

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 to 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 repre-

sentative 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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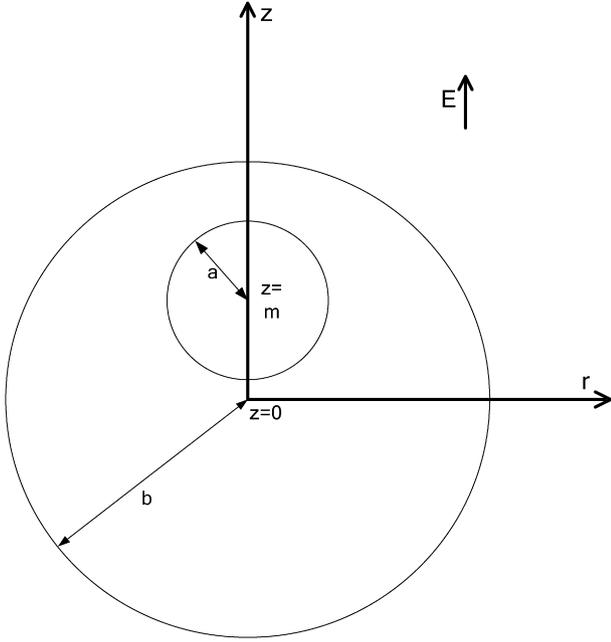


Fig. 1. Schematic representation of the problem where a sphere of radius a is placed in a spherical cavity of radius b . An electric field \mathbf{E} parallel to the z -axis is applied. The center of the particle is at $z = m$ and that of the cavity at $z = 0$.

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

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

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

$$\nabla \cdot \mathbf{v} = 0, \quad (3)$$

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

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,

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

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

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

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

$$\nabla^{*2} g_1^* - \phi_r \nabla^* \phi_1^* \cdot \nabla^* g_1^* = \phi_r^2 \text{Pe}_1 \mathbf{v}^* \cdot \nabla^* \phi_1^*, \quad (8)$$

$$\nabla^{*2} g_2^* + \alpha \phi_r \nabla^* \phi_1^* \cdot \nabla^* g_2^* = \phi_r^2 \text{Pe}_2 \mathbf{v}^* \cdot \nabla^* \phi_1^* \quad (9)$$

$$n_1^* = \exp(\phi_r \phi_1^*) [1 - \phi_r (\phi_2^* + g_1^*)], \quad (10)$$

$$n_2^* = \exp(\alpha \phi_r \phi_1^*) [1 + \alpha \phi_r (\phi_2^* + g_2^*)]. \quad (11)$$

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 $\zeta_a = 0$. $n_j^* = n_j / n_{j0}$, $\phi_j^* = \phi_j / \zeta_k$, $\text{Pe}_j = \varepsilon (z_j e / k_B T)^2 / \eta D_j$, which is the electrical Péclet number of ion species j , and $g_j^* = g_j / \zeta_k$, $j = 1, 2$; $\kappa = [\sum_{j=1}^2 n_{j0} (e z_j)^2 / \varepsilon k_B T]^{1/2}$ 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

$$\nabla \cdot \mathbf{v}^* = 0, \quad (12)$$

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

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

Suppose that both the sphere and the cavity surface are non-conductive, 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

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

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

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

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

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

$$g_j^* = -\phi_2^*, \quad j = 1, 2 \quad \text{on the cavity surface,} \quad (19)$$

$$\mathbf{v}^* = (v/U_E)\mathbf{e}_z \quad \text{on the sphere surface,} \quad (20)$$

$$\mathbf{v}^* = 0 \quad \text{on the cavity surface.} \quad (21)$$

In these expressions, $E_z^* = E_z/(\zeta_k/a)$ is the scaled strength of the applied electric field, \mathbf{n} is the unit normal vector directed into the liquid phase, and \mathbf{e}_z is the unit vector in the z -direction.

Following the treatment of O'Brien and White [19], the present problem is decomposed into two subproblems. In the first subproblem, a sphere moves at a constant velocity in the absence of \mathbf{E} , and in the second subproblem the sphere is fixed in the space when \mathbf{E} is applied. Let \mathbf{F}_i be the total force acting on a sphere in subproblem i , and let F_i be its magnitude; then $F_1 = \chi V^*$ and $F_2 = \beta E_z^*$, where χ is independent of V^* and β is independent of E_z^* , and $V^* = v/U_E$ is the scaled velocity. The fact that the sum of F_1 and F_2 must vanish at the steady state yields

