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Diffusiophoresis and Electrophoresis in Concentrated Suspensions of Charged Colloidal Spheres

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The diffusiophoretic and electrophoretic motions of homogeneous suspensions of identical, charged, spherical particles in the solution of a symmetrically charged electrolyte are analyzed under conditions of small Reynolds numbers. The thickness of the electric double layers surrounding the particles is assumed to be small relative to the radius of each particle and to the gap width between two neighboring particles, but the effect of polarization of the mobile ions in the diffuse layer is taken into account. The effects of interaction among individual particles are taken into explicit account by employing a unit cell model which is known to provide good predictions for the sedimentation of monodisperse suspensions of spherical particles. The appropriate equations of conservation of electrochemical potential energies of ionic species and fluid momentum are solved for each cell, in which a spherical particle is envisaged to be surrounded by a concentric shell of suspending fluid, and the diffusiophoretic and electrophoretic velocities of the particle are calculated for various cases. Analytical expressions of these mean particle velocities are obtained in closed form as functions of the volume fraction of the particles. Comparisons between the approximate ensemble-averaged diffusiophoretic and electrophoretic velocities of a test particle in a dilute suspension and our cell-model results are made.

1. Introduction

The transport behavior of small particles in a continuous medium at low Reynolds numbers is of much fundamental and practical interest. In general, driving forces for motions of colloidal particles 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 were treated extensively in the past. Another category of driving forces for the locomotions of colloidal particles involves a nonuniform imposed field (such as electric potential, temperature, or solute concentration) that interacts with the surface of each particle. The particle motions associated with this mechanism, known as "phoretic motions", have received a considerable amount of attention recently.[1-3]

Perhaps the most familiar example of various phoretic motions is electrophoresis, which results from the interaction between an external electric field and the electric double layer surrounding a charged particle and is widely used for the particle characterization and separation in a variety of colloidal and biological systems. The electrophoretic velocity $\mathbf{U}_0$ of a single nonconducting particle suspended in an unbounded electrolyte solution is simply related to the uniformly applied electric field $\mathbf{E}^\infty$ by the Smoluchowski equation,[4,5]

$$\mathbf{U}_0 = \frac{\epsilon\zeta}{4\pi\eta}\mathbf{E}^\infty \tag{1}$$

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 diffusiophoresis, which is the migration of a particle in response to the macroscopic concentration gradient of a solute and was applied to certain latex-particle coating processes.[6] 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 unbounded solution of a symmetrically charged binary electrolyte with a constant concentration gradient ∇n^∞, the diffusiophoretic velocity of a charged particle is[7]

$$\mathbf{U}_0 = \frac{\epsilon\zeta}{4\pi\eta}\frac{kT}{Ze}\frac{\nabla n^\infty}{n^\infty(\mathbf{0})}(\lambda + \bar{\zeta}^{-1}\ln\cosh\bar{\zeta}) \tag{2}$$

with

$$\lambda = \frac{D_2 - D_1}{D_2 + D_1} \tag{3}$$

$$\bar{\zeta} = \frac{Ze\zeta}{4kT} \tag{4}$$

Here, $n^\infty(\mathbf{0})$ is the macroscopic electrolyte concentration measured at the particle center $\mathbf{0}$ 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. For the special case of $D_2 = D_1$, eq 2 predicts that the particle movement (due to chemiphoresis only) is in the direction of increasing electrolyte concentration regardless of the sign of ζ and the particle velocity is a monotonic increasing function of the magnitude of ζ.

Equations 1 and 2 indicate that the electrophoretic and diffusiophoretic velocities of a dielectric particle having

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a uniform zeta potential on its surface are independent of the particle size and shape (and there is no rotational motion of the particle). 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 electric double layer at the particle surface and that the effect of polarization (relaxation effect) of the diffuse ions in the double layer due to nonuniform "osmotic" flow is negligible. In fact, important advances were made in the past 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[8] obtained a numerical calculation for the electrophoretic velocity of a dielectric sphere of radius a in a KCl solution which was applicable to arbitrary values of ζ and κa, where κ^{-1} is the Debye screening length

$$\kappa = \left(\frac{8\pi Z^2 e^2 n^\infty}{\epsilon kT}\right)^{1/2} \qquad (5)$$

On the other hand, Dukhin and Derjaguin[6] obtained an analytical expression for the electrophoretic mobility of a spherical particle surrounded by a thin but polarized double layer in the solution of a symmetrically charged electrolyte. Later, O'Brien[9] generalized this analysis to the case of electrophoretic motion of a colloidal sphere in the solution containing an arbitrary combination of electrolytes. The essence of this thin-layer polarization approach is that a thin diffuse layer can still transport a significant amount of solute molecules so as to affect the solute transport outside the diffuse layer. The result for the electrophoretic velocity of a sphere with a thin but polarized double layer in a symmetric electrolyte solution can be expressed as[10]

$$\mathbf{U}^{(0)} = \frac{\epsilon\zeta}{12\pi\eta}\,\mathbf{E}^\infty[2 + c_1 + c_2 + (c_1 - c_2)\bar{\zeta}^{-1}\ln\cosh\bar{\zeta}] \qquad (6)$$

where coefficients c_1 and c_2 are functions of κa defined by eq 21. A comparison of eq 6 with the numerical results for the KCl solution shows that the thin-layer polarization model is quite good over a wide range of zeta potentials when $\kappa a > 20$. If $|\bar{\zeta}|$ 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

$$(\kappa a)^{-1}\exp(2|\bar{\zeta}|) \to 0 \qquad (7)$$

$c_1 = c_2 = 1/2$ and eq 6 reduces to the Smoluchowski equation (eq 1). In general, the electrophoretic velocity given by eq 6 is not a monotonic function of $\bar{\zeta}$ for a finite value of κa, unlike the prediction of eq 1.

In contrast, Prieve and Roman[11] obtained a numerical solution of the diffusiophoretic velocity over a broad range of $\bar{\zeta}$ and κa for a charged sphere in concentration gradients of symmetric electrolytes (KCl or NaCl) using the method of O'Brien and White.[8] Recently, analytical expressions for the velocity of a dielectric sphere with a thin but polarized double layer undergoing diffusiophoresis in

electrolyte solutions have also been derived.[3,12] The result for this diffusiophoretic velocity in a symmetric electrolyte solution is

$$\mathbf{U}^{(0)} = \frac{\epsilon\zeta}{12\pi\eta}\frac{kT}{Ze}\frac{\nabla n^\infty}{n^\infty(\mathbf{0})}\{c_1' - c_2' + \lambda(2 + c_1 + c_2) + $$
$$[2 + c_1' + c_2' + \lambda(c_1 - c_2)]\bar{\zeta}^{-1}\ln\cos\bar{\zeta}\} \qquad (8)$$

where coefficients c_1' and c_2' are functions of κa defined by eq 22. When $\kappa a > 20$, the agreement between eq 8 and the numerical solution is excellent for all reasonable values of the zeta potential. In the limiting situation given by eq 7, the effect of double-layer polarization disappears, $c_1 = c_2 = c_1' = c_2' = 1/2$, and eq 8 reduces to eq 2. Even for the case of $D_2 = D_1$, the particle velocity given by eq 8 for a finite value of κa may not be a monotonic function of the magnitude of $\bar{\zeta}$ and its direction can reverse (toward lower electrolyte concentration) when $|\bar{\zeta}|$ becomes large.

It could be found from eqs 6 and 8 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 diffuse ions within the double layer reduces the local electrolyte gradient or electric field along the particle surface. Numerical calculations of eqs 6 and 8 show that, even when κa is as large as 300, the effect of ion transport inside the diffuse layer cannot be ignored if $|\zeta|$ equals several kT/e.

In practical applications of diffusiophoresis and electrophoresis, collections of particles are usually encountered, and effects of particle interactions will be important. In the limiting case that eqs 1 and 2 are applicable, the normalized velocity field of the immense fluid that is dragged by a particle during diffusiophoresis is the same as for electrophoresis of the particle;[1] thus, the particle interaction effects in electrophoresis under the situation of infinitesimally thin double layer (satisfying eq 7), which were studied extensively in the past,[2,13–16] can be taken to interpret those in diffusiophoresis.

