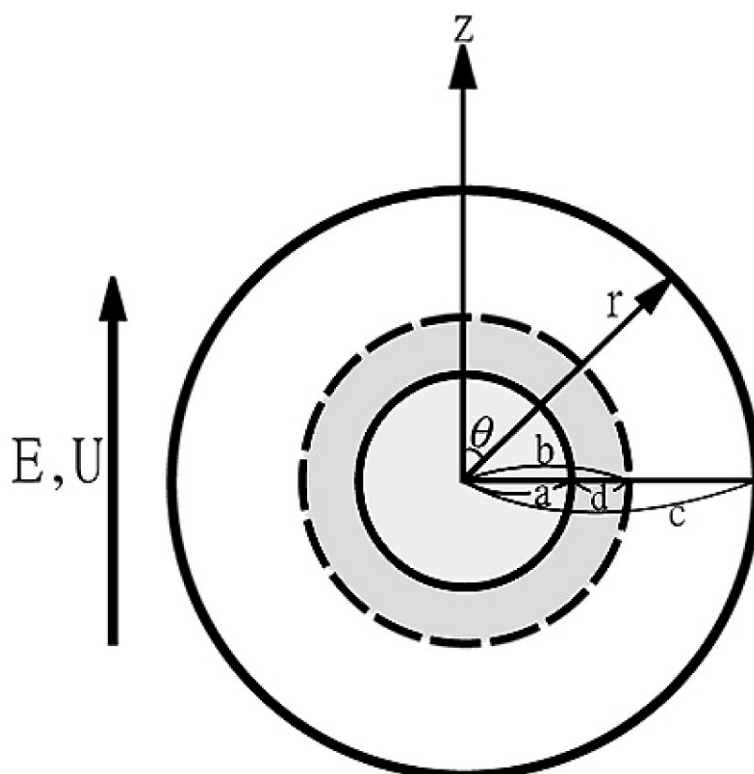


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# Electrophoresis of a Membrane-Coated Sphere in a Spherical Cavity

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The boundary effect on the electrophoresis of particles covered by a membrane layer is discussed by considering a spherical particle in a spherical cavity under the conditions where the effect of double-layer polarization can be significant. The influence of the key parameters of the system under consideration on the electrophoretic mobility of a particle is investigated. These include the surface potential; the thickness of the double layer; the relative size of the cavity; and the thickness, the fixed charge density, and the friction coefficient of the membrane layer. The fixed charge in the membrane layer of a particle is found to have a significant influence on its electrophoretic behavior. For instance, depending upon the amount of fixed charge in the membrane layer, the mobility of a particle may exhibit a local minimum as the thickness of the double layer varies.

## Introduction

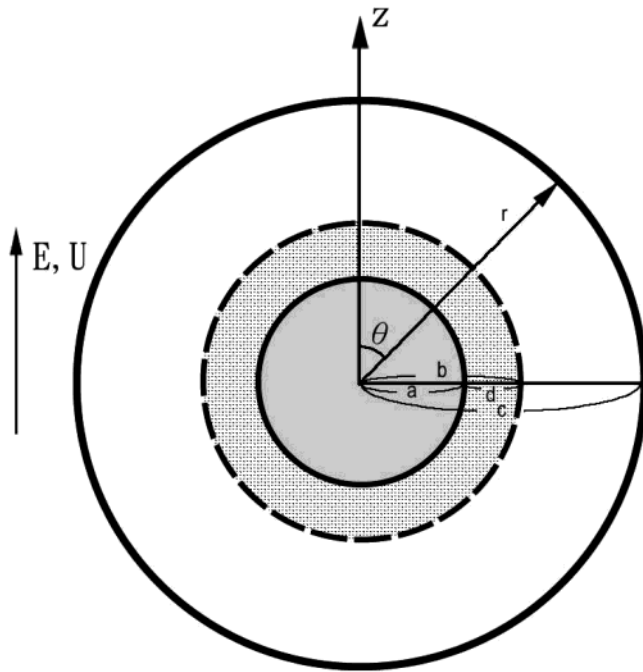
Electrophoresis has been applied widely to estimate the surface properties of charged entities and in various separation processes. Its fundamental and practical significances have drawn the attention of researchers in many fields since the last century, and it has been studied extensively, both theoretically and experimentally. von Smoluchowski,<sup>1</sup> for example, was able to derive an analytic expression for the electrophoretic mobility of a rigid particle. Although it is based on drastic assumptions such as low surface potential, weak applied electric field, and a thin double layer, the result of von Smoluchowski is concise and has been used widely to elaborate experimental observations. The analysis of von Smoluchowski was extended by many investigators to take account of more general conditions.<sup>2–4</sup> In addition to the electrophoresis of rigid particles, that of porous particles such as polyelectrolytes and particles comprising a rigid core and an ion-penetrable membrane or polymer layer, the so-called soft or fuzzy particles,<sup>5–9</sup> has also been studied. The former can be viewed as a limiting case of the latter by letting the size of the rigid core vanish. The presence of a membrane layer on the surface of a particle can have an appreciable influence on its electrophoretic behavior. The density of the ionic cloud of counterions near the rigid core of a particle can increase appreciably because of the presence of a membrane layer, even if it is thin. From the

hydrodynamic point of view, because the presence of an uncharged membrane layer yields an extra drag, the movement of a particle is slowed. However, the influence of the membrane layer can be profound if it is charged. The problem becomes even more complicated when the surface potential is high, when the effect of double-layer polarization can be significant.<sup>10,11</sup> Solving the electrophoresis of a soft particle can be nontrivial because the governing equations in the membrane layer and those in the liquid phase must be solved simultaneously. In general, an appropriate numerical scheme is necessary so that the problem can be solved efficiently and accurately. Ohshima<sup>12</sup> solved analytically the electrophoresis of a soft particle under the conditions that the effect of double-layer polarization is negligible. Hill et al.<sup>10</sup> and Saville<sup>11</sup> pointed out, however, that this effect cannot be ignored when the surface potential is not low. In practice, electrophoresis is often conducted under situations where the presence of a boundary can be important. A typical example includes the electrophoresis performed in a porous medium to avoid possible natural convection. In separation through electrophoresis, microporous gels or membranes are designed to have a strong enough electric field so that separation efficiency can be raised.<sup>13</sup> Apparently, the boundary effect can play a role in these cases. While theoretical analyses relevant to the boundary effect on electrophoresis are ample in the literature, many of them are limited to the case of infinitely thin double layers.<sup>14,15</sup> Zydny<sup>16</sup> analyzed the electrophoresis of a rigid sphere at the center of a spherical cavity for the case of low electric potential and finite double-layer thickness. Although this geometry is an idealized one, it is capable

