Electroosmotic Flow of a General Electrolyte Solution through a Fibrous Medium

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The electroosmotic flow of a general electrolyte solution through a fibrous medium is modeled theoretically taking the effect of double-layer polarization into account. The result obtained is applicable to an arbitrary level of electrical potential. We show that if the effect of double-layer polarization is neglected using the linearized Poisson–Boltzmann equation will underestimate electroosmotic velocity. The deviation becomes inappreciable, however, if κa is either very large or very small, κ and a being, respectively, the reciprocal Debye length and the radius of a fiber. If the surface potential is high, the variation of electroosmotic velocity as a function of κa may exhibit a local maximum and a local minimum, and the larger the porosity of the fibrous medium the lower the level of surface potential for the local extremals to occur. If κa is small, the effect of surface potential on the electroosmotic velocity is more significant than that of double-layer polarization, and the reverse is true if κa is large. © 2000 Academic Press

Key Words: electroosmotic flow; electrolyte solution; fibrous medium; electrokinetic equations; double-layer polarization.

INTRODUCTION

Electroosmosis, the flow of liquid induced by an applied electric field, is one of the basic electrokinetic phenomena that finds many applications in practice. The flow of fluid occurs when an electric field is applied across a porous medium having a charged surface. The application of the electric field causes the ions in the double layer near the charged surface to migrate toward either cathode or anode. Since the ions are predominantly of one sign, their motion gives rise to a body force, which exerts on the liquid in the double layer, and the flow of liquid occurs.

Levine and Neale (1–3) analyzed both the electrophoresis and the electroosmosis of a swarm of spheres under the condition of low electrical potential. Their results are applicable for double layers of arbitrary thickness. They showed that the overlapping of adjacent double layers leads to a drastic decrease in both electrophoretic mobility and electroosmosis velocity. Kozak and Davis (4, 5) extended the analysis of Levine and Neale for electrophoresis to all levels of electrical potential taking the effect of double-layer polarization into account. The interaction between adjacent double layers, however, is neglected. The result

obtained in their analysis, therefore, is appropriate for thin double layers only. Ohshima (6) proposed an approximate method in which the tedious integration in the evaluation of electrophoretic mobility in Levine and Neale (3) can be avoided, and a simple analytic formula was derived. The deviation of the approximate analytical expression from the original one is less than 4%. The analysis of Levine and Neale was also extended by Lee *et al.* (7) in a recent study to an arbitrary thickness of double layer and all levels of surface potential taking the effect of double-layer polarization into account. Their results reveal that both surface potential and double-layer polarization have a significant effect on the electrophoretic behavior of a concentrated colloidal dispersion. Kozak and Davis (8) applied the theory of Levine and Neale (3) to examine the electroosmotic phenomenon in a fibrous, porous medium under the condition that the effect of double-layer polarization is negligible. The medium is simulated by an array of circular cylinders, and the flow of the liquid phase to the axes of the cylinders is normal. Their results are applicable to an arbitrary thickness of double layer, but are limited to low electrical potential. Ohshima (9) proposed an approximate method similar to that of Ohshima (6) to arrive at a simple analytic electroosmotic velocity for flow through a fibrous, porous medium at low electrical potential. The deviation of the approximate result from that of Kozak and Davis is less than 6%.

In this study, the analysis of Levine and Neale (3) is extended to an arbitrary level of potential and double-layer thickness; the effect of double-layer polarization is taken into account also. The general electrokinetic equations, which include the Poisson–Boltzmann equation for electrical field and the Navier–Stokes equation for flow field, are solved simultaneously by employing the pseudospectral method based upon Chebyshev polynomials proposed in our previous studies for the case of a sphere in a spherical cavity (10, 11) and spheres in a concentrated suspension (7).

THEORY

Let us consider a liquid containing $z_1 : z_2$ electrolyte flow through an array of parallel, charged cylinders of radius a , z_1 and z_2 being, respectively, the valences of cations and anions. Referring to Fig. 1, the flow of liquid to the axes of the cylinders is normal and is parallel to an applied electrical field $\vec{E}$. The

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FIG. 1. Schematic representation of the system under consideration. The fibrous medium is simulated by parallel cylinders of radius a . The flow of liquid to the axes of the cylinders is normal, and the electric field $\vec{E}$ is in the direction of flow.

unit cell model proposed by Kuwabara (12) is adopted where the system under consideration is simulated by a representative cylinder of radius a surrounded by a fluid envelope of radius b . The porosity of the fibrous medium, H , is obtained by

$$H = 1 - (a/b)^2. \quad [1]$$

The cylindrical coordinates (r, θ, z) , with their origin located at the center of the representative cylinder, are adopted in the discussion below. Suppose that the liquid phase is incompressible and has constant physical properties, then the electroosmotic behavior of the system can be described by the set of electrokinetic equations describing the electric and flow fields.

