Electrophoresis of a concentrated dispersion of spherical particles covered by an ion-penetrable membrane layer

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Abstract

The electrophoretic behavior of a concentrated dispersion of soft spherical particles is investigated theoretically, taking the effects of double-layer overlapping and double-layer polarization into account. Here, a particle comprises a rigid core and an ion-penetrable layer containing fixed charge, which mimics biocolloids and particles covered by artificial membrane layers. A cell model is adopted to simulate the system under consideration, and a pseudo-spectral method based on Chebyshev polynomials is chosen for the resolution of the governing electrokinetic equations. The influence of the key parameters, including the thickness of the double layer, the concentration of particles, the surface potential of the rigid core of a particle, and the thickness, the amount of fixed charge, and the friction coefficient of the membrane layer of a particle on the electrophoretic behavior of the system under consideration is discussed. We show that while the result for the case of a dispersion containing rigid particles can be recovered as the limiting case of a dispersion containing soft particles, qualitative behaviors that are not present in the former are observed in the latter.

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1. Introduction

Electrophoresis has found wide applications in numerous areas. For the case of an isolated rigid entity in an infinite fluid under conditions of low surface potential and weak applied electric field, an analytical expression for the electrophoretic mobility of the entity can be derived if the double layer surrounding it is either infinitely thin or infinitely thick [1]. Many attempts have been made to consider more general and/or realistic cases. These include, for example, the electrophoresis in which the effect of double-layer polarization/relaxation, the level of surface potential, the level of applied electric field, the effect of double-layer overlapping, the presence of a boundary, and the concentration of particles may be significant [2–7]. In particular, the development

of computing tools and software makes the analysis of a complicated electrophoresis problem feasible. While classic electrophoresis analysis focused mainly on rigid particles, particles of a nonrigid nature such as drops and entities covered by a porous layer are also not uncommon in practice. The latter is of particular importance in biological science, where electrophoresis may be conducted on microorganisms and cells. Apparently, representing these entities by a rigid particle is inadequate, and adopting a more realistic representation is necessary. To this end, an ion-penetrable layer model or the so-called soft-particle model [8–11] is often used, where a particle comprises a rigid core and a porous or ion-penetrable membrane layer. The peripheral zone of the human blood cell, for instance, has a glycoprotein layer about 15 nm thick, which contains ionogenic functional groups. The influence of this layer on the electrophoresis of the associated entity is twofold. First, because the dissociation of functional groups yields a fixed charge [12], the mobility of the entity may either increase or de-

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crease, depending on the sign of the fixed charge. Second, the hydrodynamic drag arising from the flow of liquid in the porous layer leads to smaller mobility. Wunderlich [9] and Levine et al. [10] concluded that if the effect of double-layer polarization is negligible, the mobility of a particle covered by an ion-penetrable layer is larger than that of the corresponding rigid particle. Under conditions of low surface potential and negligible double-layer polarization, Ohshima [13,14] was able to derive an analytical expression for the electrophoretic mobility of an ion-penetrable sphere, which was justified by experimental observations. In a study of the electrophoresis of an isolated, ion-penetrable sphere in an infinite fluid, Saville [15] and Hill et al. [16] concluded that the effect of double-layer polarization is important. Applying a network method, Lopez-Garcia et al. solved numerically the electrophoresis of a soft particle in a static electric field [17] and that in a dynamic electric field [18].

In this study, we extend previous analyses of the electrophoresis of particles covered by ion-penetrable layers to a general case, which takes account of the effects of particle concentration, double-layer polarization, and the overlapping of neighboring double layers. The unit cell model of Kuwabara [19] is adopted for the description of a concentrated dispersion, and the pseudo-spectral method based on Chebyshev polynomials is used to solve the governing electrokinetic equations subject to the associated boundary conditions. A brief introduction to the pseudo-spectral method can be found in Lee et al. [20]. The influence of the key parameters, including the thickness of the double layer, the concentration of particles, the surface potential of the rigid core of a particle, and the thickness, the amount of fixed charge, and the friction coefficient of the membrane layer of a particle, on the electrophoretic behavior of the system under consideration is discussed.

2. Theory

Referring to Fig. 1, we consider a concentrated dispersion of spherical particles each of which comprises a rigid core of radius a and a uniform ion-penetrable membrane layer of thickness d . The surface of the former is positively charged and the latter carries a fixed charge, which may arise from, for example, the dissociation of the functional groups. The unit cell model of Kuwabara [19] is adopted, where a dispersion is simulated by a representative cell of radius c composed of a particle of radius b ($= a + d$) and a liquid shell of thickness $c - b$. The spherical coordinates (r, θ, φ) are adopted with their origin located at the center of the particle. An electric field E is applied, which is parallel to $\theta = 0$, and U is the electrophoretic velocity of the particle. The liquid phase contains a $z_1 : z_2$ electrolyte, z_1 and z_2 being respectively the valence of cations and that of anions. Let $z_2 = -\alpha z_1$ and $H = (b/c)^3$; the latter is a measure for the volume fraction of particles.

