Diffusiophoresis and Electrophoresis of Colloidal Spheroids

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Received January 4, 1993; accepted May 25, 1993

An analytical study is presented for the diffusiophoresis and electrophoresis of a rigid nonconducting spheroid in a uniform applied field that is oriented arbitrarily with respect to its axis of revolution. The range of the interaction between the solute species and the particle surface is assumed to be small relative to the dimension of the particle, but the effect of polarization of the diffuse species in the thin solute-particle interaction layer is incorporated. To solve the conservative equations governing the system, a slip velocity of fluid and normal fluxes of solute species at the outer edge of the thin diffuse layer which balance convection and diffusion of the solute species along the particle surface are used as the boundary conditions for the fluid domain outside the diffuse layer. Explicit expressions for the migration velocity of the spheroidal particle are obtained for the cases of diffusiophoresis in a nonionic solute concentration gradient, diffusiophoresis in a concentration gradient of symmetric electrolyte, and electrophoresis in an external electric field. An interesting feature is found that the diffusiophoretic or electrophoretic velocity of the particle decreases with the reduction of the maximum length of the particle in the direction of migration. Also, the average migration velocity for an ensemble of identical, non-interacting spheroids with random orientation distribution is obtained for each case considered. © 1993 Academic Press, Inc.

1. INTRODUCTION

Driving forces for transport of colloidal particles generally include concentration gradients of the particles themselves (diffusion), bulk velocities of the disperse medium (convection), and gravitational or centrifugal fields (sedimentation). Problems of the colloidal transport induced by these well-known driving forces have been treated extensively in the past. Another category of driving forces for the locomotion of colloidal particles, which caught less attention, involves a nonuniform imposed field (such as, electrical potential, temperature, or solute concentration) that interacts with the surface of each particle. An excellent review summarizing the current state of knowledge concerning particle motions associated with this mechanism, known as "phoretic motions," is given by Anderson (1).

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Perhaps the most familiar example of the various phoretic motions of colloids is electrophoresis which results from the interaction between an external electric field and the electrical double layer surrounding a charged particle. The electrophoretic velocity U_0 of a single nonconducting particle suspended in an unbounded fluid is related to the uniformly applied electric field E^∞ by the Smoluchowski equation (2, 3),

$$U_0 = \frac{\epsilon \zeta}{4\pi\eta} E^\infty. \quad [1.1]$$

Here, $\epsilon/4\pi$ is the fluid permittivity, η is the fluid viscosity, and ζ is the zeta potential of the particle surface.

Another example of phoretic motions is termed "diffusiophoresis" (3, 4), which is the migration of a solid particle in response to the macroscopic concentration gradient of a molecular solute; the solute can be nonionic or ionic. The particle moves toward or away from a region of higher solute concentration, depending on some long-range interactions between the solute molecules and the particle. In an immense solution with a constant solute concentration gradient ∇n^∞ , the diffusiophoretic velocity of a particle is

$$U_0 = \frac{kT}{\eta} L^* K \nabla n^\infty \quad [1.2]$$

for the case of nonionic solute (5), and

$$U_0 = \frac{\epsilon \zeta}{4\pi\eta} \frac{kT}{Ze} \left[\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\zeta} \ln \cosh \left(\frac{Ze\zeta}{4kT} \right) \right] \frac{\nabla n^\infty}{n^\infty(0)} \quad [1.3]$$

for the case of symmetric electrolyte solute (6). Here, L^* is a characteristic length for the range of particle-solute interactions, K is the Gibbs adsorption length characterizing the strength of the adsorption (K and L^* are defined by Eqs. [3.7a] and [3.7d]), $n^\infty(0)$ is the macroscopic solute concentration measured at the particle center 0 in the absence of the particle, D_1 and D_2 are the diffusion coefficients of the

anion and cation, respectively, Z is the absolute value of the valences of ions, e is the charge of a proton, k is the Boltzmann constant, and T is the absolute temperature.

Equations [1.1]–[1.3] indicate that the electrophoretic and diffusiophoretic velocities of a particle are independent of particle size and shape. However, their validity is based on the assumptions that the local radii of curvature of the particle are much larger than the thickness of the particle–solute interaction layer at the particle surface and the effect of polarization (relaxation effect) of the diffuse solute species in the interfacial layer due to the nonuniform “osmotic” flow is negligible. The subscript “0” of the particle velocity U_0 in Eqs. [1.1]–[1.3] emphasizes that these expressions are only valid in the limit of these assumptions. Recently, important advances have been made in the evaluation of the phoretic velocities of colloidal particles relaxing these assumptions.

Taking the double-layer distortion from equilibrium as a perturbation, O'Brien and White (7) obtained a numerical calculation for the electrophoretic velocity of a dielectric sphere of radius a which was applicable to arbitrary values of ζ and κa ; κ^{-1} is the Debye screening length defined by

$$\kappa^{-1} = \left(\frac{\epsilon k T}{8 \pi e^2 I} \right)^{1/2}, \quad [1.4]$$

where I is the ionic strength in the bulk solution. On the other hand, Dukhin and Derjaguin (3) obtained an analytical expression for the electrophoretic mobility of a spherical particle with a thin but polarized double layer in a solution of symmetrically charged, binary electrolyte. Later, O'Brien (8) generalized this analysis to the case of electrophoretic motion of a sphere in a solution containing an arbitrary combination of electrolytes. The result for the electrophoretic velocity in a symmetric electrolyte solution can be expressed as (9)

$$U = \frac{\epsilon \zeta}{4 \pi \eta} E^\infty \left[\frac{1}{3} (2 + c_1 + c_2) + \frac{4 k T}{3 Z e \zeta} (c_1 - c_2) \ln \cosh \left(\frac{Z e \zeta}{4 k T} \right) \right], \quad [1.5]$$

with

$$c_1 = \frac{1}{2 a^2 \Delta} (a^2 + a \beta_{22} + 3 a \beta_{12} - 2 a \beta_{11} + 2 \beta_{12} \beta_{21} - 2 \beta_{11} \beta_{22}), \quad [1.6a]$$

$$c_2 = \frac{1}{2 a^2 \Delta} (a^2 + a \beta_{11} + 3 a \beta_{21} - 2 a \beta_{22} + 2 \beta_{12} \beta_{21} - 2 \beta_{11} \beta_{22}), \quad [1.6b]$$

and

$$\Delta = \frac{1}{a^2} (a^2 + a \beta_{11} + a \beta_{22} + \beta_{11} \beta_{22} - \beta_{12} \beta_{21}), \quad [1.7]$$

where β_{11} , β_{12} , β_{21} , and β_{22} are defined by Eqs. [4.3]. If $|\zeta|$ is small and κa is large, the interaction between the diffuse counterions and the particle surface is weak and the polarization of the double layer is also weak. In the limit of

$$(\kappa a)^{-1} \exp \left(\frac{Z e |\zeta|}{2 k T} \right) \rightarrow 0, \quad [1.8]$$

$c_1 = c_2 = 0.5$ ($\beta_{11}/a = \beta_{12}/a = \beta_{21}/a = \beta_{22}/a = 0$) and Eq. [1.5] reduces to the Smoluchowski equation [1.1].

For the case of diffusiophoretic motion of a sphere with a thin but polarized interaction layer in a gradient of non-electrolyte solute, the formula for the particle velocity has been analytically derived (10),

$$U = \frac{k T}{\eta} L^* K \left[1 + (1 + \nu \text{Pe}) \frac{K}{a} \right]^{-1} \nabla n^\infty, \quad [1.9]$$

where the definitions of ν and Pe are given by Eqs. [3.7b] and [3.7c]. For a strongly adsorbing solute, the ratio K/a can be much greater than unity. In the limit of $K/a \rightarrow 0$ (weak adsorption), the polarization of the diffuse solute in the interfacial region vanishes and Eq. [1.9] reduces to Eq. [1.2].

On the other hand, Prieve and Roman (11) obtained a numerical solution of the diffusiophoretic velocity over a broad range of ζ and κa for a rigid insulating sphere in concentration gradients of symmetric electrolytes (KCl or NaCl) using the method of O'Brien and White (7). Extending the analyses (3, 8, 9) for the electrophoresis of a spherical particle, Keh and Chen (12) recently obtained the following analytical expression for the diffusiophoretic velocity of a dielectric sphere with a thin polarized double layer in a symmetric electrolyte solution:

$$U = \frac{\epsilon \zeta}{4 \pi \eta} \frac{k T}{Z e} \frac{\nabla n^\infty}{n^\infty(0)} \left[\frac{2}{3} \left(\frac{D_2 - D_1}{D_2 + D_1} + b_1 - b_2 \right) + \frac{8 k T}{3 Z e \zeta} (1 + b_1 + b_2) \ln \cosh \left(\frac{Z e \zeta}{4 k T} \right) \right], \quad [1.10]$$

where

$$b_1 = \frac{D_2}{D_2 + D_1} c_1 - \frac{3}{2 a \Delta} \beta_{12}, \quad [1.11a]$$

$$b_2 = \frac{D_1}{D_2 + D_1} c_2 - \frac{3}{2 a \Delta} \beta_{21}, \quad [1.11b]$$

and c_1 and c_2 are defined by Eqs. [1.6]. In the limiting situation as given in Eq. [1.8], Eq. [1.10] reduces to Eq. [1.3].

It could be found from Eqs. [1.5], [1.9], and [1.10] that the effect of polarization of the diffuse layer is to decrease the particle velocity. The reason for this consequence is that the transport of the solute inside the particle-solute interaction layer reduces the field along the particle surface.

The phoretic theories of nonspherical particles differ from those of spheres in that there is an orientational problem. In general, under polarized conditions, the phoretic mobility of a nonspherical particle is anisotropic and the velocity of the particle is no longer collinear with the applied field. The phoretic motions of a long circular cylinder with a thin but distorted particle-solute interaction layer have been studied for both cases of electrophoresis (12-14) and diffusiophoresis (12). A remarkable feature was found that the diffusiophoretic or electrophoretic velocity of the cylinder in a transversely imposed field is exactly the same as the corresponding velocity of a rigid sphere with an equal radius. Although the electrophoresis of a spheroidal particle with a thin polarized double layer was investigated to some extent (15, 16), the effect of polarization of the diffuse layer on the diffusiophoresis of a spheroidal particle has not yet been examined. In this paper we present a common analysis of the diffusiophoretic (in gradients of non-electrolytes or electrolytes) and electrophoretic motions of a colloidal spheroid with a thin but polarized diffuse layer at the particle surface. The spheroidal particle can be oriented arbitrarily with respect to the imposed field. The particle velocities are determined for various cases as functions of relevant parameters.

