] \left( \frac{Ze\zeta}{kT} \right)^2 + O(\zeta^3) \quad (34)$$

$$\frac{u_\infty}{U^*} = \beta \frac{Ze\zeta}{kT} + \frac{1}{8} \left( \frac{Ze\zeta}{kT} \right)^2 + O(\zeta^3) \quad (35)$$

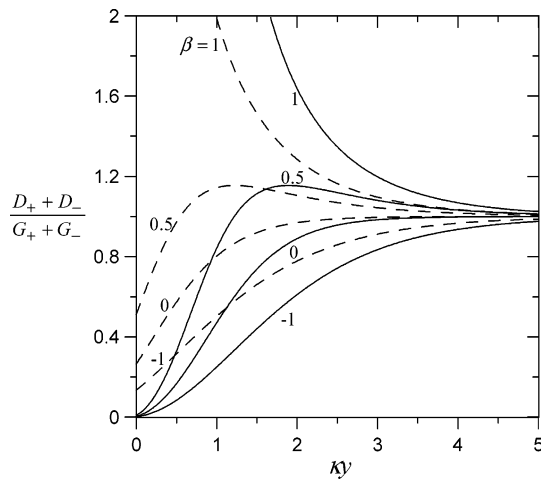
respectively.

Equations 33–35 illustrate that both the effect of the lateral distribution of the induced electric field and the chemiosmotic effect (always directs the fluid toward lower electrolyte concentration) are of the order  $\zeta^2$ . The two effects contribute to the fluid flow in opposite directions,

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**Figure 2.** Plots of the normalized electric field induced by an electrolyte gradient along a plane wall as calculated from eq 11 versus the electrokinetic coordinate  $\kappa\gamma$  for various values of the parameter  $\beta$ . The solid curves represent the case  $Ze\zeta/kT = 2$ , and the dashed curves denote the case  $Ze\zeta/kT = 6$ .



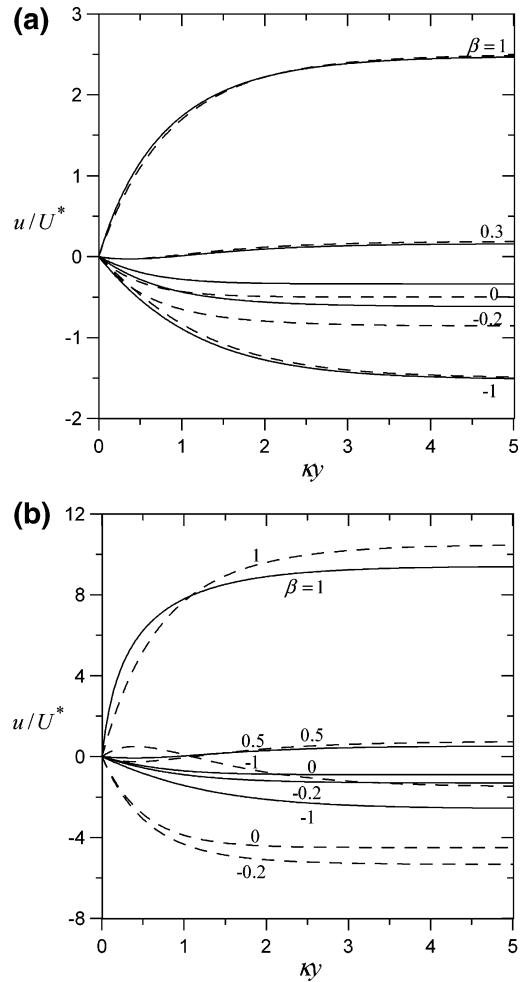
**Figure 3.** Plots of the normalized net diffusivity of the electrolyte tangential to a plane wall as calculated from eq 14 versus the electrokinetic coordinate  $\kappa\gamma$  for various values of the parameter  $\beta$ . The solid curves represent the case  $Ze\zeta/kT = 6$ , and the dashed curves denote the case  $Ze\zeta/kT = 2$ .

and the former is dominant in most practical situations. Note that the  $O(\zeta)$  and  $O(\zeta^2)$  terms in eqs 33 and 34 may act either in concert or in competition to produce the net diffusioosmotic flow, depending on the sign of  $\beta\zeta(2\beta^2 - 1)$ .