Fig. 1. An electric field E is applied to a concentrated spherical dispersion of particles, each of them comprises a rigid core of radius a and an ion-penetrable membrane layer of thickness d . The surface of the rigid core of a particle is positively charged and the membrane layer carries fixed charge. The system is simulated by a represented cell of radius c , which is composed of a particle of radius b ($= a + d$) and a liquid shell of thickness $c - b$. U is the electrophoretic velocity of the particle, and r and θ are the radial and the azimuthal angle of the spherical coordinates chosen.

The equations governing the present phenomenon comprise those for the electric, concentration, and flow fields. The so-called electrokinetic equations are coupled nonlinear differential equations. On the basis of Gauss's law, it can be shown that the electric potential ϕ is described by the Poisson equation,

$$\nabla^2 \phi = -\frac{\rho + \rho_{\text{fix}}}{\epsilon}, \quad a < r < b, \quad (1)$$

$$\nabla^2 \phi = -\frac{\rho}{\epsilon}, \quad b < r < c, \quad (2)$$

where $\rho = \sum_j n_j z_j e$ is the density of mobile ions, ∇ is the gradient operator, e is the elementary charge, n_j and z_j are respectively the number concentration and the valence of the ionic species j , and ϵ and ρ_{fix} are respectively the permittivity of the liquid phase and the fixed charge density in the membrane layer. We assume that both ϵ and ρ_{fix} are constant. The conservation of ionic species yields [20]

$$\nabla^2 n_j + \frac{z_j e}{kT} (\nabla n_j \cdot \nabla \phi + n_j \nabla^2 \phi) - \frac{1}{D_j} \mathbf{v} \cdot \nabla n_j = 0, \quad (3)$$

where D_j is the diffusivity of the ionic species j , k and T are respectively the Boltzmann constant and the absolute temperature, and $\mathbf{v}$ is the liquid velocity.

Suppose that the liquid phase is an incompressible Newtonian fluid with constant physical properties. For the present problem, the flow of liquid is in the creeping-flow regime, and, therefore, the flow field can be described by the continuity equation and the Navier–Stokes equations,

$$\nabla \cdot \mathbf{v} = 0, \quad (4)$$

$$-\nabla p + \eta \nabla^2 \mathbf{v} - \rho \nabla \phi - \gamma \mathbf{v} = 0, \quad a < r < b, \quad (5)$$

$$-\nabla p + \eta \nabla^2 \mathbf{v} - \rho \nabla \phi = 0, \quad b < r < c, \quad (6)$$

where p is the pressure, η is the viscosity of the liquid, and γ is the frictional coefficient of the membrane layer.

Following the treatment of O'Brien and White [4], the electrical potential ϕ is expressed as the sum of the electrical potential in the absence of the applied electric field (or the equilibrium electrical potential), ϕ_1 , and that outside a particle arising from the applied electric field, ϕ_2 ; that is, $\phi = \phi_1 + \phi_2$. Also, the effect of double-layer polarization is taken into account by expressing n_j as

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

where g_j is a perturbed potential and n_{j0} is the bulk number concentration of ionic species j . It should be pointed out that the decomposition of ϕ into ϕ_1 and ϕ_2 is for convenience only; it may not have actual physical meaning. Substituting Eq. (7) into Eqs. (1) and (2) and applying the relation $\phi = \phi_1 + \phi_2$, we obtain

$$\nabla^2 \phi_1 = -\sum_{j=1}^2 \frac{z_j e n_{j0}}{\varepsilon} \exp\left(-\frac{z_j e \phi_1}{kT}\right) - \frac{\rho_{\text{fix}}}{\varepsilon}, \quad a < r < b, \quad (8)$$

$$\nabla^2 \phi_1 = -\sum_{j=1}^2 \frac{z_j e n_{j0}}{\varepsilon} \exp\left(-\frac{z_j e \phi_1}{kT}\right), \quad b < r < c, \quad (9)$$

$$\begin{aligned} \nabla^2 \phi_2 &= \nabla^2 \phi - \nabla^2 \phi_1 \\ &= -\sum_{j=1}^2 \frac{z_j e n_{j0}}{\varepsilon} \left(\exp\left(-\frac{z_j e(\phi_1 + \phi_2 + g_j)}{kT}\right) - \exp\left(-\frac{z_j e \phi_1}{kT}\right) \right). \end{aligned} \quad (10)$$

Also, substituting Eq. (7) into Eq. (3) yields

$$\begin{aligned} \nabla^2 g_j - \frac{z_j e}{kT} \nabla \phi_1 \cdot \nabla g_j &= \frac{1}{D_j} \mathbf{v} \cdot \nabla \phi + \frac{1}{D_j} \mathbf{v} \cdot \nabla g_j \\ &+ \frac{z_j e}{kT} \nabla \phi_2 \cdot \nabla g_j + \frac{z_j e}{kT} \nabla g_j \cdot \nabla g_j. \end{aligned} \quad (11)$$