2. BASIC EQUATIONS FOR PHORETIC MOTIONS

Consider the diffusiophoretic or electrophoretic motion of a rigid particle of arbitrary shape in an unbounded liquid solution containing M chemical species (ionic or nonionic). The layer of interaction between the solute species and the particle surface is assumed to be thin in comparison with the particle dimension. Hence, the fluid phase can be divided into two regions: an "inner" region defined as the interaction layer adjacent to the particle surface and an "outer" region defined as the remainder of the fluid.

In the outer region, the equations of conservation of the solute species and fluid momentum can be expressed by the Laplace equation (12),

$$\nabla^2 \mu_m = 0, \quad m = 1, 2, \dots, M, \quad [2.1]$$

and the Stokes equations,

$$\eta \nabla^2 \mathbf{v} - \nabla p = \mathbf{0}, \quad [2.2a]$$

$$\nabla \cdot \mathbf{v} = 0. \quad [2.2b]$$

In Eq. [2.1], μ_m is the modified chemical potential energy of species m defined as

$$\mu_m = \mu_m^0 + kT \ln n_m + \Phi_m, \quad [2.3]$$

where μ_m^0 is a constant; n_m is the concentration of species m ; Φ_m represents all kinds of potential energy resulting from van der Waals forces, electrical forces, etc., for the interaction between type- m species and the particle surface. In Eqs. [2.2], $\mathbf{v}$ is the fluid velocity field and p is the dynamic pressure.

The governing equations [2.1] and [2.2] in the outer region ought to satisfy the following boundary conditions at the particle surface (S_p^+) obtained by solving for the fluid velocity and the modified chemical potentials of the solute species in the inner region (balancing convection and diffusion of the solute species along the surface) and using a matching procedure to ensure a continuous solution in the whole fluid phase (8, 12):

$$\text{on } S_p^+, \quad \mathbf{n} \cdot \nabla \mu_m = - \sum_{i=1}^M \beta_{mi} \mathbf{l} : \nabla_s \nabla_s \mu_i, \quad m = 1, 2, \dots, M, \quad [2.4]$$

$$\mathbf{v} = \mathbf{U} + \boldsymbol{\Omega} \times \mathbf{r} + \mathbf{v}_s, \quad [2.5]$$

with

$$\begin{aligned} \beta_{mi} = & \delta_{mi} \int_0^\infty [\exp(-\Phi_m^0/kT) - 1] dy_n \\ & + \frac{kT}{\eta D_m} n_i^\infty \int_0^\infty [\exp(-\Phi_m^0/kT) - 1] \\ & \times \int_0^{y_n} \int_{y_n'}^\infty [\exp(-\Phi_i^0/kT) - 1] dy_n'' dy_n' dy_n \quad [2.6] \end{aligned}$$

and

$$\mathbf{v}_s = - \frac{1}{\eta} \sum_{m=1}^M \nabla_s \mu_m \int_0^\infty y_n [n_m^0 - n_m^\infty(\mathbf{0})] dy_n. \quad [2.7]$$

In Eqs. [2.4]–[2.7], n_m^0 and Φ_m^0 , functions of y_n (or y_n''), are the equilibrium concentration and potential energy, respectively, of species m ; y_n (or y_n'') is the distance measured from the particle surface along $\mathbf{n}$, which is the unit vector outwardly normal to the surface; $n_m^\infty(\mathbf{0})$ is the bulk concentration of species m measured at the particle center $\mathbf{0}$ in the absence of the particle; $\mathbf{r}$ is the position vector from the particle center; $\mathbf{l}$ is the unit dyadic; $\nabla_s = (\mathbf{l} - \mathbf{nn}) \cdot \nabla$ represents the gradient operator along the particle surface; δ_{mi} denotes the Kronecker delta which is unity if i equals m , and zero otherwise; $\mathbf{U}$ and $\boldsymbol{\Omega}$ are the translational and angular velocities of the particle to be determined. Here, the term "surface"

means outer limit of the thin interaction layer surrounding the particle. If the fluid is only slightly nonuniform in the undisturbed solute concentrations n_m^∞ on the length scale of the particle dimension, the equilibrium concentration of any species is related to its equilibrium potential energy by the Boltzmann distribution

$$n_m^0 = n_m^\infty(\mathbf{0}) \exp(-\Phi_m^0/kT). \quad [2.8]$$

The modified chemical potentials far away from the particle approach the undisturbed values and the fluid is motionless there. Thus, μ_m and $\mathbf{v}$ must obey

$$|\mathbf{r}| \rightarrow \infty: \mu_m \rightarrow \mu_m^0 + kT \ln n_m^\infty + \Phi_m^\infty, \quad [2.9]$$

$$\mathbf{v} \rightarrow \mathbf{0}. \quad [2.10]$$

In Eq. [2.9], $\Phi_m^\infty = 0$ for the case of diffusiophoresis and $\nabla\Phi_m^\infty = -ez_m E^\infty$ for the case of electrophoresis, where z_m is the valence of type- m ions.

Because there is no effective external field exerted beyond the outer edge of the solute-particle interaction layer, the particle (plus its adjacent diffuse layer of solute species) is force and torque free; that is,

$$\mathbf{F} = \iint_{S_p^+} \mathbf{n} \cdot \boldsymbol{\pi} dS = \mathbf{0}, \quad [2.11a]$$

$$\mathbf{T} = \iint_{S_p^+} \mathbf{r} \times (\mathbf{n} \cdot \boldsymbol{\pi}) dS = \mathbf{0}, \quad [2.11b]$$

where $\boldsymbol{\pi}$ is the fluid stress tensor. With this constraint, one can calculate the particle velocities $\mathbf{U}$ and $\boldsymbol{\Omega}$ after solving Eqs. [2.1]–[2.10] for the modified chemical potentials and the fluid velocity.

The application of an external field to a nonspherical particle will, in general, give rise to a nonzero $\boldsymbol{\Omega}$. For the motion of a spheroidal particle, however, there can be no rotation due to the linearity of the governing equations [2.1]–[2.10] and the symmetry of the particle shape. Even so, the problem of solving the Stokes equations [2.2] with the boundary conditions [2.5] and [2.10] may not be a simple one for the migration of a spheroid. Fortunately, the particle velocity can be calculated without the need for obtaining the details of the flow field everywhere. This calculation, which involves the use of Eqs. [2.11] and the Lorentz reciprocal theorem for the Stokes flow (17), gives the formula for the case of a spheroidal particle (18),

$$\mathbf{U} = -\frac{1}{3V_p} \iint_{S_p^+} (\mathbf{n} \cdot \mathbf{r}) \mathbf{v}_s dS, \quad [2.12]$$

where V_p is the volume of the spheroid. This expression applies to both diffusiophoresis and electrophoresis for which

the slip velocity $\mathbf{v}_s$ is known at all points on the particle surface from Eq. [2.7] after solving Eqs. [2.1], [2.4], and [2.9] for the modified chemical potentials μ_m .

3. DIFFUSIOPHORESIS OF A SPHEROID IN A NONELECTROLYTE SOLUTE GRADIENT

In this section we consider the diffusiophoretic motion of a spheroid suspended in an unbounded solution of a nonelectrolyte solute ($M = 1$) with a constant concentration gradient ∇n^∞ . It is assumed that $(a^2 + b^2)^{1/2} |\nabla n^\infty| / n^\infty(\mathbf{0}) \ll 1$ and $L(a^{-2} + b^{-2})^{1/2} \ll 1$, where a and b are the half-length along the axis of revolution and the maximum cross sectional radius, respectively, of the spheroid, and L is the characteristic thickness of the solute-particle interaction layer (which is approximately the molecular dimension of the solute). The interaction between a single solute molecule and the particle surface is described by the potential energy $\Phi(y_n)$, which decays to zero when $y_n/L \gg 1$. The solute gradient ∇n^∞ can be taken as a combination of the longitudinal component $(\nabla n^\infty)_l$ and the transversal component $(\nabla n^\infty)_t$ with respect to the orientation of the spheroid. Thus, the general problem can be divided into two subproblems due to the linearity and they will be separately solved. The total diffusiophoretic velocity of the spheroid can be obtained by the vectorial addition of the two component results.

We first consider the diffusiophoresis of a spheroid along its axis of revolution due to the axial component of the solute gradient, $(\nabla n^\infty)_l$, which is directed along the z axis in the rectangular coordinate system (x, y, z) . Thus, the surface of the spheroid (or S_p^+) is represented by the equation

$$\frac{z^2}{a^2} + \frac{x^2 + y^2}{b^2} = 1. \quad [3.1]$$

The modified chemical potential energy of the solute, μ , outside the interaction layer is governed by the Laplace equation [2.1]. A solution of it that satisfies the far-field boundary condition [2.9] is (15)

$$\mu = \mu^0 + kT \ln n^\infty(\mathbf{0}) + \frac{kT(\nabla n^\infty)_l}{n^\infty(\mathbf{0})} \left[c \sum_{n=1}^{\infty} A_n P_n(\omega) Q_n(\lambda) + z \right], \quad [3.2]$$

where P_n and Q_n are the Legendre functions of the first and second kinds, respectively, ω and λ are the variables related to the bifocal-coordinate transformations, and A_n are the unknown coefficients to be determined. For prolate spheroid the coordinate transformation used is

$$x = c \sinh \xi \sin \varphi \cos \phi, \quad [3.3a]$$

$$y = c \sinh \xi \sin \varphi \sin \phi, \quad [3.3b]$$

$$z = c \cosh \xi \cos \varphi, \quad [3.3c]$$

$$\lambda = \cosh \xi, \quad [3.3d]$$

$$\omega = \cos \varphi, \quad [3.3e]$$

$$a = c \cosh \xi_0, \quad [3.3f]$$

$$b = c \sinh \xi_0, \quad [3.3g]$$

$$c = \sqrt{a^2 - b^2}, \quad [3.3h]$$

while for oblate spheroid the coordinate transformation used is

$$x = ic \cosh \xi \sin \varphi \cos \phi, \quad [3.4a]$$

$$y = ic \cosh \xi \sin \varphi \sin \phi, \quad [3.4b]$$

$$z = ic \sinh \xi \cos \varphi, \quad [3.4c]$$

$$\lambda = i \sinh \xi, \quad [3.4d]$$

$$\omega = \cos \varphi, \quad [3.4e]$$

$$a = ic \sinh \xi_0, \quad [3.4f]$$

$$b = ic \cosh \xi_0, \quad [3.4g]$$

$$c = -i\sqrt{b^2 - a^2}. \quad [3.4h]$$

Here, we employ the bifocal coordinate system (ξ, φ, ϕ) with the origin (midpoint between the foci) at the center of the spheroid. These coordinates range over the values $0 \leq \xi < \infty$, $0 \leq \varphi \leq \pi$, and $0 \leq \phi < 2\pi$. The coordinate surface $\xi = \xi_0$ corresponds to the surface of the spheroid.