When the polarization effect of diffuse ions in the double layers surrounding the particles is considered, the particle interaction behavior in diffusiophoresis can be quite different from that in electrophoresis, due to the fact that the particle size and some other factors are involved in each transport mechanism.[3] Through the use of a boundary collocation method, the electrophoresis of multiple spheres with thin but polarized double layers in an arbitrary configuration was examined.[10,17] The thin-layer polarization model and the boundary collocation technique were also used to investigate the axisymmetric diffusiophoresis of a chain of dielectric spheres in electrolyte solutions.[18] In these studies, numerical results of the electrophoretic and diffusiophoretic velocities of the particles were presented for various cases. Using a method of reflections, Tu and Keh[19] obtained the diffusiophoretic and electrophoretic velocities of two spherical particles with arbitrary zeta potentials, arbitrary sizes, and arbitrary orientation with respect to the imposed electrolyte concentration

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gradient or electric field correct to $O(r_{12}{}^{-7})$, where r_{12} is the particles' center-to-center spacing. On the basis of the concept of statistical mechanics, this reflection result of interaction effects between pairs of spheres with thin but polarized double layers was also used to calculate approximately the average diffusiophoretic and electrophoretic velocities of particles in a relatively dilute, statistically homogeneous suspension subjected to a uniform electrolyte concentration gradient or electric field to the first order of the volumn fraction of particles. However, the effects of particle volume fraction on the diffusiophoretic or electrophoretic mobility for a relatively concentrated suspension of charged particles with thin but polarized double layers have not been investigated yet.

A unit cell model has been employed successfully (and tested against the experimental data) to predict the effect of particle concentration on the mean sedimentation rate[20-22] and electrophoretic mobility[23-25] in bounded suspensions of identical spherical particles. This model involves the concept that an assemblage can be divided into a number of identical cells, one sphere occupying each cell at its center. The boundary-value problem for multiple spheres is thus reduced to the consideration of the behavior of a single sphere and its bounding envelope. Although different shapes of cells can be employed, the assumption of a spherical shape for the fictitious envelope of suspending fluid surrounding each spherical particle is of great convenience. Although the Brownian motion of small particles is not included in its analysis, the cell model is of great applicability in relatively concentrated suspensions, where the boundary effect will not be important. In this work, the cell model is used to describe the interactions among diffusiophoretic and electrophoretic spheres with thin but polarized double layers in a monodisperse suspension subjected to a constant electrolyte concentration gradient or electric field. The analytical solutions in closed form obtained with this model enable the average diffusiophoretic and electrophoretic velocities to be predicted as functions of the volume fraction of the particles for various cases.

2. Analysis for Diffusiophoresis

We consider the steady diffusiophoretic motion of a uniform three-dimensional distribution of identical spherical particles in a solution of a symmetric electrolyte. The particles are charged uniformly on the surfaces. The thin electric double layers surrounding the particles can be polarized but do not overlap with one another. The fluid phase is assumed to be incompressible and Newtonian. The applied electrolyte concentration gradient ∇n^{∞} is a constant equal to $|\nabla n^{\infty}|\mathbf{e}_z$ and the diffusiophoretic velocity of the particles is $U\mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector in the positive z direction. As shown in Figure 1, we employ a unit cell model in which each particle of radius a is surrounded by a concentric spherical shell of suspending fluid having an outer radius of b such that the particle/cell volume ratio is equal to the particle volume fraction φ throughout the entire suspension; viz., $\varphi = (a/b)^3$. The origin of the spherical coordinate system (r,θ,ϕ) is set at the center of the particle. Our objective is to determine

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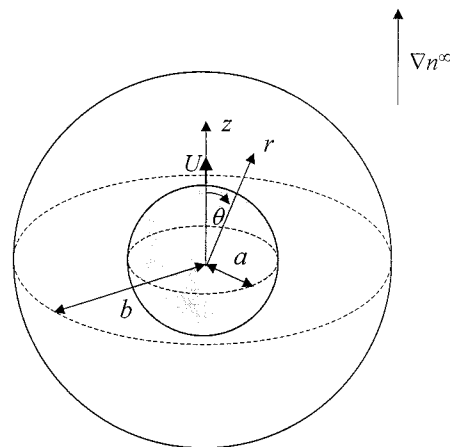(25) Ding, J. M.; Keh, H. J. *J. Colloid Interface Sci.,* in press.

Figure 1. Geometrical sketch for the diffusiophoretic motion of a spherical particle at the center of a spherical cell.

the particle velocity U in a cell induced by the diffusiophoretic driving force in the limit of small Peclet and Reynolds numbers.

The fluid phase in a cell can be divided into two regions: an "inner" region defined as the thin double layer surrounding the particle and an "outer" region defined as the remainder of the fluid which is neutral. In the outer region, the equations of conservation of each ionic species and the fluid momentum are the Laplace equation[3]

$$\nabla^2 \mu_m = 0, \quad m = 1, 2 \tag{9}$$

and the Stokes equation for viscous axisymmetric flows

$$E^2(E^2\Psi) = 0 \tag{10}$$

In eq 9, $\mu_m(r,\theta)$ is the electrochemical potential energy of species m defined by

$$\mu_m = \mu_m{}^0 + kT \ln n_m + z_m e\Phi \tag{11}$$

where $\mu_m{}^0$ is a constant, $n_m(r,\theta)$ and z_m are the concentration and valence, respectively, of type m ions, and $\Phi(r,\theta)$ is the electric potential. m equal to 1 and 2 refers to the anion and cation, respectively, so $-z_1 = z_2 = Z$. Note that, in the outer region, $n_1 = n_2 = n$, and both n and Φ also satisfy Laplace's equation. In eq 10, $\Psi(r,\theta)$ is the Stokes stream function, and, in spherical coordinates, the Stokesian operator E^2 is given by

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right) \tag{12}$$

The stream function Ψ is related to the r and θ components of the velocity field by

$$v_r = -\frac{1}{r^2\sin\theta}\frac{\partial\Psi}{\partial\theta} \tag{13a}$$

$$v_\theta = \frac{1}{r\sin\theta}\frac{\partial\Psi}{\partial r} \tag{13b}$$

The governing eqs 9 and 10 in the outer region satisfy the following boundary conditions at the particle surface (outer edge of the thin double layer) obtained by solving for the electrochemical potentials and fluid velocity in the

inner region and using a matching procedure to ensure a continuous solution in the whole fluid phase:[3,9]

$r = a$:

$$\frac{\partial \mu_m}{\partial r} = -\sum_{i=1}^{2} \beta_{mi} \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \mu_i}{\partial \theta}\right), \quad m = 1, 2 \quad (14)$$

$$v_r = U \cos \theta \quad (15a)$$

$$v_\theta = -U \sin \theta - \frac{\epsilon kT}{2\pi\eta Z^2 e^2 r}\left[(\bar{\zeta} + \ln \cosh \bar{\zeta})\frac{\partial \mu_1}{\partial \theta} + (-\bar{\zeta} + \ln \cosh \bar{\zeta})\frac{\partial \mu_2}{\partial \theta}\right] \quad (15b)$$

where the relaxation coefficients

$$\beta_{11} = \frac{1}{\kappa}\left[4\left(1 + \frac{3f_1}{Z^2}\right)\exp(\bar{\zeta}) \sinh \bar{\zeta} - \frac{12f_1}{Z^2}(\bar{\zeta} + \ln \cosh \bar{\zeta})\right] \quad (16a)$$

$$\beta_{12} = -\frac{1}{\kappa}\left(\frac{12f_1}{Z^2}\right)\ln \cosh \bar{\zeta} \quad (16b)$$

$$\beta_{21} = -\frac{1}{\kappa}\left(\frac{12f_2}{Z^2}\right)\ln \cosh \bar{\zeta} \quad (16c)$$

$$\beta_{22} = \frac{1}{\kappa}\left[-4\left(1 + \frac{3f_2}{Z^2}\right)\exp(-\bar{\zeta}) \sinh \bar{\zeta} + \frac{12f_2}{Z^2}(\bar{\zeta} - \ln \cosh \bar{\zeta})\right] \quad (16d)$$

$f_m = \epsilon k^2 T^2/6\pi\eta e^2 D_m$, $\bar{\zeta}$ was defined by eq 4, and U is the diffusiophoretic velocity of the particle to be determined. The physical meaning of eq 14 is that the net tangential ionic fluxes along the particle surface must be balanced by the normal ionic fluxes occurring just beyond the double layer to prevent accumulation of the ionic species. The apparent slip velocity given by the second term on the right-hand side of eq 15b results from the "diffusio-osmotic" flow caused by the electrostatic interaction between the particle and the diffuse ions in the double layer and by the tangential gradients $\partial \mu_m/r\partial \theta$ along the particle surface. To obtain eqs 14−16, it was assumed that the fluid is only slightly nonuniform in the undisturbed electrolyte concentration on the length scale of a and the concentration of each ionic species within the double layer is related to the electric potential by a Boltzmann distribution.

