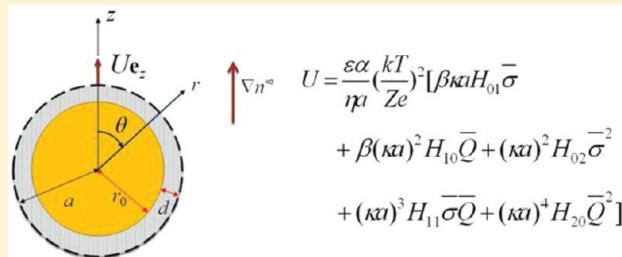


Diffusiophoresis of a Spherical Soft Particle in Electrolyte Gradients

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ABSTRACT: An analytical study of the diffusiophoresis (consisting of electrophoresis and chemiphoresis) of a charged soft particle (or composite particle) composed of a spherical rigid core and a surrounding porous shell in an electrolyte solution prescribed with a uniform concentration gradient is presented. In the solvent-permeable and ion-penetrable porous surface layer of the particle, idealized frictional segments with fixed charges are assumed to distribute at a constant density. The electrokinetic equations that govern the electric potential profile, ionic concentration distributions, and fluid flow field inside and outside the porous layer of the particle are linearized by assuming that the system is only slightly distorted from equilibrium. Using a regular perturbation method, these linearized equations are solved with the fixed charge densities on the rigid core surface and in the porous shell as the small perturbation parameters. An analytical expression for the diffusiophoretic mobility of the soft sphere in closed form is obtained from a balance between its electrostatic and hydrodynamic forces. This expression, which is correct to the second order of the fixed charge densities, is valid for arbitrary values of κa , λa , and r_0/a , where κ is the reciprocal of the Debye screening length, λ is the reciprocal of the length characterizing the extent of flow penetration inside the porous layer, a is the radius of the soft sphere, and r_0 is the radius of the rigid core of the particle. It is shown that a soft particle bearing no net charge can undergo diffusiophoresis (electrophoresis and chemiphoresis), and the direction of its diffusiophoretic velocity is decided by the fixed charges in the porous surface layer of the particle. In the limiting cases of large and small values of r_0/a , the analytical solution describing the diffusiophoretic mobility for a charged soft sphere reduces to that for a charged rigid sphere and for a charged porous sphere, respectively.



1. INTRODUCTION

When a colloidal particle is suspended in a fluid solution possessing a solute concentration gradient that interacts with its surface, it will move in the direction of increasing or decreasing concentration. This motion is known as diffusiophoresis^{1–5} and has been demonstrated experimentally for both charged^{6–8} and uncharged⁹ solutes. Being an efficient means to drive particles in nonuniform solutions, diffusiophoresis is of considerable importance in numerous practical applications, such as particle characterization or separation,¹⁰ latex paint coating processes,¹¹ particle manipulation in microfluidic or lab-on-a chip devices,^{12,13} autonomous motions of micro/nanomotors,^{14–18} and DNA sequencing.^{19–22} In a solution of nonionic solute, the solute molecules interact with the particle through the van der Waals and dipole forces. For charged particles in an electrolyte solution, the particle-solute interaction is electrostatic in nature, and its range is the Debye screening length κ^{-1} . Particles with ζ potentials of order kT/e (~ 25 mV; e is the charge of a proton, k is Boltzmann's constant, and T is the absolute temperature) in electrolyte gradients of order 0.1 M/mm will move by diffusiophoresis at speeds of several micrometers per second.

Analytical studies on electrokinetic diffusiophoresis are limited, in comparison with those on electrophoresis, and mostly restricted to cases of thin electric double layer.^{1–4} When the double-layer distortion from equilibrium was taken as a small perturbation, Prieve and Roman²³ obtained a numerical solution for the diffusiophoresis of a dielectric sphere of radius a in

concentration gradients of 1:1 electrolytes (KCl or NaCl), which was applicable to a broad range of the ζ potential, ζ , and electrokinetic radius, κa , of the particle. On the other hand, analytical formulas in closed forms were obtained for the diffusiophoretic mobilities of a rigid sphere²⁴ and a porous sphere²⁵ in symmetric electrolytes at low fixed charge densities and arbitrary κa , and the results of the former case²⁴ are in good agreement with the numerical calculations²³ for the entire range of ζ up to 50 mV.

The surface of a colloidal particle is generally not hard and smooth as assumed in many theoretical models. For example, surface layers are purposely formed by adsorbing long-chain polymers to make the suspended particles stable against flocculation.²⁶ Even the surfaces of model colloids such as silica and polystyrene latex are “hairy” with a gel-like polymeric layer extending a substantial distance into the suspending medium from the bulk material inside the particle.^{27,28} In particular, the surface of a biological cell is not a hard smooth wall, but rather is a permeable rough surface with various appendages ranging from protein molecules on the order of nanometers to cilia on the order of micrometers.²⁹ Such particles can be modeled as a soft particle (or composite particle) having a central rigid core and an outer porous shell.^{30–33} When the rigid core vanishes, the

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particle reduces to a permeable one, such as polymer coils or colloidal flocs. Although general expressions were derived for the electrophoretic mobility of a spherical soft particle,^{34–36} the effects of fixed charges on the diffusiophoretic velocity of soft particles have not yet been analyzed.

In this article, the diffusiophoretic motion of a charged soft sphere in an unbounded solution of a symmetrically charged electrolyte with a constant imposed concentration gradient is analyzed. The densities of the fixed charges and the hydrodynamic frictional segments are assumed to be uniform throughout the porous surface layer of the soft particle, but no assumption is made for the thickness of the electric double layer and of the porous layer relative to the dimension of the particle. The basic electrokinetic equations are linearized assuming that the electrolyte ion concentrations, the electrostatic potential, and the fluid pressure have only slight deviations from equilibrium due to the application of the electrolyte concentration gradient. Through the use of a regular perturbation method with the fixed charge densities on the rigid core and inside the porous shell of the soft particle as the small perturbation parameters, the ion concentration (or electrochemical potential energy), electrostatic potential, fluid velocity, and dynamic pressure profiles are determined by solving these linearized electrokinetic equations subject to the appropriate boundary conditions. A closed-form expression for the diffusiophoretic velocity of the charged soft sphere is obtained in eq 23 from a balance between its electrostatic and hydrodynamic forces.

2. ELECTROKINETIC EQUATIONS

We consider the steady diffusiophoresis of a charged soft sphere of radius a in a solution of a symmetrically charged electrolyte. As illustrated in Figure 1, the soft particle has a porous surface layer

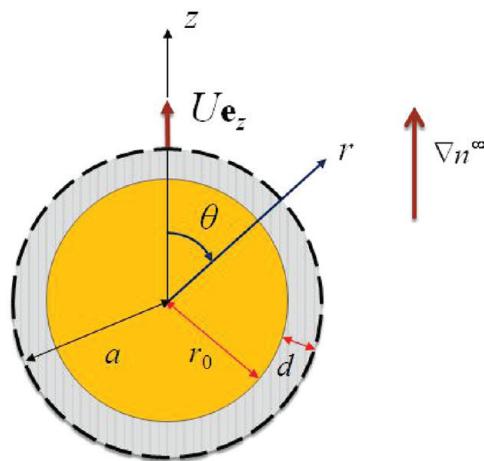


Figure 1. Geometric sketch for the diffusiophoresis of a charged soft sphere.

of constant thickness d so that the radius of the rigid core is $r_0 = a - d$. The applied electrolyte concentration gradient ∇n^∞ is a constant equal to $|\nabla n^\infty| \mathbf{e}_z$, and the diffusiophoretic velocity of the particle to be determined is $U \mathbf{e}_z$, where \mathbf{e}_z is the unit vector in the z direction. The origin of the spherical coordinate system (r, θ, ϕ) is taken at the center of the particle, and the polar axis $\theta = 0$ points toward the positive z direction. Evidently, the problem is axially symmetric about the z -axis.

2.1. Governing Equations. It is assumed that the magnitude of ∇n^∞ or the particle velocity is not large and hence that the

system is only slightly distorted from the equilibrium state, where no bulk electrolyte gradient is imposed and the particle and fluid are at rest. Therefore, the ionic concentration (number density) distributions $n_\pm(r, \theta)$, the electrostatic potential distribution $\psi(r, \theta)$, and the dynamic pressure distribution $p(r, \theta)$ can be expressed as

$$n_\pm = n_\pm^{(\text{eq})} + \delta n_\pm \quad (1a)$$

$$\psi = \psi^{(\text{eq})} + \delta\psi \quad (1b)$$

$$p = p^{(\text{eq})} + \delta p \quad (1c)$$

where $n_\pm^{(\text{eq})}(r)$, $\psi^{(\text{eq})}(r)$, and $p^{(\text{eq})}(r)$ are the equilibrium distributions of ionic concentrations, electrostatic potential, and dynamic pressure, respectively, and $\delta n_\pm(r, \theta)$, $\delta\psi(r, \theta)$, and $\delta p(r, \theta)$ are the small deviations from the equilibrium state. Here, the subscripts $+$ and $-$ refer to the cation and anion, respectively. The equilibrium concentrations $n_\pm^{(\text{eq})}$ are related to the equilibrium potential $\psi^{(\text{eq})}$ by the Boltzmann distribution.

It can be shown that the small perturbed quantities δn_\pm , $\delta\psi$, and δp together with the fluid velocity field $\mathbf{u}(r, \theta)$, which is also a small quantity, satisfy the following set of linearized electrokinetic equations:²⁵

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

$$\begin{aligned} \nabla^2 \nabla \times \mathbf{u} - h(r) \lambda^2 \nabla \times \mathbf{u} \\ = -\frac{\varepsilon}{\eta} \nabla \times (\nabla^2 \psi^{(\text{eq})} \nabla \delta\psi + \nabla^2 \delta\psi \nabla \psi^{(\text{eq})}) \end{aligned} \quad (3)$$

$$\nabla^2 \delta\mu_\pm = \pm \frac{Ze}{kT} \left\{ \nabla \psi^{(\text{eq})} \cdot \nabla \delta\mu_\pm - \frac{kT \nabla \psi^{(\text{eq})} \cdot \mathbf{u}}{[1 - (1 - \omega)h(r)] D_\pm} \right\} \quad (4)$$

$$\begin{aligned} \nabla^2 \delta\psi = \frac{Zen^\infty}{\varepsilon kT} & \left[\exp\left(\frac{Zen^\infty}{kT}\right) (\delta\mu_- + Ze\delta\psi) \right. \\ & \left. - \exp\left(-\frac{Zen^\infty}{kT}\right) (\delta\mu_+ - Ze\delta\psi) \right] \end{aligned} \quad (5)$$

Here, $\delta\mu_\pm(r, \theta)$ is defined as a linear combination of δn_\pm and $\delta\psi$ on the basis of the concept of the electrochemical potential energy,³⁷

$$\delta\mu_\pm = kT \frac{\delta n_\pm}{n_\pm^{(\text{eq})}} \pm Ze\delta\psi \quad (6)$$

n_0^∞ is the value of the prescribed electrolyte concentration n^∞ at the position with $z = 0$, which can be experimentally taken as the mean bulk concentration of the electrolyte in the vicinity of the diffusiophoretic particle; η and ε are the viscosity and permittivity, respectively, of the fluid; D_\pm and ωD_\pm (with $0 \leq \omega \leq 1$) are the diffusion coefficients of the ionic species outside and inside the porous surface layer, respectively; Z is the valence of the symmetric electrolyte, which is positive; $\lambda = (f/\eta)^{1/2}$, where f is the hydrodynamic friction coefficient inside the surface layer per unit volume of the fluid (which accounts for the hindrance to the convective transport of the fluid caused by the immobile frictional charged segments); $h(r)$ is a unit step function that equals unity if $r_0 < r < a$ (inside the surface layer), and zero if $r > a$ (outside the soft particle). The values of η , ε , D_\pm , ω , and λ are taken to be constant.

Equation 3 results from a combination of the Stokes and Brinkman equations modified with the electrostatic effect.^{34,35} The reciprocal of the parameter λ is the shielding length characterizing the extent of flow penetration inside the porous surface layer. For some model porous particles made of steel wool (in glycerin–water solution)³⁸ and plastic foam slab (in silicon oil),³⁹ experimental values of $1/\lambda$ can be as high as 0.4 mm, whereas in the surface regions of human erythrocytes,⁴⁰ rat lymphocytes,⁴¹ and grafted polymer microcapsules⁴² in salt solutions, values of $1/\lambda$ were found to be about 3 nm. Note that $1/\lambda^2$ is the “permeability” of the porous medium in the Brinkman equation, which is related to its pore size and porosity and characterizes the dynamic behavior of the viscous fluid in it.

2.2. Boundary Conditions. The boundary conditions at the surface of the dielectric rigid core of the soft sphere are

$$r = r_0: \quad \mathbf{u} = 0 \quad (7a)$$

$$\mathbf{e}_r \cdot \nabla \delta\psi = 0 \quad (7b)$$

$$\mathbf{e}_r \cdot \nabla \delta\mu_{\pm} = 0 \quad (7c)$$

where \mathbf{e}_r is the unit vector in the r direction. These conditions imply that no fluid and ions can penetrate into the rigid core and the Gauss condition holds at its surface.