At the particle surface (outer edge of the interaction layer) the solution of the modified chemical potential obeys Eq. [2.4], which can be written as

$$\text{on } S_p^+: \frac{\partial \mu}{\partial \lambda} = -\frac{\beta}{c\sqrt{\lambda^2 - 1}} \left[\frac{\partial}{\partial \omega} \left(\frac{1 - \omega^2}{\sqrt{\lambda^2 - \omega^2}} \frac{\partial \mu}{\partial \omega} \right) + \frac{\sqrt{\lambda^2 - \omega^2}}{(\lambda^2 - 1)(1 - \omega^2)} \frac{\partial^2 \mu}{\partial \phi^2} \right], \quad [3.5]$$

where

$$\beta = (1 + \nu \text{Pe})K, \quad [3.6]$$

with

$$K = \int_0^\infty [\exp(-\Phi(y_n)/kT) - 1] dy_n, \quad [3.7a]$$

$$\nu = (L^* K^2)^{-1}$$

$$\times \int_0^\infty \left\{ \int_{y_n}^\infty [\exp(-\Phi(y'_n)/kT) - 1] dy'_n \right\}^2 dy_n, \quad [3.7b]$$

$$\text{Pe} = \frac{kT}{\eta D} L^* K n^\infty(0), \quad [3.7c]$$

and

$$L^* = K^{-1} \int_0^\infty y_n [\exp(-\Phi(y_n)/kT) - 1] dy_n. \quad [3.7d]$$

Here, D is the solute diffusion coefficient, K is the Gibbs adsorption length, Pe is the Peclet number, and νPe accounts for the effect of convection on the solute distribution just outside the adsorption layer.

To generate the equations needed to evaluate the unknown constants A_n in Eq. [3.2], we substitute Eq. [3.2] into Eq. [3.5], multiply the result by the Legendre function $P_j(\omega)$, integrate with respect to ω from -1 to 1 , and utilize the orthogonality properties of the Legendre functions in the interval to obtain

$$\sum_{n=1}^{\infty} L_{jn}(\lambda_0) A_n = R_j(\lambda_0), \quad j = 1, 2, \dots, \quad [3.8]$$

where

$$L_{jn}(\lambda) = \frac{\beta}{c} B_{1jn}(\lambda) + B_{2jn}(\lambda), \quad [3.9a]$$

$$R_j(\lambda) = \frac{\beta}{c} C_{1j}(\lambda) + C_{2j}(\lambda), \quad [3.9b]$$

and λ_0 equals λ with $\xi = \xi_0$. The functions $B_{1jn}(\lambda)$, $B_{2jn}(\lambda)$, $C_{1j}(\lambda)$, and $C_{2j}(\lambda)$ in Eqs. [3.9] are defined by Eqs. [A.1]–[A.4] in the Appendix. Because coefficients A_n should approach zero as n becomes large, they can be determined by setting $A_n = 0$ for $n > N$ and then solving the finite set of Eq. [3.8] obtained by putting $j = 1, 2, \dots$, and N . The accuracy of this truncation technique can be improved to any degree by taking a sufficiently large value of N . In general cases, the series in Eq. [3.2] converges quite rapidly, and very good accuracy can be achieved with only a small number of N .

Substitution of Eq. [3.2] into Eq. [2.7] leads to the slip velocity at the outer edge of the thin interaction layer surrounding the particle,

$$\mathbf{v}_s = \mathbf{e}_\varphi \frac{kT}{\eta} L^* K (\nabla n^\infty)_t \frac{\sqrt{1 - \omega^2}}{\sqrt{\lambda_0^2 - \omega^2}} \times \left[\lambda_0 + \sum_{n=1}^{\infty} A_n Q_n(\lambda_0) \frac{dP_n(\omega)}{d\omega} \right], \quad [3.10]$$

where $\mathbf{e}_\varphi$, together with $\mathbf{e}_\xi$ and $\mathbf{e}_\phi$ are the unit vectors in the bifocal coordinate system. On replacing $\mathbf{v}_s$ in Eq. [2.12] by the form of Eq. [3.10] and integrating over the particle sur-

face we have the final result for the migration velocity of a general spheroid undergoing diffusiophoresis along its axis of symmetry,

$$U_l = \mathbf{e}_z U_l = \mathbf{e}_z \frac{kT}{\eta} L^* K(\nabla n^\infty)_l \lambda_0 \left[\lambda_0 - (\lambda_0^2 - 1) \coth^{-1} \lambda_0 + \frac{1}{2} \sum_{n=1}^{\infty} A_n Q_n(\lambda_0) \int_{-1}^1 \frac{1 - \omega^2}{\lambda_0^2 - \omega^2} \frac{dP_n(\omega)}{d\omega} d\omega \right]. \quad [3.11]$$

We now consider the diffusiophoresis of a spheroid perpendicular to its axis of revolution due to the transverse component of the solute gradient, $(\nabla n^\infty)_t$, which is directed along the x axis. For this case, a solution of the modified chemical potential of the solute that satisfies the Laplace equation and the far-field condition is (15)

$$\mu = \mu^0 + kT \ln n^\infty(\mathbf{0}) + \frac{kT(\nabla n^\infty)_t}{n^\infty(\mathbf{0})} \left[c \sum_{n=1}^{\infty} \bar{A}_n P_n^1(\omega) Q_n^1(\lambda) \cos \phi + x \right]. \quad [3.12]$$

Here, P_n^1 and Q_n^1 are the associated Legendre functions of the first and second kinds, respectively, of order one and degree n ; $\bar{A}_n$ are the unknown constants to be determined using Eq. [3.5], the boundary condition at the outer edge of the thin interaction layer adjacent to the particle surface.

Substituting Eq. [3.12] into Eq. [3.5], multiplying the result by $P_j^1(\omega)/\cos \phi$, integrating with respect to ω from -1 to 1 , and using the orthogonality properties of the associated Legendre functions, one obtains

$$\sum_{n=1}^{\infty} \bar{L}_{jn}(\lambda_0) \bar{A}_n = \bar{R}_j(\lambda_0), \quad j = 1, 2, \dots, \quad [3.13]$$

where

$$\bar{L}_{jn}(\lambda) = \frac{\beta}{c} \bar{B}_{1jn}(\lambda) + \bar{B}_{2jn}(\lambda), \quad [3.14a]$$

$$\bar{R}_j(\lambda) = \frac{\beta}{c} \bar{C}_{1j}(\lambda) + \bar{C}_{2j}(\lambda), \quad [3.14b]$$

and the definitions of the functions $\bar{B}_{1jn}(\lambda)$, $\bar{B}_{2jn}(\lambda)$, $\bar{C}_{1j}(\lambda)$, and $\bar{C}_{2j}(\lambda)$ are given by Eqs. [A.5]–[A.8]. Since coefficients $\bar{A}_n$ are small for large n , they can be determined by setting $\bar{A}_n = 0$ for $n > N$ and solving the first N equations of the set [3.13], provided that N is sufficiently large that an increase in N does not change the calculated values appreciably.

Substitution of Eq. [3.12] into Eq. [2.7] yields the slip velocity at the particular surface,

$$\mathbf{v}_s = \frac{kT}{\eta} L^* K(\nabla n^\infty)_t \left\{ -\mathbf{e}_\phi \frac{\cos \phi}{\sqrt{\lambda_0^2 - \omega^2}} \left[\sqrt{\lambda_0^2 - 1} \omega - \sqrt{1 - \omega^2} \sum_{n=1}^{\infty} \bar{A}_n Q_n^1(\lambda_0) \frac{dP_n^1(\omega)}{d\omega} \right] + \mathbf{e}_\phi \sin \phi \left[1 + \frac{1}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} \times \sum_{n=1}^{\infty} \bar{A}_n Q_n^1(\lambda_0) P_n^1(\omega) \right] \right\}. \quad [3.15]$$

After substituting Eq. [3.15] into Eq. [2.12] and performing the integration we then obtain the diffusiophoretic velocity of a general spheroid in the direction normal to its axis of revolution,

$$U_t = \mathbf{e}_x U_t = \mathbf{e}_x \frac{kT}{\eta} L^* K(\nabla n^\infty)_t \times \left\{ \frac{1}{2} (\lambda_0^2 - 1) (\lambda_0 \coth^{-1} \lambda_0 - 1) + \frac{1}{2} + \frac{1}{4} \sum_{n=1}^{\infty} \bar{A}_n Q_n^1(\lambda_0) \left[\int_{-1}^1 \frac{P_n^1(\omega)}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} d\omega - \sqrt{\lambda_0^2 - 1} \int_{-1}^1 \frac{\omega \sqrt{1 - \omega^2}}{\lambda_0^2 - \omega^2} \frac{dP_n^1(\omega)}{d\omega} d\omega \right] \right\}. \quad [3.16]$$

Note that, when the solute molecules are weakly adsorbing, i.e., $K \ll a$ and $K \ll b$, Eqs. [3.11] and [3.16] will reduce to the simpler form of Eq. [1.2].

The overall diffusiophoretic velocity of the spheroid is the sum of the longitudinal and transversal contributions,

$$\mathbf{U} = \mathbf{U}_l + \mathbf{U}_t. \quad [3.17]$$

Thus, in general, the direction of the particle migration will not be parallel to the prescribed solute gradient.