The electrochemical potentials undisturbed by the presence of the particle in a cell can be expressed as

$$\mu_m^\infty = \mu_m^0 + kT[1 - (-1)^m\lambda] \ln n^\infty \quad (17)$$

where λ was defined by eq 3 and $n^\infty(z)$ is the linear concentration distribution of the electrolyte prescribed in the absence of the particle. It is understood that diffusiophoresis of a charged particle in an electrolyte solution results from a linear combination of two effects: (i) chemiphoresis due to the nonuniform adsorption of counterions in the electric double layer over the particle surface, which is analogous to diffusiophoresis in nonionic media;[1,3] (ii) electrophoresis due to the macroscopic electric field generated by the concentration gradient of the

electrolyte and the difference in mobilities of the cation and anion of the electrolyte, given by the second term in the brackets of eq 17.[6,7,26] The terms in eqs 2 and 8 proportional to λ represent the contribution from electrophoresis, while the remainder terms are the chemiphoretic component.

At the outer (virtual) surface of the cell, the local electrochemical potential gradient of type m ions is parallel to the gradient $\nabla\mu_m^\infty$. Thus

$r = b$:

$$\frac{\partial \mu_m}{\partial r} = kT[1 - (-1)^m\lambda]\frac{|\nabla n^\infty|}{n_0} \cos \theta, \quad m = 1, 2 \quad (18)$$

where n_0 is the electrolyte concentration measured at the particle center in the absence of the particle. It is assumed that $a|\nabla n^\infty|/n_0 \ll 1$. The solution to eqs 9, 14, and 18 is

$$\mu_m = \mu_m^0 + kT[1 - (-1)^m\lambda] \ln n_0 + \left(A_{m1}r + A_{m2}\frac{a^3}{r^2}\right)kT\frac{|\nabla n^\infty|}{n_0} \cos \theta \quad (19)$$

where

$$A_{m1} = 1 - (-1)^m\lambda + 2\varphi A_{m2} \quad (20a)$$

$$A_{m2} = \frac{1}{\Delta}[c_m'\Delta_1 - 2\Delta_3\varphi - (-1)^m\lambda(c_m\Delta_1 - 2\Delta_3\varphi)] \quad (20b)$$

In eq 20

$$c_1 = \frac{1}{2a^2\Delta_1}(a^2 - 2a\beta_{11} + 3a\beta_{12} + a\beta_{22} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}) \quad (21a)$$

$$c_2 = \frac{1}{2a^2\Delta_1}(a^2 - 2a\beta_{22} + 3a\beta_{21} + a\beta_{11} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}) \quad (21b)$$

$$c_1' = c_1 - 3\frac{\beta_{12}}{a\Delta_1} \quad (22a)$$

$$c_2' = c_2 - 3\frac{\beta_{21}}{a\Delta_1} \quad (22b)$$

$$\Delta = \Delta_1 - 2\Delta_2\varphi + 4\Delta_3\varphi^2 \quad (23)$$

$$\Delta_1 = \frac{1}{a^2}(a^2 + a\beta_{11} + a\beta_{22} - \beta_{12}\beta_{21} + \beta_{11}\beta_{22}) \quad (24a)$$

$$\Delta_2 = \frac{1}{2}(c_1 + c_1' + c_2 + c_2')\Delta_1 \quad (24b)$$

$$\Delta_3 = \frac{9}{4} - (\Delta_1 + \Delta_2) \quad (24c)$$

and $\varphi = (a/b)^3$.

The boundary condition of the electrochemical potential of type m ions at the virtual surface $r = b$ may be taken as the distribution giving rise to the gradient $\nabla \mu_m^\infty$ in the cell when the particle does not exist. In this case, eq 18

(26) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962.

becomes

$r = b$:

$$\mu_m = \mu_m{}^0 + kT[1 - (-1)^m\lambda]\left(\ln n_0 + \frac{|\nabla n^\infty|}{n_0} r \cos \theta\right)$$

$$m = 1, 2 \qquad (25)$$

The solution of the governing eq 9 subject to the boundary conditions 14 and 25 is also given by the form of eq 19, but with coefficients A_{mi} defined as

$$A_{m1} = 1 - (-1)^m\lambda - \varphi A_{m2} \qquad (26a)$$

$$A_{m2} = \frac{1}{\Delta'}[c_m'\Delta_1 + \Delta_3\varphi - (-1)^m\lambda(c_m\Delta_1 + \Delta_3\varphi)] \qquad (26b)$$

where

$$\Delta' = \Delta_1 + \Delta_2\varphi + \Delta_3\varphi^2 \qquad (27)$$

In the limit of $c_1 = c_2 = c_1' = c_2' = 0$ and $\Delta_1 = 9/4$ (or $\beta_{11}/a = \beta_{22}/a = 1/2$ and $\beta_{12}/a = \beta_{21}/a = 0$), both eq 20 and eq 26 give $A_{11} = 1 + \lambda$, $A_{21} = 1 - \lambda$, and $A_{12} = A_{22} = 0$, and the concentration gradient in the fluid resulting from eq 19 equals the constant imposed value everywhere.

With knowledge of the solution for the electrochemical potential distributions (so that the apparent slip velocity given by eq 15b is known), we can now proceed to find the flow field in a cell. On the outer (virtual) boundary of the cell, the Happel model[20] assumes that the radial velocity and the shear stress are zero; viz.

$r = b$: $v_r = 0$ (28a)

$$\tau_{r\theta} = \eta\left[r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{1}{r}\frac{\partial v_r}{\partial \theta}\right] = 0 \qquad (28b)$$

A solution to eq 10 suitable for satisfying boundary conditions on the spherical surfaces is[27]

$$\Psi = (Cr^{-1} + Dr + Er^2 + Fr^4)\sin^2\theta \qquad (29)$$

where the constants C, D, E, and F are to be determined from eqs 15 and 28 using eqs 13 and 19. The procedure is straightforward, with the result

$$C = a^3\omega[U - 4A(1 - \varphi^{1/3})V] \qquad (30a)$$

$$D = - a\omega[(3 + 2\varphi^{5/3})U - 4A(1 - \varphi^{5/3})V] \qquad (30b)$$

$$E = \omega[(3\varphi^{1/3} + 2\varphi^2)U - 4A(\varphi^{1/3} - \varphi^2)V] \qquad (30c)$$

$$F = -a^{-2}\omega[\varphi^{5/3}U - 4A(\varphi^{5/3} - \varphi^2)V] \qquad (30d)$$

where V is a characteristic velocity of the particle defined by

$$V = \frac{\epsilon}{4\pi\eta}\left(\frac{kT}{Ze}\right)^2\frac{|\nabla n^\infty|}{n_0} \qquad (31)$$

$$\omega = (4 - 6\varphi^{1/3} + 6\varphi^{5/3} - 4\varphi^2)^{-1} \qquad (32)$$

$$A = (\bar{\zeta} + \ln\cosh\bar{\zeta})(A_{11} + A_{12}) + (-\bar{\zeta} + \ln\cosh\bar{\zeta})(A_{21} + A_{22}) \qquad (33)$$

and A_{11}, A_{12}, A_{21}, and A_{22} are given by eqs 20 or 26. With

this solution, the components of the fluid velocity in this axisymmetric flow (with $v_\phi = 0$) can be calculated by using eq 13.

