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Electrophoresis of a Sphere along the Axis of a Cylindrical Pore: Effects of Double-Layer Polarization and Electroosmotic Flow

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The electrophoresis of a rigid sphere along the axis of a cylindrical pore is investigated theoretically. Previous analysis is extended to the case where the effects of double-layer polarization and electroosmotic flow can be significant. The influences of the surface potential, the thickness of the double layer, and the relative size of a pore on the electrophoretic behavior of a sphere are discussed. Some interesting results are observed. For example, if both a sphere and a pore are positively charged, then the mobility of the sphere has a local minimum as the thickness of its double layer varies. Depending upon the level of the surface potential of a sphere and the degree of significance of the boundary effect, the mobility of the sphere may change its sign twice as the thickness of its double layer varies. This result can play a significant role in electrophoresis measurements.

1. Introduction

Electrophoresis has many applications in various fields. It is not only adopted often to characterize the charged conditions of entities of colloidal size but also used widely in both conventional and modern operations. One of the key effects in conducting electrophoresis and electrophoresis-related operations is the presence of a boundary. Electrophoresis conducted in a narrow space such as capillary electrophoresis is a typical example of the former, and electrodeposition where charged particles are driven by an applied electric field toward electrodes is an example of the latter. The charged conditions on a boundary can make things even more complicated because the associated electroosmotic flow will influence not only the magnitude of the electrophoretic velocity of a particle but also its direction.

The boundary effect on electrophoresis has been studied extensively in the last few decades, and various types of problems have been investigated. These include the electrophoresis of a sphere parallel to a plate,1–4 along the axis of a cylindrical pore,5–6 positioned eccentrically in a cylindrical pore,5–9 through a converging-diverging pore,10 along the center line between two parallel plates,2,4 and in a spherical cavity.11–14 Although the presence of a boundary simply yields an extra viscous force on a particle arising from the nonslip condition on the boundary, the influences of other effects such as the level of surface potential, the thickness of the double layer, and the relative size of a pore on the boundary condition can be profound. For instance, if a boundary is charged, an electroosmotic flow is generated that will influence both qualitatively and quantitatively the electrophoretic behavior of a particle.2 The interaction between the double layer of a particle with a boundary can also lead to complicated results.6

In this study, previous analysis of the electrophoresis of a sphere along the axis of a cylindrical pore under the conditions of low surface potential and weak applied electric field6 is extended to the case of arbitrary surface potential and double-layer thickness. Also, the surface of a sphere and that of a pore can be charged. This implies that the effects of double-layer polarization and electroosmotic flow, both of practical significance,15–16 can be important and should be taken into account.
2. Theory

Let us consider the electrophoresis of a rigid sphere of radius \( a \) along the axis of a long cylindrical pore of radius \( b \) shown in Figure 1. The liquid phase is an incompressible Newtonian fluid with constant physical properties. The cylindrical coordinates \((r, \theta, z)\) are chosen with the origin located at the center of the sphere. A uniform electric field \( E \) is applied in the \( z \) direction, and \( U \) is the corresponding electrophoretic velocity of the sphere. The symmetric nature of the system under consideration suggests that only the \((r, z)\) domain has to be considered. For the present case, the electrical potential \( \phi \) can be described by the Poisson equation

\[
\nabla^2 \phi = -\frac{\rho}{\epsilon} = -\sum_j z_j e n_j \tag{1}
\]

Here, \( \nabla^2 \) is the Laplace operator, \( \epsilon \) is the permittivity of the liquid phase, \( \rho \) is the space charge density, \( e \) is the elementary charge, and \( n_j \) and \( z_j \) are the number concentration and the valence of ionic species \( j \), respectively. If we let \( D_j, k_B \), \( T \), and \( v \) be the diffusivity of ionic species \( j \), the Boltzmann constant, the absolute temperature, and the liquid velocity, respectively, then the conservation of ionic species at steady state leads to

\[
\nabla \cdot \left[ -D_j \left( \nabla n_j + \frac{z_j e}{k_B T} \nabla \phi \right) + n_j v \right] = 0 \tag{2}
\]