## 5. Results and Discussion

**5.1. Induced Electric Field Distribution.** The distribution of the macroscopic electric field  $\mathbf{E}(y)$  induced by a concentration gradient of a symmetric electrolyte prescribed parallel to a plane wall is expressed by eq 11. This induced electric field normalized by its bulk-phase quantity,  $(G_+ - G_-)/(G_+ + G_-)\beta$  [equal to  $(\omega^4 - x^4)(\omega^4 + 1)/(\omega^4 + x^4)(\omega^4 - 1)$ ], as a function of the electrokinetic distance  $\kappa\gamma$  from the wall is plotted in Figure 2 for several values of the dimensionless parameters  $Ze\zeta/kT$  and  $\beta$ . As expected, the value of the normalized induced electric field equals unity in the limit of  $\beta = \pm 1$  and its magnitude becomes infinity for the special case of  $\beta = 0$ , irrespective of the parameters  $Ze\zeta/kT$  and  $\kappa\gamma$ , which are expected from eq 15.

The normalized induced electric field approaches unity as  $\kappa\gamma \geq 5$ , with a typical value at the wall (with  $\kappa\gamma = 0$ )



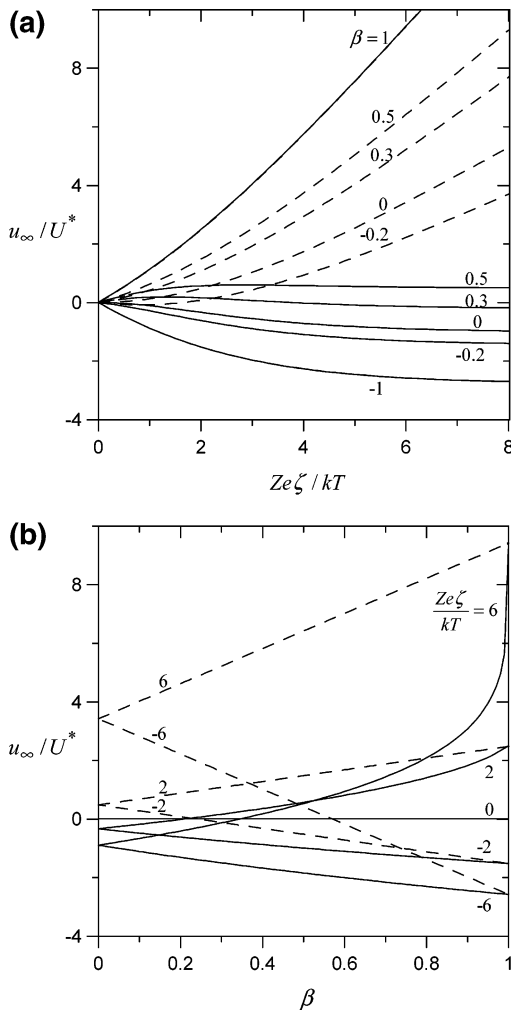
**Figure 4.** Plots of the normalized diffusioosmotic velocity along a plane wall as calculated from eqs 27 (solid curves) and 33 (dashed curves) versus the electrokinetic coordinate  $\kappa\gamma$  for various values of the parameter  $\beta$ : (a)  $Ze\zeta/kT = 2$ ; (b)  $Ze\zeta/kT = 6$ .

as  $-\zeta/|\zeta|\beta$  if  $Ze|\zeta|/kT \gg 1$ . The magnitude of  $(G_+ - G_-)/(G_+ + G_-)\beta - 1$  (or the deviation of the induced electric field from its bulk-phase quantity) decreases with an increase in  $\kappa\gamma$ , increases with an increase in  $Ze|\zeta|/kT$ , and decreases with an increase in  $|\beta|$ , for an otherwise specified condition.

**5.2. Position-Dependent Electrolyte Diffusivity.** The profile of the net diffusivity  $D(y)$  of a symmetric electrolyte in the direction parallel to a plane wall is given by eq 14. Figure 3 shows this net diffusivity normalized by its bulk-phase quantity,  $(D_+ + D_-)/(G_+ + G_-)$  [equal to  $(\omega^4 + 1)x^2/(\omega^4 + x^4)$ ], as a function of the electrokinetic position  $\kappa\gamma$  with  $Ze\zeta/kT$  and  $\beta$  as parameters. Note that each curve with specified values of  $-Ze\zeta/kT$  and  $\beta$  in Figures 2 and 3 would be identical to that with the values  $Ze\zeta/kT$  and  $-\beta$ .