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**Figure 1.** Schematic representation of the problem considered where a hard sphere of radius  $a$  coated with a membrane layer of thickness  $d$  is placed at the center of a spherical cavity of radius  $c$ .  $\mathbf{E}$  is the applied electric field, and  $\mathbf{U}$  is the electrophoretic velocity of the particle. The spherical coordinates  $(r, \theta, \varphi)$  are adopted with its origin located at the center of the particle.

of providing insight about the boundary effect on electrophoresis. The analysis of Zydney<sup>16</sup> was extended by Lee et al.<sup>17</sup> to the case of arbitrary surface potential and when double-layer polarization can be significant. The latter was further extended by Chu et al.<sup>18</sup> to the case of an arbitrary level of applied electric field.

In this study, the boundary effect on electrophoresis is investigated for the case of soft particles under conditions where the effect of double-layer polarization can be significant. The sphere-in-spherical-cavity geometry of Zydney<sup>16</sup> is adopted, and the influences of the key parameters, including the thickness of the double layer, the relative size of the cavity, and the thickness, the fixed charge density, and the friction coefficient of the membrane layer, on the electrophoretic behavior of a particle are examined.

### Theory

The problem under consideration is illustrated in Figure 1, where a spherical particle comprises a rigid core of radius  $a$  and a membrane layer of thickness  $d$  is placed at the center of a spherical cavity of radius  $c$ . Let  $b = a + d$ . The cavity is filled with an aqueous solution containing  $z_1:z_2$  electrolyte, where  $z_1$  and  $z_2$  are respectively the valence of cations and that of anions. An electric field  $\mathbf{E}$  in the positive  $z$  direction is applied, and  $\mathbf{U}$  is the electrophoretic velocity of the particle. The spherical coordinates  $(r, \theta, \varphi)$  are adopted with its origin located at the center of the particle.

The electric field of the system under consideration  $\phi$  can be described by the Poisson equation

$$\nabla^2 \phi = -\frac{\rho + i\rho_{\text{fix}}}{\epsilon} \quad (1)$$

$\rho = \sum_j n_j z_j e$  is the spatial variation of mobile ions,  $\rho_{\text{fix}}$  is the fix charge density in the membrane layer,  $\epsilon$  is the permittivity of the liquid phase,  $n_j$  and  $z_j$  are respectively the number concentration and the valence of ionic species  $j$ , and  $i = 1$  for  $a < r < b$  and  $i = 0$  for  $b < r < c$ . For convenience,  $\phi$  is decomposed into the electrical potential in the absence of  $\mathbf{E}$  or the equilibrium potential  $\phi_1$  and a potential which arises from the applied electric field,  $\phi_2$ , that is,  $\phi = \phi_1 + \phi_2$ . If the effect of double-layer polarization is significant, the double layer surrounding the particle is no longer spherically symmetric. To account for this effect, the spatial distribution of mobile ions is expressed as<sup>2</sup>

$$\rho = \sum_j z_j e n_{j0} \exp\left[-\frac{z_j e (\phi_1 + \phi_2 + g_j)}{k_B T}\right] \quad (2)$$

where  $g_j$  represents a perturbed potential, which accounts for the effect of fluid flow on the concentration of mobile ions,  $n_{j0}$  is the bulk concentration of ionic species  $j$ ,  $e$  is the elementary charge,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. The equilibrium potential can be described by

$$\nabla^2 \phi_1 = -\sum_{j=1}^2 \frac{z_j e n_{j0}}{\epsilon} \exp\left(-\frac{z_j e \phi_1}{k_B T}\right) - \frac{i\rho_{\text{fix}}}{\epsilon} \quad (3)$$

where  $i = 1$  for  $a < r < b$  and  $i = 0$  for  $b < r < c$ . Suppose that the surface of the rigid core of a particle ( $r = a$ ) remains at a constant potential, both the electrical potential and the electric field are continuous on the ion-penetrable layer-liquid interface ( $r = b$ ), and the cavity wall ( $r = c$ ) is held to be uncharged. Therefore, the boundary conditions for the equilibrium potential  $\phi_1$  are

$$\phi_1 = \zeta_a, \quad r = a \quad (4)$$

$$\phi_1|_{r=b^-} = \phi_1|_{r=b^+}, \quad r = b \quad (5)$$

$$\frac{\partial \phi_1}{\partial r}\bigg|_{r=b^-} = \frac{\partial \phi_1}{\partial r}\bigg|_{r=b^+}, \quad r = b \quad (6)$$

$$\phi_1 = 0, \quad r = c \quad (7)$$

The governing equation for  $\phi_2$  can be obtained by eq 3 and  $\phi = \phi_1 + \phi_2$  as

$$\begin{aligned} \nabla^2 \phi_2 &= \nabla^2 \phi - \nabla^2 \phi_1 \\ &= -\sum_{j=1}^2 \frac{z_j e n_{j0}}{\epsilon} \left[ \exp\left(-\frac{z_j e (\phi_1 + \phi_2 + g_j)}{k_B T}\right) - \exp\left(-\frac{z_j e \phi_1}{k_B T}\right) \right] \end{aligned} \quad (8)$$

The following boundary conditions are assumed for  $\phi_2$ :

$$\frac{\partial \phi_2}{\partial r} = 0, \quad r = a \quad (9)$$

$$\phi_2|_{r=b^-} = \phi_2|_{r=b^+}, \quad r = b \quad (10)$$

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$$\left. \frac{\partial \phi_2}{\partial r} \right|_{r=b^-} = \left. \frac{\partial \phi_2}{\partial r} \right|_{r=b^+}, \quad r = b \quad (11)$$

$$\frac{\partial \phi_2}{\partial r} = -E_z \cos \theta, \quad r = c \quad (12)$$

The first condition arises from that the rigid core of a particle is nonconductive and is impermeable to ionic species. The last condition implies that  $\phi_2$  is assumed to reach the applied electric field.