$$\mu_m^* = \frac{V^*}{E_z^*} = -\frac{\beta}{\chi}, \quad (22)$$

where μ_m^* is the scaled mobility of a sphere. For the present problem, the total force acting on a sphere in the z -direction \mathbf{F} , includes the electrical force \mathbf{F}_e and the hydrodynamic force \mathbf{F}_d . If we let F_{ei} and F_{di} be respectively the z -components of \mathbf{F}_e , and \mathbf{F}_d in subproblem i , then

$$F_i = F_{ei} + F_{di}, \quad i = 1, 2. \quad (23)$$

F_{ei} can be evaluated by [20]

$$F_{ei} = \int_S (\boldsymbol{\sigma}^E \cdot \mathbf{n}) \cdot \mathbf{e}_z dS, \quad (24)$$

where S denotes the spherical surface, $\mathbf{E} = -\nabla\phi$, $\boldsymbol{\sigma}^E \equiv \varepsilon(\mathbf{E}\mathbf{E} - \frac{1}{2}E^2\mathbf{I})$ is the Maxwell stress tensor, and \mathbf{I} is the unit tensor. It can be shown that, in terms of scaled symbols, Eq. (24)

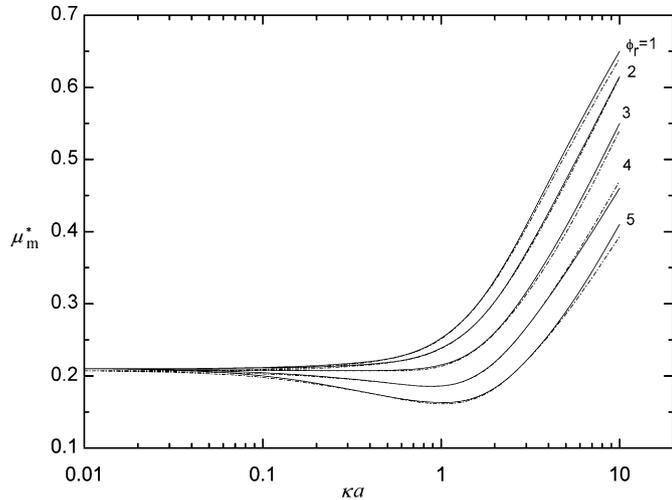


Fig. 2. Variation of the scaled mobility μ_m^* as a function of κa at various levels of the scaled surface potential ϕ_r for the case where a positively charged sphere is in an uncharged cavity. Solid curves: results based on the present method; dashed curves: results based on a pseudo-spectral method (8). Parameters used are $Pe_1 = Pe_2 = 0.1$, $\alpha = 1$, and $\lambda = 0.5$.

leads to [20,21]

$$F_{ei}^* = \frac{F_{ei}}{\varepsilon\zeta_k^2 a^2} = \int_S \frac{\partial\phi_1^*}{\partial n} \frac{\partial\phi_2^*}{\partial z} - \frac{\partial\phi_1^*}{\partial t} \frac{\partial\phi_2^*}{\partial t} dS^*, \quad (25)$$

where n and t are the magnitude of the unit normal vector and that of the unit tangential vector, respectively. F_{di} can be evaluated by [22]

$$F_{di} = \int_S (\boldsymbol{\sigma}^H \cdot \mathbf{n}) \cdot \mathbf{e}_z dS, \quad (26)$$

where $\boldsymbol{\sigma}^H \equiv -p\mathbf{I} + \eta[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]$ and the superscript T denotes matrix transpose. In terms of the scaled symbols, Eq. (26) can be rewritten as

$$F_{di}^* = \frac{F_{di}}{\varepsilon\zeta_k^2 a^2} = \int_S (\boldsymbol{\sigma}^{*H} \cdot \mathbf{n}) \cdot \mathbf{e}_z dS^*. \quad (27)$$

3. Results and discussions

FlexPDE [23], a commercial program based on a finite element method, is adopted to solve the governing equations and