When the product of  $\zeta$  and  $\beta$  is negative, the normalized net diffusivity increases with an increase in  $\kappa\gamma$ , decreases with an increase in  $Ze|\zeta|/kT$ , and decreases with an increase in  $|\beta|$ , for an otherwise fixed condition. When  $\zeta\beta$  is positive, the value of the normalized net diffusivity at a position near the wall can be much greater than unity and its dependence on  $\kappa\gamma$  is not necessarily monotonic, depending on the combination of  $Ze\zeta/kT$  and  $\beta$ .

For a constant value of  $\kappa\gamma$ , the normalized net diffusivity increases with an increase in  $\beta$  for the case of  $\zeta > 0$  but decreases with it for the case of  $\zeta < 0$ . As expected, the



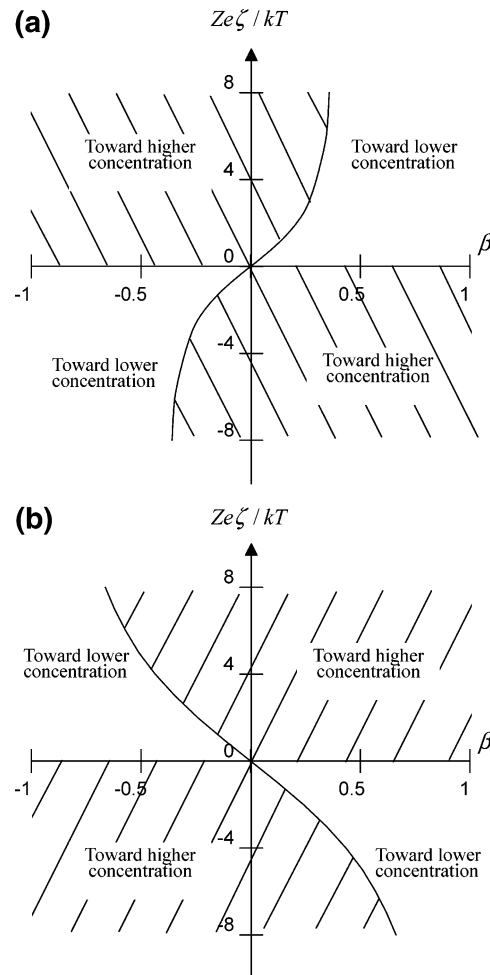
**Figure 5.** Normalized bulk-phase diffusioosmotic velocity along a plane wall as calculated from eqs 31 (solid curves) and 32 (dashed curves): (a) plots versus the dimensionless surface potential  $Ze|\zeta|/kT$  for various values of the parameter  $\beta$ ; (b) plots versus  $\beta$  for various values of  $Ze|\zeta|/kT$ .

value of  $(D_+ + D_-)/(G_+ + G_-)$  gets close to unity as  $\kappa y \geq 5$  and vanishes at the wall if  $Ze|\zeta|/kT \rightarrow \infty$  and  $\beta\zeta/|\zeta| \neq 1$ .

**5.3. Fluid Velocity Distribution.** The normalized diffusioosmotic velocity distribution  $u(\kappa y)/U^*$  of an electrolyte solution along a plane wall is given by eq 27 for the general case and by eq 33 for the case of a small magnitude of the zeta potential up to  $O(\zeta^2)$ . It can be seen from the  $O(\zeta^2)$  term of eq 33 that the fluid flows contributed from chemosmosis (involving the coefficient  $1/8$ ) and electroosmosis [involving the coefficient  $-(1 - \beta^2)/4$ ] are always in the opposite directions, and for the case of small  $\beta^2$ , the net flow is dominated by the electroosmotic effect (having the direction of increasing electrolyte concentration). The results of both eq 27 and eq 33 are plotted in Figure 4 for several values of the parameters  $Ze|\zeta|/kT$  and  $\beta$ .