Taking the curl on both sides of Eqs. (5) and (6), applying Eq. (4), and introducing the stream function ψ , it can be shown that Eqs. (5) and (6) become, respectively,

$$\begin{aligned} E^4 \psi - \gamma E^2 \psi &= -\frac{\sin \theta}{\eta} \nabla \times [\rho \nabla(\phi_1 + \phi_2)], \\ a < r < b, \end{aligned} \quad (12)$$

and

$$E^4 \psi = -\frac{\sin \theta}{\eta} \nabla \times [\rho \nabla(\phi_1 + \phi_2)], \quad b < r < c, \quad (13)$$

where $E^4 = E^2 E^2$, with

$$E^2 = \frac{\partial}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right). \quad (14)$$

Note that in terms of ψ , the r -component of the liquid velocity, v_r , and the θ -component of the liquid velocity, v_θ , can be expressed respectively as $v_r = -(1/r^2 \sin \theta)(\partial \psi / \partial \theta)$ and $v_\theta = (1/r \sin \theta)(\partial \psi / \partial r)$.

3. Boundary conditions

Suppose that the surface of the rigid core of a particle ($r = a$) is kept at a constant potential, both the electrical potential and the electric field are continuous on the membrane–liquid interface ($r = b$), and there is no net current across the surface of a cell ($r = c$). Therefore, the boundary conditions for the equilibrium potential ϕ_1 are

$$\phi_1 = \zeta_a, \quad r = a, \quad (15)$$

$$\phi_1|_{r=b^-} = \phi_1|_{r=b^+}, \quad r = b, \quad (16)$$

$$\frac{\partial \phi_1}{\partial r} \Big|_{r=b^-} = \frac{\partial \phi_1}{\partial r} \Big|_{r=b^+}, \quad r = b, \quad (17)$$

$$\frac{\partial \phi_1}{\partial r} = 0, \quad r = c. \quad (18)$$

The boundary conditions for the potential ϕ_2 are assumed to be

$$\frac{\partial \phi_2}{\partial r} = 0, \quad r = a, \quad (19)$$

$$\phi_2|_{r=b^-} = \phi_2|_{r=b^+}, \quad r = b, \quad (20)$$

$$\frac{\partial \phi_2}{\partial r} \Big|_{r=b^-} = \frac{\partial \phi_2}{\partial r} \Big|_{r=b^+}, \quad r = b, \quad (21)$$

$$\frac{\partial \phi_2}{\partial r} = -E_z \cos \theta, \quad r = c. \quad (22)$$

The first condition arises from the rigid core of a particle being nonconductive and impermeable to ionic species. The last condition implies that a Neumann-type condition is assumed for ϕ_2 [21].

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 membrane–liquid interface, and the concentration of ionic species reaches the bulk value on the cell surface. Therefore, the boundary conditions for the concentration field are

$$\mathbf{f}_j \cdot \mathbf{n} = \mathbf{f}_j \cdot \boldsymbol{\delta}_r = 0, \quad r = a, \quad (23)$$

$$n_j|_{r=b^-} = n_j|_{r=b^+}, \quad r = b, \quad (24)$$

$$\mathbf{f}_j|_{r=b^-} = \mathbf{f}_j|_{r=b^+}, \quad r = b, \quad (25)$$

$$n_j = n_{j0}, \quad r = c, \quad (26)$$

where $\mathbf{f}_j$ is the concentration flux of ionic species j , $\mathbf{n}$ is the unit normal vector, and $\boldsymbol{\delta}_r$ is the unit vector in the r -direction.

We assume that the surface of the rigid core of a particle is no-slip. Also, the velocity of the liquid and its normal and tangential stresses are continuous on the membrane–liquid interface. On the outer boundary of a cell (the virtual surface), the vorticity of the fluid velocity vanishes, and there is no net fluid flow across it. Therefore, the boundary conditions for the flow field are

$$v_r = U \cos \theta, \quad v_\theta = -U \sin \theta, \quad r = a, \quad (27)$$

$$v_r|_{r=b^-} = v_r|_{r=b^+}, \quad v_\theta|_{r=b^-} = v_\theta|_{r=b^+}, \quad r = b, \quad (28)$$

$$\begin{aligned}\sigma_{r\theta}^H|_{r=b^-} &= \sigma_{r\theta}^H|_{r=b^+}, & \sigma_{rr}^T|_{r=b^-} &= \sigma_{rr}^T|_{r=b^+}, \\ \sigma_{rr}^E|_{r=b^-} &= \sigma_{rr}^E|_{r=b^+}, & r &= b, \\ \nabla \times \mathbf{v} &= 0, & v_r &= 0, & r &= c.\end{aligned}\quad (29)$$

$$\nabla \times \mathbf{v} = 0, \quad v_r = 0, \quad r = c. \quad (30)$$

In these expressions, $\sigma_{r\theta}^H$ is the $r\theta$ -component of the hydrodynamic stress σ^H , σ_{rr}^E is the rr -component of the Maxwell stress σ^E , and σ_{rr}^T is the rr -component of the total stress $\sigma^T = \sigma^H + \sigma^E$.