The boundary conditions at the surface of the soft particle ($r = a$) are

$$\mathbf{u} \text{ and } \mathbf{e}_r \cdot \boldsymbol{\sigma} \text{ are continuous} \quad (8a)$$

$$\delta\psi \text{ and } \nabla \delta\psi \text{ are continuous} \quad (8b)$$

$$\delta\mu_{\pm} \text{ and } [1 - (1 - \omega)h(r)]\nabla \delta\mu_{\pm} \text{ are continuous} \quad (8c)$$

where $\boldsymbol{\sigma}$ is the hydrodynamic stress tensor of the fluid. The continuity requirements of the fluid velocity and stress in eq 8a, of the electric potential and electric field in eq 8b, and of the concentrations and fluxes of the ionic species in eq 8c at the particle surface are physically realistic and mathematically consistent for the present problem.^{43–45} The continuity of the hydrodynamic stress comes from the continuous Maxwell stress, and the continuity of the electric field results from the assumption that the permittivity of the solution takes the same value both inside and outside the porous surface layer.

The boundary conditions far from the particle are

$$r \rightarrow \infty: \quad \mathbf{u} \rightarrow -U\mathbf{e}_z \quad (9a)$$

$$\delta\psi \rightarrow -\frac{kT}{Ze}\beta\alpha\frac{r}{a}\cos\theta \quad (9b)$$

$$\delta\mu_{\pm} \rightarrow kT(1 \mp \beta)\alpha\frac{r}{a}\cos\theta \quad (9c)$$

where $\alpha = a|\nabla n^{\infty}|/n_0^{\infty}$ and $\beta = (D_+ - D_-)/(D_+ + D_-)$. Equations 7a and 9a take a reference frame that the particle is at rest and the velocity of the fluid at infinity is the particle velocity in the opposite direction. Equation 9b for the induced potential field, which arises spontaneously due to the imposed electrolyte gradient and the difference in mobilities of the cation and anion of the electrolyte, is derived from the requirement that the total fluxes of cations and anions are balanced in order to have no electric current generated in the bulk solution.^{1,46}

3. SOLUTION FOR THE DIFFUSIOPHORETIC VELOCITY

3.1. Equilibrium Electric Potential. Before solving for the problem of diffusiophoresis of the charged soft sphere in a

solution of a symmetric electrolyte with a constant bulk concentration gradient ∇n^{∞} , we need to determine the equilibrium electrostatic potential first. The equilibrium potential $\psi^{(eq)}$ satisfies the Poisson–Boltzmann equation and appropriate boundary conditions (taking the Gauss condition at the surface of the rigid core of the soft particle, continuous electric potential and electric field at the particle surface, and zero potential far from the particle). It can be shown that, for a charged soft sphere with a constant surface charge density σ on the rigid core and a uniform space charge density Q inside the porous shell,

$$\psi^{(eq)}(r) = \psi_{eq01}\bar{\sigma} + \psi_{eq10}\bar{Q} + O(\bar{\sigma}^3, \bar{\sigma}^2\bar{Q}, \bar{\sigma}\bar{Q}^2, \bar{Q}^3) \quad (10)$$

Here, $\bar{\sigma} = Ze\sigma/\epsilon kT$ and $\bar{Q} = ZeQ/\epsilon kT$ are the dimensionless fixed charge densities,

$$\psi_{eq01} = \frac{kT}{Ze} \left(\frac{\kappa r_0}{1 + \kappa r_0} \right) \frac{r_0}{r} e^{-\kappa(r-r_0)} \quad (11)$$

$$\psi_{eq10} = \frac{kT}{Ze} \left\{ 1 - \left(1 + \frac{1}{\kappa a} \right) \frac{e^{-\kappa d}}{1 + \kappa r_0} [\kappa r_0 \cosh(\kappa r - \kappa r_0) + \sinh(\kappa r - \kappa r_0)] \frac{a}{r} \right\} \quad \text{if } r_0 \leq r \leq a \quad (12a)$$

$$\psi_{eq10} = \frac{kT}{Ze} \left\{ 1 - \left(1 + \frac{1}{\kappa a} \right) \frac{e^{-\kappa d}}{1 + \kappa r_0} [\kappa r_0 \cosh(\kappa d) + \sinh(\kappa d)] \right\} \frac{a}{r} e^{-\kappa(r-a)} \quad \text{if } r \geq a \quad (12b)$$

and $\kappa = [2Z^2e^2n_0^{\infty}/\epsilon kT]^{1/2}$ is the Debye screening parameter. The expression in eq 10 for $\psi^{(eq)}$ as a power series in $\bar{\sigma}$ and \bar{Q} up to $O(\bar{\sigma}, \bar{Q})$ is the equilibrium solution for the linearized Poisson–Boltzmann equation that is valid for small values of the electric potential (the Debye–Hückel approximation). That is, the fixed charge densities σ and Q of the soft particle must be sufficiently small for the potential to remain small. Note that the contribution from the effects of $O(\bar{\sigma}, \bar{\sigma}\bar{Q}, \bar{Q}^2)$ to $\psi^{(eq)}$ disappears only for the case of symmetric electrolytes. The cases of a soft particle with $\sigma = 0$ and $Q = 0$ represent an uncharged rigid core with a charged porous surface layer and a charged rigid core with an uncharged surface layer, respectively.

Experimental data for the surface layers of human erythrocytes,⁴⁰ rat lymphocytes,⁴¹ and poly(*N*-isopropylacrylamide) hydrogels⁴⁷ in electrolyte solutions indicate that the magnitude of Q ranges from quite low to as high as $8.7 \times 10^6 \text{ C/m}^3$, depending on the pH value and ionic strength of the electrolyte solution. As to the surface charge density, an experimental study on the AgI surface in contact with aqueous solutions reported that the value of σ changes from 0 to -0.035 C/m^2 upon increasing the pAg from 5.6 to 11.⁴⁸ It is widely understood that the Debye length $1/\kappa$ is in the range from less than a nanometer to about a micrometer, depending on the ionic strength of the solution. For a soft particle with $\sigma = 2 \times 10^{-3} \text{ C/m}^2$ and $Q = 2 \times 10^6 \text{ C/m}^3$ in an aqueous solution of a univalent electrolyte with $1/\kappa = 1 \text{ nm}$, one obtains the dimensionless charge density $\bar{\sigma} \cong 0.1$ and $\bar{Q} \cong 0.1$.

3.2. Perturbation Solution of the Electrokinetic Equations. To solve for the small quantities \mathbf{u} , δp , $\delta\mu_{\pm}$, and $\delta\psi$ in terms of the particle velocity U when the parameters $\bar{\sigma}$ and

\bar{Q} are small, these variables are written as perturbation expansions in powers of $\bar{\sigma}$ and \bar{Q} ,

$$\mathbf{u} = \mathbf{u}_{01}\bar{\sigma} + \mathbf{u}_{10}\bar{Q} + \mathbf{u}_{02}\bar{\sigma}^2 + \mathbf{u}_{11}\bar{\sigma}\bar{Q} + \mathbf{u}_{20}\bar{Q}^2 + \dots \quad (13a)$$

$$\delta p = p_{01}\bar{\sigma} + p_{10}\bar{Q} + p_{02}\bar{\sigma}^2 + p_{11}\bar{\sigma}\bar{Q} + p_{20}\bar{Q}^2 + \dots \quad (13b)$$

$$\begin{aligned} \delta\mu_{\pm} &= \mu_{00\pm} + \mu_{01\pm}\bar{\sigma} + \mu_{10\pm}\bar{Q} + \mu_{02\pm}\bar{\sigma}^2 + \mu_{11\pm}\bar{\sigma}\bar{Q} \\ &\quad + \mu_{20\pm}\bar{Q}^2 + \dots \end{aligned} \quad (13c)$$

$$\delta\psi = \psi_{00} + \psi_{01}\bar{\sigma} + \psi_{10}\bar{Q} + \psi_{02}\bar{\sigma}^2 + \psi_{11}\bar{\sigma}\bar{Q} + \psi_{20}\bar{Q}^2 + \dots \quad (13d)$$

$$U = U_{01}\bar{\sigma} + U_{10}\bar{Q} + U_{02}\bar{\sigma}^2 + U_{11}\bar{\sigma}\bar{Q} + U_{20}\bar{Q}^2 + \dots \quad (13e)$$

where the functions \mathbf{u}_{ijp} , p_{ijp} , $\mu_{ij\pm}$, ψ_{ijp} , and U_{ij} are independent of $\bar{\sigma}$ and \bar{Q} . The zeroth-order terms of \mathbf{u} , δp , and U disappear because an uncharged particle will not move by applying an electrolyte concentration gradient if only the electrostatic interaction is involved.

Substituting the expansions given by eq 13 and $\psi^{(eq)}$ given by eq 10 into the governing equations given by eqs 2–5 and boundary conditions in eqs 7–9, and equating like powers of $\bar{\sigma}$ and \bar{Q} on both sides of the respective equations, one can derive a group of linear differential equations and boundary conditions for each set of the functions \mathbf{u}_{ijp} , p_{ijp} , $\mu_{ij\pm}$, and ψ_{ijp} . After solving these perturbation equations, the results for the r and θ components of \mathbf{u} , δp (to the orders of $\bar{\sigma}^2$, $\bar{\sigma}\bar{Q}$, and \bar{Q}^2), $\delta\mu_{\pm}$, and $\delta\psi$ (to the orders of $\bar{\sigma}$ and \bar{Q}) can be obtained as

$$\begin{aligned} u_r &= \left[\left[U_{01}F_{00r}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{01r}(r) \right] \bar{\sigma} \right. \\ &\quad + \left[U_{10}F_{00r}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{10r}(r) \right] \bar{Q} \\ &\quad + \left[U_{02}F_{00r}(r) + \frac{kT}{\eta a^2}\alpha F_{02r}(r) \right] \bar{\sigma}^2 \\ &\quad + \left[U_{11}F_{00r}(r) + \frac{kT}{\eta a^2}\alpha F_{11r}(r) \right] \bar{\sigma}\bar{Q} \\ &\quad \left. + \left[U_{20}F_{00r}(r) + \frac{kT}{\eta a^2}\alpha F_{20r}(r) \right] \bar{Q}^2 \right] \cos\theta \end{aligned} \quad (14a)$$

$$\begin{aligned} u_\theta &= \left[\left[U_{01}F_{00\theta}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{01\theta}(r) \right] \bar{\sigma} \right. \\ &\quad + \left[U_{10}F_{00\theta}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{10\theta}(r) \right] \bar{Q} \\ &\quad + \left[U_{02}F_{00\theta}(r) + \frac{kT}{\eta a^2}\alpha F_{02\theta}(r) \right] \bar{\sigma}^2 \\ &\quad + \left[U_{11}F_{00\theta}(r) + \frac{kT}{\eta a^2}\alpha F_{11\theta}(r) \right] \bar{\sigma}\bar{Q} \\ &\quad \left. + \left[U_{20}F_{00\theta}(r) + \frac{kT}{\eta a^2}\alpha F_{20\theta}(r) \right] \bar{Q}^2 \right] \sin\theta \end{aligned} \quad (14b)$$

$$\begin{aligned} \delta p &= \frac{\eta}{a} \left\{ \left[U_{01}F_{p00}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{p01}(r) - \frac{\varepsilon\kappa^2akT}{\eta Ze} \right. \right. \\ &\quad \times \beta\alpha\psi_{eq01}(r)F_{\psi00}(r) \left. \right] \bar{\sigma} + \left[U_{10}F_{p00}(r) - \frac{kT}{\eta a^2}\beta\alpha F_{p10}(r) \right. \\ &\quad - \frac{\varepsilon\kappa^2akT}{\eta Ze} \beta\alpha\psi_{eq10}(r)F_{\psi00}(r) \left. \right] \bar{Q} \\ &\quad + \left[U_{02}F_{p00}(r) + \frac{kT}{\eta a^2}\alpha F_{p02}(r) + \frac{\varepsilon\kappa^2akT}{\eta Ze}\alpha\psi_{eq01}(r) \right. \\ &\quad \times F_{\psi01}(r) \left. \right] \bar{\sigma}^2 + \left[U_{11}F_{p00}(r) + \frac{kT}{\eta a^2}\alpha F_{p11}(r) \right. \\ &\quad + \frac{\varepsilon\kappa^2akT}{\eta Ze}\alpha(\psi_{eq01}(r)F_{\psi10}(r) + \psi_{eq10}(r)F_{\psi01}(r)) \left. \right] \bar{\sigma}\bar{Q} \\ &\quad + \left[U_{20}F_{p00}(r) + \frac{kT}{\eta a^2}\alpha F_{p20}(r) + \frac{\varepsilon\kappa^2akT}{\eta Ze}\alpha\psi_{eq10}(r) \right. \\ &\quad \times F_{\psi10}(r) \left. \right] \bar{Q}^2 \} \cos\theta \end{aligned} \quad (14c)$$

$$\delta\mu_{\pm} = kT(1 \mp \beta)\alpha[F_{\mu00}(r) \mp F_{\mu01}(r)\bar{\sigma} \mp F_{\mu10}(r)\bar{Q}] \cos\theta \quad (15)$$

$$\delta\psi = \frac{kT}{Ze}\alpha[-\beta F_{\psi00}(r) + F_{\psi01}(r)\bar{\sigma} + F_{\psi10}(r)\bar{Q}] \cos\theta \quad (16)$$

Here, $F_{ijr}(r)$, $F_{ij\theta}(r)$, $F_{pij}(r)$ [with (i,j) equal to (0,1), (1,0), (0,2), (1,1), and (2,0)], $F_{\mu00}(r)$, $F_{\psi00}(r)$, $F_{\mu01}(r)$, $F_{\mu10}(r)$, $F_{\psi01}(r)$, and $F_{\psi10}(r)$ are dimensionless functions of r defined by eqs A1–A6 and A13–A16 in the Appendix. Note that the solutions for $\delta\mu_{\pm}$ and $\delta\psi$ to $O(\bar{\sigma}, \bar{Q})$ will be sufficient for the calculation of the particle velocity to $O(\bar{\sigma}^2, \bar{\sigma}\bar{Q}, \bar{Q}^2)$.