At steady state, the conservation of ionic species yields

$$\nabla^2 n_j + \frac{z_j e}{k_B T} (\nabla n_j \cdot \nabla \phi + n_j \nabla^2 \phi) - \frac{1}{D_j} \mathbf{v} \cdot \nabla n_j = 0 \quad (13)$$

where  $D_j$  is the diffusivity of ionic species  $j$ . In terms of  $g_j$ , we have

$$\begin{aligned} \nabla^2 g_j - \frac{z_j e}{k_B T} \nabla \phi_1 \cdot \nabla g_j = \frac{1}{D_j} \mathbf{v} \cdot \nabla g_j + \frac{1}{D_j} \mathbf{v} \cdot \nabla g_j + \\ \frac{z_j e}{k_B T} \nabla \phi_2 \cdot \nabla g_j + \frac{z_j e}{k_B T} \nabla g_j \cdot \nabla g_j \end{aligned} \quad (14)$$

We assume that the surface of the rigid core of a particle is impermeable to ions, both the concentration of ionic species and its flux are continuous on the ion-penetrable membrane layer–liquid interface, and the concentration of ionic species reaches the equilibrium value on the cavity wall. Therefore, the boundary conditions for the concentration field are

$$\mathbf{f}_j \cdot \hat{\mathbf{n}} = \mathbf{f}_j \cdot \delta_r = 0, \quad r = a \quad (15)$$

$$n_j|_{r=b^-} = n_j|_{r=b^+}, \quad r = b \quad (16)$$

$$\mathbf{f}_j|_{r=b^-} = \mathbf{f}_j|_{r=b^+}, \quad r = b \quad (17)$$

$$n_j = n_{j0}, \quad r = c \quad (18)$$

In these expressions,  $\hat{\mathbf{n}}$  is the unit normal vector,  $\delta_r$  is the unit vector in the  $r$  direction, and  $\mathbf{f}_j$  is the flux of ionic species  $j$  defined by

$$\mathbf{f}_j = -D_j \left[ \nabla n_j + \frac{z_j e n_j}{k_B T} \nabla \phi \right] + n_j \mathbf{v} \quad (19)$$

We assume that the flow field can be described by the Navier–Stokes equation in the creeping flow regime. In terms of the stream function  $\psi$ , it can be shown that the governing equation for the flow field is

$$\eta \mathbf{E}^4 \psi - i\gamma \mathbf{E}^2 \psi = -\nabla \times [\rho \nabla (\phi_1 + \phi_2)] \sin \theta \quad (20)$$

where  $i = 1$  for  $a < r < b$  and  $i = 0$  for  $b < r < c$  and  $\gamma$  is the frictional coefficient of the membrane layer.  $\mathbf{E}^4 = \mathbf{E}^2 \mathbf{E}^2$ , with

$$\mathbf{E}^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) \quad (21)$$

In terms of  $\psi$ , the  $r$  and the  $\theta$  components of  $\mathbf{v}$ ,  $v_r$  and  $v_\theta$ , can be expressed respectively as  $v_r = -(1/r^2 \sin \theta) (\partial \psi / \partial \theta)$  and  $v_\theta = (1/r \sin \theta) (\partial \psi / \partial r)$ . We assume that both the surface of the rigid core of a particle and that of a cavity are nonslip. Also, the velocity of liquid and both its normal and tangential stresses are continuous on the membrane

layer–liquid interface. These assumptions lead to the following boundary conditions:

$$\frac{\partial \psi}{\partial \theta} = -r^2 \sin \theta \cos \theta \mathbf{U} \quad \text{and}$$

$$\frac{\partial \psi}{\partial r} = -r \sin^2 \theta \mathbf{U}, \quad r = a \quad (22)$$

$$\left. \frac{\partial \psi}{\partial \theta} \right|_{r=b^-} = \left. \frac{\partial \psi}{\partial \theta} \right|_{r=b^+}, \quad r = b \quad (23)$$

$$\left. \frac{\partial \psi}{\partial r} \right|_{r=b^-} = \left. \frac{\partial \psi}{\partial r} \right|_{r=b^+}, \quad r = b \quad (24)$$

$$\frac{1}{r \sin \theta} \left. \frac{\partial^2 \psi}{\partial r^2} \right|_{r=b^-} = \frac{1}{r \sin \theta} \left. \frac{\partial^2 \psi}{\partial r^2} \right|_{r=b^+}, \quad r = b \quad (25)$$

$$\begin{aligned} \frac{\eta}{\sin \theta} \left. \frac{\partial}{\partial r} (\mathbf{E}^2 \psi) \right|_{r=b^-} - \frac{\gamma}{\sin \theta} \left. \frac{\partial \psi}{\partial r} \right|_{r=b^-} = \\ \frac{\eta}{\sin \theta} \left. \frac{\partial}{\partial r} (\mathbf{E}^2 \psi) \right|_{r=b^+}, \quad r = b \end{aligned} \quad (26)$$

$$\frac{\partial \psi}{\partial \theta} = 0 \quad \text{and} \quad \frac{\partial \psi}{\partial r} = 0, \quad r = c \quad (27)$$