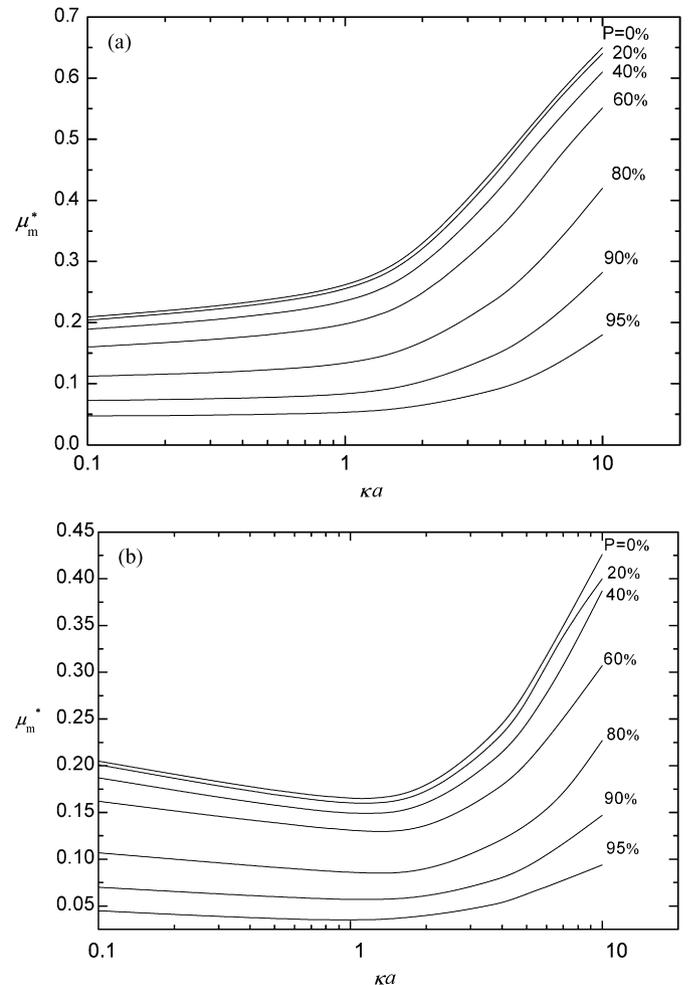


Fig. 3. Variation of the scaled mobility μ_m^* as a function of κa for various values of the position parameter P for the case where a positively charged sphere is in an uncharged cavity at $\lambda = 0.5$. (a) $\phi_r = 1$, (b) $\phi_r = 5$.