The drag force (in the z direction) exerted by the fluid on the particle is[27]

$$F_d = 8\pi\eta D \qquad (34)$$

Because the particle (with its thin double layer) is freely suspended in the fluid, the net force exerted by the fluid on the particle must vanish; viz., $D = 0$. With this constraint, eq 30b yields the diffusiophoretic velocity of the particle

$$U = 4A(1 - \varphi^{5/3})(3 + 2\varphi^{5/3})^{-1}V \qquad (35)$$

If the Kuwabara model[21] for the boundary conditions of the fluid flow at the virtual surface of the cell, which assumes that the radial velocity and the vorticity are zero, is used, eq 28b is replaced by

$$r = b: \qquad (\nabla \times \mathbf{v})_\phi = \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} - \frac{1}{r}\frac{\partial v_r}{\partial \theta} = 0 \qquad (36)$$

With this change, the stream function Ψ can still be expressed in the form of eq 29, and the coefficients C, D, E, and F should be determined by boundary conditions 15, 28a, and 36. The result is

$$C = a^3\omega'[(5 - 2\varphi)U - 4A(5 - 6\varphi^{1/3} + \varphi)V] \qquad (37a)$$

$$D = -5a\omega'[3U - 4A(1 - \varphi)V] \qquad (37b)$$

$$E = \omega'[(18\varphi^{1/3} - 5\varphi + 2\varphi^2)U - 4A(6\varphi^{1/3} - 5\varphi - \varphi^2)V] \qquad (37c)$$

$$F = -a^{-2}\omega'[3\varphi U - 4A(\varphi - \varphi^2)V] \qquad (37d)$$

where

$$\omega' = (20 - 36\varphi^{1/3} + 20\varphi - 4\varphi^2)^{-1} \qquad (38)$$

The fact that there is no drag force exerted on the particle requires $D = 0$, and eq 37b gives the particle velocity as

$$U = \frac{4}{3}A(1 - \varphi)V \qquad (39)$$

For the sedimentation of a suspension of identical spherical particles, both the Happel and the Kuwabara models give qualitatively same flow fields and approximately comparable drag forces. However, the Happel model has an advantage in that it does not require an exchange of mechanical energy between the cell and the environment.[27]

3. Results for Diffusiophoresis

Due to the differences in the boundary conditions for the electrochemical potential and fluid velocity distributions at the virtual surface $r = b$ of the unit cell, four cases of the cell model can be defined: case I, the Happel model with a specified electrochemical potential gradient at the virtual surface (the boundary conditions at $r = b$ are described by eqs 18 and 28); case II, the Happel model

(27) Happel, J.; Brenner, H. *Low Reynolds Number Hydrodynamics*; Nijhoff: The Netherlands, 1983.

with a specified electrochemical potential profile at the virtual surface (the boundary conditions at $r = b$ are described by eqs 25 and 28); case III, the Kuwabara model with a specified electrochemical potential gradient at the virtual surface (the boundary conditions at $r = b$ are described by eqs 18, 28a, and 36); case IV, the Kuwabara model with a specified electrochemical potential profile at the virtual surface (the boundary conditions at $r = b$ are described by eqs 25, 28a, and 36). The analytical solutions of the ionic electrochemical potentials and the fluid flow in the unit cell and the diffusiophoretic velocity of the particle with a thin but polarized electric double layer have been obtained in the previous section for all of the four cases.

In case I, the particle velocity is given by eq 35 with coefficient A defined by eqs 33 and 20. This migration velocity can be expressed as

$$U = U^{(0)}(1 - \varphi^{5/3})\left[1 + \frac{1}{\Delta}(h\varphi - 4\Delta_3\varphi^2)\right]\left(1 + \frac{2}{3}\varphi^{5/3}\right)^{-1}$$
(40)

where

$$U^{(0)} = \frac{Ze\zeta}{3kT}gV$$
(41)

which is the diffusiophoretic velocity of the particle in the limit $\varphi = 0$ as given by eq 8; the parameters g and h are

$$g = c_1' - c_2' + \lambda(2 + c_1 + c_2) + [2 + c_1' + c_2' + \lambda(c_1 - c_2)]\bar{\zeta}^{-1}\ln\cosh\bar{\zeta} \quad (42)$$

$$h = \frac{2}{g}\{(c_1' - c_2')(\Delta_1 + \Delta_2) + \lambda[(c_1 + c_2)(\Delta_1 + \Delta_2) - 2\Delta_3] + [(c_1' + c_2')(\Delta_1 + \Delta_2) - 2\Delta_3 + \lambda(c_1 - c_2)(\Delta_1 + \Delta_2)]\bar{\zeta}^{-1}\ln\cosh\bar{\zeta}\} \quad (43)$$

In the limiting situation given by eq 7, $\Delta_1 = \Delta_2 = h = 1$, $\Delta_3 = 1/4$, and the normalized particle velocity $U/U^{(0)}$ depends on φ only. The particle velocity U can also be written as the following power expansion in φ:

$$U = U^{(0)}[1 + \alpha\varphi + \gamma\psi^{5/3} + O(\varphi^2)]$$
(44)

A comparison between eqs 40 and 44 leads to the coefficients α and γ

$$\alpha = h/\Delta_1$$
(45a)

$$\gamma = -5/3$$
(45b)

Note that α is a function of the properties of the particle and the electrolyte solution but γ is a constant not related to these properties.

In case II, the diffusiophoretic velocity of the particle can be evaluated by eq 35 with A given by eqs 33 and 26, and its expression parallel to eq 40 for case I is

$$U = U^{(0)}(1 - \varphi^{5/3})\left[1 - \frac{1}{2\Delta'}(h\varphi + 2\Delta_3\varphi^2)\right]\left(1 + \frac{2}{3}\varphi^{5/3}\right)^{-1}$$
(46)

This particle velocity can also be expressed in the expansion form of eq 44, with the coefficients α and γ

given by

$$\alpha = -h/2\Delta_1$$
(47a)

$$\gamma = -5/3$$
(47b)

Here, γ is the same as that in case I but α has an opposite sign and a half magnitude of that in case I.

In case III, the diffusiophoretic velocity of the particle can be obtained by the eqs 39, 33, and 20, with the result

$$U = U^{(0)}(1 - \varphi)\left[1 + \frac{1}{\Delta}(h\varphi - 4\Delta_3\varphi^2)\right]$$
(48)

When this velocity is expressed in the expansion form of eq 44, one has

$$\alpha = \frac{h}{\Delta_1} - 1$$
(49a)

$$\gamma = 0$$
(49b)

In case IV, the particle velocity is given by eq 39 with A defined by eqs 33 and 26, and it can be expressed as

$$U = U^{(0)}(1 - \varphi)\left[1 - \frac{1}{2\Delta'}(h\varphi + 2\Delta_3\varphi^2)\right]$$
(50)

When this formula is written in the form of eq 44, one has

$$\alpha = -\frac{h}{2\Delta_1} - 1$$
(51a)

$$\gamma = 0$$
(51b)

Note that α in each case of the Kuwabara model equals the value of α in the corresponding case of the Happel model minus 1.

It can be found from eqs 40−51 that the mean diffusiophoretic velocity in a homogeneous suspension of identical spherical particles predicted by the cell model is quite sensitive to the boundary conditions specified at the virtual surface of the cell. The boundary condition for the electrolyte concentration at the virtual surface $r = b$ determines the dependence of the normalized particle velocity (or mobility) $U/U^{(0)}$ as a function of the properties of the particle and the electrolyte solution, while the boundary condition for the fluid velocity at $r = b$ controls the connection of $U/U^{(0)}$ with the remainder part.