For a simpler treatment, subsequent discussions are based on scaled symbols. To this end, the governing equations and the associated boundary conditions are rewritten in dimensionless form. The following symbols are chosen for the characteristic variables: the radius of the rigid core of a particle, a , the surface potential on the core, ζ_a , the bulk number concentration of the ionic species j , n_{j0} , and the electrophoretic velocity based on Smoluchowski's theory when an electric field ζ_a/a is applied, $U_E = \varepsilon \zeta_a^2 / \eta a$. Also, we define the following symbols: the scaled radius, $r^* = r/a$, the scaled number concentration of ionic species j , $n_j^* = n_j/n_{j0}$, the scaled electric field, $E_Z^* = E_Z/(\zeta_a/a)$, the scaled velocity, $v^* = v/U_E$, the scaled terminal velocity, $U^* = U/U_E$, the scaled equilibrium potential, $\phi_1^* = \phi_1/\zeta_a$, the scaled perturbed potentials, $\phi_2^* = \phi_2/\zeta_a$ and $g_j^* = g_j/\zeta_a$, and the scaled stream function, $\psi^* = \psi/U_E a$. Applying the method of separation of variables, the two-dimensional dependent variables, ϕ_2^* , g_1^* , g_2^* , and ψ^* , can make one-dimensional. For the present problem, the following expressions are applicable [19]: $\phi_2^* = \Phi_2(r) \cos \theta$, $g_1^* = G_1(r) \cos \theta$, $g_2^* = G_2(r) \cos \theta$, $\psi^* = \Psi(r) \sin^2 \theta$. On the basis of these expressions and the assumption that the applied electric field is weak relative to that induced by a particle, it can be shown that the resultant governing equations for ϕ_2^* , g_1^* , g_2^* , and ψ^* become

$$\nabla^{*2} \phi_1^* = -\frac{(\kappa a)^2}{(1+\alpha)\phi_r} [\exp(-\phi_r \phi_1^*) - \exp(\alpha \phi_r \phi_1^*)] - Q_{\text{fix}}, \quad a < r < b, \quad (31)$$

$$\nabla^{*2} \phi_1^* = -\frac{(\kappa a)^2}{(1+\alpha)\phi_r} [\exp(-\phi_r \phi_1^*) - \exp(\alpha \phi_r \phi_1^*)], \quad b < r < c, \quad (32)$$

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

$$L^2 G_1 - \phi_r^2 \frac{d\phi_1^*}{dr^*} = Pe_1 \phi_r^2 v_r^* \frac{d\phi_1^*}{dr^*}, \quad (34)$$

$$L^2 G_2 + \alpha \phi_r^2 \frac{d\phi_1^*}{dr^*} = Pe_2 \phi_r^2 v_r^* \frac{d\phi_1^*}{dr^*}, \quad (35)$$

$$D^4 \Psi - (\lambda a)^2 D^2 \Psi = -\frac{(\kappa a)^2}{1+\alpha} \left[(n_1^* G_1 + n_2^* G_2) \frac{d\phi_1^*}{dr^*} \right], \quad a < r < b, \quad (36)$$

$$D^4 \Psi = -\frac{(\kappa a)^2}{1+\alpha} \left[(n_1^* G_1 + n_2^* G_2) \frac{d\phi_1^*}{dr^*} \right], \quad b < r < c. \quad (37)$$

In these expressions, $Q_{\text{fix}} = \rho_{\text{fix}} a^2 / \varepsilon \zeta_a$ is the scaled total amount of fixed charge, $\phi_r = z_1 e \zeta_a / kT$ is the scaled surface potential of particle, $\kappa^{-1} = [\varepsilon kT / \sum n_{j0} (ez_j)^2]^{1/2}$ is the Debye length, $Pe_j = U_E a / Dj$, $j = 1, 2$, is the electric Peclet number of ionic species j , and $(\lambda a)^2 = (\gamma a^2 / \eta)$ is the dimensionless group for the friction coefficient of the membrane layer. The linear operators L^2 and D^4 are defined respectively by

$$L^2 \equiv \frac{d^2}{dr^{*2}} + \frac{2}{r^*} \frac{d}{dr^*} - \frac{2}{r^{*2}} \quad (38)$$

and

$$D^4 = D^2 D^2 = \left(\frac{d^2}{dr^{*2}} - \frac{2}{r^{*2}} \right)^2. \quad (39)$$

The associated boundary conditions become

$$\frac{d\Phi_2}{dr^*} = 0, \quad r^* = 1, \quad (40)$$

$$\Phi_2|_{r^*=b^-/a} = \Phi_2|_{r^*=b^+/a}, \quad r^* = \frac{b}{a}, \quad (41)$$

$$\frac{d\Phi_2}{dr^*} \Big|_{r^*=b^-/a} = \frac{d\Phi_2}{dr^*} \Big|_{r^*=b^+/a}, \quad r^* = \frac{b}{a}, \quad (42)$$

$$\frac{d\Phi_2}{dr^*} = -E_z^*, \quad r^* = \frac{c}{a}, \quad (43)$$

$$\frac{dG_j}{dr^*} = 0, \quad r^* = 1, \quad j = 1, 2, \quad (44)$$

$$G_j|_{r^*=b^-/a} = G_j|_{r^*=b^+/a}, \quad r^* = \frac{b}{a}, \quad j = 1, 2, \quad (45)$$