For a more concise presentation, the governing equations and the associated boundary conditions are rewritten in terms of dimensionless variables scaled by the following quantities: the radius of the rigid core of a particle,  $a$ , the surface potential on the core,  $\zeta_a$ , the bulk number concentration of ionic species 1,  $n_{10}$ , and the electrophoretic velocity based on von Smoluchowski's theory<sup>1</sup> when an electric field  $\zeta_a/a$  is applied,  $U_E = \epsilon \zeta_a^2 / \eta a$ . Also, we define  $r^* = r/a$ ,  $n_j^* = n_j / n_{10}$ ,  $E_z^* = E_z / (\zeta_a/a)$ ,  $\mathbf{v}^* = \mathbf{v} / U_E$ ,  $U^* = \mathbf{U} / U_E$ ,  $\phi_1^* = \phi_1 / \zeta_a$ ,  $\phi_2^* = \phi_2 / \zeta_a$ ,  $\mathbf{g}_j^* = \mathbf{g}_j / \zeta_a$ , and  $\psi^* = \psi / U_E a$ . In terms of scaled symbols, the governing equations for the equilibrium electric potential become

$$\begin{aligned} \nabla^{*2} \phi_1^* = - \frac{(\kappa a)^2}{(1 + \alpha) \phi_r} [\exp(-\phi_1 \phi_1^*) - \\ \exp(\alpha \phi_1 \phi_1^*)] - iQ \end{aligned} \quad (28)$$

where  $Q = (\rho_{\text{fix}} a^2 / \epsilon \zeta_a)$ , which is the scaled fix charge density in membrane layer, and  $\phi_r = z_i e \zeta_a / k_B T$ , the scaled surface potential of the rigid core of a particle,  $i = 1$  for  $a < r < b$ , and  $i = 0$  for  $b < r < c$ . The associated boundary conditions are

$$\phi_1^* = 1, \quad r^* = 1 \quad (29)$$

$$\phi_1^*|_{r^*=b/a} = \phi_1^*|_{r^*=b/a}, \quad r^* = b/a \quad (30)$$

$$\left. \frac{\partial \phi_1^*}{\partial r^*} \right|_{r^*=b/a} = \left. \frac{\partial \phi_1^*}{\partial r^*} \right|_{r^*=b/a}, \quad r^* = b/a \quad (31)$$

$$\phi_1^* = 0, \quad r^* = c/a \quad (32)$$

The two-dimensional dependent variables  $\phi_2^*$ ,  $\mathbf{g}_1^*$ ,  $\mathbf{g}_2^*$ , and  $\psi^*$  can be made one-dimensional by applying the method of separation of variables. The following expressions were used for the present problem:  $\phi_2^* = \Phi_2(r) \cos \theta$ ,  $\mathbf{g}_1^* = G_1(r) \cos \theta$ ,  $\mathbf{g}_2^* = G_2(r) \cos \theta$ , and  $\psi^* = \Psi(r) \sin^2 \theta$ . On the basis of these expressions, it can be shown that the resultant governing equation for  $\phi_2^*$  becomes

$$L^2 \Phi_2 - \frac{(\kappa a)^2}{1 + \alpha} [\exp(-\phi_r \phi_1^*) + \alpha \exp(\alpha \phi_r \phi_1^*)] \Phi_2 = \frac{(\kappa a)^2}{1 + \alpha} [\exp(-\phi_r \phi_1^*) G_1 + \alpha \exp(\alpha \phi_r \phi_1^*) G_2] \quad (33)$$

where

$$L^2 \equiv \frac{d^2}{dI^{*2}} + \frac{2}{I^*} \frac{d}{dI^*} - \frac{2}{I^{*2}}$$

The associated boundary conditions are

$$\frac{d\Phi_2}{dI^*} = 0, \quad I^* = 1 \quad (34)$$

$$\Phi_2|_{I^*=b/a} = \Phi_2|_{I^*=b^+/a}, \quad I^* = b/a \quad (35)$$

$$\left. \frac{d\Phi_2}{dI^*} \right|_{I^*=b/a} = \left. \frac{d\Phi_2}{dI^*} \right|_{I^*=b^+/a}, \quad I^* = b/a \quad (36)$$

$$\frac{d\Phi_2}{dI^*} = -E_z^*, \quad I^* = c/a \quad (37)$$

The governing equations for the concentration field become

$$L^2 G_1 - \phi_r^2 \frac{d\phi_1^*}{dI^*} = P e_1 \phi_r^2 v_r^* \frac{d\phi_1^*}{dI^*} \quad (38)$$

$$L^2 G_2 + \alpha \phi_r^2 \frac{d\phi_1^*}{dI^*} = P e_2 \phi_r^2 v_r^* \frac{d\phi_1^*}{dI^*} \quad (39)$$

where  $P e_j = U_{Ea} D_j$  is the electric Peclet number of ionic species  $j$ . The corresponding boundary conditions are

$$\frac{dG_1}{dI^*} = 0, \quad I^* = 1 \quad (40)$$

$$G_1|_{I^*=b/a} = G_1|_{I^*=b^+/a}, \quad I^* = b/a \quad (41)$$

$$\left. \frac{dG_1}{dI^*} \right|_{I^*=b/a} = \left. \frac{dG_1}{dI^*} \right|_{I^*=b^+/a}, \quad I^* = b/a \quad (42)$$

$$G_1 = -\Phi_2, \quad I^* = c/a \quad (43)$$

$$\frac{dG_2}{dI^*} = 0, \quad I^* = 1 \quad (44)$$

$$G_2|_{I^*=b/a} = G_2|_{I^*=b^+/a}, \quad I^* = b/a \quad (45)$$

$$\left. \frac{dG_2}{dI^*} \right|_{I^*=b/a} = \left. \frac{dG_2}{dI^*} \right|_{I^*=b^+/a}, \quad I^* = b/a \quad (46)$$

$$G_2 = -\Phi_2, \quad I^* = c/a \quad (47)$$

The governing equation for the flow field becomes

$$D^4 \Psi - i(\lambda a)^2 D^2 \Psi = - \frac{(\kappa a)^2}{1 + \alpha} \left[ (n_1^* G_1 + n_2^* G_2) \frac{d\phi_1^*}{dI^*} \right] \quad (48)$$

where  $(\lambda a)^2 = (\gamma a^2 / \eta)$ , which is a scaled shear parameter in the membrane layer,  $i = 1$  for  $a < r < b$ ,  $i = 0$  for  $b < r < c$ , and  $D^4 = D^2 D^2 = (d^2/dI^{*2} - 2/I^{*2})^2$ . The associated boundary conditions are

$$\Psi = -\frac{1}{2} I^{*2} U^* \quad \text{and} \quad \frac{d\Psi}{dI^*} = -I^* U^*, \quad I^* = 1 \quad (49)$$