3.3. Forces Acting on the Particle. The total force acting on a charged soft sphere undergoing diffusiophoresis in an electrolyte solution can be expressed as the sum of the electric force and the hydrodynamic drag force. The electric force exerted on the soft sphere can be represented by the integral of the electrostatic force density over the fluid volume outside the particle. Due to the fact that the net electric force acting on the particle at the equilibrium state is zero, the leading order of the electric force is given by

$$\mathbf{F}_e = -2\pi\varepsilon \int_0^\pi \int_a^\infty (\nabla^2\psi^{(eq)}\nabla\delta\psi + \nabla^2\delta\psi\nabla\psi^{(eq)})r^2 \times \sin\theta dr d\theta \quad (17)$$

Substituting eqs 1b, 10, and 16 into eq 17, we obtain

$$\begin{aligned} \mathbf{F}_e = 4\pi \frac{kT}{a} \alpha & \left\{ -\beta \left[\frac{\varepsilon \kappa^2 a^3}{3Ze} \psi_{eq01}(a) F_{\psi 00}(a) + J_{01}^{(3)}(\infty) \right] \bar{\sigma} \right. \\ & - \beta \left[\frac{\varepsilon \kappa^2 a^3}{3Ze} \psi_{eq10}(a) F_{\psi 00}(a) + J_{10}^{(3)}(\infty) \right] \bar{Q} \\ & + \left[\frac{\varepsilon \kappa^2 a^3}{3Ze} \psi_{eq01}(a) F_{\psi 01}(a) + J_{02}^{(3)}(\infty) \right] \bar{\sigma}^2 \\ & + \left[\frac{\varepsilon \kappa^2 a^3}{3Ze} (\psi_{eq01}(a) F_{\psi 10}(a) + \psi_{eq10}(a) F_{\psi 01}(a)) \right. \\ & \left. + J_{11}^{(3)}(\infty) \right] \bar{\sigma} \bar{Q} + \left[\frac{\varepsilon \kappa^2 a^3}{3Ze} \psi_{eq10}(a) F_{\psi 10}(a) + J_{20}^{(3)}(\infty) \right] \\ & \times \bar{Q}^2 + O(\bar{\sigma}^3, \bar{\sigma}^2 \bar{Q}, \bar{\sigma} \bar{Q}^2, \bar{Q}^3) \left. \right\} \mathbf{e}_z \end{aligned} \quad (18)$$

where the functions $J_{ij}^{(3)}(r)$ are defined by eq A11a.

The hydrodynamic drag force exerted on the soft sphere is given by the integral of the hydrodynamic stress over the particle surface,

$$\mathbf{F}_h = 2\pi a^2 \int_0^\pi \{-\delta p \mathbf{e}_r + \eta [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \cdot \mathbf{e}_r\} \sin \theta \, d\theta \quad (19)$$

Substitution of eq 14 into the above equation results in

$$\begin{aligned} \mathbf{F}_h = -4\pi & \left\{ \left[\eta a C_{006} U_{01} - \frac{kT}{a} \beta \alpha C_{016} - \frac{\varepsilon(\kappa a)^2}{3} \frac{kT}{Ze} \beta \right. \right. \\ & \times \alpha \psi_{eq01}(a) F_{\psi 00}(a) \left. \right] \bar{\sigma} + \left[\eta a C_{006} U_{10} - \frac{kT}{a} \beta \alpha C_{106} \right. \\ & - \frac{\varepsilon(\kappa a)^2}{3} \frac{kT}{Ze} \beta \alpha \psi_{eq10}(a) F_{\psi 00}(a) \left. \right] \bar{Q} \\ & + \left[\eta a C_{006} U_{02} + \frac{kT}{a} \alpha C_{026} + \frac{\varepsilon(\kappa a)^2}{3} \frac{kT}{Ze} \alpha \psi_{eq01}(a) \right. \\ & \times F_{\psi 01}(a) \left. \right] \bar{\sigma}^2 + \left[\eta a C_{006} U_{11} + \frac{kT}{a} \alpha C_{116} \right. \\ & + \frac{\varepsilon(\kappa a)^2}{3} \frac{kT}{Ze} \alpha (\psi_{eq01}(a) F_{\psi 10}(a) + \psi_{eq10}(a) F_{\psi 01}(a)) \left. \right] \bar{\sigma} \bar{Q} \\ & + \left[\eta a C_{006} U_{20} + \frac{kT}{a} \alpha C_{206} + \frac{\varepsilon(\kappa a)^2}{3} \frac{kT}{Ze} \alpha \psi_{eq10}(a) \right. \\ & \times F_{\psi 10}(a) \left. \right] \bar{Q}^2 + O(\bar{\sigma}^3, \bar{\sigma}^2 \bar{Q}, \bar{\sigma} \bar{Q}^2, \bar{Q}^3) \left. \right\} \mathbf{e}_z \end{aligned} \quad (20)$$

where the coefficients C_{ij6} are given by eqs A7f and A8f.

3.4. Velocity of the Particle. At the steady state, the total force exerted on the diffusiophoretic particle is zero. Applying this constraint to the summation of eqs 18 and 20, we obtain

$$U_{ij} = \frac{\varepsilon \beta^{(2-i-j)} \alpha}{\eta a} \left(\frac{kT}{Ze} \right)^2 (\kappa a)^{2i+j} H_{ij} \quad (21)$$

where (i,j) equal to $(0,1)$, $(1,0)$, $(0,2)$, $(1,1)$, and $(2,0)$, and H_{ij} are dimensionless functions of r_0/a , κa , and λa defined by

$$H_{ij} = (-1)^{i+j-1} \frac{(Ze)^2}{\varepsilon a k T} \frac{1}{(\kappa a)^{2i+j}} \frac{1}{C_{006}} [C_{ij6} - J_{ij}^{(3)}(\infty)] \quad (22)$$

From eqs 13e and 21, the diffusiophoretic velocity of the charged soft sphere can be expressed as

$$\begin{aligned} U = & \frac{\varepsilon \alpha}{\eta a} \left(\frac{kT}{Ze} \right)^2 [\beta \kappa a H_{01} \bar{\sigma} + \beta (\kappa a)^2 H_{10} \bar{Q} + (\kappa a)^2 H_{02} \bar{\sigma}^2 \\ & + (\kappa a)^3 H_{11} \bar{\sigma} \bar{Q} + (\kappa a)^4 H_{20} \bar{Q}^2 \\ & + O(\bar{\sigma}^3, \bar{\sigma}^2 \bar{Q}, \bar{\sigma} \bar{Q}^2, \bar{Q}^3)] \end{aligned} \quad (23)$$

Note that $(\kappa a) \bar{\sigma}$ ($= a Z e \sigma / \varepsilon k T$) and $(\kappa a)^2 \bar{Q}$ ($= a^2 Z e Q / \varepsilon k T$) are independent of κ or n_0^∞ for constant fixed charge densities σ and Q .

When there is no permeable layer on the surface of the rigid core of the particle, one has $d = 0$ and $r_0 = a$. Then, eq 22 reduces to

$$H_{01} = \frac{1}{\kappa a + 1} \{1 - e^{\kappa a} [5E_7(\kappa a) - 2E_5(\kappa a)]\} \quad (24a)$$

$$\begin{aligned} H_{02} = & \frac{1}{8(\kappa a + 1)^2} \left\{ 1 + \frac{1}{3} e^{2\kappa a} [10E_6(2\kappa a) + 7E_8(2\kappa a)] \right. \\ & - 40e^{2\kappa a} E_7(\kappa a) [E_3(\kappa a) - E_5(\kappa a)] \\ & + \frac{4}{3} e^{\kappa a} [3E_3(\kappa a) + 9E_4(\kappa a) - 7E_5(\kappa a) \\ & \left. - 15E_6(\kappa a)] \right\} \end{aligned} \quad (24b)$$

and $H_{10} = H_{20} = H_{11} = 0$, where

$$E_n(x) = \int_1^\infty t^{-n} e^{-xt} dt \quad (25)$$

The diffusiophoretic velocity given by eqs 23 and 24 with $H_{10} = H_{20} = H_{11} = 0$ or $Q = 0$ is the same as that of a charged rigid sphere derived previously.²⁴

When the particle is a homogeneous porous sphere, one has $r_0 = 0$ and $d = a$. For the particular case of a charged porous sphere with $\lambda a \rightarrow \infty$ and $\omega = 1$, eq 22 reduces to

$$H_{10} = \frac{2}{3} (\kappa a)^{-3} e^{-\kappa a} \alpha_1(\kappa a) \quad (26a)$$

$$\begin{aligned} H_{20} = & \frac{1}{9} (\kappa a)^{-3} \alpha_1(\kappa a) [E_5(\kappa a) - E_3(\kappa a)] + \frac{1}{12} (\kappa a)^{-6} e^{-2\kappa a} \\ & \times [\alpha_1(\kappa a)]^2 \end{aligned} \quad (26b)$$

and $H_{01} = H_{02} = H_{11} = 0$, where $\alpha_1(x)$ is defined by eq A9a in the Appendix. The diffusiophoretic velocity given by eqs 23 and 26 with $H_{01} = H_{02} = H_{11} = 0$ or $\sigma = 0$ is identical to that of a charged porous sphere obtained in the literature.²⁵

A typical soft particle is a charged rigid core adsorbing a surface layer of oppositely and equivalently charged polyelectrolytes. For a soft sphere of this type with zero net charge, one has

$$4\pi r_0^2 \sigma + \frac{4}{3} \pi (a^3 - r_0^3) Q = 0 \quad \text{or} \quad \bar{\sigma} = -\gamma \kappa a \bar{Q} \quad (27)$$

where $\gamma = [(a/r_0)^2 - (r_0/a)]/3$. Analytical studies^{49,50} have predicted that a nonuniformly charged but “neutral” impermeable sphere (with zero area-averaged ζ potential) can be driven to move by externally applied electric fields. It would be of interest

to know whether and how charged but “neutral” soft spheres undergo electrophoresis or diffusiophoresis. For such spherically symmetric soft particles with zero net charge, eq 23 with the substitution of eq 27 becomes

$$U = \frac{e\alpha}{\eta a} \left(\frac{kT}{Ze} \right)^2 [\beta(\kappa a)^2 H_1 \bar{Q} + (\kappa a)^4 H_2 \bar{Q}^2 + O(\bar{Q}^3)] \quad (28)$$

where

$$H_1 = H_{10} - \gamma H_{01} \quad (29a)$$

$$H_2 = H_{20} - \gamma H_{11} + \gamma^2 H_{02} \quad (29b)$$

In the limit of $r_0/a = 1$ (the porous surface layer of the particle disappears), $\gamma = 0$ and eq 29 reduces to $H_1 = H_{10} = 0$ and $H_2 = H_{20} = 0$.

Because the governing equations in the analysis have been linearized, diffusiophoresis of a charged particle in an electrolyte solution can be considered as a linear combination of two effects:² (i) chemiphoresis due to the nonuniform adsorption of counterions and depletion of co-ions over the surface of the particle and (ii) electrophoresis due to the macroscopic electric field generated by the electrolyte concentration gradient given by eq 9b. In eqs 23 and 28 for the diffusiophoretic velocity, the first-order terms (involving the parameter β) result from the contribution of electrophoresis, whereas the second-order terms represent the chemiphoretic contribution. Thus, eqs 23 and 28 with only the first-order terms in the brackets and the replacement of $\beta \alpha kT / Zea$ by an applied electric field can also be used to express the electrophoretic velocity of the charged soft sphere.