$$\frac{dG_j}{dr^*} \Big|_{r^*=b^-/a} = \frac{dG_j}{dr^*} \Big|_{r^*=b^+/a}, \quad r^* = \frac{b}{a}, \quad j = 1, 2, \quad (46)$$

$$G_1 = -\Phi_2 \quad \text{and} \quad G_2 = -\Phi_2, \quad r^* = \frac{c}{a}, \quad (47)$$

$$\Psi^* = -\frac{1}{2} r^{*2} U^* \quad \text{and} \quad \frac{d\Psi^*}{dr^*} = -r^* U^*, \quad r^* = 1, \quad (48)$$

$$\Psi^*|_{r^*=b^-/a} = \Psi^*|_{r^*=b^+/a} \quad \text{and}$$

$$\frac{d\Psi^*}{dr^*} \Big|_{r^*=b^-/a} = \frac{d\Psi^*}{dr^*} \Big|_{r^*=b^+/a}, \quad r^* = \frac{b}{a}, \quad (49)$$

$$\frac{d^2 \Psi^*}{dr^{*2}} \Big|_{r^*=b^-/a} = \frac{d^2 \Psi^*}{dr^{*2}} \Big|_{r^*=b^+/a}, \quad r^* = \frac{b}{a}, \quad (50)$$

$$\begin{aligned} \left[\frac{d^3 \Psi^*}{dr^{*3}} - (\lambda a)^2 \frac{d\Psi^*}{dr^*} \right]_{r^*=b^-/a} &= \left[\frac{d^3 \Psi^*}{dr^{*3}} \right]_{r^*=b^+/a}, \\ r^* &= \frac{b}{a}, \end{aligned} \quad (51)$$

$$\Psi^* = 0 \quad \text{and} \quad \left(\frac{d^2}{dr^{*2}} - \frac{2}{r^{*2}} \right) \Psi^* = 0, \quad r^* = \frac{c}{a}. \quad (52)$$

According to O'Brien and White [4], the present problem can be divided into two subproblems. In the first problem, the particle moves in the absence of E , and in the second problem E is applied, but the particle is kept fixed. In the first problem the total force acting on a particle, F_1 , is proportional to its terminal velocity, and in the second problem,

the total force acting on the particle, F_2 , is proportional to the applied electric field. Therefore have $F_1 = U^* f_1$ and $F_2 = E_z^* f_2$, where f_1 is independent of U^* , and f_2 is independent of E_z^* . The scaled electrophoretic mobility can be defined as $\mu_m^* = U^*/E_z^* = \eta U/\varepsilon \zeta_a E_z$. Because $F_1 + F_2 = 0$ at steady state, μ_m^* can be expressed as

$$\mu_m^* = \frac{U^*}{E_z^*} = -\frac{f_2}{f_1}. \quad (53)$$

Since f_1 is independent of U^* and f_2 is independent of E_z^* , we choose $|U^*| = 1$ and $|E_z^*| = 1$, for simplicity, and, therefore, $f_1 = F_1$ and $f_2 = F_2$. The forces acting on a particle $\mathbf{F}$ comprises the electrical force $\mathbf{F}_e$ and the hydrodynamic force $\mathbf{F}_d$. Let F_{zi} be the magnitude of $\mathbf{F}$ in problem i in the z -direction, and F_{ez} and F_{dz} be respectively the components of $\mathbf{F}_e$ and $\mathbf{F}_d$ in the z -direction. We have

$$F_{zi} = (F_{ez} + F_{dz})_i = f_i, \quad i = 1, 2. \quad (54)$$

The electric force acting on a particle can be evaluated by

$$\mathbf{F}_e = \iint_{r=b} \boldsymbol{\sigma}^E \cdot \mathbf{n} \, ds, \quad (55)$$

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

$$F_{ez} = \mathbf{F}_e \cdot \boldsymbol{\delta}_z = \iint_{r=b} (\boldsymbol{\sigma}^E \cdot \mathbf{n}) \cdot \boldsymbol{\delta}_z \, ds, \quad (56)$$

where $\boldsymbol{\delta}_z$ is the unit vector in the z -direction. In terms of scaled symbols, it can be shown that

$$F_{ez} = \frac{4}{3}\pi\varepsilon\zeta_a^2 \left[r^{*2} \left(\frac{d\phi_1^*}{dr^*} \right) \left(\frac{d\phi_2}{dr^*} \right) + 2r^* \left(\frac{d\phi_1^*}{dr^*} \right) \Phi_2 \right]_{r^*=b/a}. \quad (57)$$

$\mathbf{F}_d$ can be evaluated by

$$\mathbf{F}_d = \iint_{r=b} \boldsymbol{\sigma}^H \cdot \mathbf{n} \, ds, \quad (58)$$

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

$$F_{dz} = \mathbf{F}_d \cdot \boldsymbol{\delta}_z = \iint_{r=b} (\boldsymbol{\sigma}^H \cdot \mathbf{n}) \cdot \boldsymbol{\delta}_z \, ds. \quad (59)$$