$$\Psi|_{I^*=b/a} = \Psi|_{I^*=b^+/a}, \quad I^* = b/a \quad (50)$$

$$\left. \frac{d\Psi}{dI^*} \right|_{I^*=b/a} = \left. \frac{d\Psi}{dI^*} \right|_{I^*=b^+/a}, \quad I^* = b/a \quad (51)$$

$$\left. \frac{d^2\Psi}{dI^{*2}} \right|_{I^*=b/a} = \left. \frac{d^2\Psi}{dI^{*2}} \right|_{I^*=b^+/a}, \quad I^* = b/a \quad (52)$$

$$\left[ \frac{d^3\Psi}{dI^{*3}} - (\lambda a)^2 \frac{d\Psi}{dI^*} \right]_{I^*=b/a} = \left[ \frac{d^3\Psi}{dI^{*3}} \right]_{I^*=b^+/a}, \quad I^* = b/a \quad (53)$$

$$\Psi = 0 \quad \text{and} \quad \frac{d\Psi}{dI^*} = 0, \quad I^* = c/a \quad (54)$$

Solving the above equations subject to the associated boundary conditions yields the flow, the electric, and the concentration fields. Following the approach of O'Brien and White,<sup>2</sup> the problem under consideration is decomposed into two sub-problems. In the first problem, a particle moves with constant velocity in the absence of the applied electric field. If we let  $F_1$  be the total force acting on the particle, then  $F_1$  is proportional to its terminal velocity, that is,  $F_1 = \chi U^*$ , where  $\chi$  is independent of  $U^*$ . In the second problem, an external electric field is applied, but the particle remains fixed. In this case, if we let  $F_2$  be the total force acting on the particle, then  $F_2$  is proportional to the applied field, that is,  $F_2 = \beta E_z^*$ , where  $\beta$  is independent of  $E_z^*$ . Because  $\chi$  is independent of  $U^*$  and  $\beta$  is independent of  $E_z^*$ , we choose  $|U^*| = 1$  and  $|E_z^*| = 1$ , for simplicity, and, therefore,  $\chi = F_1$  and  $\beta = F_2$ . The forces acting on a particle  $\mathbf{F}$  comprises the electrical force  $\mathbf{F}_e$  and the hydrodynamic force  $\mathbf{F}_d$ . If we let  $F_{zi}$  be the magnitude of  $\mathbf{F}$  in problem  $i$  in the  $z$  direction, and  $F_{ez}$  and  $F_{dz}$  be the components of  $\mathbf{F}_e$  and  $\mathbf{F}_d$  in the  $z$  direction, then

$$F_{zi} = (F_{ez} + F_{dz})_i = F_i, \quad i = 1, 2 \quad (55)$$

The electric force acting on a particle can be evaluated by

$$\mathbf{F}_e = \int_{I=b}^I \int \sigma^E \cdot \hat{\mathbf{n}} \, ds \quad (56)$$

where  $\sigma^E \equiv \epsilon(\mathbf{E}\mathbf{E} - 1/2 \mathbf{E}^2 \mathbf{I})$  and  $\mathbf{E} = -\nabla\phi$ .  $F_{ez}$  can be expressed as

$$F_{ez} = \mathbf{F}_e \cdot \delta_z = \int_{I=b}^I \int (\sigma^E \cdot \hat{\mathbf{n}}) \cdot \delta_z \, ds \quad (57)$$

where  $\delta_z$  is the unit vector in the  $z$  direction. In terms of scaled symbols, it can be shown that

$$F_{ez} = \frac{4}{3} \pi \epsilon \zeta_a^2 \left[ I^{*2} \frac{d\phi_1^*}{dI^*} \frac{d\Phi_2}{dI^*} + 2 I^* \frac{d\phi_1^*}{dI^*} \Phi_2 \right]_{I^*=b/a} \quad (58)$$

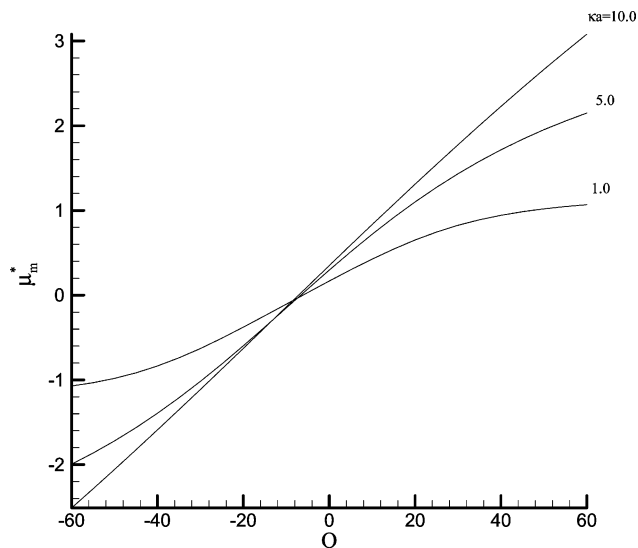
$\mathbf{F}_d$  can be evaluated by<sup>19</sup>

$$\mathbf{F}_d = \int_{I=b}^I \int \sigma^H \cdot \hat{\mathbf{n}} \, ds \quad (59)$$

where  $\sigma^H \equiv -p\mathbf{I} + \eta[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]$ .  $F_{dz}$  can be expressed as

$$F_{dz} = \mathbf{F}_d \cdot \delta_z = \int_{I=b}^I \int (\sigma^H \cdot \hat{\mathbf{n}}) \cdot \delta_z \, ds \quad (60)$$

(19) Happel, J.; Brenner, H. In *Low-Reynolds Number Hydrodynamics*; Nijhoff, M., Ed.; Kluwer: Boston, MA, 1983.



**Figure 2.** Effect of fixed charge density  $Q$  on mobility at various  $\kappa a$  for the case when  $\phi_r = 1.0$ ,  $\lambda a = 5.0$ ,  $d/a = 2.0$ , and  $d/a = 0.5$ .