Electrical Potential

Suppose that the time scale for double-layer relaxation is much smaller than that of the motion of fluid, then the spatial variation of the electrical potential ϕ can be described by the Poisson–Boltzmann equation

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon}, \quad [2]$$

with

$$\rho = \sum_i n_i z_i e, \quad [3]$$

where ∇ represents the gradient operator, ε and ρ are, respectively, the permittivity of the liquid phase and the space charge density.

Conservation of Ions

At steady state, the conservation of ions leads to

$$\nabla \cdot \left\{ D_j \left[\nabla n_j + \frac{z_j e n_j}{kT} \nabla \phi \right] - n_j \vec{v} \right\} = 0, \quad [3]$$

where D_j , n_j , and z_j are the diffusivity, the number concentration, and the valence of ion species j ; e and ϕ are, respectively, the elementary charge and the electrical potential; and k and T are the Boltzmann constant and the absolute temperature, respectively.

Flow Field

The flow field is described by the Navier–Stokes equation. Assuming creeping flow, we have

$$\mu \nabla^2 \vec{v} - \nabla p - \rho \nabla \phi = 0 \quad [4]$$

$$\nabla \cdot \vec{v} = 0, \quad [5]$$

where p and μ are, respectively, the pressure and the viscosity of the liquid phase.

Suppose that ϕ can be decomposed as (13)

$$\phi = \phi_1 + \phi_2, \quad [6]$$

where ϕ_1 and ϕ_2 represent, respectively, the electrical potential that would exist in the absence of an electrical field and that due to the imposed electrical field. According to O'Brien and White (13), the effect of double-layer polarization can be simulated by considering

$$n_j = n_{j0} \exp \left[\frac{-z_j e}{kT} (\phi_1 + \phi_2 + g_j) \right], \quad j = 1, 2, \quad [7]$$

where g_j denotes a perturbation term which accounts for the effect of fluid flow on the concentration of ions. If ϕ_2 and g_j are small compared to both kT/e and ϕ_1 , Eq. [7] can be approximated by

$$n_j = n_{j0} \exp \left(-\frac{z_j e \zeta_a}{kT} \phi_1^* \right) \left[1 - \frac{z_j e \zeta_a}{kT} (\phi_1^* + g_j^*) \right], \quad j = 1, 2, \quad [8]$$

where $\phi_j^* = \phi_j / \zeta_a$, $g_j^* = g_j / \zeta_a$, $j = 1, 2$, ζ_a being the zeta potential. ϕ_1^* represents the scaled electric potential at equilibrium. As pointed out by O'Brien and White (13), that ϕ_2 and g_j are small does not imply that their effects are insignificant.

For an easier mathematical treatment, scaled properties are used in the following analyses where the radius of the representative cylinder a is chosen as the characteristic length and $U_E (= \varepsilon \zeta_a^2 / \mu a)$ is chosen as the characteristic velocity. The latter is the electrophoretic velocity of an isolated cylinder evaluated by Smoluchowski's theory (14).

Adopting the approach of Lee *et al.* (7), Eq. [4] is transformed by taking curl to yield the governing equation for the corresponding stream function Ψ . The r and θ components of $\vec{v}$, v_r and v_θ , can be evaluated from Ψ by $v_r = -(\partial \Psi / \partial \theta) / r$ and $v_\theta = \partial \Psi / \partial r$, respectively. For convenience, a scaled stream potential $\Psi^* = \Psi / a U_E$ is defined. The symmetric nature of

the problem suggests that ϕ_2^* , g_1^* , g_2^* , and Ψ^* can be expressed respectively by $\phi_2^* = \Phi_2(r) \cos \theta$, $g_1^* = G_1(r) \cos \theta$, $g_2^* = G_2(r) \cos \theta$, and $\Psi^* = \Omega(r) \sin \theta$. It can be shown that the variation of ϕ_1^* is described by (7)

$$L\phi_1^* = -\frac{(\kappa a)^2}{(1+\alpha)\phi_r} [\exp(-\phi_r \phi_1^*) - \exp(\alpha \phi_r \phi_1^*)], \quad [9]$$

where the scaled surface potential ϕ_r , the linear operator L , and the Debye–Hückel parameter κ are defined, respectively, by

$$\phi_r = \zeta_a z_1 e / kT \quad [9a]$$

$$L = \frac{d^2}{dr^{*2}} + \frac{1}{r^*} \frac{d}{dr^*} - \frac{1}{r^{*2}} \quad [9b]$$

and

$$\kappa^2 = \frac{e \sum n_{i0} z_i}{\varepsilon kT} = \frac{(1+\alpha)e^2 n_{10} z_1^2}{\varepsilon kT}. \quad [9c]$$