In terms of scaled symbols, it can be shown that

$$F_{dz} = \frac{4}{3}\pi\varepsilon\zeta_a^2 \left[r^{*2} \frac{\partial}{\partial r^*} (D^2\psi) - 2r^* (D^2\psi) \right]_{r^*=b/a} + \frac{4}{3}\pi\varepsilon\zeta_a^2 \frac{(\kappa a)^2}{(1+\alpha)\phi_r} \left\{ r^{*2} \Phi_2 [\exp(-\phi_r \phi_1^*) - \exp(\alpha\phi_r \phi_1^*)] \right\}_{r^*=b/a}. \quad (60)$$

μ_m^* can be evaluated by substituting the results obtained from Eqs. (57) and (60) into Eqs. (53) and (54) with

$$f_i = \begin{pmatrix} [r^{*2} \left(\frac{\partial \phi_1^*}{\partial r^*} \right) \left(\frac{\partial \Phi_2}{\partial r^*} \right) + 2r^* \left(\frac{\partial \phi_1^*}{\partial r^*} \right) \Phi_2]_{r^*=b/a} \\ + [r^{*2} \frac{\partial}{\partial r^*} (D^2\psi) - 2r^* (D^2\psi)]_{r^*=b/a} \\ + \frac{(\kappa a)^2}{(1+\alpha)\phi_r} \{ r^{*2} \Phi_2 [\exp(-\phi_r \phi_1^*) \\ - \exp(\alpha\phi_r \phi_1^*)] \}_{r^*=b/a} \end{pmatrix}_{\text{problem } i}, \quad i = 1, 2. \quad (61)$$

4. Results and discussions

The applicability of the numerical scheme adopted in this study is justified by reproducing the result of Lee et al. [21], where the electrophoresis of a concentrated rigid spherical dispersion is analyzed. Fig. 2 illustrates the variation of the scaled mobility μ_m^* as a function of $(\lambda a)^2$ for the case when the membrane layer is uncharged. In this case, if $(\lambda a)^2 \rightarrow 0$, the membrane layer is frictionless to the flow of liquid, and the present case should reduce to that of Lee et al. [21], which is justified in Fig. 2. On the other hand, if $(\lambda a)^2 \rightarrow \infty$, the membrane layer is impermeable to the liquid phase, and the present problem is equivalent to that for the case of rigid spherical dispersions of radius b . Note that μ_m^* approaches a constant value when $(\lambda a)^2 \rightarrow \infty$, as it should be. The qualitative behavior of μ_m^* shown in Fig. 2 is similar to that observed by Saville [15].

The influences of the key parameters of the present problem, including the thickness of double layer κa , the relative thickness of membrane layer d/a , the scaled friction coefficient of the membrane layer $(\lambda a)^2$, the concentration of particles estimated by H , and the scaled surface potential on

Fig. 2. Variation of scaled mobility μ_m^* as a function of $(\lambda a)^2$ for the case when $Q_{\text{fix}} = 0$, $\kappa a = 1.0$, $\phi_r = 4.0$, $H = 0.421875$, and $d/a = 0.5$. Dashed line, result of Lee et al. [21]; solid line, present result.

the rigid core of a particle ϕ_r , on the mobility of a particle are examined through numerical simulation. For illustration, the following values are chosen: $\varepsilon_r = 78.5$, $\eta = 8.904 \times 10^{-3}$ poise, $\rho_f = 0.99704$ g/cm³, $\rho_p = 1.05$ g/cm³, $z_1 = 1$, $z_2 = -1$, $T = 298.15$ K, $D_1 = 1.962297 \times 10^{-5}$ cm²/s, $D_2 = 2.037051 \times 10^{-5}$ cm²/s. These values are based on an aqueous KCl solution at $T = 298.15$ K. The nature and the amount of the fixed charge carried by a particle depends largely on the nature of its membrane layer, and we consider two general cases, $Q_{\text{fix}} = 0$ and $Q_{\text{fix}} \neq 0$.

4.1. Case 1. $Q_{\text{fix}} = 0$

In this case, the membrane layer is free of fixed charge. Fig. 3 shows that if $d/a \neq 0$, μ_m^* increases with κa , in general, and depending on the magnitude of d/a , μ_m^* may have a local maximum, a local minimum, and an inflection point. This can be explained as follows. If κa is small, the double layer surrounding a particle is thick, and the overlap between adjacent double layers is significant. Also, because the spatial distribution of ionic species is relatively uniform, the influence of the applied electric field is weak. These factors are disadvantageous to the movement of a particle. As κa increases, the retardation arising from the presence of double layer decreases, and the mobility increases accordingly. The decrease of μ_m^* in the range $1 \leq \kappa a \leq 10$ arises from the effects of double-layer polarization and the flow field in the membrane layer. In the former, the deformation of double layer yields an induced electric field, which is in the reverse direction from that of the applied electric field. In the latter, because the double layer is thinner than the membrane layer, the effective flow region in the membrane layer becomes larger, and the friction resistance due to the presence of the membrane layer is also large. Therefore, μ_m^* decreases with the increase in κa . However, if κa exceeds about 10, the increase in the absolute value of the