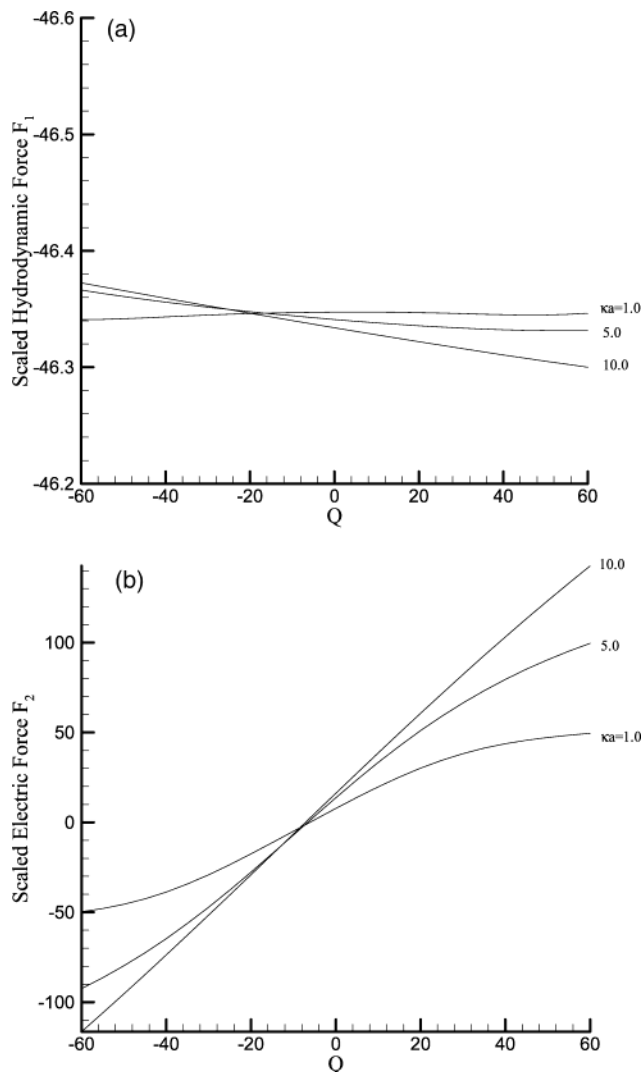
or, in terms of scaled symbols

$$F_{dz} = \frac{4}{3}\pi\epsilon\zeta_a^2 \left[ r^{*2} \frac{\partial}{\partial r^*} (D^2\Psi) - 2r^* (D^2\Psi) \right]_{r^*=b/a} + \frac{4}{3}\pi\epsilon\zeta_a^2 \frac{(\kappa a)^2}{(1+\alpha)\phi_r} \left\{ r^{*2} \Phi_2 [\exp(-\phi_r \phi_1^*) - \exp(\alpha\phi_r \phi_1^*)] \right\}_{r^*=b/a} \quad (61)$$

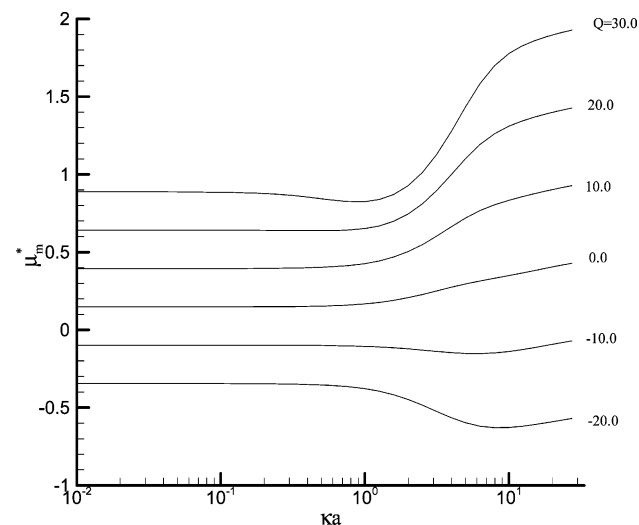
The sum of  $F_1$  and  $F_2$  vanishes at steady state, and the magnitude of the scaled electrophoretic velocity of a particle,  $\mu_m^*$ , can be expressed as  $\mu_m^* = U^*/E_z^* = -\beta/\chi = -F_2/F_1$ .

### Results and Discussions

The governing equations and the associated boundary conditions are solved numerically by a pseudo-spectral method based on Chebyshev polynomials. The performance of this approach for solving electrophoresis problems in a spherical cavity was found to be satisfactory.<sup>17,18</sup> The influence of the key parameters of the system under consideration on the mobility of a particle is investigated through numerical simulation. These include the thickness of the double layer; the relative size of cavity; and the thickness, the fixed charge density, and the friction coefficient of the membrane layer. The influence of the scaled fix charge density  $Q$  on the electrophoretic behavior of a particle is illustrated in Figure 2, where the variation of the scaled mobility of a particle  $\mu_m^*$  as a function of  $Q$  at various  $\kappa a$  is presented. This figure reveals that while  $\mu_m^*$  varies nonlinearly with  $Q$ , in general, the  $\mu_m^*-Q$  relation is roughly linear if  $\kappa a$  is sufficiently large, that is, the concentration of electrolyte is sufficiently high or the double layer surrounding a particle is sufficiently thin. Figure 3 illustrates the variations of the scaled hydrodynamic force  $F_1$  and the scaled electric force  $F_2$  as a function of  $Q$  at various  $\kappa a$ . This figure indicates that  $F_1$  is much more insensitive to the variation in both  $Q$  and  $\kappa a$  than  $F_2$  is, which implies that the behavior of  $\mu_m^*$  in Figure 2 is dominated by  $F_2$ . As will be discussed later, the nonlinear  $\mu_m^*-Q$  relation in Figure 2 arises mainly from the effect of double-layer polarization that occurs for  $\kappa a$  in the range [1.0, 5.0]. This effect becomes insignificant when  $\kappa a$  is sufficiently large. On the other hand, if  $\kappa a$  is small, both the hydrodynamic retardation