4. RESULTS AND DISCUSSION

According to eq 23, the diffusiophoretic velocity of a charged soft sphere in an electrolyte solution prescribed with a constant concentration gradient can be calculated to the second orders σ^2 , σQ , and Q^2 of its fixed charge densities. In this section, we first discuss the dimensionless coefficients H_{ij} given by eq 22 for the general case, then present the dimensionless coefficients H_1 and H_2 given by eq 29 for a charged but “neutral” soft sphere, and finally exhibit the diffusiophoretic velocity given by eqs 23 and 28. For conciseness and without loss in physical insight, as indicated in the analytical result for the diffusiophoresis of a charged porous particle,²⁵ $\omega = 1$ (the same diffusion coefficient for each ion inside and outside the porous surface layer of the soft particle) will be taken in all the calculations. It is understood that the particle velocity is hardly dependent on ω at small κa , since under this condition the particle behaves electrically like a point charge, and the detail of what happens (such as the diffusion of ions) inside the surface layer of the particle is unimportant for the determination of its mobility by a balance between its electrostatic and hydrodynamic forces.

4.1. The First-Order Coefficients H_{01} and H_{10} for Electrophoresis. The first-order coefficients H_{01} and H_{10} in eq 23 for the diffusiophoretic/electrophoretic velocity of a charged soft sphere (which also represent the dimensionless electrophoretic mobilities of a charged rigid core with an uncharged porous surface layer and an uncharged rigid core with a charged surface layer, respectively) calculated using eq 22 are plotted in Figures 2 and 3, respectively, as functions of the electrokinetic radius κa , the shielding parameter λa , and the radius ratio r_0/a of the particle. As expected, the coefficients H_{01}

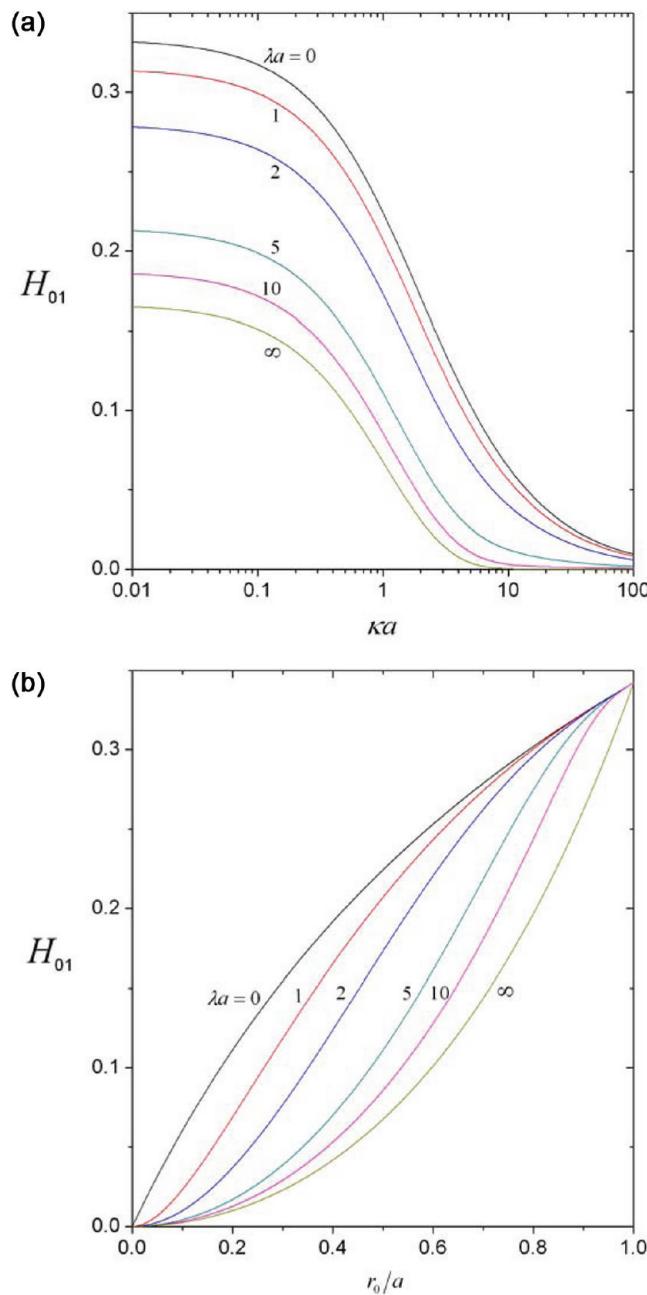


Figure 2. Plots of the coefficient H_{01} given by eq 22 for the diffusiophoretic/electrophoretic velocity of a charged soft sphere with various values of λa , κa , and r_0/a : (a) H_{01} versus κa at $r_0/a = 0.5$; (b) H_{01} versus r_0/a at $\kappa a = 1$.

and H_{10} for the electrophoretic contributions are always positive, and thus the directions of the diffusiophoresis of the particle caused by these contributions are determined by the signs of the products of the parameter β (which determines the direction of the induced electric field according to eq 9b) and the fixed charge densities σ and Q , respectively. The values of H_{01} and H_{10} , which are in the same order of magnitude for the typical case of $r_0/a = 0.5$, decrease [whereas those of $\kappa a H_{01}$ and $(\kappa a)^2 H_{10}$ may increase] monotonically with an increase in κa for specified values of r_0/a and λa , similar to the results of their limiting cases.^{24,25}

Figures 2 and 3 illustrate that the coefficients H_{01} and H_{10} decrease monotonically with an increase in λa for given values

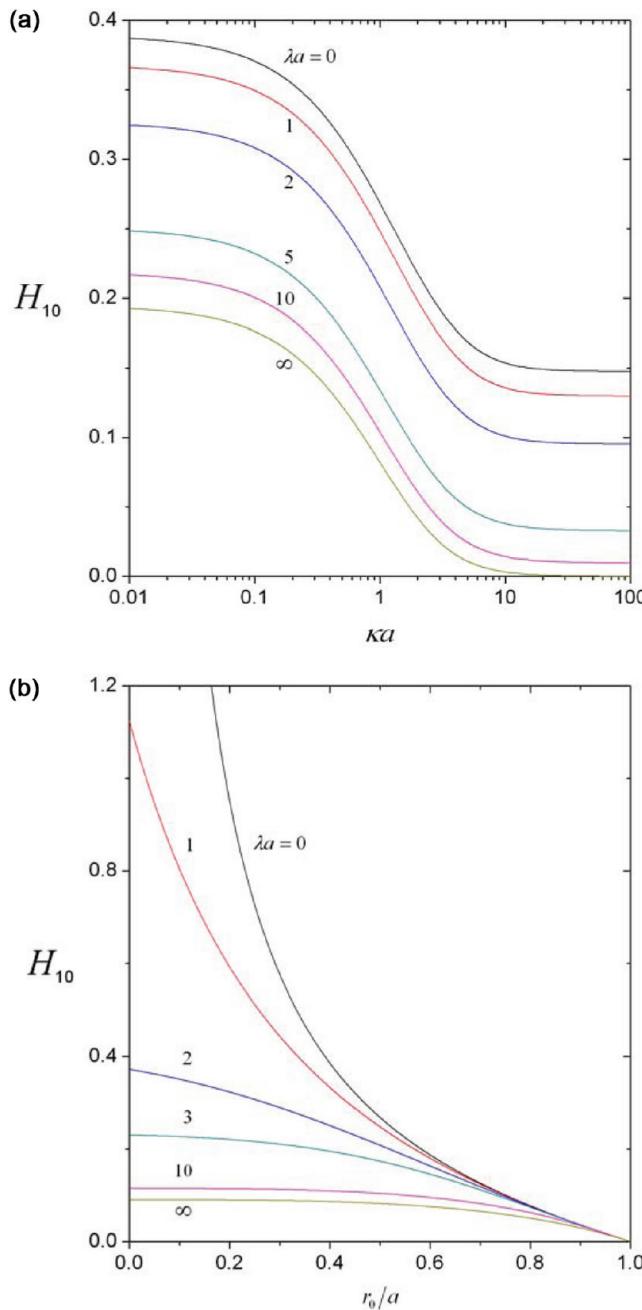


Figure 3. Plots of the coefficient H_{10} given by eq 22 for the diffusiophoretic/electrophoretic velocity of a charged soft sphere with various values of λa , κa , and r_0/a : (a) H_{10} versus κa at $r_0/a = 0.5$; (b) H_{10} versus r_0/a at $\kappa a = 1$.

of r_0/a and κa . When $\lambda a \rightarrow \infty$, the resistance to the fluid motion inside the porous surface layer of the soft particle is infinitely large, and the relative fluid velocity in the surface layer vanishes (the electrolyte ions can still penetrate the surface layer and the equilibrium potential distribution $\psi^{(eq)}$ is still given by eq 10). Therefore, for given values of r_0/a and κa with $\lambda a \rightarrow \infty$, H_{01} and H_{10} approach constant minimal values. When $\lambda a = 0$, the surface layer does not exert resistance to the fluid motion, and H_{01} and H_{10} for given values of r_0/a and κa approach constant maximal values. Note that H_{01} and H_{10} are sensitive functions of λa over its range of 1–10.

As expected, Figure 2b shows that the coefficient H_{01} , which represents the contribution to the electrophoretic velocity of the

soft particle from the surface charge density σ of its impermeable core, is a monotonic increasing function of r_0/a (or the volume fraction of the impermeable core in the soft particle) for fixed values of κa and λa . In the special case of $r_0/a = 0$, the soft particle degenerates to a homogeneous porous sphere and H_{01} must equal zero. Obviously, H_{01} is independent of λa in the special case of $r_0/a = 1$ in which the soft particle reduces to an impermeable sphere with no porous surface layer. Conversely, as shown in Figure 3b, the coefficient H_{10} , which denotes the contribution to the electrophoretic velocity of the soft particle from the space charge density Q of its porous surface layer, decreases monotonically with increasing r_0/a and vanishes when $r_0/a = 1$. In the general case of moderate values of r_0/a , the fixed charge densities σ and Q contribute comparably to the diffusiophoretic/electrophoretic velocity of the soft sphere.

4.2. The Second-Order Coefficients H_{02} , H_{11} , and H_{20} for Chemiphoresis. The second-order coefficients H_{02} , H_{11} , and H_{20} for the diffusiophoretic/chemiphoretic velocity of a charged soft sphere (where H_{02} and H_{20} also represent the dimensionless chemiphoretic mobilities of a charged rigid core with an uncharged porous surface layer and an uncharged rigid core with a charged surface layer, respectively) can also be calculated using eq 22, and their results as functions of the parameters κa , λa , and r_0/a are plotted in Figures 4–6. Again, for fixed values of r_0/a and κa , the coefficients H_{02} , H_{11} , and H_{20} generally decrease monotonically with an increase in λa and are sensitive functions of λa over its range of 1–10. Note that the values of H_{02} , H_{11} , and H_{20} , which have the same order of magnitude for the typical case of $r_0/a = 0.5$, in general are also positive (thus, the contributions of H_{02} and H_{20} cause the chemiphoresis of the particle toward the side of higher electrolyte concentration, but the contribution of H_{11} to the direction of chemiphoresis is determined by the sign of the product of σ and Q) and about 2 orders of magnitude smaller than those of H_{01} and H_{10} .

For fixed values of κa and λa , as illustrated in Figures 4b and 6b, the coefficient H_{02} , which represents the contribution to the chemiphoresis of the soft particle from the surface charge density σ of its impermeable core, in general increases with an increase in the value of r_0/a (or the volume fraction of the impermeable core in the soft particle), becomes zero as $r_0/a = 0$, and is independent of λa as $r_0/a = 1$, similar to the trend of the coefficient H_{01} , whereas the coefficient H_{20} , which denotes the contribution to the chemiphoresis of the soft particle from the space charge density Q of its porous surface layer, generally decreases with an increase in the value of r_0/a and vanishes as $r_0/a = 1$, similar to the trend of the coefficient H_{10} . On the other hand, the coefficient H_{11} , which is the contribution to the chemiphoresis of the soft particle from the interaction between the fixed charge densities σ and Q , equals zero in both limiting cases of $r_0/a = 0$ and $r_0/a = 1$, and thus there exists a maximal value of H_{11} in between the limits for specified values of κa and λa , as shown in Figure 5b. The location of the maximum shifts to greater r_0/a as λa increases, since large volume fraction of the impermeable core (small volume fraction of the porous surface layer) in the soft particle favors its movement when the resistance to the fluid motion inside the surface layer is large. In the general case of moderate values of r_0/a , the three second-order terms of the fixed charge densities in eq 23 contribute to the diffusiophoretic/chemiphoretic velocity of the soft sphere comparably.