Fig. 3. Variation of scaled mobility μ_m^* as a function of κa at various d/a for the case when $Q_{\text{fix}} = 0$, $\lambda a = 5$, $\phi_r = 1.0$, and $H = 0.421875$.

gradient of electrical potential near the core of a particle becomes more important than the above two negative effects, and μ_m^* increases with the increase in κa . Note that for a rigid particle, as κa increases, the double layer surrounding it becomes thin, the absolute value of the potential gradient near its surface is large, which implies that the electric force acting on it is large, and its mobility becomes large. In the limit as $\kappa a \rightarrow \infty$, the mobility approaches that predicted by the classic Smoluchowski result; that is, we must have $\mu_m^* \rightarrow 1$ as $\kappa a \rightarrow \infty$. For the present case, although situations become more complicated, similar reasoning is still applicable; that is, if κa is sufficient large, μ_m^* should increase with κa and approach a constant value as $\kappa a \rightarrow \infty$. Fig. 3 also suggests that if κa is small, the thicker the membrane layer the larger the μ_m^* is, but the reverse is true if κa is large. The former is because that although the overlapping of double layers yields a decrease in the mobility, the presence of a membrane layer alleviates this effect. Therefore, it is possible that the thicker the membrane layer the larger the mobility is. The latter is because the thicker the membrane layer the greater is the friction resistance due to its presence. The result corresponding to $d/a = 0$ is similar to that of Lee et al. [21] for the case of a dispersion containing rigid particles. This is expected because if $d/a = 0$, the membrane layer is absent.

The influences of the friction coefficient of the membrane layer of a particle, measured by λa , and the scaled surface potential on its rigid core, ϕ_r , on the scaled mobility of a particle, μ_m^* , are presented in Fig. 4. Fig. 4a reveals that for a fixed κa , μ_m^* decreases with the increase in λa , which is expected since the larger the λa the greater the frictional resistance due to the presence of the membrane layer. Note that if λa has a medium value, the variation of μ_m^* as a function of κa has both a local maximum and a local minimum, if λa is sufficiently large, μ_m^* has a local maximum only; and if λa is small, μ_m^* increases monotonically with κa . These behaviors can be explained by the same reasoning as that employed in the discussion of Fig. 3. Fig. 4a reveals that the variation of μ_m^* becomes insensitive to λa when it exceeds about 100. This is because if λa exceeds a certain value, the fluid in the membrane layer is almost stagnant, and a further increase in λa has a negligible influence on the flow field inside. The qualitative behavior of μ_m^* presented in Fig. 4b is similar to that for the case of a rigid spherical dispersion [21]. Again, the specific behavior of μ_m^* in the range $1 \leq \kappa a \leq 10$ arises from the effect of double-layer polarization.

4.2. Case 2. $Q_{\text{fix}} \neq 0$

In this case, the membrane layer carries a fixed charge. Fig. 5 illustrates the variation of the scaled mobility μ_m^* as a function κa at various values of d/a for two levels of Q_{fix} . This figure indicates that for the case where Q_{fix} is small, if κa is large, the thicker the membrane layer the smaller the μ_m^* , as shown in Fig. 5a, but the reverse is true if Q_{fix} is

Fig. 4. Variation of scaled mobility μ_m^* as a function of κa at various λa (a) and various ϕ_r (b) for the case when $Q_{\text{fix}} = 0$, $H = 0.421875$, and $d/a = 0.5$. $\phi_r = 1.0$ in (a) and $\lambda a = 5$ in (b).

large, as illustrated in Fig. 5b. As the thickness of the membrane layer increases, both the friction of liquid flow inside and the total amount of fixed charge increase. The former is disadvantageous to the movement of a particle, but the latter is advantageous. The behavior of μ_m^* shown in Fig. 5 reflects the net result of these two competing factors. Note that in Fig. 5a, although the influence of membrane friction is more important than that of total amount of fixed charge, μ_m^* increases with d/a if κa is small. This is because if κa is sufficiently small, since the double layer extends to the outside of the membrane layer, the flow of liquid inside it becomes relatively insignificant, that is, the influence of friction is relatively unimportant to that of total amount of fixed charge.

The influence of the friction coefficient of the membrane layer of a particle, measured by λa , on its electrophoretic be-

Fig. 5. Variation of scaled mobility μ_m^* as a function of κa at various d/a at two values of Q_{fix} for the case when $\lambda a = 10$, $\phi_r = 1.0$, and $H = 0.421875$. (a) $Q_{\text{fix}} = 0.5$, (b) $Q_{\text{fix}} = 5$.

havior is presented in Fig. 6. Here, μ_m^* is negative because the membrane layer is negatively charged. Fig. 6 indicates that for a fixed κa , $|\mu_m^*|$ decreases with the increase in λa , and for a fixed λa , μ_m^* exhibits a local minimum as κa varies. The former is expected since the larger the λa , the more significant the friction of the membrane layer, and the latter can be explained as follows. If κa is small, the overlapping between neighboring double layers is significant and the spatial distribution of mobile ions is relatively uniform. Since both of these factors are disadvantageous to the movement of a particle, $|\mu_m^*|$ is small. As κa increases, those factors become less significant, and $|\mu_m^*|$ increases accordingly. The rationale behind the presence of a local minimum in μ_m^* for κa in the range 1 to 10 is similar to that for the case when