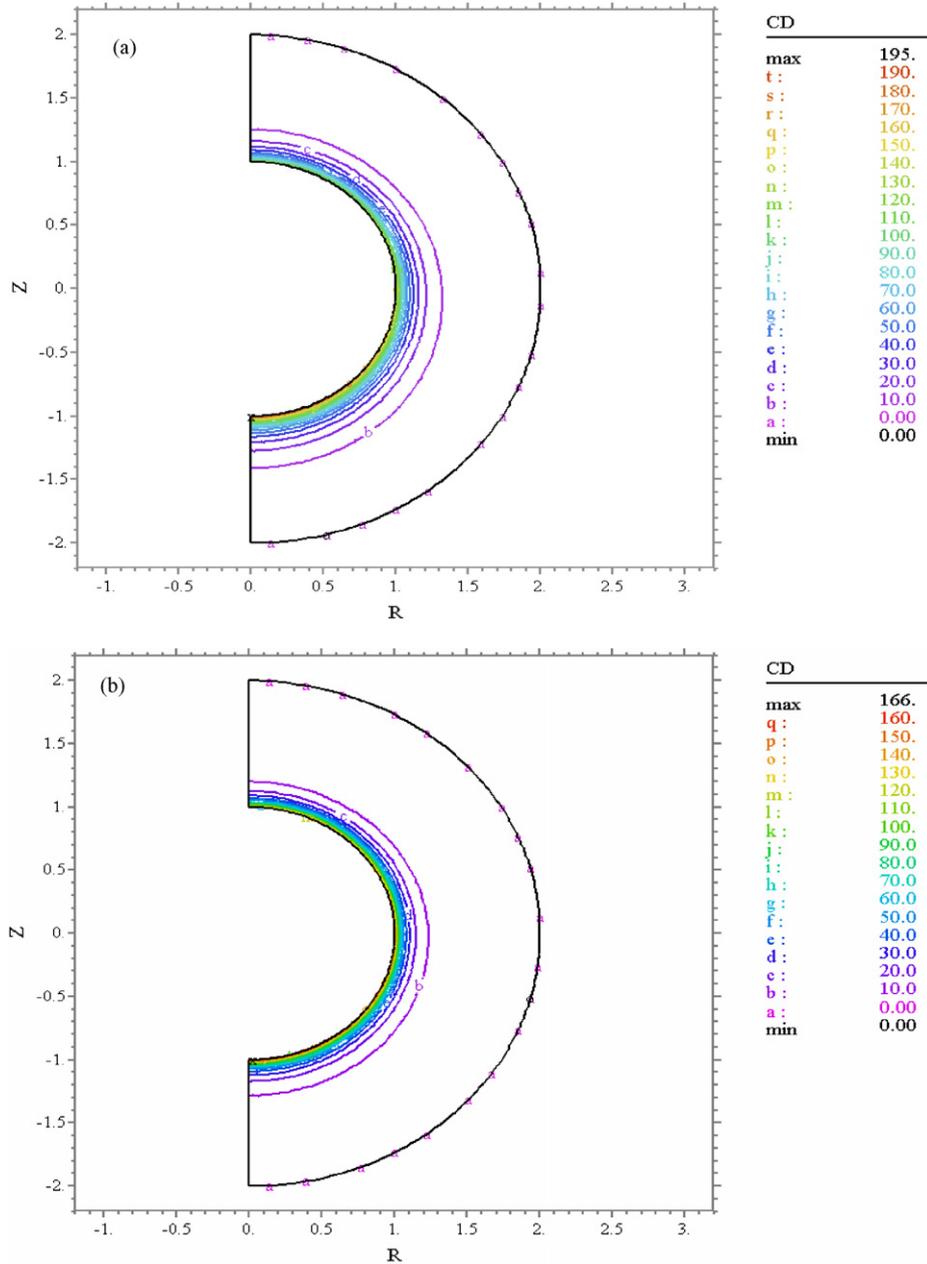


Fig. 4. Contours of the scaled net ionic concentration $CD (=n_1^* - n_2^*)$ at two levels of κa for the case where a positively charged sphere is in an uncharged cavity at $\lambda = 0.5$ and $\phi_r = 5$. (a) $\kappa a = 0.7$, (b) $\kappa a = 1.5$.

the associated boundary conditions, and the results obtained are used to calculate the mobility of a particle; the detailed procedure can be found in [8,19]. Our previous experience indicates that this program is efficient and sufficiently accurate for the resolution of the boundary value problem of the present type [24]. Its applicability is further justified by reanalyzing the problem considered by Lee et al. [8], the electrophoresis of a sphere at the center of a spherical cavity, where a pseudo-spectral method based on Chebyshev polynomials is adopted for the resolution of the governing equations and the associated boundary conditions. Fig. 2 shows that the performance of the present numerical scheme is satisfactory.

In subsequent discussion, numerical simulations are conducted to examine the electrophoretic behavior of a sphere

under various conditions. For illustration, we consider two typical cases, namely, a positively charged sphere in an uncharged cavity and an uncharged sphere in a positively charged cavity. Also, we assume $Pe_1 = Pe_2 = 0.1$ and $z_1 = z_2$; that is, $\alpha = 1$. For convenience, a position parameter $P = 100m/(b - a)\%$ is defined; if $P = 0\%$, a sphere is at the center of a cavity, and $P = 100\%$ if a sphere touches the north pole of a cavity.

3.1. Positively charged sphere in uncharged cavity

Let us consider first the case in which a positively charged sphere is placed in an uncharged cavity. Fig. 3a shows the variation of the scaled mobility of a sphere μ_m^* as a function of double-layer thickness κa at various values of the position para-