For specified values of r_0/a and λa , as shown in Figures 4a, 5a, and 6a, the values of the coefficients H_{02} , H_{11} , and H_{20} are maximal at some values of κa between 0.1 and 1, and fade out as the value of κa gets small or large. Both the limits $\kappa a = 0$ and

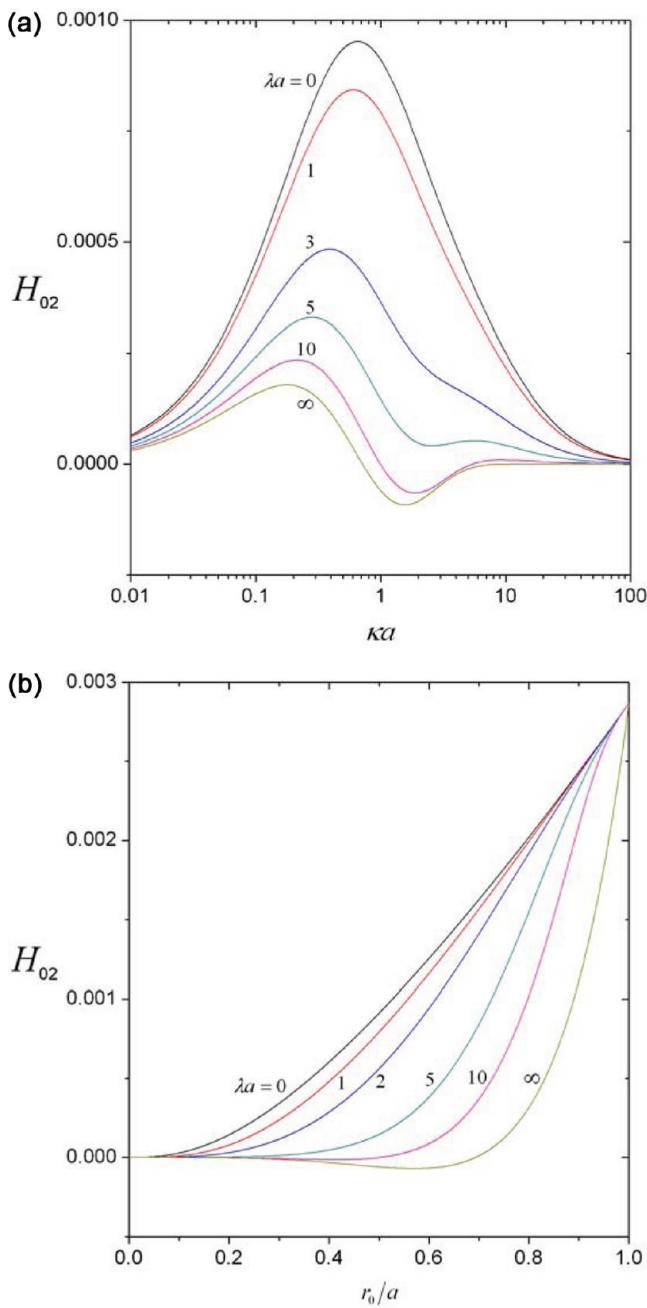


Figure 4. Plots of the coefficient H_{02} given by eq 22 for the diffusiophoretic/chemiphoretic velocity of a charged soft sphere with various values of λa , κa , and r_0/a : (a) H_{02} versus κa at $r_0/a = 0.5$; (b) H_{02} versus r_0/a at $\kappa a = 1$.

$\kappa a \rightarrow \infty$ result in $H_{02} = H_{11} = H_{20} = 0$ (but the contribution from the chemiphoretic effect vanishes only for the case of $\kappa a = 0$, as indicated by eq 23). Interestingly, when the value of λa is sufficiently large (e.g., $\lambda a > 10$), H_{02} , H_{11} , and H_{20} decrease first, reach minima (at some values of κa between 1 and 3), which in general are negative (the direction of the chemiphoresis of the particle is reversed), and then increase monotonically to zero as κa increases from its values at the maximal points to infinity. The locations of the minima (if they exist) and maxima in H_{02} , H_{11} , and H_{20} shift to smaller κa as λa increases.

The negative behavior of the second-order coefficients H_{02} , H_{11} , and H_{20} in some cases can be explained as follows. For the diffusiophoresis/chemiphoresis of a soft particle, the diffusion of

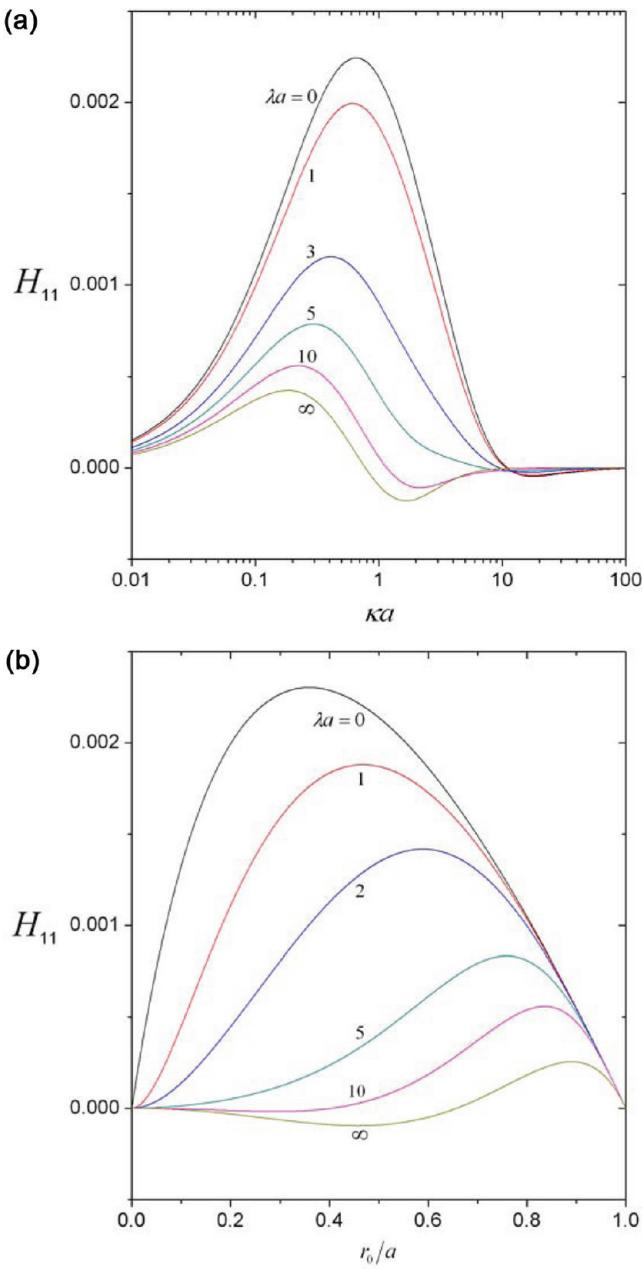


Figure 5. Plots of the coefficient H_{11} given by eq 22 for the diffusiophoretic/chemiphoretic velocity of a charged soft sphere with various values of λa , κa , and r_0/a : (a) H_{11} versus κa at $r_0/a = 0.5$; (b) H_{11} versus r_0/a at $\kappa a = 1$.

the solute species in the fluid solution affects the particle's movement through two mechanisms. Evidently, the concentration gradient of the solute along the external surface of the particle leads to a diffusioosmotic/chemiosmotic flow, which drives the soft particle to move in the direction of the concentration gradient as that for the corresponding motion of an impermeable particle. On the other hand, the diffusion of the solute species inside the porous surface layer drags the ambient fluid, which then drives the soft particle to move in the opposite direction. For the cases with intermediate κa , large λa , and small r_0/a , the contribution from the diffusion of the solute species inside the porous surface layer can be dominant over the contribution from the osmotic flow along the external surface of the particle so that the values of H_{02} , H_{11} , and H_{20} are negative.

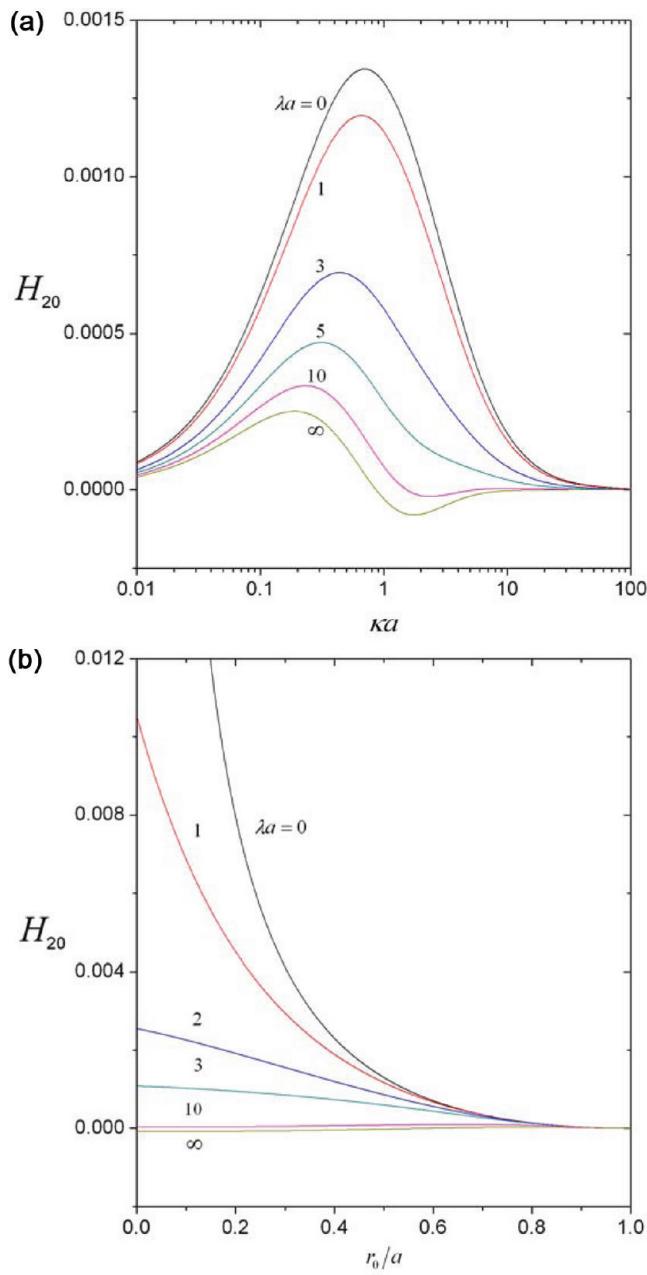


Figure 6. Plots of the coefficient H_{20} given by eq 22 for the diffusiophoretic/chemiphoretic velocity of a charged soft sphere with various values of λa , κa , and r_0/a : (a) H_{20} versus κa at $r_0/a = 0.5$; (b) H_{20} versus r_0/a at $\kappa a = 1$.

4.3. The Coefficients H_1 and H_2 for a Neutral Soft Particle. The coefficients H_1 and H_2 in eq 28, which represent the dimensionless electrophoretic and chemiphoretic velocities, respectively, of a charged but “neutral” soft sphere, expressed in terms of the fixed charge density in its porous surface layer and calculated using eqs 29 and 22 are plotted as functions of the parameters κa , λa , and r_0/a in Figures 7 and 8, respectively. It can be seen that both H_1 and H_2 are always positive and, as expected, vanish as $r_0/a = 1$ (the porous layer of the particle disappears). Thus, the “neutral” soft sphere can experience electrophoresis and chemophoresis under an electrolyte concentration gradient, and the directions of the electrophoretic and chemiphoretic velocities are decided by the fixed charges in the porous layer (rather than the surface charges of the rigid core, whose effect is

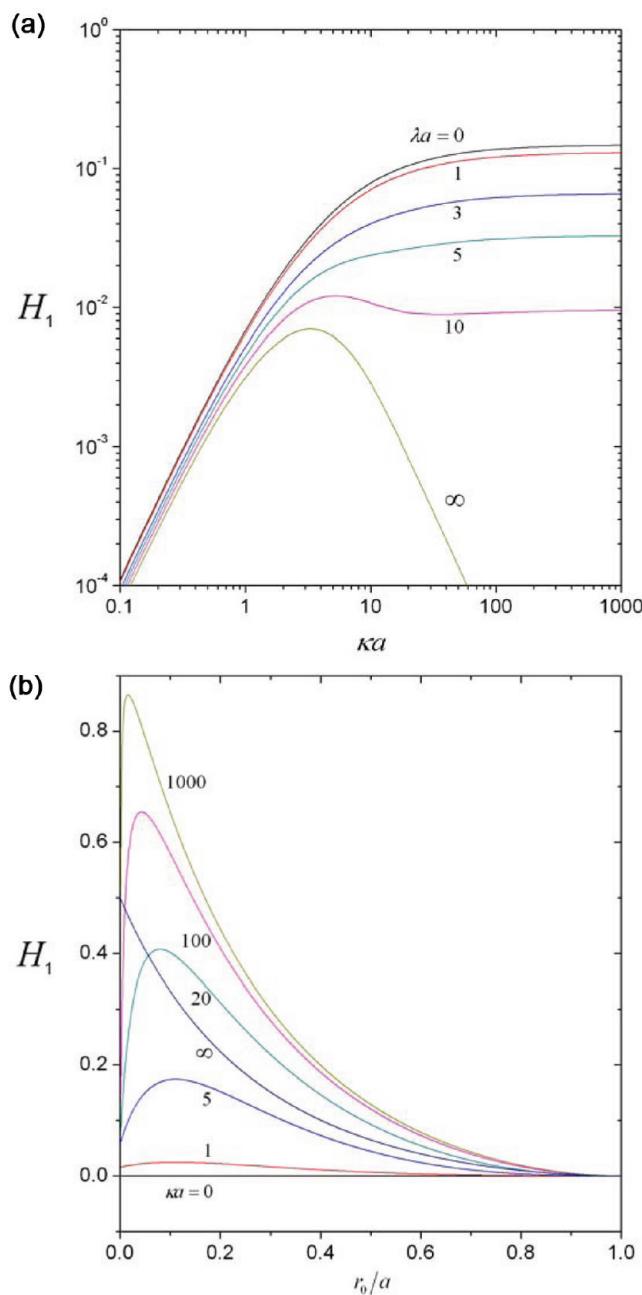


Figure 7. Plots of the coefficient H_1 given by eq 29a for the electrophoretic mobility of a soft sphere with zero net charge with various values of λa , κa , and r_0/a : (a) H_1 versus κa at $r_0/a = 0.5$; (b) H_1 versus r_0/a at $\lambda a = 1$.

screened entirely by part of the charged porous layer) of the soft particle. In the limit $\kappa a = 0$, the effects of the positive and negative fixed charges on the rigid core and inside the surface layer on the electrophoresis of the soft particle cancel out with each other, which leads to $H_1 = 0$. Since $H_{02} = H_{11} = H_{20} = 0$ in both the limits $\kappa a = 0$ and $\kappa a \rightarrow \infty$; $H_2 = 0$ also in these limits according to eq 29b (but the contribution from the chemiphoretic effect vanishes only for the case of $\kappa a = 0$, as indicated by eq 28). For specified values of r_0/a and λa , as shown in Figure 8a, the value of H_2 is maximal at some value of κa between 1 and 10.