Usually, experimental values of the diffusiophoretic velocity are average results. For an ensemble of identical, non-interacting spheroids with random orientation distribution, the average particle velocity (aligned with the direction of ∇n^∞) can be calculated from the longitudinal and transversal mobilities,

$$\mathbf{U}_{av} = \frac{1}{3} \left[\frac{U_l}{(\nabla n^\infty)_l} + 2 \frac{U_t}{(\nabla n^\infty)_t} \right] \nabla n^\infty. \quad [3.18]$$

The coefficients A_n in Eq. [3.11] and $\bar{A}_n$ in Eq. [3.16] have been calculated for various values of the aspect ratio a/b and the relaxation parameter β/a (or β/b , which indicates the strength of the solute adsorption to the particle surface)

using Eqs. [3.8] and [3.13], respectively, by a DEC 5000/240 work station. For a typical case with $a/b = 10$ and $\beta/b = 1$, N equal to about 30 is sufficiently large that the $(N + 1)$ th terms in the infinite series in Eqs. [3.11] and [3.16] are negligible and increases in N do not alter the calculated particle velocities appreciably. Numerical results of U_l and U_t for a diffusiophoretic spheroid with aspect ratio approaching unity ($a/b = 0.9, 0.99, 1.01$, and 1.1) are presented in Table I for various values of β/a or β/b . The magnitudes of the diffusiophoretic velocities are normalized by the corresponding values with negligible effect of the diffuse layer polarization, given by (from Eq. [1.2])

$$U_{l0} = \frac{kT}{\eta} L^* K(\nabla n^\infty)_l, \quad [3.19a]$$

$$U_{t0} = \frac{kT}{\eta} L^* K(\nabla n^\infty)_t. \quad [3.19b]$$

All of the results converge to at least four significant digits as shown. The exact solutions of the normalized diffusiophoretic velocity of a spherical particle (with $a/b = 1$) resulted from Eq. [1.9] are also listed in the last column of Table I for comparison. It can be seen that our results for the prolate and oblate spheroids with $a/b \rightarrow 1$ agree very well in tendency with the exact values for the sphere.

An interesting feature is obtained in Table I: the normalized velocity U_l/U_{l0} is a much less sensitive function of the aspect ratio a/b for a fixed value of β/a than for a fixed value of β/b , while U_t/U_{t0} is a much less sensitive function of a/b for a given β/b than a given β/a . Namely, the maximum length of the particle in the direction of diffusiophoresis is the major factor of the particle dimension influencing

the magnitude of the diffusiophoretic velocity. In general, the particle velocity decreases with the decrease of this length. This behavior is consistent with the observation in the phoretic motions of a circular cylinder (12).

The normalized velocities U_l/U_{l0} and U_t/U_{t0} of the spheroid as a function of the aspect ratio a/b (in the range from 0.1 to 10) are plotted by solid curves in Figs. 1a and 1b, respectively. Three constant values, 0.1, 1, and 10, are chosen for the parameter β/a or β/b in these curves. Again, these curves demonstrate that U_l/U_{l0} does not vary too much with a/b for a given β/a and U_t/U_{t0} is not a sensitive function of a/b for a fixed β/b . In general, these normalized velocities are not monotonic functions of a/b . It can be seen from Table I and Figs. 1a and 1b that the migration velocity of the particle decreases monotonically with the increase of the relaxation parameter β/a or β/b .

It was usually deemed that the terms after the first one in the infinite series in Eqs. [3.11] and [3.16] make little contribution to the magnitudes of the series and are negligible in the calculations (15, 16). In Figs. 1a and 1b, the results of the particle velocities versus a/b obtained by neglecting the terms after the first one in these infinite series are also plotted by dashed curves for comparison. Although the values of the particle velocities displayed by these dashed curves agree very well with the exact results when the aspect ratio is close to unity, their errors can be significant if a/b deviates much from unity. For example, the particle velocities calculated by neglecting the terms after the first one in the infinite series in Eqs. [3.11] and [3.16] can be as much as 20% higher than the exact solutions for the case of $a/b = 10$ and $\beta/a = 1$ (or $\beta/b = 1$).

The average diffusiophoretic velocity in a dilute suspension of identical spheroids can be evaluated using Eq. [3.18], and

TABLE I
The Normalized Diffusiophoretic Mobilities of a Spheroid in Nonelectrolyte Concentration Gradients in the Longitudinal and Transversal Directions, as Computed from Eqs. [3.11] and [3.16]

β/a	β/b	$a/b = 0.9$		$a/b = 0.99$		$a/b = 1.01$		$a/b = 1.1$		$a/b = 1$
		U_l/U_{l0}	U_t/U_{t0}	U_l/U_{l0}	U_t/U_{t0}	U_l/U_{l0}	U_t/U_{t0}	U_l/U_{l0}	U_t/U_{t0}	U/U_0
0.01		0.9905	0.9912	0.9901	0.9902	0.9901	0.9900	0.9897	0.9890	0.9901
	0.01	0.9894	0.9902	0.9900	0.9901	0.9902	0.9901	0.9906	0.9900	
0.1		0.9119	0.9181	0.9094	0.9100	0.9088	0.9082	0.9063	0.8998	0.9091
	0.1	0.9030	0.9099	0.9085	0.9092	0.9096	0.9090	0.9141	0.9080	
0.5		0.6724	0.6911	0.6672	0.6691	0.6661	0.6643	0.6617	0.6431	0.6667
	0.5	0.6486	0.6681	0.6650	0.6668	0.6683	0.6665	0.6826	0.6646	
1		0.5055	0.5277	0.5005	0.5027	0.4995	0.4973	0.4955	0.4743	0.5000
	1	0.4791	0.5013	0.4980	0.5002	0.5020	0.4998	0.5192	0.4981	
2		0.3377	0.3582	0.3337	0.3357	0.3330	0.3310	0.3300	0.3111	0.3333
	2	0.3144	0.3344	0.3315	0.3335	0.3352	0.3332	0.3513	0.3318	
10		0.0923	0.1003	0.0910	0.0918	0.0908	0.0901	0.0899	0.0829	0.0909
	10	0.0838	0.0912	0.0902	0.0909	0.0916	0.0909	0.0980	0.0905	
100		0.0101	0.0110	0.0099	0.0099	0.0099	0.0098	0.0098	0.0090	0.0099
	100	0.0091	0.0099	0.0098	0.0099	0.0100	0.0099	0.0108	0.0098

FIG. 1. Plots of the normalized diffusiophoretic mobilities of a spheroidal particle in a nonelectrolyte solution versus the aspect ratio for various values of the relaxation parameter: (a) migration in the longitudinal direction; (b) migration in the transversal direction. The dashed curves are plotted for the mobilities calculated by neglecting the terms after the first one in the infinite series in Eqs. [3.11] and [3.16] for comparison.

the numerical results of its normalized magnitude for three different values of β/a and β/b are plotted versus a/b in Fig. 2. Again, this average velocity is not necessarily a monotonic function of a/b . In general, U_{av}/U_0 varies less sensitively with a/b for a given value of β/b than for a given value of β/a .

4. DIFFUSIOPHORESIS OF A SPHEROID IN A CONCENTRATION GRADIENT OF SYMMETRIC ELECTROLYTES

We now consider the diffusiophoretic motion of a uniformly charged spheroid when immersed in a solution of symmetrically charged, binary electrolyte ($M = 2$) with a constant concentration gradient ∇n^∞ ($n_1^\infty = n_2^\infty = n^\infty$, where subscripts 1 and 2 refer to the anion and cation, respectively). Again we assume $(a^2 + b^2)^{1/2} |\nabla n^\infty| / n^\infty(0) \ll 1$. The electrical double layer (similar to the solute-particle interaction layer in the previous section), which is characterized by the Debye length κ^{-1} , is assumed to be much thinner than the particle dimension, but the effect of double layer relaxation is incorporated. The interaction between the solute ions and the charged surface of the spheroid is dominated by the electrical energies $\Phi_m = ez_m\Phi_e$, where z_m is the valence of ions m ($m = 1$ or 2) and Φ_e is the electrical potential.

Because n^∞ is not uniform, it is required that the total fluxes of cations and anions are equal in order to have no current arising from the diffusive fluxes of the solute ions in an electrically neutral solution. So an electric field arises spontaneously due to the difference in mobilities of the cation

and the anion (6),

$$\mathbf{E}^\infty = -\nabla\Phi_e^\infty = \frac{kT}{Ze} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \nabla \ln n^\infty. \quad [4.1]$$

Since all the governing equations and boundary conditions are linear, diffusiophoresis can be considered a linear combination of two effects: (1) "chemiphoresis" due to the non-

FIG. 2. Plots of the normalized average diffusiophoretic mobility in a dilute suspension of identical spheroids with a nonelectrolyte concentration gradient versus the aspect ratio for various values of the relaxation parameter.

uniform adsorption of counterions over the surface of the particle, which is analogous to diffusiophoresis of nonelectrolytes considered in the previous section, and (2) "electrophoresis" due to the macroscopic electric field generated by the gradient of electrolyte concentration given by Eq. [4.1]. Similar to the analysis in Section 3, we can decompose ∇n^∞ into the longitudinal and transversal components, $(\nabla n^\infty)_l$ and $(\nabla n^\infty)_t$, and analyze the diffusiophoretic motion due to each separately.

First, we consider the motion due to the axial component, $(\nabla n^\infty)_l$, which is directed along the z axis. The modified chemical potentials (known as electrochemical potentials (19)) of the ions outside the double layer satisfy the Laplace equation [2.1]. A solution of them in terms of the bifocal coordinates that satisfies the far-field boundary condition [2.9] is

$$\mu_m = \mu_m^0 + kT \ln n^\infty(\mathbf{0}) + \frac{kT(\nabla n^\infty)_l}{n^\infty(\mathbf{0})} \times \left\{ c \sum_{n=1}^{\infty} A_{mn} P_n(\omega) Q_n(\lambda) + \left[1 - \frac{z_m}{Z} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \right] z \right\}, \quad [4.2]$$

where $m = 1$ or 2 , and A_{1n} and A_{2n} are unknown constants to be determined by using the boundary condition at the particle surface. In addition to the contribution of the electrolyte gradient to μ_m , as is given by Eq. [3.2], a part due to the induced electric field given by Eq. [4.1] is also included in Eq. [4.2].