When the product of  $\zeta$  and  $\beta$  is negative,  $u$  is also negative (due to the electroosmotic contribution, as can be seen from eq 15 or eq 33), meaning that the diffusioosmotic flow is in the direction of increasing electrolyte concentration. The magnitude of  $u/U^*$  increases monotonically with an increase in the electrokinetic distance  $\kappa y$  from the wall, with an increase in  $Ze|\zeta|/kT$  and with an increase in  $|\beta|$ , for an otherwise specified condition, which is expected from eq 33.

When  $\zeta\beta$  is positive, the direction of the diffusioosmotic flow depends on the combination of parameters  $Ze|\zeta|/kT$ ,



**Figure 6.** Maps showing the direction of the bulk-phase diffusioosmotic velocity along a plane wall: (a) as calculated from eq 31; (b) as calculated from eq 32.

$\beta$ , and  $\kappa y$ . If the magnitude of  $\beta$  is sufficiently large [the  $O(\zeta^2)$  term of the fluid velocity in eq 33 is dominated by the chemosmotic effect], the fluid flows against the electrolyte concentration gradient ( $u$  is positive) and  $u/U^*$  are still a monotonic increasing function of  $\kappa y$  and of  $Ze|\zeta|/kT$ . If the magnitude of  $\beta$  is sufficiently small [the  $O(\zeta)$  term of the fluid velocity in eq 33 is dominated by the electroosmotic effect, which overcomes the contribution from the  $O(\zeta^2)$  term], the fluid flows toward the opposite direction ( $u$  is negative) and the magnitude of  $u/U^*$  are also a monotonic increasing function of  $\kappa y$  and of  $Ze|\zeta|/kT$ . For a specified value of  $Ze|\zeta|/kT$  with an intermediate magnitude of  $\beta$ , the diffusioosmotic flow may reverse its direction from along the concentration gradient to against it as the value of  $\kappa y$  increases not much from zero.

For fixed values of  $Ze|\zeta|/kT$  and  $\beta$ , the value of  $u/U^*$  approaches a constant as  $\kappa y \geq 5$ , which is expected from eq 33. Evidently, the asymptotic formula of eq 33 for  $u/U^*$  from the Debye–Hückel approximation (depicted by dashed curves in Figure 4) agrees reasonably well with the exact result of eq 27 for the case of small magnitude of the zeta potential (say,  $Ze|\zeta|/kT \leq 2$ ), but the accuracy of this approximation deteriorates rapidly, as expected, when the value of  $Ze|\zeta|/kT$  becomes large.

**5.4. Bulk Fluid Velocity.** In Figure 5, the normalized diffusioosmotic velocity  $u_\infty/U^*$  of the electrolyte solution far away from the plane wall given by eq 31 is plotted versus the parameters  $Ze|\zeta|/kT$  and  $\beta$ . A map showing the direction of this velocity is also provided in Figure 6a. The dependence of  $u_\infty/U^*$  on  $Ze|\zeta|/kT$  and  $\beta$  is quite similar to

that of  $u/U^*$  for a given value of  $\kappa\gamma$ . When the product of  $\zeta$  and  $\beta$  is negative (inside the second and fourth quadrants in Figure 6a),  $u_\infty$  is negative and the electrolyte solution flows toward higher concentration. When the product of  $\zeta$  and  $\beta$  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  $Ze|\zeta|/kT$  increases not much from zero for the case of a small magnitude of  $\beta$  (in addition to a reversal that occurred at  $\zeta = 0$ ), or as  $|\beta|$  decreases from 1 to 0 for a given value of  $Ze\zeta/kT$ .

For comparison, the result of  $u_\infty/U^*$  given by eq 32 without accounting for the effect of the lateral distribution of the induced tangential electric field in the electric double layer adjacent to the plane wall is also plotted in Figures 5 and 6b. Surprisingly, the difference between this previously obtained bulk-phase diffusioosmotic velocity and the presently obtained quantity is quite substantial unless the magnitude of  $\beta$  approaches unity. Thus, the effect of the lateral distribution of the induced electric field always exists and cannot be neglected even as  $\kappa\gamma \rightarrow \infty$ .