Similar to the coefficients H_{10} and H_{20} presented in Figures 3 and 6, both H_1 and H_2 decrease monotonically with an increase

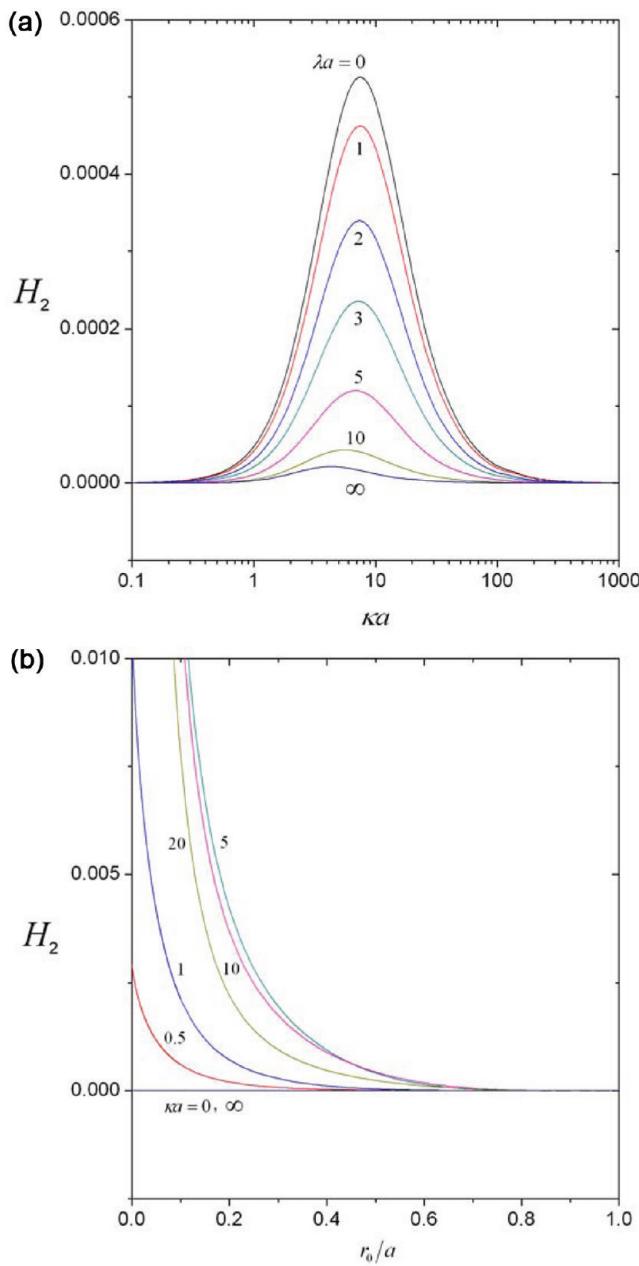


Figure 8. Plots of the coefficient H_2 given by eq 29b for the chemophoretic mobility of a soft sphere with zero net charge with various values of λa , κa , and r_0/a : (a) H_2 versus κa at $r_0/a = 0.5$; (b) H_2 versus r_0/a at $\lambda a = 1$.

in λa for given values of κa and r_0/a , and H_2 decreases monotonically with an increase in r_0/a for fixed values of κa and λa . However, H_1 is not necessarily a monotonic function of either κa or r_0/a . For given values of κa and λa , there is a maximum of H_1 at some small value of r_0/a , and this maximum shifts to smaller r_0/a as κa increases (which favors the electrophoretic contribution from the porous surface layer rather than that from the rigid core of the soft particle). The trend of the dependence of H_1 on κa and r_0/a is quite different from that of H_{10} presented in Figure 3. When κa is large (greater than about 10), the coefficients H_1 and H_{10} have the same order of magnitude. However, when κa is as small as 0.1, the value of H_1 is about 3 orders of magnitude smaller than that of H_{10} . In general, the coefficients H_2 and H_{20} have the same order of magnitude.

4.4. Diffusiophoretic Velocity. The dependence of the diffusiophoretic velocity of a charged but neutral soft sphere on its dimensionless fixed charge density $(\kappa a)^2 \bar{Q} = a^2 Z e Q / \epsilon k T$ with various values of κa and r_0/a at $\lambda a = 1$ for the case in which the cation and anion diffusivities are equal ($\beta = 0$) is shown in Figure 9.

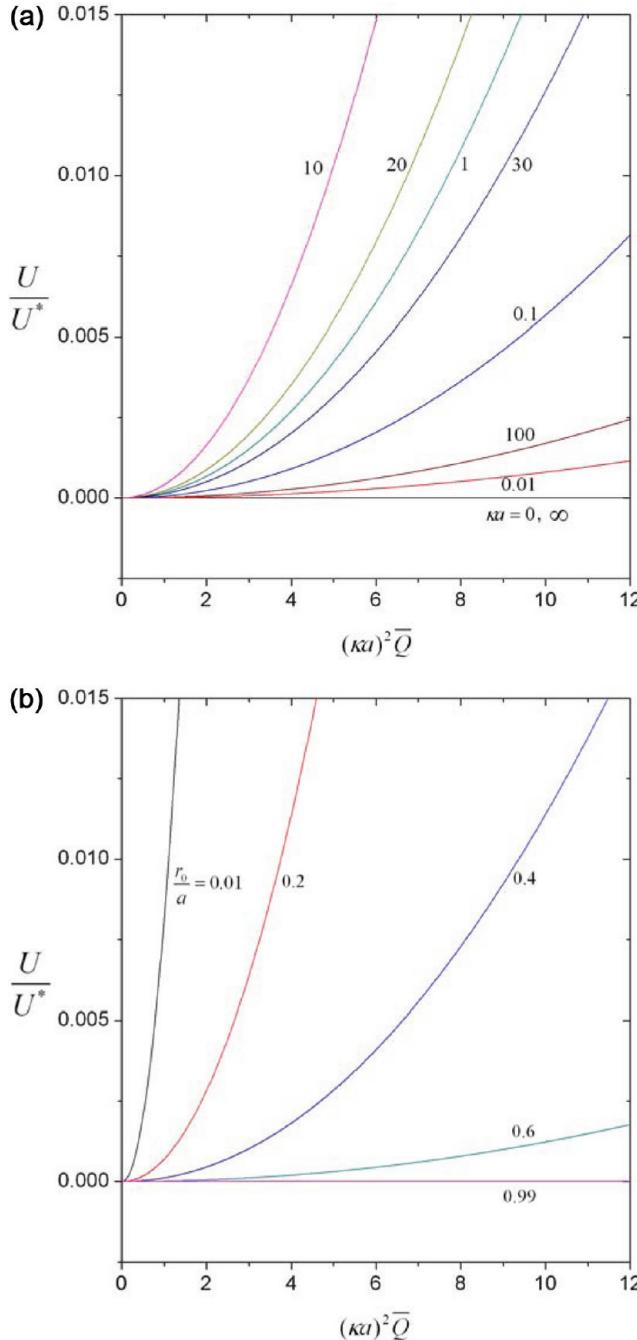


Figure 9. Plots of the normalized diffusiophoretic mobility of a charged soft sphere with zero net charge in a symmetric electrolyte solution with $\beta = 0$ versus the dimensionless fixed charge density $(\kappa a)^2 \bar{Q}$: (a) $\lambda a = 1$ and $r_0/a = 0.5$; (b) $\kappa a = 1$ and $\lambda a = 1$.

The magnitude of the diffusiophoretic velocity is normalized by a characteristic value given by

$$U^* = \frac{\epsilon a}{\eta a} \left(\frac{k T}{Z e} \right)^2 \quad (30)$$

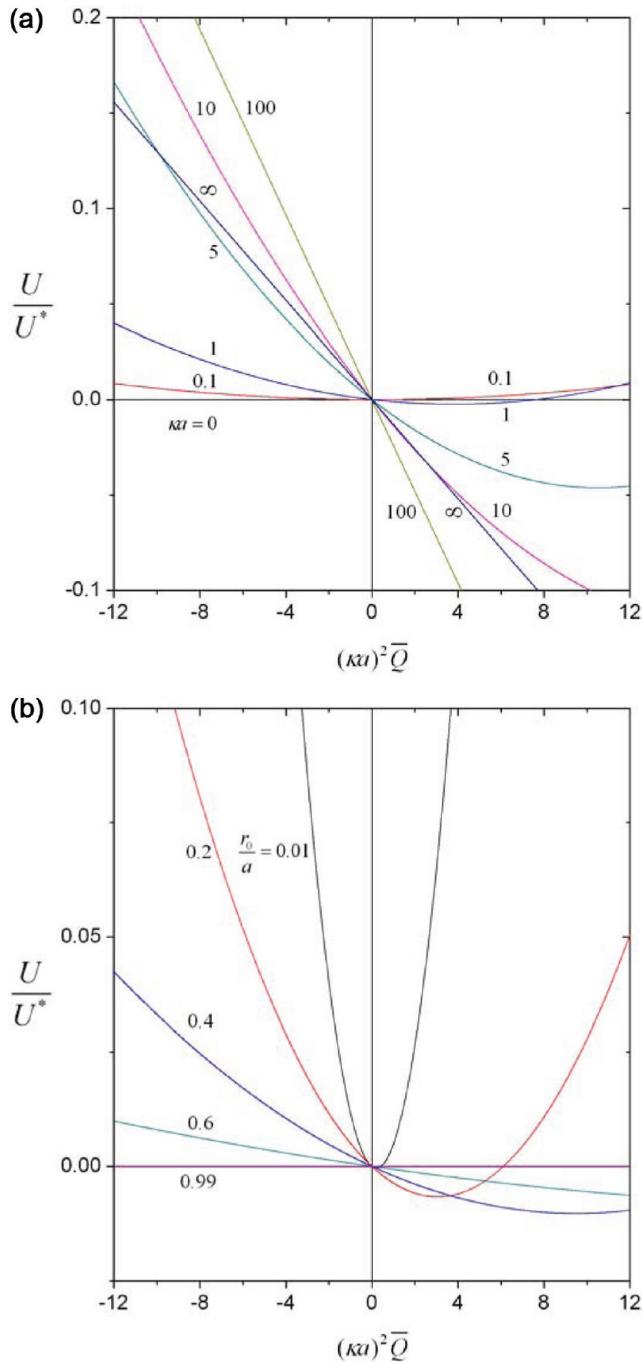


Figure 10. Plots of the normalized diffusiophoretic mobility of a charged soft sphere with zero net charge in a symmetric electrolyte solution with $\beta = -0.2$ versus the dimensionless fixed charge density $(\kappa a)^2 \bar{Q}$: (a) $\lambda a = 1$ and $r_0/a = 0.5$; (b) $ka = 1$ and $\lambda a = 1$.