We assume that the unit cell as a whole is electrically neutral and that there is no net current flow between adjacent cells. Therefore the boundary conditions associated with Eq. [9] are

$$\phi_1^* = 1 \quad \text{at } r^* = 1 \quad [9d]$$

$$\frac{d\phi_1^*}{dr^*} = 0 \quad \text{at } r^* = b/a. \quad [9e]$$

We need to solve Eq. [8] along with the following equations (7):

$$\left[L - \frac{(\kappa a)^2}{1+\alpha} [\exp(-\phi_r \phi_1^*) + \alpha \exp(\alpha \phi_r \phi_1^*)] \right] \Phi_2 = \frac{(\kappa a)^2}{1+\alpha} [G_1 \exp(-\phi_r \phi_1^*) + \alpha G_2 \exp(\alpha \phi_r \phi_1^*)] \quad [10]$$

$$LG_1 - \phi_r \frac{d\phi_1^*}{dr^*} \frac{dG_1}{dr^*} = \text{Pe}_1 v_r^* \frac{d\phi_1^*}{dr^*} \quad [11]$$

$$LG_2 + \alpha \phi_r \frac{d\phi_1^*}{dr^*} \frac{dG_2}{dr^*} = \text{Pe}_2 v_r^* \frac{d\phi_1^*}{dr^*} \quad [12]$$

$$\nabla^4 \Omega = -\frac{1}{r^*} \frac{(\kappa a)}{1+\alpha} \left[(n_1^* G_1 + \alpha n_2^* G_2) \frac{d\phi_1^*}{dr^*} \right]. \quad [13]$$

In these expressions $\text{Pe}_j = \varepsilon (z_1 e / kT)^2 / \mu D_j$, $j = 1, 2$, is the electric Peclet number of ion species j , $n_1^* = \exp(-\phi_r \phi_1^*)$, $n_2^* = \exp(\alpha \phi_r \phi_1^*)$, and the operator ∇^4 is defined by

$$\nabla^4 = (\nabla^2)^2 = \left(\frac{d^2}{dr^{*2}} + \frac{1}{r^*} \frac{d}{dr^*} - \frac{1}{r^{*2}} \right)^2. \quad [13a]$$

We assume the following: (a) the representative cylinder is non-conducting, (b) ion species achieve the equilibrium value at the virtual surface ($r = b$), (c) the fluid is moving at constant velocity U , and (d) the virtual surface is steady and satisfies Kuwabara's

model of zero vorticity. Therefore the boundary conditions associated with Eqs. [10]–[13] are

$$\frac{d\Phi_2}{dr^*} = 0 \quad \text{at } r^* = 1 \quad [13b]$$

$$\frac{d\Phi_2}{dr^*} = -E_x^* \quad \text{at } r^* = b/a \quad [13c]$$

$$\frac{dG_j}{dr^*} = 0 \quad \text{at } r^* = 1, j = 1, 2 \quad [13d]$$

$$G_j = -\Phi_2 \quad \text{at } r^* = b/a, j = 1, 2 \quad [13e]$$

$$\Omega = 0 \quad \text{and} \quad \frac{d\Omega}{dr^*} = 0 \quad \text{at } r^* = 1 \quad [13f]$$

$$L\Omega = 0 \quad \text{and} \quad \Omega = Ur^* \quad \text{at } r^* = b/a. \quad [13g]$$

In these expressions $L = \nabla^2$, $E_x^* = E_x a / \zeta_a$, and $U^* = U / U_E$, E_x and U being, respectively, the x component of the electric field and the bulk velocity of liquid. The choice of zero vorticity rather than zero shear stress at the cell boundary is based on the consideration that the former leads to Smoluchowski's result for an isolated charged fiber. The choice of the boundary condition expressed in Eq. [13c] is based on the assumption of Levine and Neale (1); that is, the local electric field is parallel to the external applied field at $r = b$. We have $-\nabla \phi_2 = \bar{E}_x$ or $-\nabla^* \phi_2^* = \bar{E}_x$. Therefore, $(\partial \phi_2^* / \partial r)_{r^*=b/a} = -E_x^* \cos \theta$. Since $\phi_2^* = \Phi_2 \cos \theta$ at $r^* = b/a$, Eq. [13c] is justified.