At the outer edge of the double layer surrounding the particle, normal gradients of the electrochemical potentials occur as described in Eq. [2.4]. Since the equilibrium electrical potential Φ_e^0 governed by the Poisson-Boltzmann equation has an analytical expression for a symmetric electrolyte (so do Φ_1^0 and Φ_2^0), the values of β_{mi} in Eq. [2.6] can be analytically determined,

$$\beta_{11} = \frac{1}{\kappa} \left[4 \left(1 + \frac{3f_1}{Z^2} \right) \exp(\bar{\xi}) \sinh \bar{\xi} - \frac{12f_1}{Z^2} (\bar{\xi} + \ln \cosh \bar{\xi}) \right], \quad [4.3a]$$

$$\beta_{12} = \frac{-1}{\kappa} \left(\frac{12f_1}{Z^2} \right) \ln \cosh \bar{\xi}, \quad [4.3b]$$

$$\beta_{21} = \frac{-1}{\kappa} \left(\frac{12f_2}{Z^2} \right) \ln \cosh \bar{\xi}, \quad [4.3c]$$

$$\beta_{22} = \frac{1}{\kappa} \left[-4 \left(1 + \frac{3f_2}{Z^2} \right) \exp(-\bar{\xi}) \sinh \bar{\xi} + \frac{12f_2}{Z^2} (\bar{\xi} - \ln \cosh \bar{\xi}) \right], \quad [4.3d]$$

where $\bar{\xi} = Ze\zeta/4kT$ and $f_m = \epsilon(kT)^2/6\pi\eta e^2 D_m$; ζ is the zeta potential of the spheroid surface.

Substituting Eq. [4.2] into Eq. [2.4], multiplying the result by the Legendre function $P_j(\omega)$, integrating with respect to ω from -1 to 1 , and utilizing the orthogonality properties of the Legendre functions yields

$$\sum_{n=1}^{\infty} [L_{1jn}(\lambda_0) A_{1n} + L_{2jn}(\lambda_0) A_{2n}] = R_{1j}(\lambda_0), \quad j = 1, 2, \dots, \quad [4.4a]$$

$$\sum_{n=1}^{\infty} [L_{3jn}(\lambda_0) A_{1n} + L_{4jn}(\lambda_0) A_{2n}] = R_{2j}(\lambda_0), \quad j = 1, 2, \dots, \quad [4.4b]$$

where

$$L_{1jn}(\lambda) = \frac{\beta_{11}}{c} B_{1jn}(\lambda) + B_{2jn}(\lambda), \quad [4.5a]$$

$$L_{2jn}(\lambda) = \frac{\beta_{12}}{c} B_{1jn}(\lambda), \quad [4.5b]$$

$$R_{1j}(\lambda) = \frac{2(\beta_{11}D_2 + \beta_{12}D_1)}{c(D_2 + D_1)} C_{1j}(\lambda) + \frac{2D_2}{D_2 + D_1} C_{2j}(\lambda); \quad [4.5c]$$

$$L_{3jn}(\lambda) = \frac{\beta_{21}}{c} B_{1jn}(\lambda), \quad [4.6a]$$

$$L_{4jn}(\lambda) = \frac{\beta_{22}}{c} B_{1jn}(\lambda) + B_{2jn}(\lambda), \quad [4.6b]$$

$$R_{1j}(\lambda) = \frac{2(\beta_{21}D_2 + \beta_{22}D_1)}{c(D_2 + D_1)} C_{1j}(\lambda) + \frac{2D_1}{D_2 + D_1} C_{2j}(\lambda). \quad [4.6c]$$

The definitions of the functions $B_{1jn}(\lambda)$, $B_{2jn}(\lambda)$, $C_{1j}(\lambda)$, $C_{2j}(\lambda)$ in Eqs. [4.5] and [4.6] are given by Eqs. [A.1]–[A.4]. The coefficients A_{1n} and A_{2n} in Eq. [4.2] can be determined by solving the first N pairs of Eqs. [4.4], provided that N is sufficiently large that A_{1n} and A_{2n} are negligible for $n > N$.

The slip velocity at the surface of the particle is obtained by the substitution of Eq. [4.2] into Eq. [2.7],

$$\mathbf{v}_s = \mathbf{e}_\varphi \frac{\epsilon \zeta}{4\pi\eta} \frac{kT(\nabla n^\infty)_l}{Ze n^\infty(\mathbf{0})} \frac{\sqrt{1 - \omega^2}}{\sqrt{\lambda_0^2 - \omega^2}} \times \left\{ \lambda_0 \left(\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} \right) \right.$$

$$+ \sum_{n=1}^{\infty} \left[\frac{1}{2} (A_{1n} - A_{2n}) + \frac{2kT}{Ze\xi} \ln \cosh \frac{Ze\xi}{4kT} (A_{1n} + A_{2n}) \right] \sum_{n=1}^{\infty} L_{3jn}(\lambda_0) A'_{1n} + L_{4jn}(\lambda_0) A'_{2n} = R'_{2j}(\lambda_0),$$

$$\times Q_n(\lambda_0) \frac{dP_n(\omega)}{d\omega} \Bigg\}. \quad [4.7] \quad j = 1, 2, \dots, \quad [4.11b]$$

The diffusiophoretic velocity of the spheroid along its axis of revolution $U_l (= U_l e_z)$ can be obtained by replacing v_s in Eq. [2.12] by the expression [4.7] and integrating over the particle surface, with the result

$$U_l = \frac{\epsilon\xi}{4\pi\eta} \frac{kT}{Ze} \frac{(\nabla n^\infty)_l}{n^\infty(\mathbf{0})} \lambda_0 \left\{ [\lambda_0 - (\lambda_0^2 - 1) \coth^{-1} \lambda_0] \right. \\ \times \left(\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\xi} \ln \cosh \frac{Ze\xi}{4kT} \right) \\ \left. + \sum_{n=1}^{\infty} \left[\frac{1}{4} (A_{1n} - A_{2n}) + \frac{kT}{Ze\xi} \ln \cosh \frac{Ze\xi}{4kT} (A_{1n} + A_{2n}) \right] \right. \\ \left. \times Q_n(\lambda_0) \int_{-1}^1 \frac{1 - \omega^2}{\lambda_0^2 - \omega^2} \frac{dP_n(\omega)}{d\omega} d\omega \right\}. \quad [4.8]$$

Due to the linearity of the diffusiophoretic problem, the particle migration velocity U_l can be expressed as

$$U_l = U_l^c + U_l^e, \quad [4.9]$$

where U_l^c and U_l^e denote the corresponding chemiphoretic and electrophoretic velocities, respectively. U_l^c can be determined from the same procedure to obtain Eq. [4.8] by setting $D_2 = D_1$ in Eq. [4.2] for μ_m ,

$$U_l^c = \frac{\epsilon\xi}{4\pi\eta} \frac{kT}{Ze} \frac{(\nabla n^\infty)_l}{n^\infty(\mathbf{0})} \lambda_0 \left\{ \frac{4kT}{Ze\xi} \ln \cosh \frac{Ze\xi}{4kT} [\lambda_0 - (\lambda_0^2 - 1) \coth^{-1} \lambda_0] \right. \\ \left. + \sum_{n=1}^{\infty} \left[\frac{1}{4} (A'_{1n} - A'_{2n}) + \frac{kT}{Ze\xi} \ln \cosh \frac{Ze\xi}{4kT} (A'_{1n} + A'_{2n}) \right] \right. \\ \left. \times Q_n(\lambda_0) \int_{-1}^1 \frac{1 - \omega^2}{\lambda_0^2 - \omega^2} \frac{dP_n(\omega)}{d\omega} d\omega \right\}. \quad [4.10]$$

Here, the coefficients A'_{1n} and A'_{2n} can be evaluated by solving the set of equations,

$$\sum_{n=1}^{\infty} L_{1jn}(\lambda_0) A'_{1n} + L_{2jn}(\lambda_0) A'_{2n} = R'_{1j}(\lambda_0),$$

$$j = 1, 2, \dots, \quad [4.11a]$$

where L_{1jn} , L_{2jn} , L_{3jn} , and L_{4jn} are defined by Eqs. [4.5] and [4.6];

$$R'_{1j}(\lambda) = \frac{\beta_{11} + \beta_{12}}{c} C_{1j}(\lambda) + C_{2j}(\lambda), \quad [4.12a]$$

$$R'_{2j}(\lambda) = \frac{\beta_{21} + \beta_{22}}{c} C_{1j}(\lambda) + C_{2j}(\lambda). \quad [4.12b]$$

U_l^e can be determined similarly by eliminating the first term in the square brackets in Eq. [4.2],

$$U_l^e = \frac{\epsilon\xi}{4\pi\eta} \frac{kT}{Ze} \frac{(\nabla n^\infty)_l}{n^\infty(\mathbf{0})} \frac{D_2 - D_1}{D_2 + D_1} \lambda_0 \\ \times \left\{ \lambda_0 - (\lambda_0^2 - 1) \coth^{-1} \lambda_0 + \sum_{n=1}^{\infty} \left[\frac{1}{4} (A''_{1n} + A''_{2n}) \right. \right. \\ \left. \left. + \frac{kT}{Ze\xi} \ln \cosh \frac{Ze\xi}{4kT} (A''_{1n} - A''_{2n}) \right] Q_n(\lambda_0) \right. \\ \left. \times \int_{-1}^1 \frac{1 - \omega^2}{\lambda_0^2 - \omega^2} \frac{dP_n(\omega)}{d\omega} d\omega \right\}. \quad [4.13]$$

The coefficients A''_{1n} and A''_{2n} can be obtained by solving

$$\sum_{n=1}^{\infty} L_{1jn}(\lambda_0) A''_{1n} - L_{2jn}(\lambda_0) A''_{2n} = R''_{1j}(\lambda_0),$$

$$j = 1, 2, \dots, \quad [4.14a]$$

$$\sum_{n=1}^{\infty} L_{3jn}(\lambda_0) A''_{1n} - L_{4jn}(\lambda_0) A''_{2n} = R''_{2j}(\lambda_0),$$

$$j = 1, 2, \dots, \quad [4.14b]$$

where

$$R''_{1j}(\lambda) = \frac{\beta_{11} - \beta_{12}}{c} C_{1j}(\lambda) + C_{2j}(\lambda), \quad [4.15a]$$

$$R''_{2j}(\lambda) = \frac{\beta_{21} - \beta_{22}}{c} C_{1j}(\lambda) - C_{2j}(\lambda). \quad [4.15b]$$