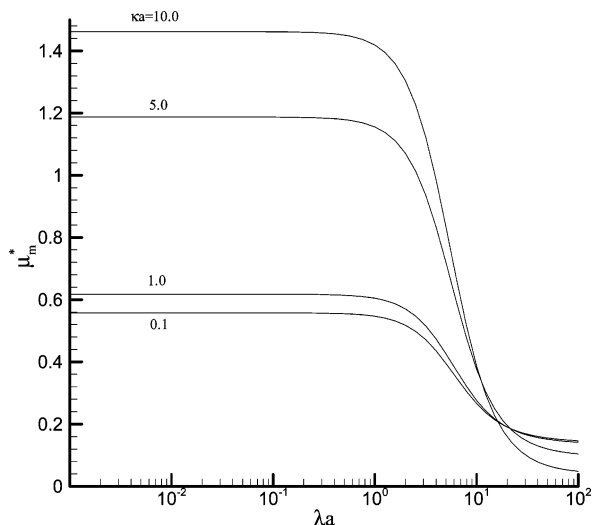


**Figure 3.** Variation of scaled hydrodynamic force  $F_1$  (a) and scaled electric force  $F_2$  (b), as a function of  $Q$  at various  $\kappa a$  for the case of Figure 2.

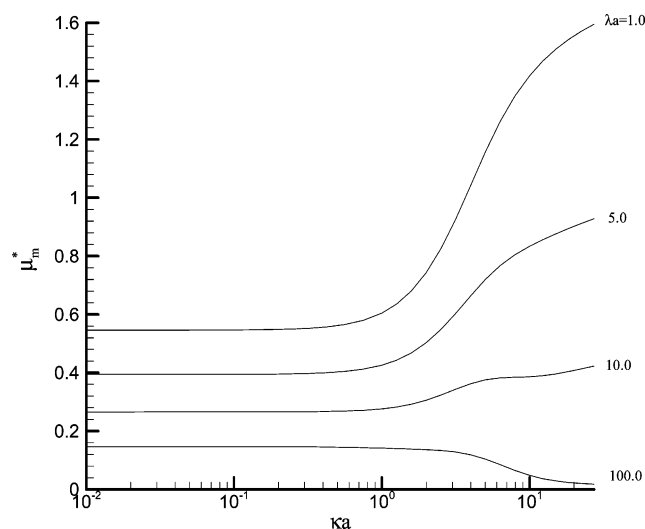


**Figure 4.** Variation of scaled mobility  $\mu_m^*$  as a function of  $\kappa a$  at various  $Q$  for the case when  $\phi_r = 1.0$ ,  $\lambda a = 5.0$ ,  $d/a = 2.0$ , and  $d/a = 0.5$ .

arising from the presence of the double layer and the effect of double-layer polarization are significant. The competition between the electric force and the hydrodynamic force



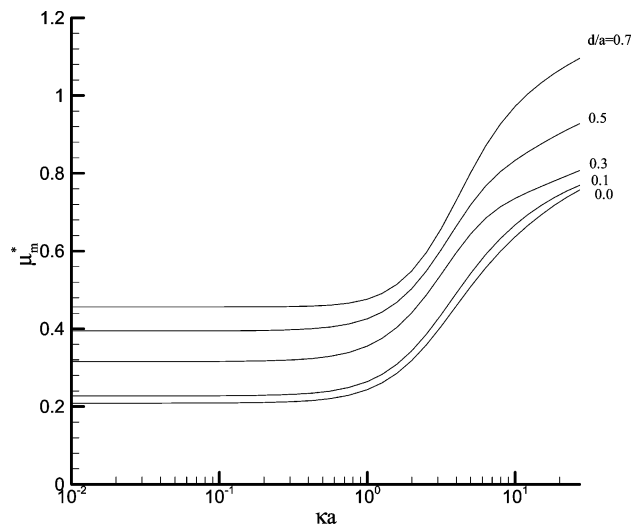
**Figure 5.** Variation of scaled mobility  $\mu_m^*$  as a function of  $\lambda a$  at various  $\kappa a$  for the case when  $\phi_r = 1.0$ ,  $Q = 10.0$ ,  $d/a = 2.0$ , and  $d/a = 0.5$ .



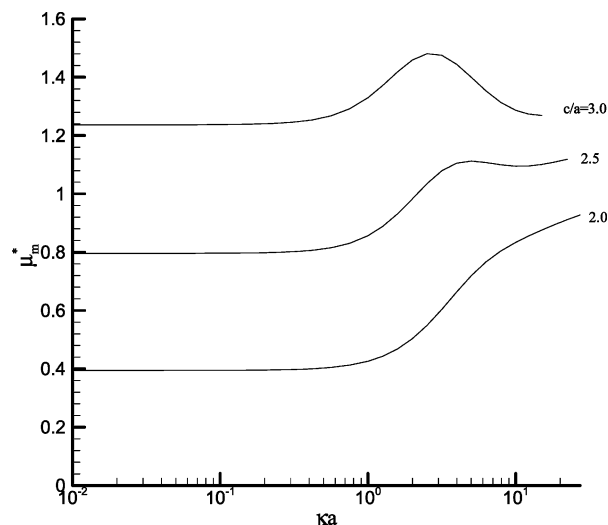
**Figure 6.** Variation of scaled mobility  $\mu_m^*$  as a function of  $\kappa a$  at various  $\lambda a$  for the case when  $\phi_r = 1.0$ ,  $Q = 10.0$ ,  $d/a = 2.0$ , and  $d/a = 0.5$ .

can be further illustrated in Figure 4. This figure shows that if  $\kappa a$  is small, the hydrodynamic retardation force dominates. In this case, although the electric force acting on a particle increases with  $\kappa a$ , the scaled mobility  $|\mu_m^*|$  remains roughly constant. If  $\kappa a$  is sufficiently large, the electric force dominates, and  $|\mu_m^*|$  increases with the increase in  $\kappa a$ . It is interesting to note that if  $Q$  is sufficiently high,  $|\mu_m^*|$  exhibits a local minimum as  $\kappa a$  varies. This phenomenon arises from the polarization of the double layer surrounding a particle, which induces a local electric field having a direction reverse of that of the applied electric field. The effect of double-layer polarization becomes appreciable when the thickness of the double layer is comparable to the linear size of a particle, that is,  $\kappa a$  ranges from 0.1 to 10, and is insignificant when  $\kappa a$  is either too small or too large. A similar phenomenon was also observed in the case of rigid particles.<sup>17</sup>