At steady state the sum of the x components of all the forces, including the electrical force F_{Ex} and the viscous force F_{Dx} , acting on a unit length of the representative cylinder vanishes. The former can be calculated by $F_{\text{Ex}} = \int_S \sigma (-\nabla \phi) dA$, and the latter can be evaluated by the method used in Kozak and Davis (8). It can be shown that

$$\begin{aligned} F_{\text{Ex}} &= \frac{2\varepsilon \zeta_a^2}{a} \int_0^\pi \left(\frac{\partial \phi^*}{\partial r^*} \right)_S \left(\frac{\partial \phi^*}{\partial r^*} \cos \theta - \frac{1}{r^*} \frac{\partial \phi^*}{\partial \theta} \sin \theta \right) r^* d\theta \\ &= \frac{\pi \varepsilon \zeta_a^2}{a} \left(\frac{d\phi_1^*}{dr^*} \right)_{r^*=1} (\Phi_2^*)_{r^*=1} \\ F_{\text{Dx}} &= 2 \int_0^\pi \left[-p \cos \theta + 2\mu \frac{\partial V_r}{\partial r} \cos \theta + \tau_{r\theta} \sin \theta \right]_{r=a} r d\theta \\ &= \frac{\pi \varepsilon \zeta_a^2}{a} \left[r^{*2} \frac{d^3 \Omega}{dr^{*3}} - 3 \frac{d\Omega}{dr^*} + \frac{3}{r^*} \Omega \right]_{r^*=1} \\ &\quad + \left[\frac{\pi \varepsilon \zeta_a^2}{a} \frac{(\kappa a)^2}{(1+\alpha)} r^* (n_1^* - n_2^*) \Phi_2 \right]_{r^*=1}. \end{aligned} \quad [14]$$

According to O'Brien and White (13), the present linear problem can be decomposed into two subproblems. In the first problem the fluid moves at a constant velocity U in the absence of the applied electric field, and in the second problem the fluid is fixed in the applied electric field. The force required to move the fluid in the first problem, f_1 , can be expressed as $f_1 = \delta U^*$, and that exerts on the fluid in the second problem, f_2 , as $f_2 = \beta E_x^*$.

That the net force vanishes implies that $U_0^* = U^*/E_x^* = -\beta/\delta$, U_0^* being the scaled electroosmotic velocity.

RESULTS AND DISCUSSIONS

Figure 2 shows the variation of the scaled electroosmotic velocity, U_0^* , as a function of κa at various scaled surface potential ϕ_r for the case $H = 0.75$. Double-layer polarization is neglected. The results of Ohshima (9) are also shown for comparison. As can be seen from Fig. 2, for fixed ϕ_r , U_0^* increases with κa . This is because for a fixed cylinder radius, the smaller the κa , the thicker the double layer, and, therefore, the more the electrical interaction between adjacent cylinders. For a fixed κa , U_0^* increases with ϕ_r as expected. Figure 2 also suggests that if the effect of double-layer polarization is neglected, that is, the result of Ohshima, using the linearized Poisson–Boltzmann equation will underestimate the electroosmotic velocity. The deviation becomes small, however, if κa is either very large or very small. If κa is very large, the result of Ohshima can be recovered from the present study; that is, if the double layer is thin, the effect of the double layer is insignificant, as expected. Also, although not shown in Fig. 2, $U_0^* \rightarrow 1$ as $\kappa a \rightarrow \infty$.

Figures 3 and 4 show the variation of scaled electroosmotic velocity U_0^* as a function of κa at various scaled surface potential ϕ_r for two levels of H ($= 1 - (a/b)^2$) for the case where double-layer polarization is considered. Also shown in these figures are the results based on Ohshima (9). Figures 3 and 4 reveal that if κa is either very small or very large, the result of Ohshima can be recovered by the present analysis. For an intermediate κa , depending upon the values of κa , H , and ϕ_r , the result of Ohshima may either underestimate or overestimate U_0^* . The deviation of the result of Ohshima from the present result is

FIG. 2. Variation of scaled electroosmotic velocity U_0^* as a function of κa at various scaled surface potential ϕ_r for the case $H = 0.75$. Double-layer polarization is neglected. Key: $a = 1$, $b = 2$, $\alpha = 1$, and $\text{Pe}_1 = \text{Pe}_2 = 0.1$. Dashed line, result of Ohshima (9); solid lines, present study.

