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Effect of charged boundary on electrophoresis: Sphere in spherical cavity at arbitrary potential and double-layer thickness

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Abstract

The boundary effect on electrophoresis is investigated by considering a spherical particle at an arbitrary position in a spherical cavity. Our previous analysis is extended to the case where the effect of double-layer polarization can be significant. Also, the effect of a charged boundary, which yields an electroosmotic flow and a pressure gradient, thereby making the problem under consideration more complicated, is investigated. The influences of the level of the surface potential, the thickness of double layer, the relative size of a sphere, and its position in a cavity on the electrophoretic behavior of the sphere are discussed. Some results that are of practical significance are observed. For example, if a positively charged sphere is placed in an uncharged cavity, its mobility may have a local minimum as the thickness of the double layer varies. If an uncharged sphere is placed in a positively charged cavity, the mobility may have a local minimum as the position of the sphere varies. Also, if the size of a sphere is fixed, its mobility may have a local minimum as the size of a cavity varies. These provide useful information for the design of an electrophoresis apparatus.

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Keywords: Electrophoresis; Boundary effect; Electroosmotic flow; Sphere in spherical cavity; Double-layer polarization

1. Introduction

Electrophoresis is one of the most important analytical tools in various fields such as colloidal, biological, biomedical, and biochemical sciences [1,2], to name a few. It is also a basic technique for the separation/processing of particles of colloidal size in practice. Recent research and development in biochip technology and electrokinetic phenomena in microchannels are also related closely to electrophoresis. In these cases, the effect of the presence of a boundary on the electrophoretic behavior of a particle becomes important and the classical result, which is based on an isolated particle in an infinite fluid, needs be modified accordingly. A considerable amount of work has been devoted to the analysis of boundary effects of various types [3–18]. Among these, a rigid sphere at the center of a spherical cavity, considered by Zydney [6] and Lee et al. [7,8], is a representative one. Although this geometry is of a one-dimensional nature, thereby considerably simplifying relevant mathematical treatments, the key influence of the presence of a boundary on the electrophoretic behavior of an entity can be taken into account. However, because the cavity surface was assumed to be uncharged in these studies, the effect of electroosmosis, an effect of practical significance, was neglected.

In a previous study, Hsu et al. [9] considered the electrophoresis of a rigid sphere at an arbitrary position in a spherical cavity under conditions of weak applied electric field and low surface potential, where the effect of double-layer polarization, an effect of fundamental significance, can be neglected. The same problem was also analyzed by Hsu et al. [10] for the case in which the cavity surface can be charged. In the present study, these analyses are further extended to the case of arbitrary surface potential and double-layer thickness; that is, the effect of double-layer polarization can be significant. Here, both the surface of a sphere and that of a cavity can be charged; that is, the effect of the electroosmotic flow arising from the presence of the latter is taken into account.

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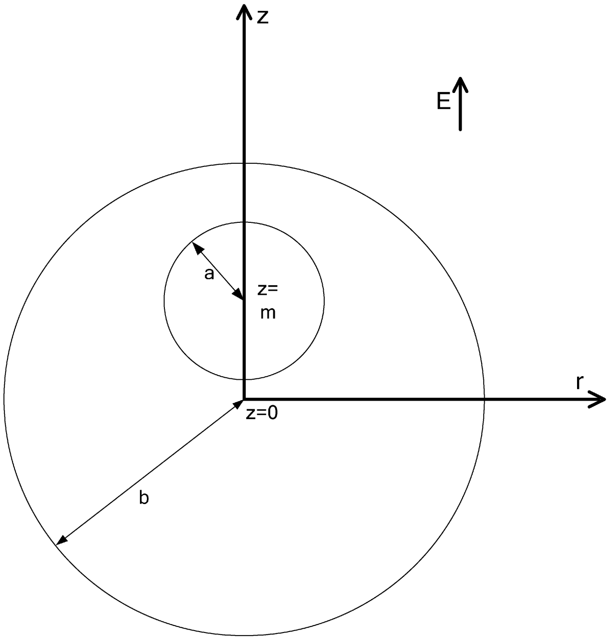

Fig. 1. Schematic representation of the problem where a sphere of radius a is placed in a spherical cavity of radius b. An electric field $\mathbf{E}$ parallel to the z-axis is applied. The center of the particle is at $z = m$ and that of the cavity at $z = 0$.

2. Theory

The problem under consideration is illustrated in Fig. 1, where a nonconducting sphere of radius a is placed at an arbitrary position in a spherical cavity of radius b. Let ζ_a and ζ_b be respectively the surface potential of the sphere and that of the cavity. Spherical coordinates (r, θ, φ) are adopted, with the origin located at the center of the cavity. The center of the particle is at $z = m$, and that of the cavity at $z = 0$. A uniform electric field $\mathbf{E}$ in the z-direction is applied. The cavity is filled with an aqueous Newtonian fluid containing z_1:z_2 electrolyte; z_1 and z_2 are respectively the valence of cations and that of anions, with $\alpha = -z_2/z_1$. Let ε be the permittivity of the liquid phase, ρ the space charge density, e the elementary charge, n_j and D_j the number concentration and the diffusivity of ionic species j respectively, k_B and T the Boltzmann constant and the absolute temperature respectively, ϕ the electrical potential, and $\mathbf{v}$, η, and p be the velocity, the viscosity, and the pressure of the liquid phase respectively. Then the phenomenon under consideration can be described by

$$\nabla^2\phi = -\frac{\rho}{\varepsilon} = -\sum_{j=1}^{2}\frac{z_j e n_j}{\varepsilon}, \tag{1}$$

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

$$\nabla \cdot \mathbf{v} = 0, \tag{3}$$

$$-\nabla p + \eta\nabla^2\mathbf{v} + \rho\nabla\phi = \mathbf{0}, \tag{4}$$

where ∇^2 and ∇ are respectively the Laplace operator and the gradient operator.