Fig. 6. Variation of scaled mobility μ_m^* as a function of κa at various λa for the case when $Q_{\text{fix}} = -10$, $\phi_r = 1.0$, $H = 0.421875$, and $d/a = 0.5$.

the membrane layer is free of fixed charge. That is, the polarization of the double layer induces an electric field, which is in the reverse direction from that of the applied electric field. Also, when the double layer is thinner than the membrane layer, the friction of the latter becomes significant. It is interesting to note that after passing the local minimum, if κa is increased further, $|\mu_m^*|$ does not increase again as that for the case the membrane layer is free of fixed charge. This is because the surface of the rigid core of a particle is positively charged, and, therefore, the thinner the double layer the greater the absolute value of the potential gradient near the surface, which leads to a higher driving force for the particle to move in the direction of the applied electric field. The negative fixed charge in the membrane layer of the particle, however, tends to balance this driving force, and the net result is that $|\mu_m^*|$ decreases with the increase in κa .

4.3. Effect of surface potential ϕ_r

The influence of the surface potential on the rigid core of a particle on its mobility is illustrated in Fig. 7, where the scaled mobility μ_m^* is plotted against κa at various ϕ_r . A comparison between Figs. 7 and 4b reveals that the influence of ϕ_r on μ_m^* for the case when the membrane layer is negatively charged is relatively less important than that for the case where it is free of fixed charge. This is because, in the former, the induced electric field arising from double-layer polarization is in the same direction as that of the electric force acting on a particle due to the presence of the fixed charge in its membrane layer, and, therefore, $|\mu_m^*|$ does not decrease significantly as ϕ_r increases.

4.4. Effect of volume fraction H

The influence of the volume fraction of particle, estimated by $H = (b/c)^3$, on its scaled mobility μ_m^* is illus-

Fig. 7. Variation of scaled mobility μ_m^* as a function of κa at various ϕ_r for the case when $Q_{\text{fix}} = -10$, $\lambda a = 5$, $H = 0.421875$, and $d/a = 0.5$.

Fig. 8. Variation of scaled mobility μ_m^* as a function of κa at various H for the case when $Q_{\text{fix}} = -10$, $\lambda a = 5$, $\phi_r = 1.0$, and $d/a = 0.5$.

trated in Fig. 8. The general behavior of μ_m^* as H varies is similar to that of rigid particle [21]; that is, the larger the H the smaller the μ_m^* . This is because, the higher the concentration of particles, the more significant the overlap between neighboring double layers and the drag acting on a particle arising from the neighboring particles, which are disadvantageous to the movement of a particle. Fig. 8 also reveals that the κa at which μ_m^* has a local minimum increases with H . This is because the larger the H the closer the particle surface to cell surface, and, therefore, a larger κa is necessary to achieve the condition that the boundary of double layer is within a cell, that is, to avoid double-layer overlap.

Fig. 9. Variation of scaled mobility μ_m^* as a function of Q_{fix} for the case when $\lambda a = 5$, $\kappa a = 1.0$, $\phi_r = 4.0$, $H = 0.125$, and $d/a = 0.5$.

4.5. Effect of Q_{fix}

Fig. 9 shows the variation of the scaled mobility of a particle μ_m^* as a function of the scaled total amount of fixed charge in its membrane layer Q_{fix} for the case where the surface of its core is positively charged. This figure indicates that if Q_{fix} exceeds about -5 , μ_m^* is positive, that is, the particle moves in the direction of the applied electric field; otherwise, it moves in the reverse direction. This is expected because if Q_{fix} is sufficiently small, the net charge carried by a particle is negative.

5. Conclusions

The electrophoresis of a concentrated dispersion of soft, spherical particles is investigated theoretically under the conditions when the effects of double-layer overlap and double-layer polarization can be significant. The results of numerical simulations can be summarized as follow: (a) If the double layer surrounding a particle is either very thick or very thin, the thinner the double layer the greater the mobility of the particle. For a medium-thick double layer, the mobility may exhibit both a local maximum and a local minimum as the thickness of the double layer varies. (b) The electrophoresis of a rigid spherical dispersion can be recovered as a special case of the present analysis by letting the friction coefficient of the membrane layer surrounding a particle approach either a very large or very small value. (c) If

the membrane layer is free of fixed charge, it is thicker for smaller mobility. On the other, if the membrane layer carries fixed charge, increasing its thickness can have either a positive effect or a negative effect on the mobility, depending on the parameters assumed. (d) If the membrane layer is free of fixed charge, the higher the surface potential of the rigid core of a particle the larger its mobility when the double layer is thick, but the reverse is true if it is thin. This phenomenon does not occur when the sign of the fixed charge in the membrane layer is the same as that on the surface of the rigid core. (e) If the sign of the fixed charge in the membrane layer is different from that on the surface of the rigid core, the direction of electrophoresis depends on the relative amount of the fixed charge on the surface of the rigid core and that in the membrane layer. (f) The more concentrate a dispersion is the smaller the mobility.

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