For convenience, \( \phi \) is decomposed into an equilibrium potential or the potential in the absence of \( E, \phi_1 \), and a perturbed potential.
arising from \(E, \phi_2\), that is, \(\phi = \phi_1 + \phi_2\). Also, \(n_j\) is expressed as

\[
n_j = n_0 \exp \left( - \frac{z_i e (\phi_1 + \phi_2 + g_j)}{k_B T} \right) \tag{3}
\]

where \(g_j\) is a perturbed potential that takes account of the deformation of the double layer surrounding a particle as it moves. Note that the form of eq 3 is assumed for convenience. Until now, \(g_j\) has been considered to be an arbitrary function. Under conditions of practical significance, the applied electric field is weak compared with that established by the sphere and/or by the cavity so that the expressions for the distortion of the double layer, the electric potential, and the flow field near the sphere can be linearized. For example, the scaled number concentrations of ions, \(n^*_1\) and \(n^*_2\), can be approximated respectively by

\[
n^*_1 = \exp(\phi_1 \phi_2^*)[1 - \phi_1 (\phi_2^* + g_1^*)] \tag{4}
\]

\[
n^*_2 = \exp(\alpha \phi_1 \phi_2^*)[1 + \alpha \phi_1 (\phi_2^* + g_2^*)] \tag{5}
\]

where \(n^*_j = n_j/n_{10}\), \(\phi_j^* = \phi_j/\zeta_1\), \(g_j^* = g_j/\zeta_2\), \(j = 1, 2\), \(\alpha = -z_j/\zeta_1\), \(\phi_1 = \zeta_1 e /k_B T\), and \(\zeta_1\) is the surface potential of the sphere. In scaled quantities, the equilibrium electrical potential can be described by

\[
\nabla^* \phi_1^* = -\frac{1}{(1 + \alpha)} \cdot \frac{(\kappa a)^2}{\phi_1^*} \cdot \left[ \exp(-\phi_1 \phi_2^*) - \exp(\alpha \phi_1 \phi_2^*) \right] \tag{6}
\]

where \(\nabla^* = \nabla^2 /\nu^2\) is the scaled Laplace operator and \(\kappa = (\sum_{j=1}^N n_{10} \langle z_j \rangle^2 /k_{B} T)^{1/2}\) is the reciprocal Debye length. It can be shown that eqs 1, 3, 4, 5, and 6 lead to

\[
\nabla^* \phi_1^* = -\frac{(\kappa a)^2}{(1 + \alpha)} \cdot \left[ \exp(-\phi_1 \phi_2^*) + \alpha \exp(\alpha \phi_1 \phi_2^*) \right] \phi_2^* = \frac{(\kappa a)^2}{(1 + \alpha)} \cdot \left[ \exp(-\phi_1 \phi_2^*) \right] g_1^* + \exp(\alpha \phi_1 \phi_2^*) \alpha g_2^* \tag{7}
\]

after neglecting terms involving products of small quantities such as \(g_1^*\), \(g_2^*\), and \(\phi_1^*\). Similarly, the variation of \(g_j^*\) can be approximated by employing eqs 3–5 to obtain

\[
\nabla^* \phi_1^* = \phi_1 \nabla^* \phi_2^* \nabla^* \phi_1^* = \phi_2^* P e \cdot \nabla^* \nabla^* \phi_1^* \tag{8}
\]

\[
\nabla^* \phi_2^* = \phi_1 \nabla^* \phi_2^* \nabla^* \phi_2^* = \phi_2^* P e \cdot \nabla^* \nabla^* \phi_1^* \tag{9}
\]

Here, \(\nabla^* = \nabla /\nu^2\) is the scaled gradient operator, \(\nu^2 = \nu /U_0\), \(U_0 = \zeta_1^2 \zeta_2 /\eta a\) is the magnitude of the velocity based on Smoluchowski’s theory when an electric field of strength \(\zeta_1 /a\) is applied, \(\eta\) is the viscosity of the liquid phase, and \(Pe = \zeta_1 (\zeta_2 /a) /\eta D\) for \(j = 1, 2\) is the electric Pecllet number of ionic species \(j\).

We assume that both the sphere and the pore are nonconductive, impermeable to ionic species, and remain at constant surface potential. Also, the concentrations of ionic species reach the bulk values at both the inlet and the outlet of a pore. These lead to the following boundary conditions:

\[
\phi_1^* \|_{r = 0} = \frac{\zeta_1}{\zeta_a} \quad \text{on the sphere surface} \tag{10}
\]

\[
\phi_2^* \|_{r = 0} = \frac{\zeta_2}{\zeta_a} \quad \text{on the pore surface} \tag{11}
\]

\[
\phi_1^* = \frac{\zeta_1}{\zeta_a} \int_{\zeta}^\infty \frac{J_1(kr)}{J_0(kr)} \quad \text{as} \quad r \to b \tag{12}
\]