FIG. 3. Variation of scaled electroosmotic velocity U_0^* as a function of κa at various scaled surface potential ϕ_r for the case $H = 0.75$. Double-layer polarization is considered. Key: same as that in Fig. 2.

the net result of two factors. As discussed in Fig. 2, using the linearized Poisson–Boltzmann equation will underestimate U_0^* . On the other hand, according to Kozak and Davis (8), the electric field induced by the representative cylinder has the effect of lessening the applied electric field. For fixed ϕ_r , the thinner the double layer, the greater the gradient of electrical potential, and the stronger the induced electric field. Therefore, if κa is large, the result of Ohshima will overestimate U_0^* , and the reverse is true if κa is small. Note that if ϕ_r is sufficiently high, there may exist a local maximum and a local minimum. A comparison between Figs. 3 and 4 shows that for a fixed κa , U_0^* increases with the increase in H . This is because the larger the H the higher the porosity of the fibrous medium and, therefore, the

FIG. 4. Variation of scaled electroosmotic velocity U_0^* as a function of κa at various scaled surface potential ϕ_r for the case $H = 0.408$. Double-layer polarization is considered. Key: same as that in Fig. 2, except $b = 1.3$.

FIG. 5. Variation of scaled electroosmotic velocity U_0^* as a function of ϕ_r at various H for the case $\kappa a = 1$, $\alpha = 1$, and $Pe_1 = Pe_2 = 0.1$.

smaller the interference between adjacent fibers and, therefore, the greater the U_0^* . Note that the larger the H the lower the level of κa required for the local extremals to occur.

Figure 5 illustrates the variation of scaled electroosmotic velocity U_0^* as a function of ϕ_r for fixed κa . This figure reveals that if H is sufficiently small, U_0^* has a local maximum as ϕ_r varies. We find that the value of H at which the local maximum exists decreases with κa .

The variations of scaled electroosmotic velocity U_0^* as a function of H at two different κa and two levels of ϕ_r are presented in Figs. 6 and 7. Also illustrated in these figures are the corresponding results based on the analysis of Ohshima (9). Figure 6 shows that for a fixed κa , U_0^* increases with H , and, for a fixed H , U_0^* increases with κa . The difference between the present

FIG. 6. Variation of scaled electroosmotic velocity U_0^* as a function of H at two different κa for the case $\phi_r = 1$. Key: same as that in Fig. 2.

FIG. 7. Variation of scaled electroosmotic velocity U_0^* as a function of H at two different κa for the case $\phi_r = 4$. Key: same as that in Fig. 2.

result and that of Ohshima is inappreciable at $\phi_r = 1$. The difference becomes appreciable, however, for a higher level of ϕ_r , as can be seen in Fig. 7. This figure also reveals that if κa is small, the effect of surface potential on the electroosmotic velocity is more significant than that of double-layer polarization. Also, the result of Ohshima will underestimate U_0^* . On the other hand, if κa is large, the reverse is true. For a high H and a medium κa , the effect of double-layer polarization on U_0^* is more significant than that of surface potential.

The variations of scaled electroosmotic velocity U_0^* as a function of κa for various H for two ϕ_r are shown in Figs. 8 and 9. The corresponding results based on the model of Ohshima (9) are also presented in the former for comparison. Again, if ϕ_r

FIG. 8. Variation of scaled electroosmotic velocity U_0^* as a function of κa for various H for the case $\phi_r = 1$. Key: $a = 1$, $b = 2$, $Pe_1 = Pe_2 = 0.1$, and $\alpha = 1$. Dashed lines are the results of Ohshima (9).

FIG. 9. Variation of scaled electroosmotic velocity U_0^* as a function of κa for various H for the case $\phi_r = 4$. Key: same as that in Fig. 8.

is small, the difference between the present model and that of Ohshima is insignificant, as illustrated in Fig. 8. On the other hand, if ϕ_r is sufficiently high, the variation of U_0^* as a function of κa may have local maximum and minimum, as can be seen in Fig. 9.

The major contribution of the present work can be summarized as follows. Levine and Neale (1–3) investigated both the electrophoretic and electroosmotic behaviors of a system containing multiple spheres. The result of Smoluchowski (14) was

extended to the case of an arbitrary thickness of double layer, but was limited to a low level of electrical potential. Kozak and Davis (8) used the linearized Poisson–Boltzmann equation and neglected double-layer polarization and overlapping, but the result obtained in the present analysis is applicable to an arbitrarily thick double layer. The integral representation for electroosmotic velocity in Kozak and Davis (8) was simplified by Ohshima (9), and an approximate analytical expression was derived. In the present study, the electrical potential can assume an arbitrary level, and the effects of double-layer polarization and the overlapping of adjacent double layers are taken into account.

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