We now consider the diffusiophoresis of a spheroid due to the transverse component of the solute gradient, $(\nabla n^\infty)_t$. For this case, a solution of the electrochemical potentials of the ions that satisfies the Laplace equation and the far-field

condition is

$$\begin{aligned} \mu_m = \mu_m^0 + kT \ln n^\infty(\mathbf{0}) \\ + \frac{kT(\nabla n^\infty)_i}{n^\infty(\mathbf{0})} \left\{ c \sum_{n=1}^{\infty} \bar{A}_{mn} P_n^1(\omega) Q_n^1(\lambda) \cos \phi \right. \\ \left. + \left[1 - \frac{z_m}{Z} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \right] x \right\}, \quad [4.16] \end{aligned}$$

where $m = 1$ or 2 . In addition to the contribution of the electrolyte gradient to μ_m , as is given by Eq. [3.12], a part due to the induced electric field given by Eq. [4.1] is also included in Eq. [4.16]. To determine the unknown coefficients $\bar{A}_{1n}$ and $\bar{A}_{2n}$, we need to substitute Eq. [4.16] into Eqs. [2.4], multiply the result by $P_j^1(\omega)/\cos \phi$, and integrate with respect to ω from -1 to 1 . The same equations as Eqs. [4.4]–[4.6] with A_{in} , B_{ijn} , and C_{ij} (where $i = 1$ and 2) being replaced by $\bar{A}_{in}$, $\bar{B}_{ijn}$, and $\bar{C}_{ij}$ (where the definitions of $\bar{B}_{1jn}$, $\bar{B}_{2jn}$, $\bar{C}_{1ij}$, and $\bar{C}_{2ij}$ are given by Eqs. [A.5]–[A.8]), respectively, can be obtained. The equations in the form of [4.4] can be solved for the first N pairs to yield the coefficients $\bar{A}_{1n}$ and $\bar{A}_{2n}$ required for the ionic electrochemical potential distributions.

Substituting Eq. [4.16] into Eq. [2.7] gives the slip velocity at the particle surface

$$\begin{aligned} \mathbf{v}_s = \frac{\epsilon \zeta}{4\pi\eta} \frac{kT(\nabla n^\infty)_i}{Ze n^\infty(\mathbf{0})} \left\{ -\mathbf{e}_\phi \frac{\cos \phi}{\sqrt{\lambda_0^2 - \omega^2}} \right. \\ \times \left[\sqrt{\lambda_0^2 - 1} \omega \left(\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} \right) \right. \\ \left. - \frac{1}{2} \sqrt{1 - \omega^2} \sum_{n=1}^{\infty} Q_n^1(\lambda_0) \frac{dP_n^1(\omega)}{d\omega} \right. \\ \times \left(\bar{A}_{1n} - \bar{A}_{2n} + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} (\bar{A}_{1n} + \bar{A}_{2n}) \right) \Bigg] \\ + \mathbf{e}_\phi \frac{\sin \phi}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} \left[\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2} \right. \\ \times \left(\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} \right) \\ \left. + \frac{1}{2} \sum_{n=1}^{\infty} Q_n^1(\lambda_0) P_n^1(\omega) \left(\bar{A}_{1n} - \bar{A}_{2n} \right. \right. \\ \left. \left. + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} (\bar{A}_{1n} + \bar{A}_{2n}) \right) \right] \Bigg\}. \quad [4.17] \end{aligned}$$

On replacing $\mathbf{v}_s$ in Eq. [2.12] by the expression [4.17] and integrating over the particle surface we obtain the diffusio-phoretic velocity of the spheroid in the transverse direction

$$\mathbf{U}_t (= U_t \mathbf{e}_x),$$

$$\begin{aligned} U_t = \frac{\epsilon \zeta}{4\pi\eta} \frac{kT(\nabla n^\infty)_i}{Ze n^\infty(\mathbf{0})} \left\{ \frac{1}{2} \left(\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} \right) \right. \\ \times [(\lambda_0^2 - 1)(\lambda_0 \coth^{-1} \lambda_0 - 1) + 1] \\ + \frac{1}{8} \sum_{n=1}^{\infty} Q_n^1(\lambda_0) \left[\bar{A}_{1n} - \bar{A}_{2n} + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} \right. \\ \times (\bar{A}_{1n} + \bar{A}_{2n}) \Bigg] \left[\int_{-1}^1 \frac{P_n^1(\omega)}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} d\omega - \sqrt{\lambda_0^2 - 1} \right. \\ \left. \times \int_{-1}^1 \frac{\omega \sqrt{1 - \omega^2}}{\lambda_0^2 - \omega^2} \frac{dP_n^1(\omega)}{d\omega} d\omega \right] \Bigg\}. \quad [4.18] \end{aligned}$$

Similarly to the case of longitudinal migration, the diffusio-phoretic velocity U_t can be taken as the sum of a chemi-phoretic velocity U_t^c and an electrophoretic velocity U_t^e , given by

$$\begin{aligned} U_t^c = \frac{\epsilon \zeta}{4\pi\eta} \frac{kT(\nabla n^\infty)_i}{Ze n^\infty(\mathbf{0})} \left\{ \frac{2kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} [(\lambda_0^2 - 1) \right. \\ \times (\lambda_0 \coth^{-1} \lambda_0 - 1) + 1] + \frac{1}{8} \sum_{n=1}^{\infty} Q_n^1(\lambda_0) \left[\bar{A}'_{1n} - \bar{A}'_{2n} \right. \\ \left. + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} (\bar{A}'_{1n} + \bar{A}'_{2n}) \right] \\ \times \left[\int_{-1}^1 \frac{P_n^1(\omega)}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} d\omega - \sqrt{\lambda_0^2 - 1} \right. \\ \left. \times \int_{-1}^1 \frac{\omega \sqrt{1 - \omega^2}}{\lambda_0^2 - \omega^2} \frac{dP_n^1(\omega)}{d\omega} d\omega \right] \Bigg\} \quad [4.19] \end{aligned}$$

and

$$\begin{aligned} U_t^e = \frac{\epsilon \zeta}{4\pi\eta} \frac{kT(\nabla n^\infty)_i}{Ze n^\infty(\mathbf{0})} \frac{D_2 - D_1}{D_2 + D_1} \left\{ \frac{1}{2} [(\lambda_0^2 - 1) \right. \\ \times (\lambda_0 \coth^{-1} \lambda_0 - 1) + 1] + \frac{1}{8} \sum_{n=1}^{\infty} Q_n^1(\lambda_0) \left[\bar{A}''_{1n} + \bar{A}''_{2n} \right. \\ \left. + \frac{4kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} (\bar{A}''_{1n} - \bar{A}''_{2n}) \right] \\ \times \left[\int_{-1}^1 \frac{P_n^1(\omega)}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} d\omega - \sqrt{\lambda_0^2 - 1} \right. \\ \left. \times \int_{-1}^1 \frac{\omega \sqrt{1 - \omega^2}}{\lambda_0^2 - \omega^2} \frac{dP_n^1(\omega)}{d\omega} d\omega \right] \Bigg\}. \quad [4.20] \end{aligned}$$

The coefficients $\bar{A}'_{1n}$ and $\bar{A}'_{2n}$ in Eq. [4.19] and $\bar{A}''_{1n}$ and $\bar{A}''_{2n}$ in Eq. [4.20] are to be determined by solving the equa-

tions in the form of Eqs. [4.11] and [4.14], respectively, with A'_{in} , A''_{in} , B_{ijn} , and C_{ij} ($j = 1$ and 2) being replaced by $\bar{A}'_{in}$, $\bar{A}''_{in}$, $\bar{B}_{ijn}$, and $\bar{C}_{ij}$, respectively.

Note that, when κa and κb are large and $|\zeta|$ is small such that Eq. [1.8] is satisfied, both Eqs. [4.8] and [4.18] reduce to the form of Eq. [1.3]; also, Eqs. [4.10] and [4.19] reduce to Eq. [1.3] with $D_2 = D_1$.

The overall diffusiophoretic velocity of an arbitrarily oriented spheroid and the ensemble-averaged mobility of the spheroid can also be determined by Eqs. [3.17] and [3.18], respectively, incorporated with Eqs. [4.8] and [4.18].

The coefficients A_{1n} and A_{2n} in Eq. [4.8] and $\bar{A}_{1n}$ and $\bar{A}_{2n}$ in Eq. [4.18] have been calculated for various values of $(D_2 - D_1)/(D_2 + D_1)$, f_1 , Z , $\zeta e/kT$, κa , and a/b using the matrix equations in the form of Eqs. [4.4]. Part of the numerical results of the diffusiophoretic velocities U_l and U_t of the spheroid (with $Z = 1$, $f_1 = 0.2$, $\zeta e/kT = 8$, $a/b = 0.9, 0.99, 1.01$, and 1.1) normalized by their corresponding magnitudes with negligible effect of the double layer polarization are presented in Table II. The analytical solutions of the diffusiophoretic velocity of a sphere as given by Eq. [1.10] are also listed in the last column of this table for comparison. It can be seen that the results for the prolate and oblate spheroids agree very well in trend with the exact values for the sphere. The diffusiophoretic mobilities are always reduced due to the polarization of the double layer. Also, the normalized velocity U_l/U_0 is a much less sensitive function of the aspect ratio a/b for a given value of κa than for a given value of κb , while U_t/U_0 is a much less sensitive function of a/b for a fixed κb than for a fixed κa . Similarly to the case of diffusiophoresis of a spheroid in nonelectrolytes considered in

the previous section, the diffusiophoretic velocity of a spheroid in electrolytes decreases with the reduction of the maximum length of the particle in the direction of diffusiophoresis. Note that the situations associated with $(D_2 - D_1)/(D_2 + D_1) = 0$ and -0.2 in Table II are very close to the diffusiophoresis in the aqueous solutions of KCl and NaCl, respectively.