Only the results at positive \bar{Q} are exhibited in Figure 9 since the particle velocity (due to the chemiphoretic effect entirely for the case $\beta = 0$) is an even function of \bar{Q} as illustrated by eq 28. As expected, the reduced diffusiophoretic velocity U/U^* increases monotonically with an increase in $(\kappa a)^2 \bar{Q}$ for given values of κa , λa , and r_0/a , with a decrease in λa for specified values of κa , r_0/a , and \bar{Q} (this result is not shown here for conciseness), and with a decrease in r_0/a for constant values of κa , λa , and \bar{Q} . For fixed values of λa , r_0/a , and $(\kappa a)^2 \bar{Q}$, the value of U/U^* is maximal at a finite value of κa , and decreases as κa

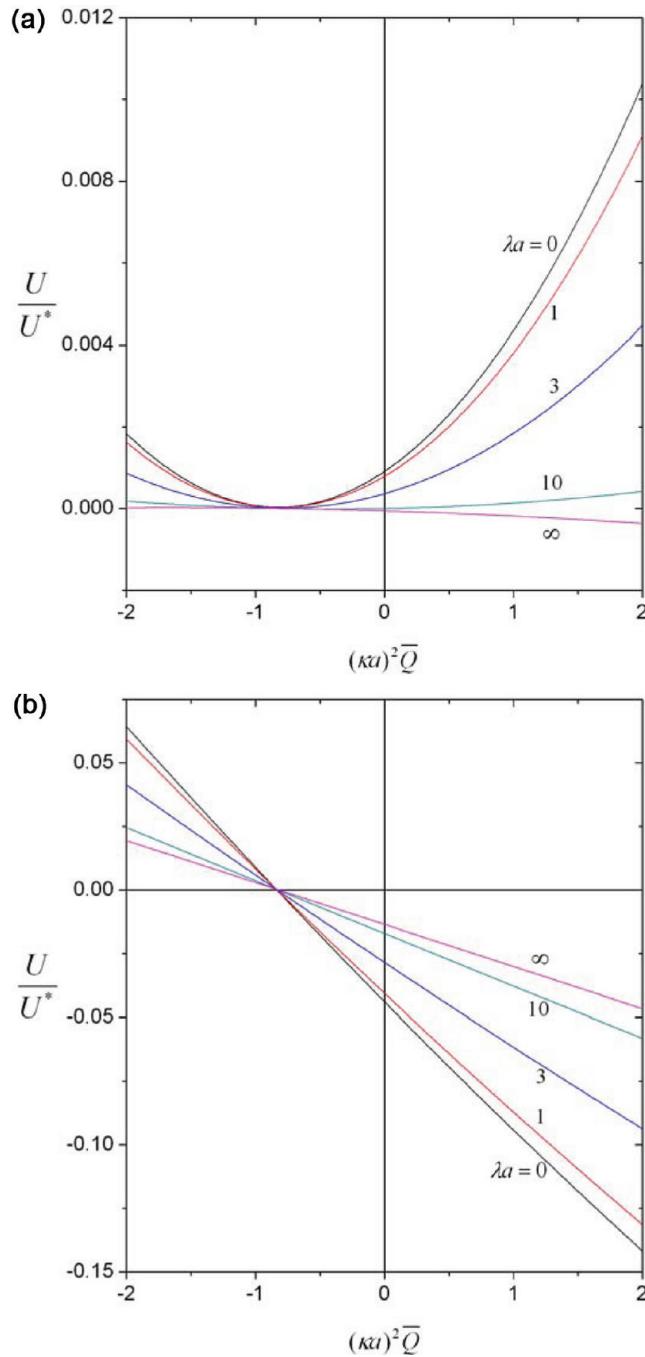


Figure 11. Plots of the normalized diffusiophoretic mobility of a charged soft sphere in a symmetric electrolyte solution with $\bar{\sigma} = 1$, $\kappa a = 1$, and $r_0/a = 0.5$ versus the dimensionless fixed charge density $(\kappa a)^2 \bar{Q}$: (a) $\beta = 0$; (b) $\beta = -0.2$.

increases or decreases from this value. There is no chemiphoretic motion of the particle for the limiting cases of $\bar{Q} = 0$ and $\kappa a = 0$.

In Figure 10, the normalized diffusiophoretic velocity U/U^* of a charged but neutral soft sphere calculated using eq 28 with various values of κa and r_0/a at $\lambda a = 1$ is plotted as a function of $(\kappa a)^2 \bar{Q}$ for a case in which the cation and anion have different diffusion coefficients with $\beta = -0.2$. In this case, both the electrophoretic and chemiphoretic effects contribute to the motion of the particle, and the net diffusiophoretic velocity is

neither an even nor an odd function of \bar{Q} . Again, for given values of λa , r_0/a , and $(\kappa a)^2 \bar{Q}$, the normalized velocity U/U^* is not a monotonic function of κa . For small values of r_0/a , the normalized particle velocity U/U^* is not a monotonic function of $(\kappa a)^2 \bar{Q}$. Some of the curves in Figure 10b show that the particle might reverse direction of movement more than once as its dimensionless fixed charge density varies from negative to positive values. The reversals occurring at the values of $(\kappa a)^2 \bar{Q}$ other than zero result from the competition between the contributions from electrophoresis and chemiphoresis. Note that the situations associated with Figures 9 and 10 ($\beta = 0$ and -0.2) taking $Z = 1$ are close to the diffusiophoresis in the aqueous solutions of KCl and NaCl, respectively.

To use eq 23 to determine the diffusiophoretic velocity for a general soft sphere, not only the parameters κa , λa , and r_0/a but also the dimensionless fixed charge densities $\bar{\sigma}$ and \bar{Q} of the particle have to be specified. Results of the reduced diffusiophoretic velocity U/U^* of a charged soft sphere with the dimensionless surface charge density of its rigid core $\bar{\sigma} = 1$ plotted versus the dimensionless space charge density $(\kappa a)^2 \bar{Q}$ of its porous layer for various values of λa at $\kappa a = 1$ and $r_0/a = 0.5$ are given in Figures 11a and 11b for the cases of $\beta = 0$ and $\beta = -0.2$, respectively. Again, the magnitude of U/U^* decreases with an increase in the value of λa . For the given case with $\bar{\sigma} = 1$, $\kappa a = 1$, and $r_0/a = 0.5$, eq 27 shows that the soft particle is “neutral” at $\bar{Q} = -6/7$, and the curves in Figure 11 indeed display minimal magnitudes of the particle velocity in its vicinity. In the range of $|\bar{Q}| < (\gamma \kappa a)^{-1} \bar{\sigma}$, the contribution to the particle velocity due to $\bar{\sigma}$ may be important, but the effect of the fixed charge at the porous layer or \bar{Q} on the diffusiophoresis of a soft particle becomes dominant beyond this range.

5. CONCLUSIONS

In this paper the steady diffusiophoresis (consisting of electrophoresis and chemiphoresis) of a charged soft sphere with arbitrary values of the electrokinetic radius κa , the shielding parameter λa , and the radius ratio r_0/a in an unbounded solution of a symmetric electrolyte with a uniformly imposed concentration gradient is analyzed. The porous shell of the soft particle is treated as a solvent-permeable and ion-penetrable layer in which fixed-charged groups and frictional segments are distributed at uniform densities. Solving the linearized Poisson–Boltzmann equation, continuity equations of ions, and modified Stokes/Brinkman equations applicable to the system by a regular perturbation method, we have obtained the electric potential profile, the ion concentration (or electrochemical potential energy) distributions, and the fluid velocity field. The requirement that the total force exerted on the soft particle is zero leads to eqs 22 and 23 for its diffusiophoretic velocity as a function of the parameters κa , λa , and r_0/a correct to the second orders of the fixed charge densities σ and Q . We found that a charged but “neutral” soft sphere can undergo diffusiophoresis (electrophoresis and chemiphoresis), and the direction of its diffusiophoretic velocity is determined by the fixed charges inside its porous surface layer. Expression 23 for the diffusiophoretic velocity of a charged soft sphere reduces to the corresponding formulas for a charged rigid sphere and a charged porous sphere, respectively, in the limiting cases of $r_0/a = 1$ and $r_0/a = 0$.

APPENDIX

The definitions of some functions in Section 3 are listed here. In eq 14,

$$F_{00r}(r) = C_{001} + [C_{002} + C_{003}\alpha_1(\lambda r) + C_{004}\beta_1(\lambda r)]\left(\frac{a}{r}\right)^3 \quad \text{if } r_0 < r < a \quad (\text{A1a})$$

$$F_{00r}(r) = C_{005}\left(\frac{a}{r}\right)^3 + C_{006}\frac{a}{r} - 1 \quad \text{if } r > a \quad (\text{A1b})$$

$$F_{00\theta}(r) = -C_{001} + \frac{1}{2}[C_{002} - C_{003}\alpha_2(\lambda r) - C_{004}\beta_2(\lambda r)]\left(\frac{a}{r}\right)^3 \quad \text{if } r_0 < r < a \quad (\text{A2a})$$

$$F_{00\theta}(r) = \frac{C_{005}}{2}\left(\frac{a}{r}\right)^3 - \frac{C_{006}}{2}\frac{a}{r} + 1 \quad \text{if } r > a \quad (\text{A2b})$$

$$F_{p00}(r) = (\lambda a)^2 \left[\frac{C_{002}}{2}\left(\frac{a}{r}\right)^2 - C_{001}\frac{r}{a} \right] \quad \text{if } r_0 < r < a \quad (\text{A3a})$$

$$F_{p00}(r) = C_{006}\left(\frac{a}{r}\right)^2 \quad \text{if } r > a \quad (\text{A3b})$$

$$F_{ijr}(r) = C_{ij1} + [C_{ij2} + C_{ij3}\alpha_1(\lambda r) + C_{ij4}\beta_1(\lambda r)]\left(\frac{a}{r}\right)^3 + \frac{6}{(\lambda a)^2(\lambda r)^3}[\alpha_1(\lambda r)J_{ij}^\beta(r) - \beta_1(\lambda r)J_{ij}^\alpha(r)] + \frac{2}{(\lambda a)^2}\left[J_{ij}^{(0)}(r) - \left(\frac{a}{r}\right)^3 J_{ij}^{(3)}(r)\right] \quad \text{if } r_0 < r < a \quad (\text{A4a})$$

$$F_{ijr}(r) = C_{ij5}\left(\frac{a}{r}\right)^3 + C_{ij6}\frac{a}{r} - J_{ij}^{(2)}(\infty) + \frac{1}{5}J_{ij}^{(0)}(\infty)\left(\frac{r}{a}\right)^2 + \frac{1}{5}\left(\frac{a}{r}\right)^3 J_{ij}^{(5)}(r) - \frac{a}{r}J_{ij}^{(3)}(r) + J_{ij}^{(2)}(r) - \frac{1}{5}\left(\frac{r}{a}\right)^2 J_{ij}^{(0)}(r) \quad \text{if } r > a \quad (\text{A4b})$$

$$F_{ij\theta}(r) = -C_{ij1} + \frac{1}{2}[C_{ij2} - C_{ij3}\alpha_2(\lambda r) - C_{ij4}\beta_2(\lambda r)]\left(\frac{a}{r}\right)^3 - \frac{3}{(\lambda a)^2(\lambda r)^3}[\alpha_2(\lambda r)J_{ij}^\beta(r) - \beta_2(\lambda r)J_{ij}^\alpha(r)] - \frac{2}{(\lambda a)^2}\left[J_{ij}^{(0)}(r) + \left(\frac{a}{r}\right)^3 J_{ij}^{(3)}(r)\right] \quad \text{if } r_0 < r < a \quad (\text{A5a})$$

$$F_{ij\theta}(r) = \frac{C_{ij5}}{2}\left(\frac{a}{r}\right)^3 - \frac{C_{ij6}}{2}\frac{a}{r} + J_{ij}^{(2)}(\infty) - \frac{2}{5}J_{ij}^{(0)}(\infty)\left(\frac{r}{a}\right)^2 + \frac{1}{10}\left(\frac{a}{r}\right)^3 J_{ij}^{(5)}(r) + \frac{a}{2r}J_{ij}^{(3)}(r) - J_{ij}^{(2)}(r) + \frac{2}{5}\left(\frac{r}{a}\right)^2 J_{ij}^{(0)}(r) \quad \text{if } r > a \quad (\text{A5b})$$

$$F_{pij}(r) = (\lambda a)^2 \left[\frac{C_{ij2}}{2} \left(\frac{a}{r} \right)^2 - C_{ij1} \frac{r}{a} \right] - 2 \frac{r}{a} J_{ij}^{(0)}(r) \\ - \left(\frac{a}{r} \right)^2 J_{ij}^{(3)}(r) \quad \text{if } r_0 < r < a \quad (\text{A6a})$$

$$F_{pij}(r) = C_{ij6} \left(\frac{a}{r} \right)^2 + 2 J_{ij}^{(0)}(\infty) \frac{r}{a} - 2 \frac{r}{a} J_{ij}^{(0)}(r) \\ - \left(\frac{a}{r} \right)^2 J_{ij}^{(3)}(r) \quad \text{if } r > a \quad (\text{A6b})$$

for $(i,j) = (0, 1), (1, 0), (0, 2), (1, 1)$, and $(2, 0)$, where

$$C_{001} = \frac{3}{\Omega} (\lambda r_0 - \lambda a \cosh \lambda a + \sinh \lambda a) \quad (\text{A7a})$$

$$C_{002} = \frac{\Gamma}{(\lambda a)^3 \Omega \Delta} + 2 C_{001} \quad (\text{A7b})$$

$$C_{003} = \frac{-3}{(\lambda a)^3 \Omega} \{ A + 3 \lambda r_0 [\beta_1(\lambda a) - \beta_1(\lambda r_0)] \} \quad (\text{A7c})$$