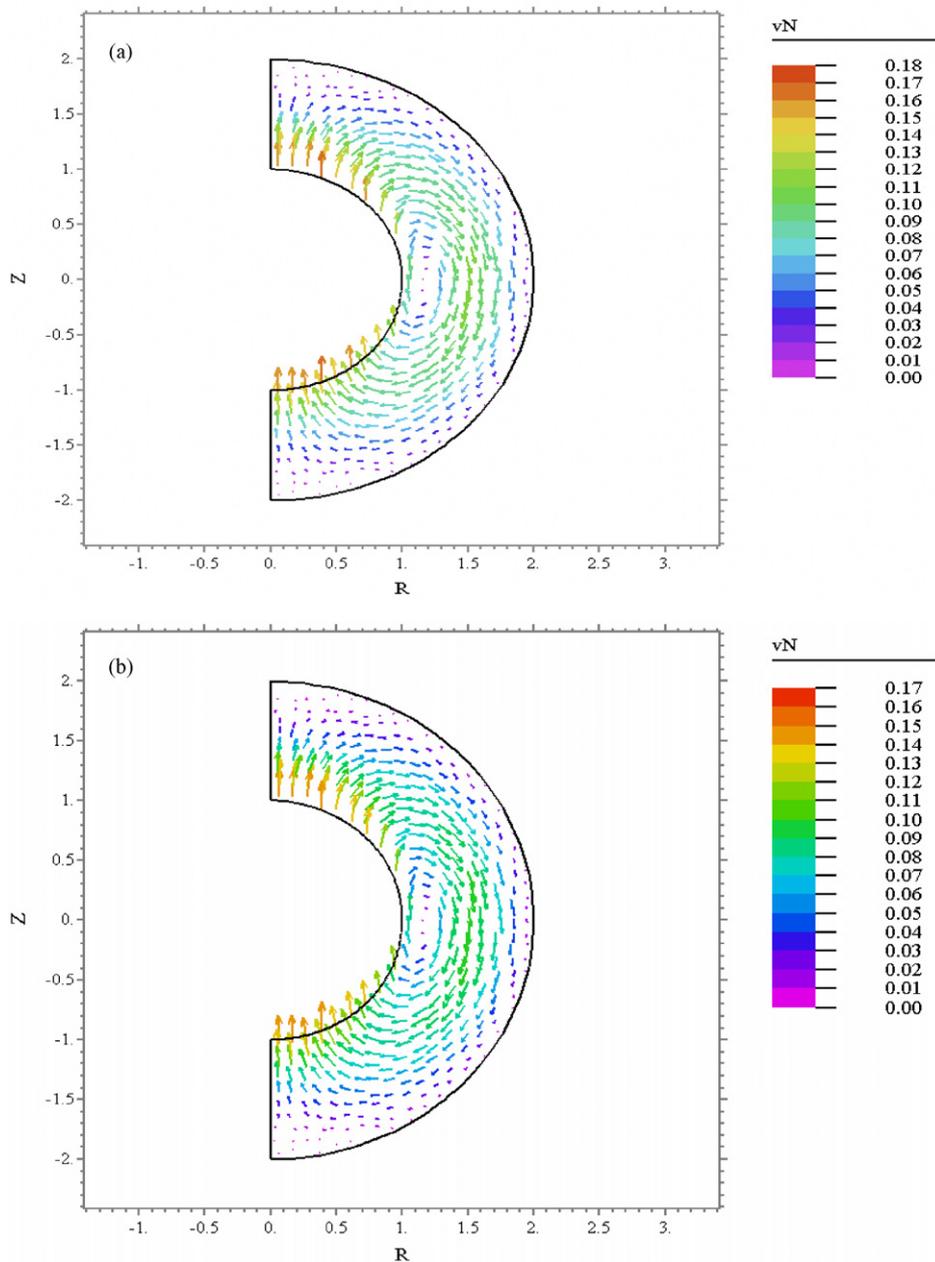


Fig. 5. Flow fields for the case of Fig. 4.

meter P for the case of a low scaled surface potential ($\phi_r = 1$), and that for the case of a high scaled surface potential ($\phi_r = 5$) is presented in Fig. 3b. Fig. 3a reveals that if ϕ_r is low μ_m^* increases monotonically with the increase in κa . This is because the smaller the κa the thinner the double layer, and the larger the absolute value of the potential gradient on the sphere surface, leading to a higher surface charge density, and therefore, the greater the electric force acting on the sphere. Fig. 3a also reveals that if κa is fixed, the larger the P the smaller the μ_m^* . This is because the closer a sphere is to a cavity, the greater the viscous retardation arises from the latter. As can be seen in Fig. 3b, the qualitative behavior of μ_m^* when ϕ_r is high becomes different from that when it is low. Here, μ_m^* has a local minimum when κa varies. This phenomenon was also observed by O'Brien and White [19] for the electrophoresis of a sphere in an

infinite fluid. The presence of the local minimum in μ_m^* arises from the fact that when κa is small the electrical driving force in subproblem 2 declines with the increase in κa due to double-layer polarization, but the hydrodynamic force F_{d2} increases with κa , and the rate of the former is higher than that of the latter. The effect of double-layer polarization becomes unimportant when κa is sufficiently large (thin double layer). Figs. 4 and 5 show some typical results for the contours of the scaled net ionic concentration, $CD (= n_1^* - n_2^*)$, and the flow field, respectively. As can be seen in Fig. 4, the thicker the double layer the more serious the effect of double-layer polarization, that is, the more asymmetric the contours of CD . Under the conditions assumed, a sphere moves upward and the concentration of anions (counterions) near its bottom is higher than that near its top. The asymmetric distribution of CD yields an internal elec-