In Figs. 3a–c, the dependence of the average diffusiophoretic velocity in a dilute dispersion of identical spheroids on their dimensionless zeta potential at various values of a/b and Z for a case that the anion and cation mobilities are equal ($D_2 - D_1 = 0$ with $f_1 = f_2 = 0.2$ and $\kappa b = 300$) is illustrated. Here, the magnitude of the diffusiophoretic velocity is normalized by a characteristic value

$$U^* = \frac{\epsilon}{4\pi\eta} \left(\frac{kT}{e} \right)^2 \frac{|\nabla n^\infty|}{n^\infty(\mathbf{0})}. \quad [4.21]$$

Only the results at positive zeta potentials are shown in Figs. 3a–c since the induced electric field given by Eq. [4.1] disappears for $D_1 = D_2$ and the diffusiophoretic velocity, which is due to the chemiphoretic effect only, is an even function of zeta potential. It can be seen that the diffusiophoretic velocity does not vary monotonically with the zeta potential or the aspect ratio of the particles and a maximum in the average mobility occurs at a value of $\zeta e/kT$ which depends on a/b and Z . When a/b decreases or when Z increases, the maximum will take place at a smaller zeta potential. Note that the downward trend for large zeta potentials continues until the direction of diffusiophoresis reverses. Figure 3c for the case of $Z = 3$ shows that the reduced diffusiophoretic

TABLE 2
The Normalized Diffusiophoretic Mobilities of a Spheroid in a Solution Containing Only One Symmetric Electrolyte with $Z = 1$, $f_1 = 0.2$, and $\zeta e/kT = 8$ in the Longitudinal and Transversal Directions, as Computed from Eqs. [4.8] and [4.18]

κa	κb	$a/b = 0.9$		$a/b = 0.99$		$a/b = 1.01$		$a/b = 1.1$		$a/b = 1$
		U_l/U_0	U_t/U_0	U_l/U_0	U_t/U_0	U_l/U_0	U_t/U_0	U_l/U_0	U_t/U_0	U/U_0
$(D_2 - D_1)/(D_2 + D_1) = 0$										
100		0.2358	0.2627	0.2303	0.2329	0.2293	0.2267	0.2250	0.2000	0.2298
	100	0.2049	0.2312	0.2274	0.2300	0.2322	0.2296	0.2532	0.2277	
300		0.5702	0.5941	0.5636	0.5660	0.5623	0.5599	0.5568	0.5331	0.5630
	300	0.5399	0.5648	0.5608	0.5632	0.5651	0.5628	0.5834	0.5604	
1000		0.8308	0.8424	0.8265	0.8277	0.8255	0.8244	0.8215	0.8094	0.8260
	1000	0.8147	0.8273	0.8250	0.8262	0.8270	0.8258	0.8355	0.8242	
$(D_2 - D_1)/(D_2 + D_1) = -0.2$										
100		0.1300	0.1606	0.1237	0.1267	0.1225	0.1195	0.1176	0.0891	0.1231
	100	0.0947	0.1247	0.1203	0.1233	0.1258	0.1229	0.1497	0.1207	
300		0.5109	0.5382	0.5035	0.5062	0.5020	0.4993	0.4957	0.4686	0.5027
	300	0.4765	0.5048	0.5002	0.5030	0.5052	0.5025	0.5260	0.4998	
1000		0.8075	0.8207	0.8026	0.8039	0.8015	0.8002	0.7969	0.7832	0.8021
	1000	0.7892	0.8035	0.8009	0.8022	0.8032	0.8019	0.8128	0.8001

FIG. 3. Plots of the normalized average diffusiophoretic mobility in a dilute suspension of identical spheroids with a symmetric-electrolyte concentration gradient versus the dimensionless zeta potential of the particles for various values of the aspect ratio a/b with $D_1 - D_2 = 0$, $f_1 = f_2 = 0.2$, and $\kappa b = 300$: (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

phoretic velocity at high zeta potentials approaches a negative constant value which is independent of the aspect ratio a/b of the particles.

Figures 4a-c are drawn for the reduced average diffusiophoretic velocity in a dilute dispersion of identical spheroids as a function of $\zeta e/kT$ at various values of a/b and Z for a case that the anion and cation have different diffusion coefficients ($(D_2 - D_1)/(D_2 + D_1) = -0.2$ with $f_1 = 0.2$ and $\kappa b = 300$). In this case, both the chemiphoretic and the electrophoretic effects contribute to the particles' movement and the net diffusiophoretic velocity is neither an even nor an odd function of ζ . The curves in Figs. 4a-c show that the diffusiophoretic velocity might reverse direction

four times as the zeta potential of the particles varies from highly negative to highly positive values. Similarly to Fig. 3c for the case of $D_1 = D_2$, the reduced diffusiophoretic velocity at large magnitudes of zeta potential for the case of $Z = 3$ converges to constant values for various aspect ratios a/b of the particles, as illustrated in Fig. 4c.

5. ELECTROPHORESIS OF A SPHEROID IN SYMMETRIC ELECTROLYTES

Considered in this section is the electrophoretic motion of a charged spheroid when a uniform external electric field E^∞ is imposed. The bulk concentrations of all ions n_m^∞ be-

FIG. 4. Plots of the normalized average diffusioelectric mobility in a dilute suspension of identical spheroids with a symmetric-electrolyte concentration gradient versus the dimensionless zeta potential of the particles for various values of the aspect ratio a/b with $(D_2 - D_1)/(D_2 + D_1) = -0.2$, $f_1 = 0.2$, and $\kappa b = 300$: (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

yond the electrical double layer are constant. The thickness of the double layer is assumed to be much smaller than the particle dimension. The potential energy Φ_m of ionic species m is equal to $ez_m\Phi_e$. Like the analyses in Sections 3 and 4, the imposed electric field can be vectorially decomposed into the longitudinal and transversal components, E_l^∞ and E_t^∞ . For simplicity, only one symmetric electrolyte in the liquid phase ($M = 2$; $-z_1 = z_2 = Z$; $n_1^\infty = n_2^\infty = n^\infty$, where subscripts 1 and 2 denote anion and cation, respectively) will be considered.

First, we examine the motion due to $E_l^\infty \mathbf{e}_z$. Outside the double layer, the electrochemical potentials, which satisfy

Laplace's equation [2.1], can be expressed as

$$\mu_m = \mu_m^0 + kT \ln n^\infty - ez_m E_l^\infty z + [c \sum_{n=1}^{\infty} A_{mn}'' P_n(\omega) Q_n(\lambda) + z], \quad [5.1]$$

where $m = 1$ or 2. This solution immediately satisfies the far-field condition, $\nabla \mu_m \rightarrow -ez_m E_l^\infty \mathbf{e}_z$. At the outer edge of the double layer, normal fluxes of ions take place as described by Eq. [2.4]. The parameters β_{mi} have been given in Eqs. [4.3]. The unknown coefficients A_{1n}'' and A_{2n}'' in Eq. [5.1]

can also be determined using Eqs. [4.14]. Following the procedure in the previous section, we can find the electrophoretic velocity $U_l (=U_l \mathbf{e}_z)$ with

$$U_l = \frac{\epsilon \zeta}{4\pi\eta} E_l^\infty \lambda_0 \times \left\{ \lambda_0 - (\lambda_0^2 - 1) \coth^{-1} \lambda_0 + \sum_{n=1}^{\infty} \left[\frac{1}{4} (A_{1n}'' + A_{2n}'') + \frac{kT}{Ze\zeta} \ln \cosh \frac{Ze\zeta}{4kT} (A_{1n}'' - A_{2n}'') \right] Q_n(\lambda_0) \times \int_{-1}^1 \frac{1 - \omega^2}{\lambda_0^2 - \omega^2} \frac{dP_n(\omega)}{d\omega} d\omega \right\}. \quad [5.2]$$

This expression can also be obtained from Eq. [4.13] with the substitution of Eq. [4.1].

Similarly, the electrophoretic velocity of the spheroid in the transverse direction $U_t (=U_t \mathbf{e}_x)$ can result from the substitution of Eq. [4.1] into Eq. [4.20],

$$U_t = \frac{\epsilon \zeta}{4\pi\eta} E_t^\infty \left\{ \frac{1}{2} [(\lambda_0^2 - 1)(\lambda_0 \coth^{-1} \lambda_0 - 1) + 1] + \frac{1}{8} \sum_{n=1}^{\infty} Q_n^1(\lambda_0) \left[\bar{A}_{1n}'' + \bar{A}_{2n}'' + \frac{4kT}{Ze\zeta} \times \ln \cosh \frac{Ze\zeta}{4kT} (\bar{A}_{1n}'' - \bar{A}_{2n}'') \right] \times \left[\int_{-1}^1 \frac{P_n^1(\omega)}{\sqrt{\lambda_0^2 - 1} \sqrt{1 - \omega^2}} d\omega - \sqrt{\lambda_0^2 - 1} \times \int_{-1}^1 \frac{\omega \sqrt{1 - \omega^2}}{\lambda_0^2 - \omega^2} \frac{dP_n^1(\omega)}{d\omega} d\omega \right] \right\}. \quad [5.3]$$

Here, the coefficients $\bar{A}_{1n}''$ and $\bar{A}_{2n}''$ are to be determined using Eqs. [4.14] with A_{in}' , B_{ijn} , and C_{ij} ($i = 1$ and 2) being replaced by $\bar{A}_{in}'$, $\bar{B}_{ijn}$, and $\bar{C}_{ij}$, respectively. In the limit of Eq. [1.8],

both Eqs. [5.2] and [5.3] reduce to the Smoluchowski equation.

The total electrophoretic velocity and the ensemble-averaged mobility of the spheroid can also be determined by Eqs. [3.17] and [3.18], with $(\nabla n^\infty)_i$, $(\nabla n^\infty)_t$, and ∇n^∞ in Eq. [3.18] being replaced by E_l^∞ , E_t^∞ , and $\mathbf{E}^\infty$, respectively.