The influence of the friction coefficient of the membrane layer on the electrophoretic mobility of a particle is illustrated in Figures 5 and 6, and that of the relative thickness of the membrane layer and the relative magnitude of the cavity on the mobility of a particle is presented



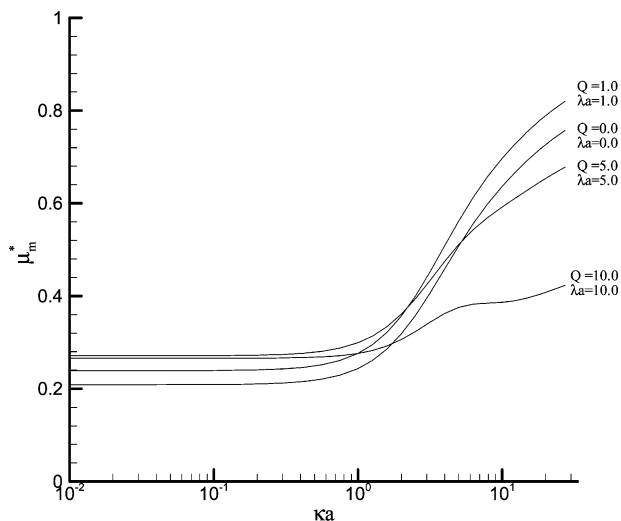
**Figure 7.** Variation of scaled mobility  $\mu_m^*$  as a function of  $\kappa a$  at various  $d/a$  for the case when  $d/a = 2.0$ ,  $\phi_r = 1.0$ ,  $Q = 10.0$ , and  $\lambda a = 5.0$ .



**Figure 8.** Variation of scaled mobility  $\mu_m^*$  as a function of  $\kappa a$  at various  $d/a$  for the case when  $d/a = 0.5$ ,  $\phi_r = 1.0$ ,  $Q = 10.0$ , and  $\lambda a = 5.0$ .

in Figures 7 and 8, respectively. Figures 5 and 6 indicate that the larger the  $\lambda a$ , the smaller the  $\mu_m^*$  is, which is expected. Figure 7 suggests that the thicker the membrane layer, the larger the mobility, and Figure 8 indicates that the smaller the cavity, the smaller the mobility. These are expected because the thicker the membrane layer, the more the total amount of fixed charge in the membrane layer, and the smaller the cavity, the more significant the steric retardation on the movement of a particle.

In practice, the membrane layer arises often from the attachment of polymer or macromolecules on the particle surface. Because the greater the amount of polymer molecules attached, the higher the density of membrane layer, it is highly possible that  $Q$  and  $\lambda a$  are positively correlated. As mentioned previously,  $Q$  is related to the magnitude of the electric force acting on a particle; the higher the  $Q$ , the greater the electric force and the larger the absolute value of mobility. On the other hand,  $\lambda a$  is related to the hydrodynamic drag; the larger the  $\lambda a$ , the greater the hydrodynamic drag and the smaller the mobility. These imply that the density of the membrane layer can have a confound influence on the mobility of a particle, as is illustrated in Figure 9. For example, with



**Figure 9.** Variation of scaled mobility  $\mu_m^*$  as a function of  $\kappa a$  at various combinations of  $Q$  and  $\lambda a$  for the case when  $\phi_r = 1.0$ ,  $d/a = 2.0$ , and  $d/a = 0.5$ .

the same  $Q/\lambda a$  ratio, while the mobility of a particle with  $Q = 1$  is greater than that with  $Q = 0$  (free of fixed charge), the mobility of a particle with  $Q = 5$  is smaller than that with  $Q = 0$ .

The present study focused on the influences of the nature of a colloidal particle as well as the presence of a boundary on its electrophoretic behavior. The membrane-coated particle adopted here simulates a wide class of nonrigid entities in practice. Polystyrene latex dispersions, for example, comprise particles that have a hairy-structured surface arising from the extension of the internal polymer chains. Surfactants are usually introduced into a colloidal dispersion to avoid coagulation. In this case, the surfactant molecules adsorbed to particle surface form a gel layer, and the resultant composite entity can be simulated by the present model. Biocolloids such as cells and microorganisms where their peripheral zone is ion-penetrable and contains dissociable functional groups are also typical examples which can be described by the present model. Boundary effect is of practical significance in electrophoresis measurements. For instance, capillary electro-

phoresis and gel electrophoresis, where this effect cannot be neglected, are widely adopted in the separation of entities such as DNA. In this study, the boundary effect is simulated by considering the presence of a cavity. Often, estimating surface properties of colloidal particles such as the zeta potential, charge density, and thickness of the surface layer on the basis of experimental observations is necessary. This can be conducted by matching the present model to experimental data, and the estimated values of the adjustable parameters provide sufficient information. Apparently, the present model can be used directly to predict the electrophoretic behavior of particles of known physical properties under specified conditions. This is of particular importance in design of an electrophoretic separation device.

### Conclusions

The electrophoresis of a membrane-coated particle in a spherical cavity is investigated theoretically. As a result of the presence of a membrane layer, particles are capable of exhibiting specific behavior that is not observed for the case of rigid particles. The physical properties of the membrane layer are characterized mainly by its fixed charge density and friction coefficient; both of them are positively correlated with the density of the membrane layer. The former is advantageous and the latter is disadvantageous to the electrophoretic movement of a particle. We show that while the mobility of a particle varies nonlinearly with fixed charge density, in general, they are roughly linearly correlated if the double layer surrounding the particle is sufficiently thin. The nonlinear relation arises mainly from the effect of double-layer polarization, becoming insignificant when the double layer is thin. Depending on the level of fixed charge density, the mobility of a particle may exhibit a local minimum as the thickness of the double layer varies, which is also observed for the case of rigid particles. The presence of a cavity has a negative influence on the electrophoretic movement of a particle.

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