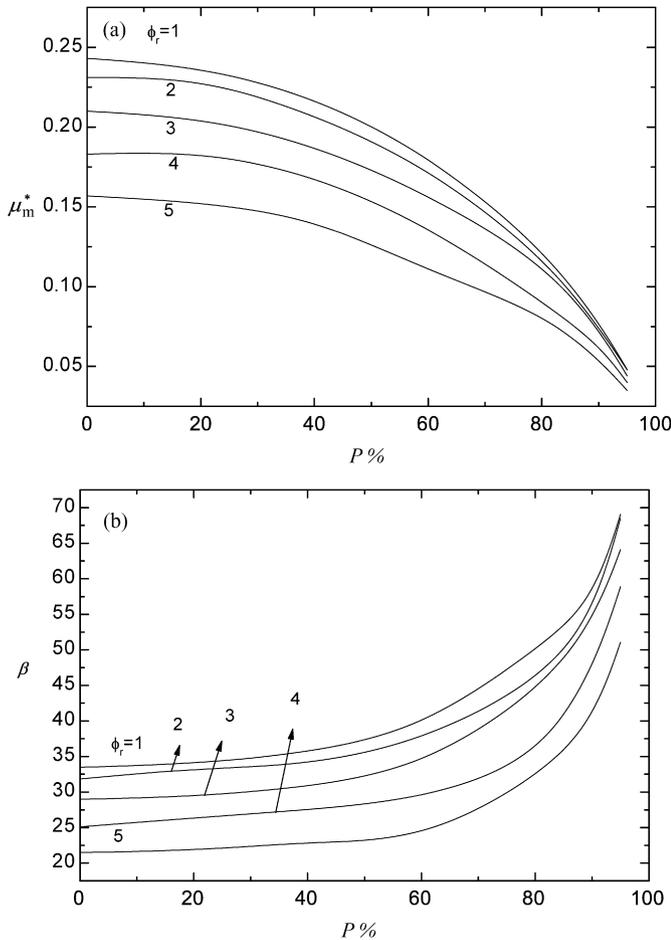


Fig. 6. Variation of the scaled mobility μ_m^* (a), and β (b), as a function of the position parameter P at various levels of the scaled surface potential ϕ_r for the case where a positively charged sphere is in an uncharged cavity at $\kappa a = 1$ and $\lambda = 0.5$.

tric field, the direction of which is opposite to that of the applied electric field, thereby reducing the mobility of the sphere. Fig. 5 shows that a clockwise (counterclockwise) vortex is generated on the right- (left-)hand side of a sphere. Also, the fluid flow at a thicker double layer can be faster than that at a thinner double layer, which was not observed for the case in which the surface potential of a sphere is low.

Fig. 6a shows that the scaled mobility of a sphere μ_m^* declines with the increase in the position parameter P , which is expected. This figure also reveals that μ_m^* decreases with the increases in the scaled surface potential ϕ_r . This is because for the value of κa considered, the effect of double-layer polarization is important and the strength of the corresponding induced electric field increases with the level of the surface potential of a particle. This phenomenon can also be explained by the variation of β , which is a measure of the net force acting on a sphere in the second subproblem, illustrated in Fig. 6b, where β decreases with the increase in ϕ_r .

The influence of the cavity wall on the electrophoretic behavior of a sphere is presented in Fig. 7. Here, the value of a is fixed, and therefore, the larger the λ ($= a/b$) the smaller the cavity and the more significant the wall effect, which leads to a smaller scaled mobility μ_m^* . For a fixed λ , μ_m^* declines with

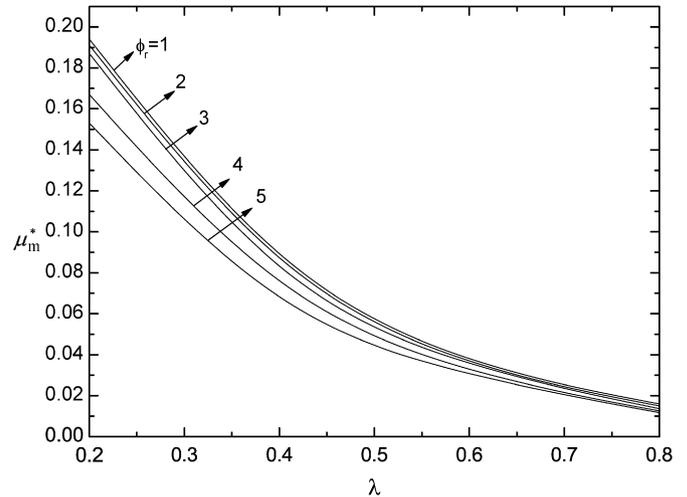


Fig. 7. Variation of the scaled mobility μ_m^* as a function of λ ($= a/b$) for various levels of the scaled surface potential ϕ_r for the case where a positively charged sphere is in an uncharged cavity at $P = 95\%$ and $\kappa a = 1$.

the increase in scaled surface potential ϕ_r due to the effect of double-layer polarization.