\[
\mathbf{n} \cdot \nabla \phi_2^* = 0 \quad \text{on the sphere surface} \tag{13}
\]

\[
\mathbf{n} \cdot \nabla \phi_2^* = 0 \quad \text{on the pore surface} \tag{14}
\]

\[
\mathbf{n} \cdot \nabla g_2^* = -E_2^* \quad \text{as} \quad r \to b \tag{15}
\]

\[
\mathbf{n} \cdot \nabla g_j^* = 0 \quad \text{as} \quad r \to b \tag{16}
\]

\[
\mathbf{n} \cdot \nabla g_j^* = 0 \quad \text{as} \quad r \to b \tag{17}
\]

\[
g_j^* = -\phi_2^* \quad j = 1, 2 \quad \text{as} \quad r \to b \tag{18}
\]

In these expressions, \(E_1^* = E_1 /\zeta_1 /a\), \(J_0\) is the zeroth-order modified Bessel function of the first kind, and \(\zeta_a\) is the surface potential of the pore.

If we let \(p\) be the hydrodynamic pressure, then the flow field can be described by

\[
\nabla \cdot \mathbf{v} = 0 \tag{19}
\]

\[
-\nabla p + \eta \nabla^2 \mathbf{v} + \rho \nabla \phi = 0 \tag{20}
\]
These expressions can be rewritten in scaled forms as

\[ \nabla \cdot \mathbf{v}^* = 0 \]  
\[ -\nabla p^* + \nabla^2 \mathbf{v}^* + \nabla^2 \phi^* \nabla \phi^* = 0 \]  

where \( p^* = p / p_{ed} \) and \( p_{ed} = \varepsilon \xi^2 / \eta^2 \).

Assuming no-slip conditions on the surfaces of the sphere and the pore, the boundary conditions associated with eqs 21 and 22 can be expressed as

\[ \mathbf{v}^* = \left( \frac{v}{U_E} \right) \mathbf{e}_z \] on the sphere surface

\[ \mathbf{v}^* = 0 \] on the pore surface

These expressions can be rewritten in scaled forms as

\[ \nabla \cdot \mathbf{v}^* = 0 \]  
\[ -\nabla p^* + \nabla^2 \mathbf{v}^* + \nabla^2 \phi^* \nabla \phi^* = 0 \]  

Here, \( v \) is the speed of the sphere in the \( z \) direction, and \( \mathbf{e}_z \) is the unit vector in the \( z \) direction. Equation 25 describes the scaled undisturbed electroosmotic velocity profile for a charged cylindrical pore in the absence of the sphere.6

The problem under consideration is decomposed into two subproblems.18 In the first subproblem, a sphere moves with a constant velocity in the absence of \( \mathbf{E} \), and in the second subproblem, a sphere is fixed in space when \( \mathbf{E} \) is applied. The total forces acting on a sphere in these two subproblems,
In our case, the force acting on a sphere in subproblem i, \( F_i \), comprises the electrical force \( F_e \) and the hydrodynamic force \( F_d \). Let \( F_{z1} \), \( F_{z2} \), and \( F_{z3} \) be the \( z \) components of \( F \), \( F_e \), and \( F_d \) in subproblem \( i \), respectively. Then

\[
F_{zi} = F_{z1} + F_{z2} = F_i \quad i = 1, 2
\]

The axisymmetric nature of the present problem suggests that only the \( z \) components of these forces need to be considered. The electrostatic force in the \( z \) direction, \( F_{z1} \), can be calculated by integrating the Maxwell stress tensor over the particle surface,

\[
F_{z1} = \int_S (\sigma^S \cdot \mathbf{n}) \mathbf{e}_z \, dS
\]

Here, \( S \) denotes the surface of a sphere, \( \mathbf{E} = -\nabla \phi \), and \( \sigma^S \equiv \epsilon (\mathbf{E} \cdot \mathbf{E}) - (1/2) \mathbf{E} \mathbf{E}^T \) is the Maxwell stress tensor. It can be shown that this expression leads to

\[
F^*_e = \frac{F_{z1}}{\epsilon_o a^2} = \int_S \frac{\partial \phi^{s1}}{\partial n} \frac{\partial \phi^{s2}}{\partial \zeta} \, dS^*
\]

where \( F^*_e \) and \( S^* \) are the scaled form of \( F_{z1} \) and \( S \), respectively (Appendix). In our case, the hydrodynamic force acting on a sphere in the \( z \) direction, \( F_{z2} \), comprises the viscous force and the pressure and can be evaluated by

\[
F_{z2} = \int_S (\sigma^H \cdot \mathbf{n}) \mathbf{e}_z \, dS
\]

where \( \sigma^H = -p I + \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \). This expression can be rewritten in terms of scaled symbols as

\[
F^*_{z2} = \frac{F_{z2}}{\epsilon_o a^2} = \int_S (\sigma^H \cdot \mathbf{n}) \mathbf{e}_z \, dS^*
\]

where \( F^*_{z2} \) is the scaled form of \( F_{z2} \).