The coefficients A_{1n}'' and A_{2n}'' in Eq. [5.2] and $\bar{A}_{1n}''$ and $\bar{A}_{2n}''$ in Eq. [5.3] have been calculated for various values of Z , $\zeta e/kT$, κa , and a/b using the appropriate matrix equations. Part of the numerical results of the electrophoretic velocities of the spheroid (with $Z = 1$, $f_1 = f_2 = 0.2$, $\zeta e/kT = 8$, $a/b = 0.9, 0.99, 1.01$, and 1.1) normalized by their corresponding magnitudes with negligible relaxation effect of the double layer are listed in Table III. The exact solutions of the electrophoretic velocity of a sphere calculated using Eq. [1.5] are also given in the last column of this table for comparison. Again, the results for the prolate and oblate spheroids can be found to agree very well in trend with the analytical solutions for the sphere. Similarly to the case of diffusiophoresis considered in the previous sections, the electrophoretic mobilities are reduced due to the polarization of the double layer. Also, the normalized electrophoretic velocity of a spheroid decreases with the reduction of the maximum length of the particle in the direction of migration. Note that only one case of the ionic mobilities is considered here since their influence on the electrophoretic velocity of particles is generally weak for most realistic aqueous systems (9).

The normalized electrophoretic velocities U_l/U_{l0} and U_t/U_{t0} of the spheroid with $f_1 = f_2 = 0.2$ and $\zeta e/kT = 5$ as a function of the aspect ratio a/b (in the range from 0.1 to 10) are plotted by solid curves for various values of Z in Figs. 5a and 5b, respectively. Again, these curves demonstrate that U_l/U_{l0} does not vary too much with a/b for a given κa and U_t/U_{t0} is not a sensitive function of a/b for a fixed κb . In general, these normalized velocities are not monotonic functions of a/b .

O'Brien and Ward (16) noted that the terms after the first one in the infinite series in Eqs. [5.2] and [5.3] contribute little to the magnitudes of the series and are negligible in the

TABLE 3

The Normalized Electrophoretic Mobilities of a Spheroid in a Solution Containing Only One Symmetric Electrolyte with $Z = 1$, $f_1 = f_2 = 0.2$, and $\zeta e/kT = 8$ in the Longitudinal and Transversal Directions, as Computed from Eqs. [5.2] and [5.3]

κa	κb	$a/b = 0.9$		$a/b = 0.99$		$a/b = 1.01$		$a/b = 1.1$		$a/b = 1$
		U_l/U_{l0}	U_t/U_{t0}	U_l/U_{l0}	U_t/U_{t0}	U_l/U_{l0}	U_t/U_{t0}	U_l/U_{l0}	U_t/U_{t0}	
100	100	0.4787	0.4968	0.4751	0.4768	0.4744	0.4726	0.4716	0.4548	0.4747
		0.4579	0.4756	0.4731	0.4748	0.4763	0.4746	0.4906	0.4734	
300	300	0.7056	0.7220	0.7012	0.7028	0.7003	0.6987	0.6966	0.6803	0.7008
		0.6850	0.7020	0.6993	0.7009	0.7022	0.7006	0.7147	0.6990	
1000	1000	0.8840	0.8919	0.8810	0.8818	0.8804	0.8796	0.8776	0.8693	0.8807
		0.8730	0.8816	0.8800	0.8808	0.8814	0.8806	0.8872	0.8795	

electrophoresis calculations. In Figs. 5a and 5b, the results of the particle velocities versus a/b obtained by neglecting the terms after the first one in these infinite series are also plotted by dashed curves for comparison. Similarly to the case of diffusiophoresis considered in Section 3, the values of the particle velocities illustrated by these dashed curves agree very well with the exact results when the aspect ratio is close to unity, but their errors can be significant if a/b deviates much from unity. For example, the particle velocities calculated by neglecting the terms after the first one in the infinite series in Eqs. [5.2] and [5.3] can be as much as 15% higher than the exact solutions for the case of $a/b = 10$ and $Z = 2$.

The average electrophoretic velocity in a dilute suspension of identical spheroids as a function of $\zeta e/kT$ at various values of a/b and Z for the case with $f_1 = f_2 = 0.2$ and $\kappa b = 300$ is depicted in Figs. 6a–c. In these figures, the magnitude of this average velocity is normalized by the characteristic value

$$U^* = \frac{\epsilon}{4\pi\eta} \left(\frac{kT}{e} \right) |\mathbf{E}^\infty|. \quad [5.4]$$

Only the results at positive zeta potentials are displayed in Figs. 6a–c since the electrophoretic velocity is an odd function of zeta potential for the situation that the anion and cation mobilities are equal. Similarly to the case of chemiophoresis as shown in Figs. 3a–c, the electrophoretic velocity does not vary monotonically with the zeta potential or the aspect ratio and a maximum in the particle mobility appears at a value of $\zeta e/kT$ which depends on a/b and Z . When a/b decreases

or when Z increases, the maximum will occur at a smaller magnitude of zeta potential. Also, Fig. 6c for the case of $Z = 3$ shows that the reduced electrophoretic velocity at high zeta potentials converges to a constant value for various aspect ratios a/b of the particles. Contrary to the case of diffusiophoresis, this constant value is always positive.

6. SUMMARY

Three problems of similar physical and mathematical structures are studied in this work: the diffusiophoresis of a spheroid in a nonelectrolyte solute gradient, the diffusiophoresis of a spheroid in an electrolyte solute gradient, and the electrophoresis of a spheroid in an external electric field. The spheroid can be oriented arbitrarily with respect to the applied field. Although the region of the interaction between the solute species and the particle surface is taken to be small relative to the particle dimension, the assumptions allow for polarization of the mobile species in the diffuse layer. The method developed for solving the electrokinetic equations in the limit of thin double layer (3, 8) has been used to solve the equations of conservation applicable to the problems.

Expressions for the diffusiophoretic and electrophoretic velocities of the spheroid were obtained in Eqs. [3.11], [4.8], and [5.2] for various longitudinal imposed fields and in Eqs. [3.16], [4.18], and [5.3] for various transversal imposed fields. An important result that the particle velocity decreases with the reduction of the maximum length of the particle in the direction of migration was deduced. Although the validity of Eqs. [4.8], [4.18], [5.2], and [5.3] is restricted for the

FIG. 5. Plots of the normalized electrophoretic mobilities of a spheroidal particle in a symmetric-electrolyte solution versus the aspect ratio for various values of Z with $f_1 = f_2 = 0.2$ and $\zeta e/kT = 5$: (a) migration in the longitudinal direction with $\kappa a = 300$; (b) migration in the transversal direction with $\kappa b = 300$. The dashed curves are plotted for the mobilities calculated by neglecting the terms after the first one in the infinite series in Eqs. [5.2] and [5.3] for comparison.

FIG. 6. Plots of the normalized average electrophoretic mobility in a dilute suspension of identical spheroids with a symmetric electrolyte in the solution versus the dimensionless zeta potential of the particles for various values of the aspect ratio a/b with $f_1 = f_2 = 0.2$ and $\kappa b = 300$: (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

case of a symmetric electrolyte solution, formulae for a fluid containing an arbitrary combination of general electrolytes can be obtained from the same procedure using O'Brien's (8) reasoning that only the most highly charged counterions play a dominant role in the ionic fluxes along the particle surface. Due to the linearity of these problems, the migration velocity of the spheroid in an arbitrarily oriented applied field can be obtained by the vectorial addition of the contributions generated from the longitudinal and transversal components of the applied field. The average diffusiophoretic or electrophoretic velocity for an ensemble of identical

spheroids can also be calculated from the longitudinal and transversal mobilities of the particle.

APPENDIX

For the purpose of conciseness the definitions of some functions in Sections 3 and 4 are listed here:

$$B_{1/n}(\lambda) = Q_n(\lambda) \int_{-1}^1 \frac{1 - \omega^2}{\sqrt{\lambda^2 - \omega^2}} \frac{dP_n(\omega)}{d\omega} \frac{dP_j(\omega)}{d\omega} d\omega, \quad [A.1]$$

$$B_{2jn}(\lambda) = -\delta_{nj} \frac{2}{2j+1} \sqrt{\lambda^2 - 1} \frac{dQ_n(\lambda)}{d\lambda}, \quad [\text{A.2}]$$

$$C_{1j}(\lambda) = -\lambda \int_{-1}^1 \frac{1 - \omega^2}{\sqrt{\lambda^2 - \omega^2}} \frac{dP_j(\omega)}{d\omega} d\omega, \quad [\text{A.3}]$$

$$C_{2j}(\lambda) = \delta_{1j} \frac{2}{2j+1} \sqrt{\lambda^2 - 1}; \quad [\text{A.4}]$$

$$\begin{aligned} \bar{B}_{1jn}(\lambda) = & -Q_n^1(\lambda) \int_{-1}^1 \frac{1 - \omega^2}{\sqrt{\lambda^2 - \omega^2}} \frac{dP_n^1(\omega)}{d\omega} \frac{dP_j^1(\omega)}{d\omega} d\omega \\ & - \frac{Q_n^1(\lambda)}{\lambda^2 - 1} \int_{-1}^1 \frac{\sqrt{\lambda^2 - \omega^2}}{1 - \omega^2} P_n^1(\omega) P_j^1(\omega) d\omega, \quad [\text{A.5}] \end{aligned}$$

$$\bar{B}_{2jn}(\lambda) = \delta_{nj} \frac{2}{2j+1} \frac{(j+1)!}{(j-1)!} \sqrt{\lambda^2 - 1} \frac{dQ_n^1(\lambda)}{d\lambda}, \quad [\text{A.6}]$$

$$\begin{aligned} \bar{C}_{1j}(\lambda) = & -\sqrt{\lambda^2 - 1} \int_{-1}^1 \frac{\omega \sqrt{1 - \omega^2}}{\sqrt{\lambda^2 - \omega^2}} \frac{dP_j^1(\omega)}{d\omega} d\omega \\ & + \frac{1}{\sqrt{\lambda^2 - 1}} \int_{-1}^1 \frac{\sqrt{\lambda^2 - \omega^2}}{\sqrt{1 - \omega^2}} P_j^1(\omega) d\omega, \quad [\text{A.7}] \end{aligned}$$

$$\bar{C}_{2j}(\lambda) = -\delta_{1j} \frac{2}{2j+1} \frac{(j+1)!}{(j-1)!} \lambda. \quad [\text{A.8}]$$

ACKNOWLEDGMENT

This research was supported by the National Science Council of the Republic of China.

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