On the basis of the analytical (approximate) solution of the hydrodynamic interaction between pairs of diffusiophoretic spheres in a uniformly prescribed electrolyte concentration gradient obtained by a method of reflections correct to $O(r_{12}^{-7})$, where r_{12} is the center-to-center distance between the spherical particles, Tu and Keh[19] derived a formula of the mean diffusiophoretic velocity in a dilute suspension of particles (say, $\varphi < 0.1$) in the expansion form of eq 44 with $\gamma = 0$ by using the concept of statistical mechanics. This ensemble-averaged result gives the coefficient α approximately as

$$\alpha = -\frac{21}{16} + \frac{1}{16g}[(c_1'^2 + c_1'c_1 - c_1c_2' + c_1'c_2' - 9c_1')G_1 + (c_2'^2 + c_2c_2' - c_1'c_2 + c_1'c_2' - 9c_2')G_2 + 9c_1'H_1 + 9c_2'H_2] + \frac{\lambda}{16g}[(c_1^2 + c_1c_1' - c_1'c_2 + c_1c_2 - 9c_1)G_1 + (-c_2^2 - c_2c_2' + c_1c_2' - c_1c_2 + 9c_2)G_2 + 9c_1H_1 - 9c_2H_2] \quad (52)$$

where

$$G_1 = 2 + c_1' + c_1 - c_2' + c_2 +$$
$$(2 + c_1' + c_1 + c_2' - c_2)\bar{\zeta}^{-1} \ln \cosh \bar{\zeta} \quad (53a)$$

$$G_2 = -2 + c_1' - c_1 - c_2' - c_2 +$$
$$(2 + c_1' - c_1 + c_2' + c_2)\bar{\zeta}^{-1} \ln \cosh \bar{\zeta} \quad (53b)$$

$$H_1 = 1 + d_1' + d_1 - d_2' + d_2 +$$
$$(1 + d_1' + d_1 + d_2' - d_2)\bar{\zeta}^{-1} \ln \cosh \bar{\zeta} \quad (54a)$$

$$H_2 = -1 + d_1' - d_1 - d_2' - d_2 +$$
$$(1 + d_1' - d_1 + d_2' + d_2)\bar{\zeta}^{-1} \ln \cosh \bar{\zeta} \quad (54b)$$

$$d_1 = \frac{1}{3a^2\Delta_1'}(a^2 - 3a\beta_{11} + 5a\beta_{12} + 2a\beta_{22} + 6\beta_{12}\beta_{21} -$$
$$6\beta_{11}\beta_{22}) \quad (55a)$$

$$d_2 = \frac{1}{3a^2\Delta_1'}(a^2 - 3a\beta_{22} + 5a\beta_{21} + 2a\beta_{11} + 6\beta_{12}\beta_{21} -$$
$$6\beta_{11}\beta_{22}) \quad (55b)$$

$$d_1' = d_1 - \frac{10\beta_{12}}{3a\Delta_1'} \quad (56a)$$

$$d_2' = d_2 - \frac{10\beta_{21}}{3a\Delta_1'} \quad (56b)$$

$$\Delta_1' = \frac{1}{a^2}(a^2 + 2a\beta_{11} + 2a\beta_{22} - 4a\beta_{12}\beta_{21} + 4\beta_{11}\beta_{22})$$
$$(57)$$

In this statistical model γ vanishes, which is similar to that in the Kuwabara cell model (case III and case IV). In the limiting situation given by eq 7 (which leads to $c_1 = c_2 = c_1' = c_2' = 1/2$ and $d_1 = d_2 = d_1' = d_2' = 1/3$), eq 52 yields $\alpha = -3/2$.

The normalized diffusiophoretic velocity in a homogeneous suspension of identical spherical particles, $U/U^{(0)}$, as calculated from eqs 40, 46, 48, and 50 for the four cases of the cell model, is plotted versus the volume fraction of the particles, φ, in Figures 2 and 3 for various values of the parameters Z, λ, $\zeta e/kT$, and κa. In all cases, $U/U^{(0)} = 1$ in the limit $\varphi = 0$. The calculations are presented up to $\varphi = 0.74$, which corresponds to the maximum attainable volume fraction for a swarm of identical spheres.[23] It is also clear that at volume fractions approaching this, coagulation due to contacts between particles may occur, and the present study does not cover this case.

In Figure 2, the normalized diffusiophoretic mobility $U/U^{(0)}$ for a suspension of identical spherical particles is plotted as a function of φ in the limit of eq 7 or $\kappa a \rightarrow \infty$. The results obtained from eq 44 for the statistical model (with $\alpha = -3/2$ and $\gamma = 0$) are also exhibited in this figure to compare with those of the cell model. It can be seen that each of the four cases of the cell model predicts a greater diffusiophoretic velocity than the statistical model does. The Kuwabara model predicts a smaller diffusiophoretic mobility than the Happel model does. The normalized particle velocity $U/U^{(0)}$ is greater than unity for case I, is a monotonically decreasing function of φ for case II and case IV, and is independent of φ for case III.

The results of $U/U^{(0)}$ as a function of φ for a monodisperse suspension of particles with a finite value of κa are plotted
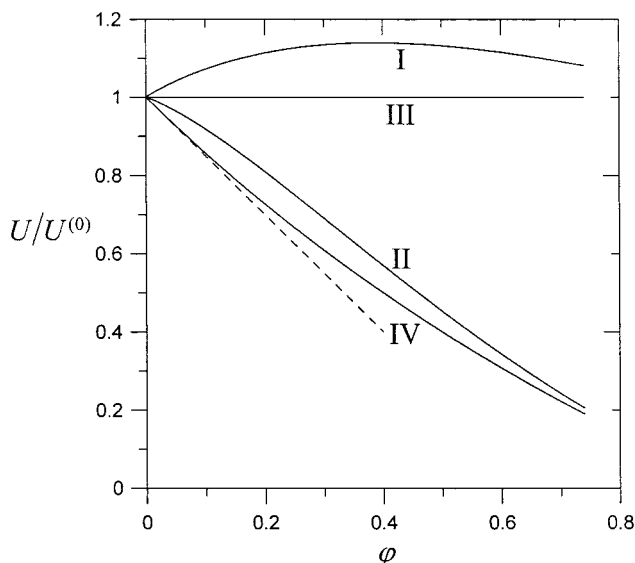

Figure 2. Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus the volume fraction of the particles in the limiting situation of eq 7 or $\kappa a \rightarrow \infty$. The solid curves with labels I, II, III, and IV represent the cell model calculations from eqs 40, 46, 48, and 50, respectively, and the dashed curve is the statistical model result calculated from eq 44 with $\alpha = -3/2$ and $\gamma = 0$.

in Figure 3 for both cases of the statistical model and the cell model. The situations associated with Figures 3a ($Z = 1$, $f_1 = f_2 = 0.2$) and 3b ($Z = 1$, $f_1 = 0.2$, $\lambda = -0.2$) are close to those of diffusiophoresis in the aqueous solutions of KCl and NaCl, respectively. It can be seen in Figures 2 and 3 that the four cases of the cell model lead to quite different results of the particle velocity. The tendency of the dependence of the normalized particle velocity $U/U^{(0)}$ on the particle volume fraction φ in case I and case III is not correct, in comparison with the ensemble-averaged results. So, the boundary condition of eq 18 is not as accurate as the boundary condition of eq 25, probably due to the fact that the angular component of the electrochemical potential gradient at the virtual surface of the cell is not specified in eq 18. In general, the diffusiophoretic velocity predicted by case IV of the cell model agrees well with that calculated from the statistical model for dilute suspensions of particles (especially in the case with $\kappa a \rightarrow \infty$). A possible reason for this outcome might be the fact that the Kuwabara boundary condition (eq 36) of zero vorticity is consistent with the irrotational-flow environment generated by a diffusiophoretic or electrophoretic particle with a thin polarized double layer.[3] Note that, however, except for the case with $\kappa a \rightarrow \infty$, the flow caused by two or more identical diffusiophoretic or electrophoretic spheres is not irrotational.[19]

In Figure 4, $U/U^{(0)}$ for a suspension of identical particles is plotted as a function of φ for case IV with Z and $\zeta e/kT$ as parameters. It can be seen that the normalized diffusiophoretic mobility can be increased or decreased by the particle interactions with the increase of φ, depending on the values of the relevant factors. Note that the particle can reverse its direction of migration due to the particle interactions.