The governing equations and the associated boundary conditions are solved numerically by FlexPDE,

\[
\text{version 2.22; PDE Solutions Inc.: Sunol, CA.}
\]

\[\text{Figure 6. Variation of the scaled electrophoretic mobility } \mu_E \text{ (defined in eq 28) as a function of } \lambda (=a/b) \text{ at various levels of } \phi_i (=\zeta_0 e_{el} k_B T) \text{ for the case when } \zeta_0^* = 0 \text{ and } \kappa a = 1. \]

\text{pore, and a positively charged sphere is placed in a positively charged pore.}

\section{Results and Discussion}

The influences of the key parameters of the system under consideration on the electrophoretic behaviors of a sphere are examined through numerical simulation. For illustration, we assume that \( a = 100 \text{ nm} \) and \( T = 298 \text{ K} \). For an aqueous solution of a common electrolyte such as KCl, we have \( D_e = 2 \times 10^{-9} \text{ m}^2/\text{s} \), \( \epsilon = 8.854 \times 10^{-12} \times 78.54688 \text{ F/m} \), \( \eta = 1 \text{ cP} \), and \( \alpha = 1 \). These lead to \( Pe_1 = Pe_2 = 0.1 \). Also, we assume that a pore is sufficiently long so that the end effects of the flow field can be neglected. To make sure that this is appropriate, the transition length of a pore \( L_{tc} \), the shortest length to achieve fully developed electroosmotic flow, is estimated under conditions of interest. The estimation of \( L_{tc} \) is based on the criteria proposed by Hsu and Ku.\textsuperscript{2} Figure 2a illustrates the variation of the scaled transition length of a pore (\( L_D/a \)) as a function of \( \kappa a \) for the case when both a sphere and a pore are positively charged, and that as a function of \( \lambda (=a/b) \) is shown in Figure 2b. According to this Figure, assuming a pore length on the order of 10\( a \) is sufficient to assuming a fully developed flow field.

\subsection{Positively Charged Sphere in an Uncharged Pore}

Let us first consider the case when a positively charged sphere is placed in an uncharged pore. The influence of the surface potential of a sphere on its mobility \( \mu_E \) at various levels of double-layer thickness, measured by \( \kappa a \), and the boundary effect, measured by \( \lambda (=a/b) \), is illustrated in Figure 3. Here, the value of \( \epsilon \) is fixed, and that of \( \kappa \) varies, that is, we fix the radius of a sphere and let the concentration of electrolytes vary. In general, for a fixed value of \( \kappa a \), the higher the surface potential, the smaller the mobility; the more important the boundary effect \( \lambda \), the smaller the mobility. The latter is expected because the presence of the pore wall has the effect of retarding the movement of a sphere. The former can be explained by the effect of double-layer polarization, which induces an internal electric field, the direction of which is opposite that of the applied electric field. Because the strength of the induced electric field increases with the increase in the surface potential of a sphere, \( \mu_E \) decreases with the increase in the scaled surface potential of a sphere \( \phi_i \). Figure 3 also indicates that for a low to medium value of \( \phi_i \), \( \mu_E \) increases with the increase in \( \kappa a \), and if \( \phi_i \) is sufficiently high, then \( \mu_E \) has a local minimum as \( \kappa a \) varies. Similar phenomena were also observed by Wiersema\textsuperscript{17} and O’Brien\textsuperscript{18} for the electrophoresis of an isolated
sphere in an infinite fluid and by Lee et al.\textsuperscript{13} for the electrophoresis of a sphere in a spherical cavity. Note that if $a$ is sufficiently small then $\zeta$ becomes independent of $r$.

Figure 4 shows the variations of $\beta$ and $F_{e}^{*}$ as a function of the double-layer thickness measured by $ka$ for the case presented in Figure 3 at $\lambda = 0.5$. According to the definitions, $\beta$ and $F_{e}^{*}$ are measures of the net driving force and the electric force acting on a sphere in the $z$ direction in the second subproblem, respectively. As can be seen in Figure 4, the qualitative trends in both $\beta$ and $F_{e}^{*}$ are the same as that of the mobility illustrated in Figure 3.

