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Diffusiophoresis in a concentrated suspension of colloidal spheres in nonelectrolyte gradients

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Abstract The diffusiophoretic motion of a homogeneous suspension of identical spherical particles is considered under conditions of small Reynolds and Peclet numbers. The effects of interaction of the 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 mass and 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 velocity of the particle is calculated for various cases. Analytical expressions of this mean particle velocity are obtained in closed form as functions of the volume fraction of the particles. Comparisons between the ensemble-averaged diffusiophoretic velocity of a test particle in a dilute suspension and our cell-model results are made.

Key words Diffusiophoresis in nonelectrolyte gradients · Concentrated suspension of spheres · Effects of particle volume fraction · Unit cell model

Introduction

Colloidal particles, when placed in a solution that is not uniform in the concentration of some molecular solute, will spontaneously migrate toward regions of higher or lower concentration of the solute as a result of physical interaction between the solute molecules and each particle. This migration is termed diffusiophoresis [1] and has been demonstrated experimentally for both charged [2] and uncharged [3] solutes. In a solution of nonionic solute with constant concentration gradient, ∇n_∞, the diffusiophoretic velocity of a particle is [4]

$$\mathbf{U}_0 = \frac{kT}{\eta} L^* K \nabla n_\infty \quad . \tag{1}$$

Here, L^* is a characteristic length for the particle–solute interaction (of order 1 nm), K is the Gibbs adsorption length characterizing the strength of the adsorption of the molecular solute (K and L^* are defined by Eqs. (6), (7), η is the fluid viscosity, k is the Boltzmann constant, and T is the absolute temperature. Equation (1) can be applied to an isolated rigid particle of arbitrary shape and size; however, its validity is based on the assumption that the local radii of curvature of the particle are much larger than the thickness of the particle–solute interaction layer (diffuse layer) at the particle surface and that the effect of the "polarization" (or relaxation) of the diffuse solute (the solute continually adsorbs at the upstream edge and desorbs at the downstream edge) in the interfacial layer surrounding the particle is negligible.

By relaxing part of this assumption, Anderson and Prieve [5] analyzed the diffusiophoresis of a colloidal sphere of radius a with a thin, but polarized, diffuse layer at the particle surface when the solution is only slightly nonuniform in solute concentration on the length scale of a ($a|\nabla n_\infty| \ll n_\infty$). They obtained for the diffusiophoretic velocity of the particle

$$\mathbf{U}^{(0)} = \frac{kT}{\eta} L^* K \left(1 + \frac{\beta}{a}\right)^{-1} \nabla n_\infty \ , \tag{2}$$

where the definition of the relaxation coefficient, β, is given by Eq. (5). For a strongly adsorbing solute (e.g., a surfactant), the relaxation parameter, β/a (or K/a), can be much greater than unity. If all the adsorbed solute were "stuck" to the surface of the particle (the diffuseness of the adsorption layer disappears), then $L^* = 0$ and there would be no diffusiophoretic migration of the particle. In the limit of $\beta/a \rightarrow 0$ (very weak adsorption), the polarization of the diffuse solute in the interfacial layer vanishes and Eq. (2) reduces to Eq. (1). It can be seen from Eqs. (1) and (2) that the effect of polarization of the diffuse layer is to lower the diffusiophoretic mobility of the particle. The reason for this consequence is that the transport of the solute inside the particle–solute interaction layer reduces the concentration gradient along the particle surface.

In practical applications of diffusiophoresis, collections of particles are usually encountered, and effects of particle interactions will be important. Recently, some progress has been made in the theoretical analysis concerning the applicability of Eq. (2) for two-sphere and multiple-sphere systems. Through the use of a boundary collocation method, the diffusiophoresis of a chain of colloidal spheres of arbitrary radii and surface properties with thin, but polarized, diffuse layers along the line through their centers has been examined [6]. Numerical results of the diffusiophoretic velocities of the particles were presented for various cases. Using a method of reflections, Keh and Luo [7] obtained the diffusiophoretic velocities of two spherical particles with arbitrary surface properties, arbitrary size ratio, and arbitrary orientation with respect to the imposed solute concentration gradient correct to $O(r_{12}^{-7})$, where r_{12} is the center-to-center spacing. Based on the concept of statistical mechanics, this reflection result of interaction effects between pairs of spheres with thin, but polarized, diffuse layers was also used to calculate approximately the average diffusiophoretic velocity of particles in a relatively dilute, statistically homogeneous suspension subjected to a uniform solute concentration gradient. However, the effects of particle volume fraction on the diffusiophoretic mobility for a relatively concentrated suspension 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 in a bounded suspension of identical spherical particles [8–10]. 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 the 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 spheres with thin, but polarized, interfacial layers in a monodisperse suspension subjected to a constant solute concentration gradient. The analytical solutions in closed form obtained with this model enable the average diffusiophoretic velocity to be predicted as functions of the volume fraction of the particles for various cases.