The normalized diffusiophoretic mobility $U/U^{(0)}$ for a suspension of identical particles is plotted versus their dimensionless zeta potential at different values of κa and Z in Figure 5 for case IV when φ is kept constant. In Figure 5a for the case of $\lambda = 0$, only the results at positive zeta potentials are displayed since the induced macroscopic electric field vanishes and the particle velocity, which is
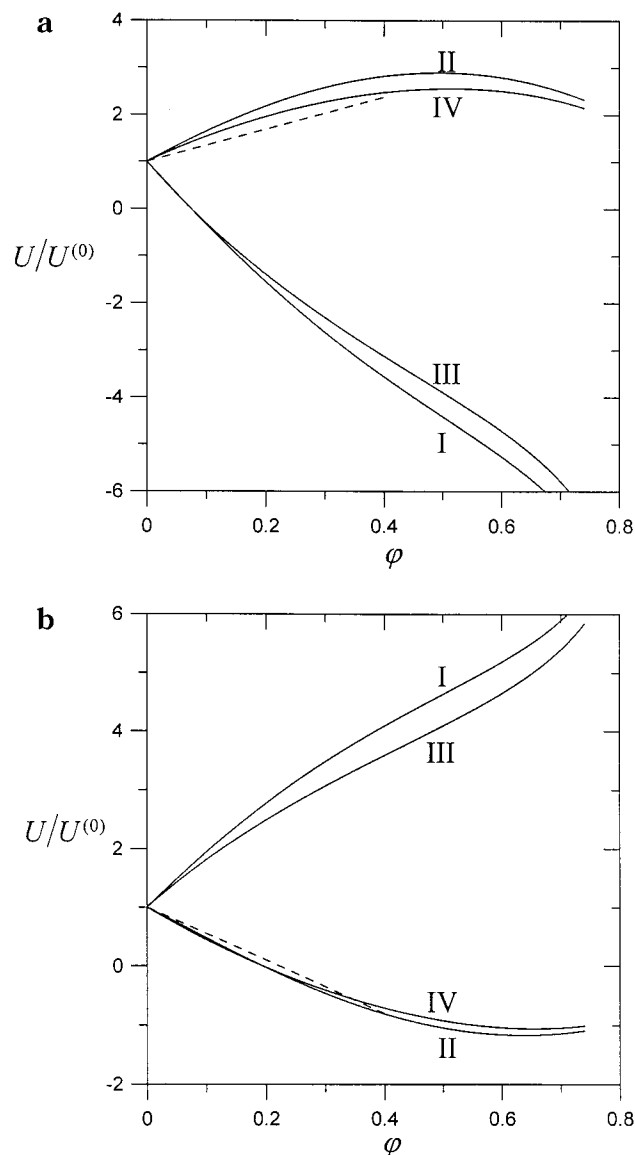
a

b

Figure 3. Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus the volume fraction of the particles with $Z = 1$, $f_1 = 0.2$, $\zeta e/kT = 8$, and $\kappa a = 50$: (a) $\lambda = 0$; (b) $\lambda = -0.2$. The solid curves with labels I, II, III, and IV represent the cell model calculations from eqs 40, 46, 48, and 50, respectively, and the dashed curves are the statistical model results calculated from eqs 44 and 52 with $\gamma = 0$.

due to the chemiphoretic effect only, will be an even function of the zeta potential. When the value of $Ze\zeta/kT$ is small (say, <6), $U/U^{(0)}$ is a monotonic increasing function of $Ze\zeta/kT$ for a finite value of κa. Also, this mobility is larger with smaller κa. However, when the value of $Ze\zeta/kT$ is increased, a maximum and a minimum of the normalized mobility would appear. As Z increases or κa decreases, the extremes occur at smaller zeta potentials. Note that the abrupt variation of the normalized particle velocity near these extremes is due to the fact that the direction of the undisturbed velocity $\mathbf{U}^{(0)}$ reverses and its magnitude is small over there,[3,11] while the interacted particle velocity $\mathbf{U}$ does not reverse synchronously. In Figure 5b for the case of $\lambda \neq 0$, both the chemiphoretic and electrophoretic effects contribute to the particles' movement and the net diffusiophoretic velocity is neither an even nor an odd function of ζ. Again, $U/U^{(0)}$ is not a monotonic function of $\zeta e/kT$. In general, no simple rule could appropriately describe the particle interactions.
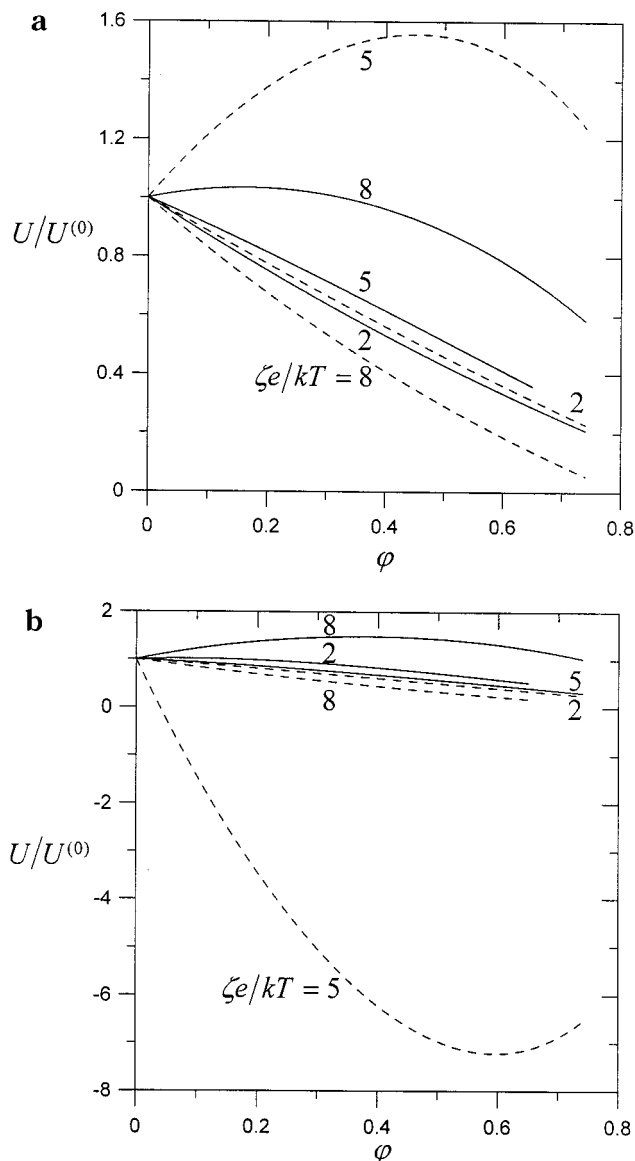
a

b

Figure 4. Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus the volume fraction of the particles for case IV with $f_1 = 0.2$ and $\kappa a = 100$: (a) $\lambda = 0$; (b) $\lambda = -0.2$. Solid curves represent the case $Z = 1$ and dashed curves denote the case $Z = 2$.

Whether the diffusiophoretic mobility is increased or decreased depends on the combination of $\zeta e/kT$, κa, Z, f_1, and f_2.

In Figure 6, $U/U^{(0)}$ for a monodisperse suspension of particles is plotted versus κa in the range from 20 to 10 000 for case IV with Z and $\zeta e/kT$ as parameters. For the case $Z = 1$, the magnitude of $U/U^{(0)}$ in general decreases steadily as κa becomes large gradually. However, when the value of $Ze\zeta/kT$ gets large (say, >6), there can be a minimum and a maximum of the particle interaction occurring at some value of κa for a given value of $\zeta e/kT$. If the particles are charged more highly (with greater magnitude in zeta potential) or the counterions have a larger absolute value of valence, the locations of these maximal particle interactions will shift toward large κa; that means larger values of κa are required to make the assumption of $\kappa a \rightarrow \infty$ valid. This behavior is in accordance with the limiting requirement given by eq 7. Although only the situation of $\lambda = 0$ is displayed in Figure 6, the plot of $U/U^{(0)}$ versus κa for cases with $\lambda \neq 0$ will indicate a similar outcome.
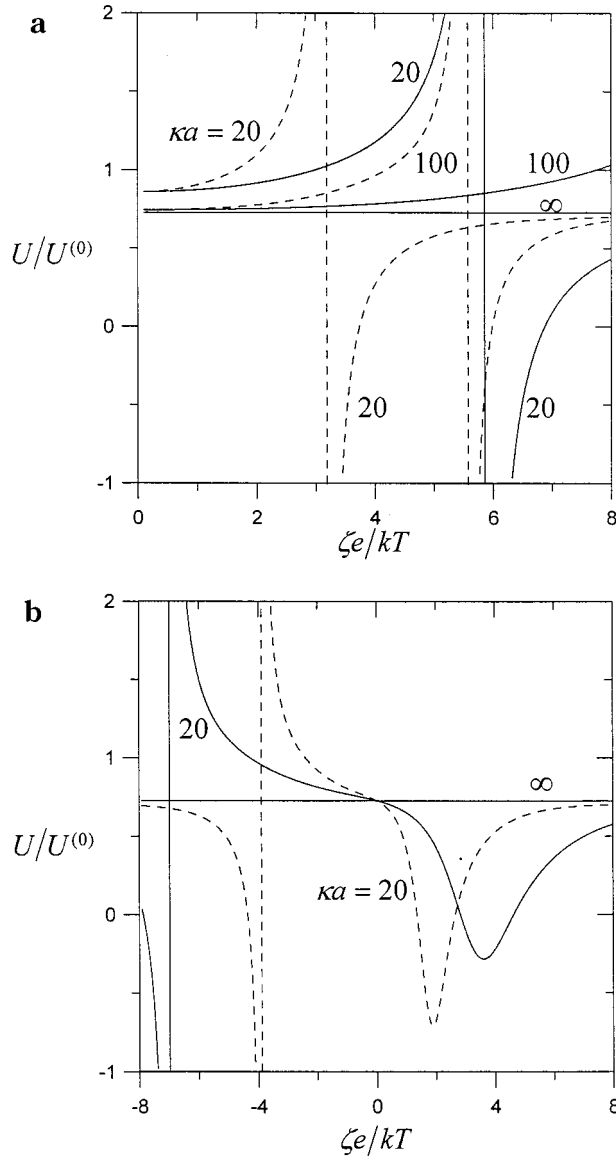
a