## 6. Concluding Remarks

An analysis of the steady diffusioosmotic flow of symmetric electrolyte solutions parallel to a charged plane wall is presented in this work. It is assumed that the fluid is only slightly nonuniform in the electrolyte concentration along the wall, but no assumption is made about the thickness of the electric double layer adjacent to the wall and the effect of lateral distributions of the electrolyte ions; the electrostatic potential on the induced tangential electric field due to the applied concentration gradient is taken into account. The plane wall may have either a constant surface potential or a constant surface charge density of an arbitrary quantity. By solving the Poisson–Boltzmann equation and the modified Navier–Stokes equation applicable to the system, the electrostatic potential distribution, the induced electric field distribution, and the pressure distribution under the influence of the imposed electrolyte gradient are determined analytically. Closed-form formulas and numerical results for the local and bulk-phase diffusioosmotic velocities as functions of relevant parameters are presented in detail.

It is shown in section 3 that the macroscopic electric field induced by the prescribed electrolyte gradient along the plane wall is a function of the lateral position rather than a constant bulk-phase quantity. The contribution to the diffusioosmotic flow made by the position dependence of the induced electric field is of the same order [ $O(\zeta^2)$ ] as, but has an opposite direction to, that made by the chemiosmotic effect, and the former is dominant in most practical situations, as indicated by eqs 33 and 34. Therefore, the effect of the deviation of the local induced tangential electric field inside the electric double layer from its bulk-phase quantity (given by the term of zeroth order in  $\psi$  in eq 15), which causes the fluid flowing toward the end of higher electrolyte concentration, cannot be neglected in the evaluation of the diffusioosmotic velocity of electrolyte solutions along a wall, even for the case of a very thin double layer.

The macroscopic electric field  $\mathbf{E}$  arising spontaneously due to an imposed concentration gradient of a symmetric electrolyte along a plane wall is provided by eq 11 or 15, and the diffusioosmotic velocity  $u$  of the electrolyte solution is obtained in eq 27 or 33; both are accurate with the primary effects only. In addition to the ionic fluxes due to diffusion and electric migration (given by eq 10), the diffusioosmotic fluid flow can generate an electric current by ionic convection (known as the relaxation effect). This electric current is not included in the current balance for the determination of  $\mathbf{E}$  in section 3. Thus, a secondary induced electric field must build up along the wall, which is just sufficient to prevent the net electric current flow. This secondary induced field, which is of  $O(\zeta^2)$ , and its contribution to the fluid flow, which is of  $O(\zeta^3)$ , can be calculated via the same approach in the calculations of the electroosmosis and streaming potential induced across a capillary in the presence of an applied electric field and pressure gradient.<sup>3,4,10,11</sup> Alternatively, distributions of ionic concentrations, electric potentials, and fluid velocity might be calculated in a general self-consistent way.<sup>10,18–20</sup> For the case of a plane wall with an arbitrary value of its zeta potential considered in the present article, however, this general approach would be somewhat complicated and could be an endeavor for future work.

In contrast to diffusioosmosis, diffusiophoresis refers to the migration of colloidal particles in response to a macroscopic gradient of solute concentration in a solution. Without considering the variation of the induced tangential electric field with the normal position inside the electric double layer,  $u_\infty$  given by eq 32 has been used as a slip velocity at the surface of a nonconductive charged particle of arbitrary shape with a very thin double layer to obtain the steady diffusiophoretic velocity of the particle.<sup>12–15</sup> This terminal velocity turned out to be equal in magnitude but opposite in direction to  $u_\infty$  expressed by eq 32. When the effect of the lateral distribution of the induced electric field in the double layer is taken into account, the correct diffusiophoretic velocity of the dielectric particle should be equal in magnitude but opposite in direction to  $u_\infty$  given by eq 31 on the basis of the same derivation.

It is worth repeating that all the results in this study are obtained on the basis of a small external gradient of the electrolyte concentration along the plane wall. If the imposed concentration gradient  $|\nabla n^\infty|$  is relatively large, then the effect of variation of the electrostatic potential  $\psi$  in the double layer adjacent to the wall with the tangential position and the relaxation effect of the diffuse electrolyte ions may not be neglected. However, it is reasonable for one to expect that these effects will lead to quantitatively rather than qualitatively different results.

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