3.2. Uncharged sphere in positively charged cavity

Fig. 8 shows the variation of scaled mobility μ_m^* as a function of double-layer thickness κa at various values of the position parameter P for the case when an uncharged sphere is placed in a positively charged cavity. This figure indicates that, if $\mu_m^* < 0$, $|\mu_m^*|$ decreases with the increase in κa , but the reverse is true if $\mu_m^* > 0$. Also, if κa is fixed, $|\mu_m^*|$ decreases with the increase in P , and if P is fixed, $|\mu_m^*|$ increases with the increase in ϕ_r . This is because negative charge is induced on the sphere surface as it approaches a positively charged cavity. Therefore, the sphere moves in the $-z$ -direction; that is, $\mu_m^* < 0$. As κa increases, the thickness of the double layer near the cavity surface decreases and the amount of induced charge on the sphere surface declines accordingly. Since the cavity is positively charged, an electroosmotic flow is generated when \mathbf{E} is applied; a clockwise vortex appears on the right-hand side of a sphere and a counterclockwise vortex appears on its left-hand side. In this case, the sphere experiences a drag force in the z -direction. Therefore, the mobility of the sphere may become positive as κa increases.

Fig. 9 shows that, in general, if the surface potential of a cavity is not high, $\mu_m^* < 0$, and $|\mu_m^*|$ decreases with the increase in P . However, if the surface potential of the cavity is sufficiently high ($\phi_r = 5$), $\mu_m^* > 0$ if P is small and $\mu_m^* < 0$ if P is large. Also, μ_m^* has a local minimum as P varies. These can be explained by the fact that if ϕ_r is not high, the movement of a sphere is dominated by the electrical driving force F_{e2} , which is in the $-z$ -direction, since negative charge is induced on its surface, and therefore, μ_m^* is negative. As P increases, although both $|F_{d2}|$ and $|F_{e2}|$ increase, the rate of increase in the former is higher than that in the latter, and therefore, $|\mu_m^*|$ decreases. If ϕ_r is sufficiently high, because the hydrodynamic force acting on a sphere arising from the electroosmotic flow, which drives

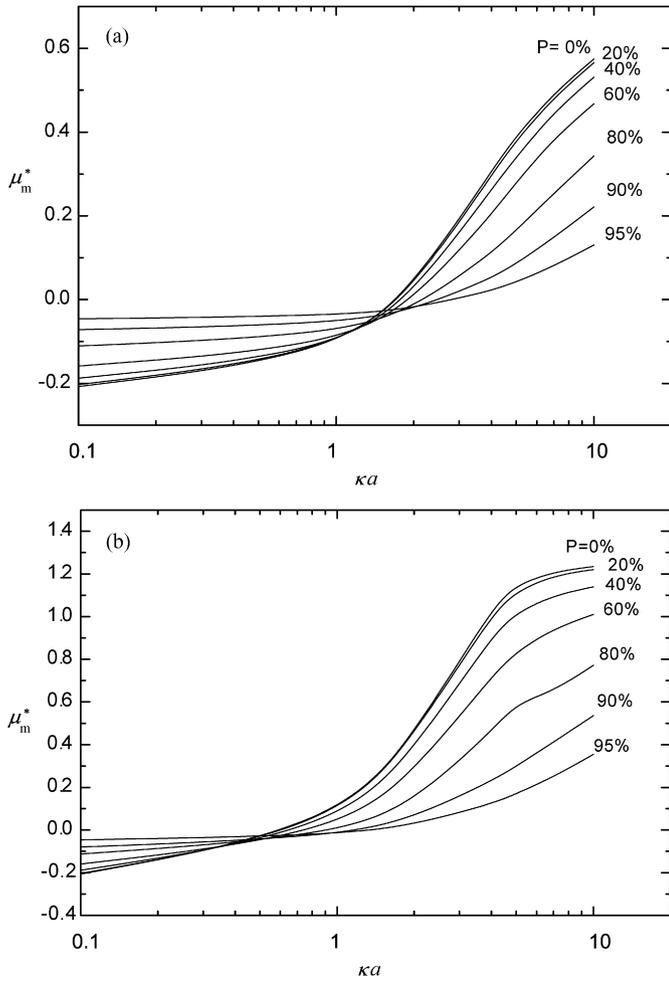


Fig. 8. Variation of the scaled mobility μ_m^* as a function of κa for various values of the position parameter P for the case where an uncharged sphere is in a positively charged cavity at $\lambda = 0.5$. (a) $\phi_r = 1$, (b) $\phi_r = 5$.