b

Figure 5. Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus the dimensionless zeta potential $\zeta e/kT$ for case IV with $f_1 = 0.2$ and $\varphi = 0.2$: (a) $\lambda = 0$; (b) $\lambda = -0.2$. Solid curves represent the case $Z = 1$ and dashed curves denote the case $Z = 2$.

4. Electrophoresis

Considered in this section is the steady electrophoresis of a homogeneous suspension of identical charged spheres in a uniform electric field $\mathbf{E}^\infty = E^\infty \mathbf{e}_z$. The electrophoretic velocity of the particles is $U\mathbf{e}_z$. The bulk concentration n^∞ of the symmetrically charged electrolyte beyond the electric double layers is constant. Like the analysis in section 2, the thickness of the double layers is assumed to be much smaller than the radius of the particles and the surface-to-surface distance between the neighboring particles, but the polarization effect in the thin diffuse layers is incorporated. Again, the unit cell model shown in Figure 1 is employed.

Outside the double layer surrounding the electrophoretic particle in a cell, the electrochemical potentials of the ions satisfy the Laplace equation (eq 9) and the boundary condition of eq 14 at the particle surface, but their undisturbed values are given by

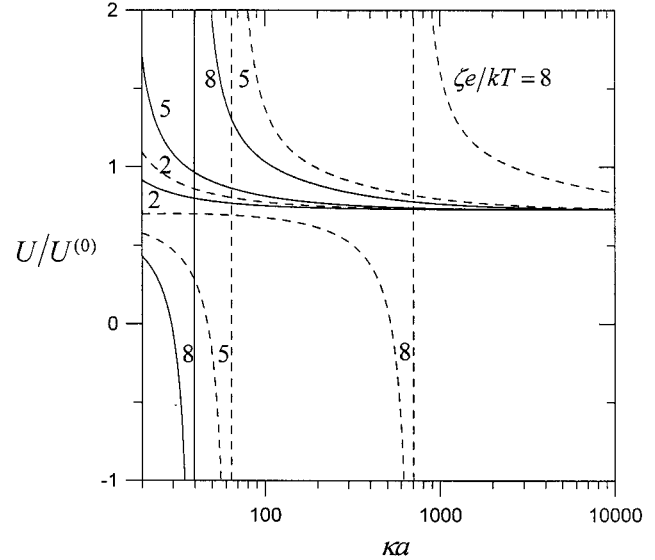$$\mu_m^\infty = \mu_m^0 + kT\ln n^\infty - (-1)^m ZeE^\infty r \cos\theta \quad (58)$$

Figure 6. Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus κa for case IV with $f_1 = f_2 = 0.2$ and $\varphi = 0.2$. Solid curves represent the case $Z = 1$ and dashed curves denote the case $Z = 2$.

in replacement of eq 17. If a boundary condition similar to eq 18 is used at the virtual surface of the cell, one has

$$r = b: \qquad \frac{\partial \mu_m}{\partial r} = -(-1)^m ZeE^\infty \cos\theta, \; m = 1, 2 \quad (59)$$

where m equal to 1 and 2 refers to the anion and cation, respectively, of the symmetric electrolyte of valence Z. The solution to eqs 9, 14, and 59 is

$$\mu_m = \mu_m^0 + kT\ln n^\infty + \left(A_{m1}r + A_{m2}\frac{a^3}{r^2}\right)ZeE^\infty \cos\theta \quad (60)$$

where, instead of eq 20

$$A_{m1} = -(-1)^m + 2\varphi A_{m2} \quad (61a)$$

$$A_{m2} = -(-1)^m \frac{1}{\Delta}(c_m\Delta_1 - 2\Delta_3\varphi) \quad (61b)$$

If a boundary condition analogous to eq 25

$$r = b: \qquad \mu_m = \mu_m^\infty, \qquad m = 1, 2 \quad (62)$$

is used, the solution of the electrochemical potentials is also given by eq 60, but now the coefficients A_{mi} are

$$A_{m1} = -(-1)^m - \varphi A_{m2} \quad (63a)$$

$$A_{m2} = -(-1)^m \frac{1}{\Delta'}(c_m\Delta_1 + \Delta_3\varphi) \quad (63b)$$

The governing equations, boundary conditions, and solution for the fluid flow field and the expression for the electrophoretic velocity of the particle have the same forms as those given in section 2, except that the characteristic
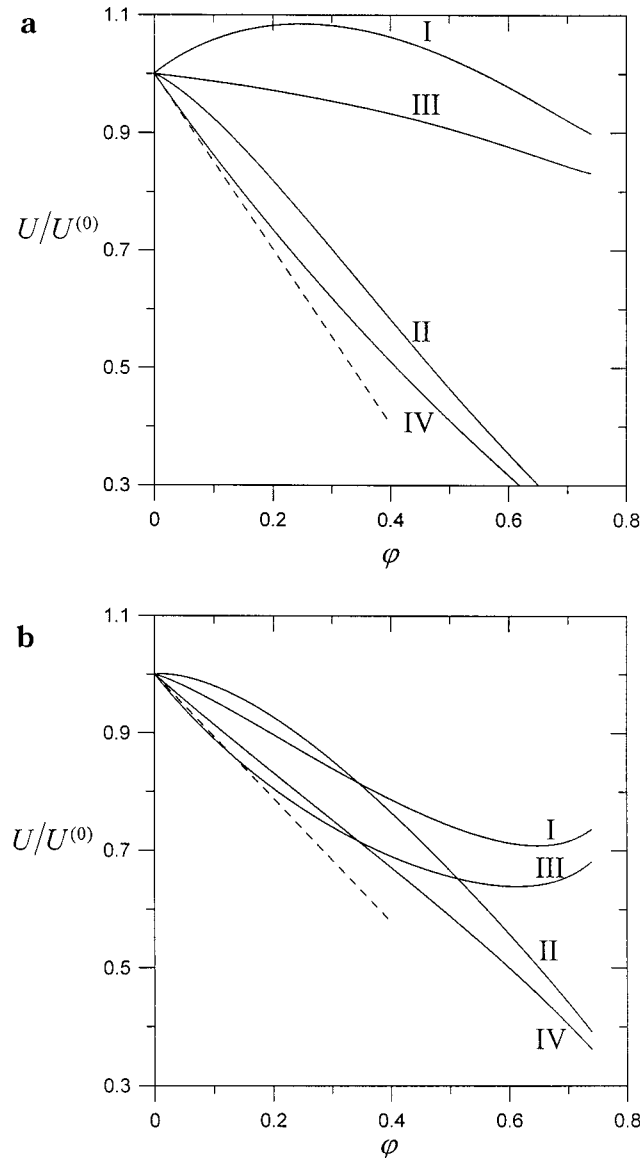
a

b

Figure 7. Plots of the normalized electrophoretic velocity in a monodisperse suspension of spherical particles versus the volume fraction of the particles with $Z = 1$, $f_1 = f_2 = 0.2$, and $\kappa a = 50$: (a) $\zeta e/kT = 2$; (b) $\zeta e/kT = 8$. The solid curves with labels I, II, III, and IV represent the cell model calculations from eqs 40, 46, 48, and 50, respectively, and the dashed curves are the statistical model results calculated from eqs 44 and 67 with $\gamma = 0$.