$$C_{004} = \frac{3}{(\lambda a)^3 \Omega} \{ [2(\lambda a)^3 + (\lambda r_0)^3] \\ \times \sinh \lambda r_0 + 3 \lambda r_0 [\alpha_1(\lambda a) - \alpha_1(\lambda r_0)] \} \quad (\text{A7d})$$

$$C_{005} = 1 + C_{001} + C_{002} + C_{003} \alpha_1(\lambda a) \\ + C_{004} \beta_1(\lambda a) - C_{006} \quad (\text{A7e})$$

$$C_{006} = \frac{\Gamma}{2 \lambda a \Omega \Delta} \quad (\text{A7f})$$

$$C_{ij1} = -\frac{\lambda^2 a^3}{3r_0} (C_{ij3} \sinh \lambda r_0 + C_{ij4} \cosh \lambda r_0) - \frac{2}{(\lambda a)^2} J_{ij}^{(0)}(r_0) \\ + \frac{2}{\lambda^3 a^2 r_0} [J_{ij}^\alpha(r_0) \cosh \lambda r_0 - J_{ij}^\beta(r_0) \sinh \lambda r_0] \quad (\text{A8a})$$

$$C_{ij2} = 2 C_{ij1} + \frac{2}{(\lambda a)^2} [C_{ij6} + 2 J_{ij}^{(0)}(\infty)] \quad (\text{A8b})$$

$$C_{ij3} = \frac{3}{(\lambda a)^3 \Omega} \{ -(A + 3 \lambda r_0 [\beta_1(\lambda a) - \beta_1(\lambda r_0)]) J_{ij}^{(2)}(\infty) \\ + (A - 3 \lambda r_0 [\lambda a \sinh \lambda a + \cosh \lambda a + \beta_1(\lambda r_0)] \\ + 6 \lambda a \cosh \lambda r_0) J_{ij}^{(0)}(\infty) + \frac{2r_0}{\lambda a^2} [2(\lambda a)^3 \\ \times \sinh \lambda a + (\lambda r_0)^2 \cosh \lambda r_0 + 3 \beta_1(\lambda a) - 3 \beta_1(\lambda r_0)] \\ \times J_{ij}^{(0)}(r_0) + 2 \lambda a \Delta J_{ij}^{(3)}(r_0) - \frac{2}{(\lambda a)^2} \\ \times [B \cosh \lambda r_0 - (\lambda r_0)^2 \sinh \lambda a \sinh \lambda r_0] J_{ij}^\alpha(r_0) \\ + \frac{2}{(\lambda a)^2} [B \sinh \lambda r_0 - (\lambda r_0)^2 \sinh \lambda a \cosh \lambda r_0 \\ + 3 \lambda r_0] J_{ij}^\beta(r_0) \} \quad (\text{A8c})$$

$$C_{ij4} = \frac{1}{(\lambda a)^3 \Delta} \{ -3 \lambda r_0 J_{ij}^{(2)}(\infty) + 3 \lambda r_0 J_{ij}^{(0)}(\infty) \\ - (\lambda a)^3 (\lambda r_0 \cosh \lambda a - \sinh \lambda r_0) C_{ij3} + \frac{6r_0}{\lambda a^2} J_{ij}^{(0)}(r_0) \\ + \frac{6}{(\lambda a)^2} [J_{ij}^\beta(r_0) \sinh \lambda r_0 - J_{ij}^\alpha(r_0) \cosh \lambda r_0] \} \quad (\text{A8d})$$

$$C_{ij5} = C_{ij1} + C_{ij2} + \alpha_1(\lambda a) C_{ij3} + \beta_1(\lambda a) C_{ij4} - C_{ij6} \\ + J_{ij}^{(2)}(\infty) - \frac{1}{5} J_{ij}^{(0)}(\infty) \quad (\text{A8e})$$

$$C_{ij6} = C_{005} J_{ij}^{(0)}(\infty) + C_{006} J_{ij}^{(2)}(\infty) - C_{001} J_{ij}^{(3)}(r_0) \\ - C_{002} J_{ij}^{(0)}(r_0) - C_{003} J_{ij}^\alpha(r_0) - C_{004} J_{ij}^\beta(r_0) \quad (\text{A8f})$$

$$\alpha_1(x) = x \cosh x - \sinh x \quad (\text{A9a})$$

$$\alpha_2(x) = (x^2 + 1) \sinh x - x \cosh x \quad (\text{A9b})$$

$$\beta_1(x) = x \sinh x - \cosh x \quad (\text{A9c})$$

$$\beta_2(x) = (x^2 + 1) \cosh x - x \sinh x \quad (\text{A9d})$$

$$\Delta = \lambda r_0 \sinh \lambda a - \cosh \lambda r_0 \quad (\text{A10a})$$

$$\Omega = -6 \lambda r_0 + [2(\lambda a)^3 + (\lambda r_0)^3 + 3 \lambda a + 3 \lambda r_0] \cosh \lambda d \\ + [3(\lambda r_0)^2 - 3] \sinh \lambda d \quad (\text{A10b})$$

$$\Gamma = 3 \lambda r_0 A - 9(\lambda r_0)^2 [\beta_1(\lambda a) + \beta_1(\lambda r_0)] + 3 \{ -\lambda a A \\ + \lambda r_0 [2(\lambda a)^3 + (\lambda r_0)^3 + 3 \lambda r_0] \beta_1(\lambda a) \\ + 3 \lambda^2 a r_0 \beta_1(\lambda r_0) \} \cosh \lambda d \\ + 3 \{ A + 3 \lambda r_0 [(\lambda r_0)^2 \beta_1(\lambda a) - \beta_1(\lambda r_0)] \} \sinh \lambda d \quad (\text{A10c})$$

$$A = [2(\lambda a)^3 + (\lambda r_0)^3] \cosh \lambda r_0 \quad (\text{A10d})$$

$$B = [2(\lambda a)^3 + (\lambda r_0)^3 + 3 \lambda a + 3 \lambda r_0] \sinh \lambda a - 3 \cosh \lambda a \quad (\text{A10e})$$

$$J_{ij}^{(n)}(r) = \int_a^r \left(\frac{r}{a} \right)^n G_{ij}(r) \, dr \quad (\text{A11a})$$

$$J_{ij}^\alpha(r) = \int_a^r \alpha_1(\lambda r) G_{ij}(r) \, dr \quad (\text{A11b})$$

$$J_{ij}^\beta(r) = \int_a^r \beta_1(\lambda r) G_{ij}(r) \, dr \quad (\text{A11c})$$

$$G_{01}(r) = \frac{\varepsilon \kappa^2 a^4}{3 Z \epsilon r} F_{\mu 00}(r) \frac{d \psi_{eq01}}{dr} \quad (\text{A12a})$$

$$G_{10}(r) = \frac{\varepsilon \kappa^2 a^4}{3 Z \epsilon r} F_{\mu 00}(r) \frac{d \psi_{eq10}}{dr} \quad (\text{A12b})$$

$$G_{02}(r) = -\frac{\varepsilon \kappa^2 a^4}{3 Z \epsilon r} W_{01}(r) \frac{d \psi_{eq01}}{dr} \quad (\text{A12c})$$

$$G_{11}(r) = -\frac{\varepsilon\kappa^2 a^4}{3Zer} \left[W_{01}(r) \frac{d\psi_{eq10}}{dr} + W_{10}(r) \frac{d\psi_{eq01}}{dr} \right] \quad (\text{A12d})$$

$$G_{20}(r) = -\frac{\varepsilon\kappa^2 a^4}{3Zer} W_{10}(r) \frac{d\psi_{eq10}}{dr} \quad (\text{A12e})$$

$$W_{ij}(r) = \left[F_{\mu ij}(r) + \frac{Ze}{kT} \psi_{eqij}(r) F_{\mu 00}(r) \right] \quad (\text{A12f})$$

In eqs 15, 16, and A12,

$$F_{\mu 00}(r) = s_2 \left[1 - \omega + \left(\frac{1}{2} + \omega \right) \left(\frac{r_0}{a} \right)^3 \right] \left(\frac{a}{r} \right)^2 + \frac{r}{a}$$

if $r > a$ (A13a)

$$F_{\mu 00}(r) = 3s_2 \left[\frac{1}{2} \left(\frac{r_0}{a} \right)^3 \left(\frac{a}{r} \right)^2 + \frac{r}{a} \right] \quad \text{if } r_0 < r < a$$

(A13b)

$$F_{\psi 00}(r) = F_{\mu 00}(r) - 3(1 - \omega)s_1s_2 \left[1 - \left(\frac{r_0}{a} \right)^3 \right]$$

$$\left\{ \left[2 + (\kappa r_0)^2 - 2\frac{r_0}{a} \right] \cosh \kappa d - \left[\frac{2}{\kappa a} - \kappa r_0 \left(2 - \frac{r_0}{a} \right) \right] \right.$$

$$\times \sinh \kappa d \left. \frac{1 + \kappa r}{(\kappa r)^2} e^{-\kappa(r-r_0)} \right\} \quad \text{if } r > a$$

(A14a)

$$F_{\psi 00}(r) = F_{\mu 00}(r) - 3(1 - \omega)s_1s_2 e^{-\kappa d} \left[1 - \left(\frac{r_0}{a} \right)^3 \right] \frac{1 + \kappa a}{\kappa^3 ar^2}$$

$$\left. \begin{aligned} & \{ \kappa[(2 + \kappa^2 r_0^2)r - 2r_0] \cosh \kappa(r - r_0) \\ & + [\kappa^2 r_0(2r - r_0) - 2] \sinh \kappa(r - r_0) \} \end{aligned} \right\} \quad \text{if } r_0 < r < a$$

(A14b)

$$F_{\mu ij}(r) = s_2 \left\{ -\frac{r}{a} K_{ij}^{(0)}(r) - s_2 \left[\left(\frac{r_0}{a} \right)^3 K_{ij}^{(0)}(r_0) + 2K_{ij}^{(3)}(r_0) \right] \right.$$

$$\times \left[\left(1 + \frac{1}{2}\omega \right) \left(\frac{a}{r} \right)^2 - (1 - \omega) \frac{r}{a} \right] + L_{ij}^{(0)}(\infty)$$

$$\times \left. \left[\left(\frac{r}{a} \right)^3 + \frac{1}{2} \left(\frac{r_0}{a} \right)^3 \right] \left(\frac{a}{r} \right)^2 + \left(\frac{a}{r} \right)^2 K_{ij}^{(3)}(r) \right\}$$

if $r_0 < r < a$ (A15a)

$$F_{\mu ij}(r) = -\frac{3}{2} \omega s_2^2 \left[\left(\frac{r_0}{a} \right)^3 K_{ij}^{(0)}(r_0) + 2K_{ij}^{(3)}(r_0) \right] \left(\frac{a}{r} \right)^2$$

$$+ \frac{1}{3} \left(\frac{a}{r} \right)^2 L_{ij}^{(3)}(r) - \frac{1}{3} \frac{r}{a} L_{ij}^{(0)}(r) + \frac{s_2}{6} \left\{ \left[2 + \left(\frac{r_0}{a} \right)^3 \right] \right.$$

$$\times \left. \left[\left(\frac{a}{r} \right)^2 + 2\frac{r}{a} \right] - 2\omega \left[1 - \left(\frac{r_0}{a} \right)^3 \right] \left[\left(\frac{a}{r} \right)^2 - \frac{r}{a} \right] \right\} L_{ij}^{(0)}(\infty)$$

if $r > a$ (A15b)

$$F_{\psi ij}(r) = -\frac{1}{\kappa r^2} \{ \alpha_1(\kappa r) M_{ij}(r) - s_1 [\alpha_2(\kappa r_0) - \alpha_1(\kappa r_0)]$$

$$\times M_{ij}(r_0)(1 + \kappa r)e^{-\kappa(r-r_0)} + (1 + \kappa r)e^{-\kappa r}$$

$$\times \int_{r_0}^r \alpha_1(\kappa r) W_{ij}(r) dr \}$$

(A16)

where

$$K_{ij}^{(n)}(r) = \frac{Ze}{kT} \int_a^r \left(\frac{r}{a} \right)^n \left[1 - \left(\frac{r_0}{r} \right)^3 \right] \frac{d\psi_{eqij}}{dr} dr$$

(A17a)

$$L_{ij}^{(n)}(r) = \frac{Ze}{kT} \int_a^r \left(\frac{r}{a} \right)^{n-3} \left\{ 2 - 3s_2 \left[2 + \left(\frac{r_0}{a} \right)^3 \right] + \left(\frac{r}{a} \right)^3 \right\}$$

$$\times \frac{d\psi_{eqij}}{dr} dr$$

(A17b)

$$M_{ij}(r) = \int_r^\infty (1 + \kappa r) e^{-\kappa r} W_{ij}(r) dr$$

(A17c)

$$s_1 = [2 + \kappa r_0(2 + \kappa r_0)]^{-1}$$

(A18a)

$$s_2 = \left[2 + \omega + (1 - \omega) \left(\frac{r_0}{a} \right)^3 \right]^{-1}$$

(A18b)

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Notes

The authors declare no competing financial interest.

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