Following the treatment of O'Brien and White [19], we let $\phi = \phi_1 + \phi_2$, where ϕ_1 and ϕ_2 are respectively the equilibrium potential or the potential in the absence of $\mathbf{E}$ and a perturbed potential arising from $\mathbf{E}$. Also,

$$n_j = n_{j0}\exp\left(-\frac{z_j e(\phi_1 + \phi_2 + g_j)}{k_B T}\right), \tag{5}$$

where g_j is a perturbed potential that simulates the deformation of the double layer.

Suppose that the applied electric field is weak compared with that established by the sphere and/or the cavity. Then the expressions for the distortion of the double layer, the electrical potential, and the flow field near a sphere can be linearized. Using Eqs. (1), (2), and (5) and the relation $\phi = \phi_1 + \phi_2$ and neglecting terms involving the product of two perturbed terms, it can be shown that the concentration and the electric fields can be described by

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

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

$$\nabla^{*2}g_1^* - \phi_r\nabla^*\phi_1^* \cdot \nabla^* g_1^* = \phi_r^2\,\mathrm{Pe}_1\,\mathbf{v}^* \cdot \nabla^*\phi_1^*, \tag{8}$$

$$\nabla^{*2}g_2^* + \alpha\phi_r\nabla^*\phi_1^* \cdot \nabla^* g_2^* = \phi_r^2\,\mathrm{Pe}_2\,\mathbf{v}^* \cdot \nabla^*\phi_1^* \tag{9}$$

$$n_1^* = \exp\left(\phi_r\phi_1^*\right)\left[1 - \phi_r\left(\phi_2^* + g_1^*\right)\right], \tag{10}$$

$$n_2^* = \exp\left(\alpha\phi_r\phi_1^*\right)\left[1 + \alpha\phi_r\left(\phi_2^* + g_2^*\right)\right]. \tag{11}$$

In these expressions, $\nabla^* = a\nabla$ is the scaled gradient operator, $\nabla^{*2} = a^2\nabla^2$ is the scaled Laplace operator, and $\phi_r = \zeta_k z_1 e/k_B T$ is the scaled surface potential, where $\zeta_k = \zeta_a$ if $\zeta_a \neq 0$, and $\zeta_k = \zeta_b$ if $\zeta_a = 0$. $n_j^* = n_j/n_{10}$, $\phi_j^* = \phi_j/\zeta_k$, $\mathrm{Pe}_j = \varepsilon(z_j e/k_B T)^2/\eta D_j$, which is the electrical Péclet number of ion species j, and $g_j^* = g_j/\zeta_k$, $j = 1, 2$; $\kappa = [\sum_{j=1}^{2} n_{j0}(ez_j)^2/\varepsilon k_B T]^{1/2}$ is the reciprocal Debye length; $\mathbf{v}^* = \mathbf{v}/U_E$; and $U_E = (\varepsilon\zeta_k^2/\eta a)$ is the magnitude of the velocity of the particle predicted by the Smoluchowski theory when an electric field of strength (ζ_k/a) is applied.

In terms of the scaled symbols, the flow field can be described by

$$\nabla \cdot \mathbf{v}^* = 0, \tag{12}$$

$$-\nabla p^* + \eta\nabla^2\mathbf{v}^* + \nabla^2\phi^*\nabla\phi^* = 0, \tag{13}$$

where $p^* = p/p_{\mathrm{ref}}$ and $\mathrm{p}_{\mathrm{ref}} = \varepsilon\zeta_k^2/a^2$.

Suppose that both the sphere and the cavity surface are nonconductive, nonslip, and impermeable to ionic species, and the concentration of ionic species reaches the bulk value on the cavity surface. Then the boundary conditions associated with Eqs. (6)–(9) and (12)–(13) can be expressed as

$$\phi_1^* = \zeta_a/\zeta_k \quad \text{on the sphere surface}, \tag{14}$$

$$\phi_1^* = \zeta_b/\zeta_k \quad \text{on the cavity surface}, \tag{15}$$

$$\mathbf{n} \cdot \nabla^*\phi_2^* = 0 \quad \text{on the sphere surface}, \tag{16}$$

$$\mathbf{n} \cdot \nabla^*\phi_2^* = -E_z^*\cos\theta \quad \text{on the cavity surface}, \tag{17}$$

$$\mathbf{n} \cdot \nabla^* g_j^* = 0, \quad j = 1, 2 \quad \text{on the sphere surface}, \tag{18}$$

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