velocity of the particle given by eq 31 should be changed into

$$V = \epsilon kTE^\infty/4\pi\eta Ze \tag{64}$$

The final results for the electrophoretic velocity of the particle for all of the four cases of the cell model also have the same forms as those presented in section 3, except that g and h in eqs 42 and 43 are replaced by

$$g = 2 + c_1 + c_2 + (c_1 - c_2)\bar{\zeta}^{-1} \ln \cosh \bar{\zeta} \tag{65}$$

$$h = \frac{2}{g}[(c_1 + c_2)(\Delta_1 + \Delta_2) - 2\Delta_3 +$$
$$(c_1 - c_2)(\Delta_1 + \Delta_2)\bar{\zeta}^{-1} \ln \cosh \bar{\zeta}] \tag{66}$$

Now, $U^{(0)}$ given by eq 41 is the electrophoretic velocity of the particle in the limit $\varphi = 0$.
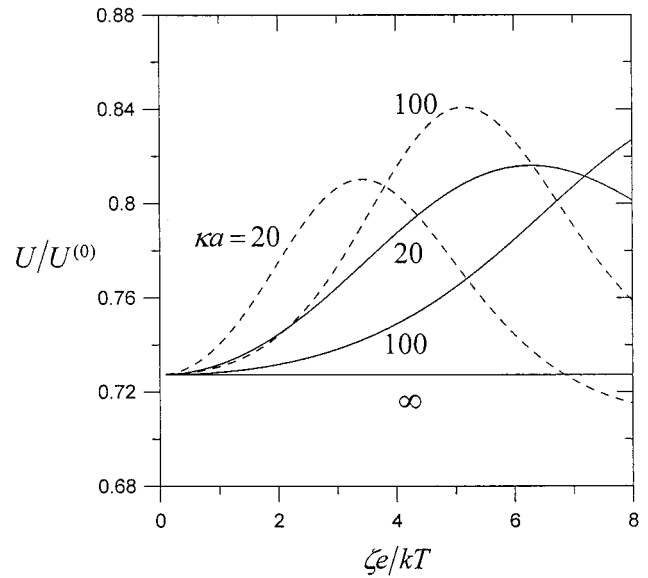

Figure 8. Plots of the normalized electrophoretic velocity in a monodisperse suspension of spherical particles versus $\zeta e/kT$ for case IV with $f_1 = f_2 = 0.2$ and $\varphi = 0.2$. Solid curves represent the case $Z = 1$ and dashed curves denote the case $Z = 2$.

Using the method-of-reflection solution for the interaction between pairs of electrophoretic spheres in an imposed electric field and the concept of statistical mechanics, Tu and Keh[19] also obtained the ensemble-averaged electrophoretic velocity in a dilute suspension of particles. This mean particle velocity can be expressed by eq 44 with $\gamma = 0$ and

$$\alpha = -\frac{21}{16} + \frac{1}{16g}[(c_1^2 + c_1 c_1' - c_1' c_2 + c_1 c_2 - 9c_1)G_1 +$$
$$(-c_2^2 - c_2 c_2' + c_1 c_2' - c_1 c_2 + 9c_2)G_2 + 9c_1 H_1 - 9c_2 H_2] \tag{67}$$

In the limiting situation given by eq 7, the dependence of the normalized particle velocity $U/U^{(0)}$ for the electrophoresis in a suspension of identical spherical particles on the particle volume fraction φ is the same as that for the diffusiophoresis, shown in Figure 2. The results of the normalized electrophoretic mobility $U/U^{(0)}$ for a suspension of particles with a finite value of κa are plotted in Figure 7 for both cases of the statistical model and the cell model. Similar to the corresponding situation of diffusiophoresis presented in the previous section, the four cases of the cell model yield somewhat different results for the particle mobility, and the result given by case IV agrees well with that obtained from eq 67 for the statistical model when φ is small. Note that, in the situation of electrophoresis, the particle velocities obtained from cases III and IV are always smaller than those obtained from cases I and II, respectively.

The normalized electrophoretic mobility $U/U^{(0)}$ for a monodisperse suspension of particles is plotted versus $\zeta e/kT$ at different values of κa and Z in Figure 8 for case IV with a constant φ. When the value of $Ze\zeta/kT$ is small (say, <6), $U/U^{(0)}$ increases monotonically with an increase in $Ze\zeta/kT$ or a decrease in κa. However, when the value of $Ze\zeta/kT$ is increased, a maximum of the normalized mobility would appear. As Z increases or κa decreases, the maximum occurs at a smaller zeta potential.

In Figure 9, the results of $U/U^{(0)}$ for a given value of φ are plotted versus κa for case IV with Z and $\zeta e/kT$ as parameters. For the case $Z = 1$, $U/U^{(0)}$ in general decreases as κa increases. However, when the value of $Ze\zeta/kT$ is
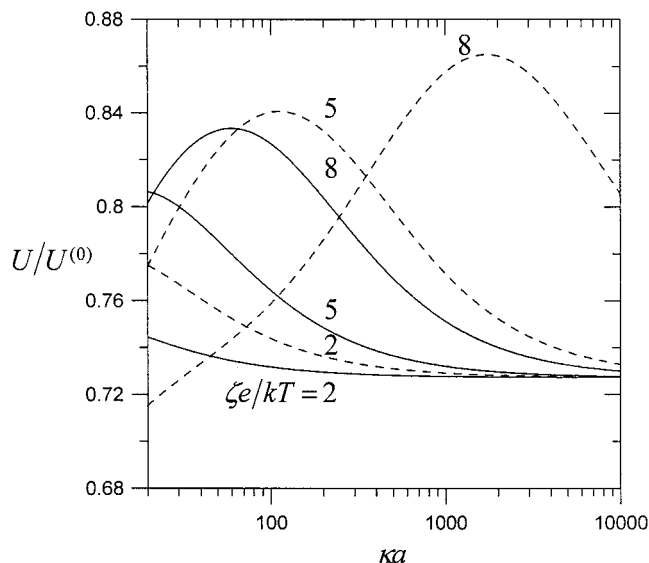
Figure 9. Plots of the normalized electrophoretic velocity in a monodisperse suspension of spherical particles versus κa for case IV with $f_1 = f_2 = 0.2$ and $\varphi = 0.2$. Solid curves represent the case $Z = 1$ and dashed curves denote the case $Z = 2$.

large (say, >6), there can be a maximum of the normalized mobility occurring at some κa for a fixed value of $\zeta e/kT$. If the value of $Ze\zeta/kT$ is increased, the locations of these maximal values will shift toward larger κa.

5. Concluding Remarks

Collections of particles are often encountered in real situations of diffusiophoresis and electrophoresis. It is important to understand if the effect of particle interactions significantly affects the movement of the particles. In this work, the diffusiophoretic and electrophoretic motions of a swarm of identical charged spheres with thin but polarized electric double layers suspended uniformly in an electrolyte solution have been analyzed using the unit cell model with various boundary conditions at the outer (virtual) surface of the cell. The electrochemical potential and fluid flow fields in the cell were analytically solved, and the particle velocities as functions of the volume fraction of the particles were obtained in the closed-form expressions 40, 46, 48, and 50. Comparisons of the results among the cell models and between the statistical model for dilute suspensions and the cell models have also been provided. It was shown that the diffusiophoretic and electrophoretic velocities predicted by case IV of the cell model agree quite well with those calculated from the statistical model. For most situations, the effects of particle interactions on the diffusiophoretic and electrophoretic mobilities are complicated functions of the properties of the particles and surrounding ions, $\zeta e/kT$, κa, Z, f_1, and f_2. In general, these effects can be quite significant under appropriate conditions. Since there is no simple rule to be able to make an adequate prediction for such complicated phenomena, the closed-form analytical results obtained here, which can be conveniently applied in the calculations for various cases with $\kappa a > 20$, should be a useful contribution to the understanding of the particle interactions in diffusiophoresis and electrophoresis. Although our analytical results are derived for the solution of a symmetric electrolyte, they can be extended to the solution containing a general electrolyte knowing its correction to eqs 6 and 8 for the undisturbed electrophoretic[9] and diffusiophoretic[12] velocities.