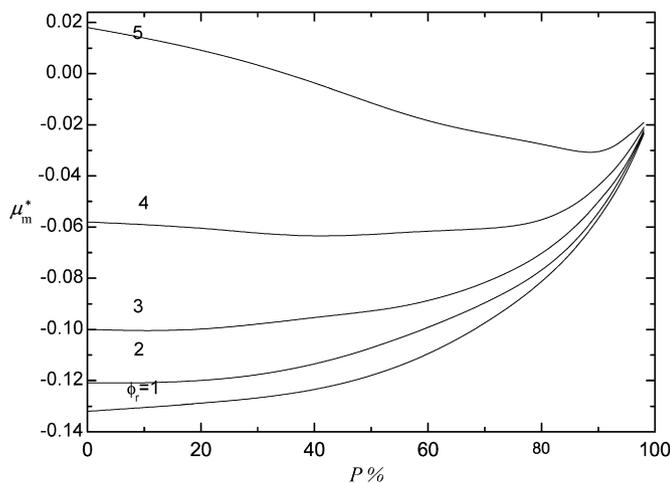


Fig. 9. Variation of the scaled mobility μ_m^* as a function of the position parameter P at various levels of the scaled surface potential ϕ_r for the case where an uncharged sphere is in a positively charged cavity at $\kappa a = 1$ and $\lambda = 0.5$.

the sphere toward the z -direction, is greater than F_{ez} , μ_m^* is positive. As P increases, since the amount of charge induced on the spherical surface increases, $|F_{e2}|$ increases, and μ_m^* declines ac-

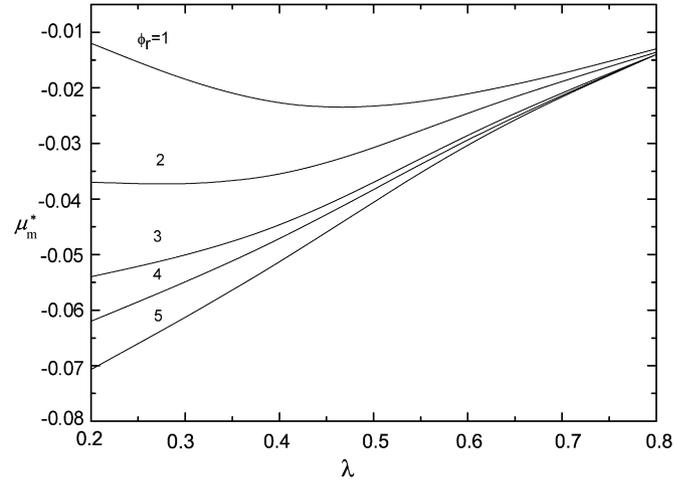


Fig. 10. Variation of the scaled mobility μ_m^* as a function of λ ($= a/b$) at various levels of the scaled surface potential ϕ_r for the case where an uncharged sphere is in a positively charged cavity at $P = 95\%$ and $\kappa a = 1$.

cordingly and becomes negative when P exceeds about 40. If a sphere is close to a cavity, F_{dz} dominates, and the nonslip condition of the cavity surface requires that μ_m^* must approach to zero, and therefore, μ_m^* has a local minimum.

Fig. 10 shows the variation of scaled mobility μ_m^* as a function of λ ($= a/b$) at various levels of the scaled surface potential ϕ_r . A comparison between Figs. 7 and 10 indicates that although $|\mu_m^*|$ declines with the increase of λ in both cases due to the hydrodynamic retardation of the cavity, μ_m^* may have a local minimum as λ varies if ϕ_r is sufficiently low in Fig. 10. The presence of the local minimum arises from the fact that if λ is small, F_{e2} dominates, and F_{d2} dominates if λ is large. If λ is small, the rate of increase in F_{e2} as λ increases is faster than that of F_{d2} , but the reverse is true if λ is large.

4. Conclusions

The electrophoretic behavior of a sphere at an arbitrary position in a spherical cavity for the case in which the effect of double-layer polarization can be important is investigated theoretically. If a positively charged sphere is in an uncharged cavity, we conclude the following. (i) If the surface potential is low, the mobility increases monotonically with the decrease in the thickness of double layer. (ii) For a fixed double-layer thickness, the closer a sphere is to a cavity the smaller the mobility is. (iii) If the surface potential is high, the mobility has a local minimum when the thickness of the double layer varies. (iv) The mobility declines with increases in the surface potential. If an uncharged sphere is placed in a positively charged cavity we conclude the following. (i) If the mobility is negative, its absolute value declines with the decrease in the thickness of the double layer, but the reverse is true if it is positive. (ii) The absolute value of the mobility increases with the increase in the surface potential. (iii) In general, if the surface potential is not high, the mobility is negative, and its absolute value declines with the decrease in the separation distance between a sphere and a cavity. However, if the surface potential is sufficiently high, the mobility is positive if a sphere is away from a cavity,

and is negative if it is close to a cavity. (iv) The mobility has a local minimum as the position of a sphere varies. For a fixed sphere size, its mobility may have a local minimum as the size of a cavity varies if the surface potential is sufficiently low.

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