Figure 5 illustrates the contours for the net scaled ionic concentration $CD$ ($= n_{1}^{*} - n_{2}^{*}$) on semiplane $\theta = \pi/2$ for two levels of the scaled surface potential of a sphere $\phi_{i}$. This Figure reveals that if $\phi_{i}$ is low then the contours are essentially symmetric around a sphere, implying that double-layer polarization is insignificant. On the other hand, if $\phi_{i}$ is sufficiently high, then it becomes significant. For the present case, a sphere moves upward, and the concentration of anions (counterions) near its bottom is higher than that near its top. An internal electric field is induced, the direction of which is opposite to that of the applied electric field.

The boundary effect on the mobility of a sphere for the case presented in Figure 3 at $ka = 1$ is summarized in Figure 6. As mentioned previously, the more important the boundary effect, the smaller the mobility. Note that the influence of the boundary effect is threefold: the squeezing of the applied electric field between a sphere and a pore, the increase in the surface charge of a sphere due to double-layer deformation, and the increase in the viscous drag on a sphere.

### 3.2. Both the Sphere and Pore are Positively Charged.

Consider next the case when a positively charged sphere is placed in a positively charged pore. Figure 7 shows the variation of the mobility $\mu_{E}$ as a function of the double-layer thickness measured by $ka$ at various combinations of the scaled surface potential of a sphere $\phi_{i}$ and the boundary effect measured by $\lambda (= a/b)$, and the corresponding variations of the net driving force measured by $\beta$ and the scaled electric force $F_{e}^{*}$, for the case in which $\lambda = 0.7$. A comparison between Figures 3 and 7 reveals that the mobility in the former is larger than that in the latter. This is because the direction of electroosmotic flow arising from the charged pore...
the increases in the surface potential. In general, the presence of numerical simulation can be summarized as follows. For a fixed double-layer thickness, the mobility decreases with the thickness of its double layer varies, which is a result of practical significance, for example, when capillary electrophoresis is chosen as a separation tool. In this case, the separation efficiency depends largely upon the bulk concentration of electrolytes.

**Appendix: Derivation of Equation 31**

For convenience, eq 30 is written as

$$
F_{sc} = \int \int_S \left( \sigma E \cdot n \right) \epsilon_z \, dS
$$

(A1)

where \( \sigma E \equiv \epsilon (EE - (1/2) E^2 I) \) and \( E = -\nabla \phi = n (\partial \phi / \partial n) + t (\partial \phi / \partial t) \). Here, \( I \) is the unit tensor, \( t \) is the unit tangential vector on the particle surface, \( n \) and \( t \) are the magnitudes of \( n \) and \( t \), respectively, and \( E^2 = E \cdot E \). Substituting \( \sigma E \) into eq A1 yields

$$
F_{sc} = \int \int_S \left( \frac{\partial \phi}{\partial n} \frac{\partial \phi}{\partial z} - \frac{1}{2} \epsilon \left[ \left( \frac{\partial \phi}{\partial n} \right)^2 + \left( \frac{\partial \phi}{\partial t} \right)^2 \right] n_z \right) dS
$$

(A2)

where \( n_z \) is the \( z \) component of \( n \). Because \( \phi = \phi_1 + \phi_2 \), eq A2 becomes, after eliminating some minor terms,

$$
F_{sc} = \int \int_S \left( \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_2}{\partial z} + \frac{\partial \phi_2}{\partial n} \frac{\partial \phi_1}{\partial z} - \epsilon \left[ \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_2}{\partial t} + \frac{\partial \phi_1}{\partial t} \frac{\partial \phi_2}{\partial n} \right] n_z \right) dS
$$

(A3)

For the present case, because the sphere is nonconducting,

$$
\int \int_S \left( \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_2}{\partial z} - \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_2}{\partial n} n_z \right) dS
$$

vanishes, and eq A3 reduces to

$$
F_{sc} = \int \int_S \left( \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_2}{\partial z} - \epsilon \left[ \frac{\partial \phi_1}{\partial t} \frac{\partial \phi_2}{\partial n} \right] n_z \right) dS
$$

(A4)

If the surface of a particle is maintained at a constant potential, then \( \partial \phi / \partial t = 0 \), and this expression can be further simplified to

$$
F_{sc} = \int \int_S \frac{\partial \phi_1}{\partial n} \frac{\partial \phi_2}{\partial z} dS
$$

(A5)

Rewriting this equation with scaled symbols leads to eq 31 in the text.

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