Analysis

We consider the steady diffusiophoretic motion of a uniform three-dimensional distribution of identical spherical particles in a solution of a nonionic solute. The thin diffuse layers surrounding the particles can be polarized but they do not overlap with one another. The uniformly imposed solute concentration gradient, ∇n_∞, equals $E_\infty \mathbf{e}_z$ 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 Fig. 1, we employ a unit cell model [8–10] 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

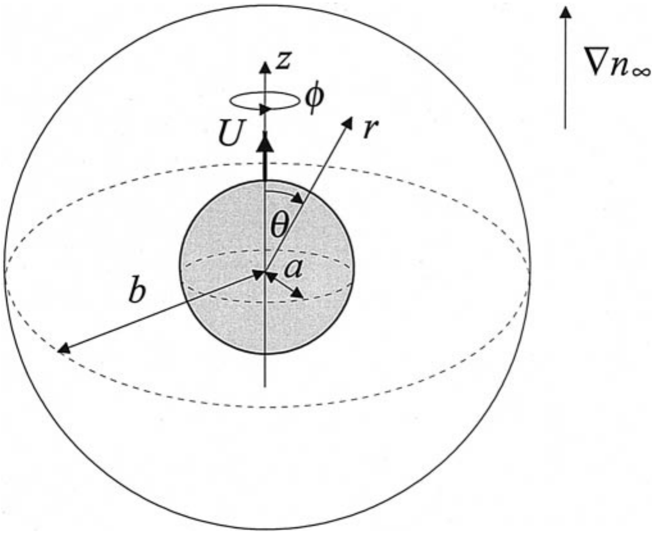

Fig. 1 Geometrical sketch for the diffusiophoretic motion of a spherical particle at the center of a spherical cell

set at the center of the particle. Our objective is to determine the particle velocity, U, in a cell induced by the diffusiophoretic driving force.

The Peclet number (Ua/D_0, where D_0 is the diffusion coefficient of the solute molecules) of this axisymmetric problem is assumed to be small. Hence, the equation of continuity governing the solute concentration distribution, $n(r,\theta)$, for the fluid is the Laplace equation

$$\nabla^2 n = 0 \ . \tag{3}$$

The boundary condition for the solute concentration at the particle surface (or, more precisely, at the outer limit of the thin, polarized interfacial layer) requires that [5–7]

$$r = a: \qquad \frac{\partial n}{\partial r} = -\beta \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial n}{\partial\theta}\right) \ , \tag{4}$$

where the relaxation coefficient

$$\beta = (1 + v\, Pe)K \ , \tag{5}$$

with

$$K = \int_0^\infty \left[\exp\left(\frac{-\Phi(y)}{kT}\right) - 1\right] \mathrm{d}y \ , \tag{6}$$

$$L^* = K^{-1} \int_0^\infty y \left[\exp\left(\frac{-\Phi(y)}{kT}\right) - 1\right] \mathrm{d}y \ , \tag{7}$$

$$v = (L^* K^2)^{-1} \int_0^\infty \left\{ \int_y^\infty \left[\exp\left(\frac{-\Phi(y)}{kT}\right) - 1\right] \mathrm{d}y \right\}^2 \mathrm{d}y \ , \tag{8}$$

$$Pe = \frac{kT}{\eta D_0} L^* K n_0 \ . \tag{9}$$

Φ represents the potential energy resulting from the interaction between a single solute molecule and the particle surface, y is the normal distance measured from the particle surface to the fluid phase, and n_0 is the solute concentration measured at the particle center in the absence of the particle. The dimensionless parameter v depends primarily on the shape of Φ rather than on its magnitude, and a typical value for it is 1/2. The adsorption length, K, is equal to the ratio of the Gibbs excess concentration of the solute in the adsorption layer to the solute concentration in the bulk solution at equilibrium, and it can be measured independently. There does not seem to be any means of quantitatively determining the length L^*, other than to say that its magnitude is comparable to the size of the solute molecule. The physical meaning of Eq. (4) is that the net tangential solute flux along the particle surface must be balanced by the normal solute flux occurring just beyond the diffuse layer to prevent accumulation of the solute. β represents the ratio of apparent surface-to-bulk diffusion coefficients [5].

At the outer (virtual) surface of the cell, the local solute concentration gradient is parallel to the uniformly applied gradient, $E_\infty \mathbf{e}_z$. Thus,

$$r = b: \qquad \frac{\partial n}{\partial r} = E_\infty \cos\theta \ . \tag{10}$$

The solution to Eqs. (3), (4), and (10) is

$$n = n_0 + A\left[1 + \frac{\beta}{a} + \left(\frac{1}{2} - \frac{\beta}{a}\right)\frac{a^3}{r^3}\right] E_\infty r \cos\theta \ , \tag{11}$$

where

$$A = \left[1 + \frac{\beta}{a} - \left(1 - 2\frac{\beta}{a}\right)\varphi\right]^{-1} \ , \tag{12}$$

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

The boundary condition of the solute concentration at the virtual surface $r = b$ may be taken as the distribution giving rise to the gradient $E_\infty \mathbf{e}_z$ in the cell when the particle does not exist. In this case, Eq. (10) becomes

$$r = b: \qquad n = n_0 + E_\infty r \cos\theta \ . \tag{13}$$

The solution of the governing equation (Eq. 3) subject to the boundary conditions (Eqs. 4, 13) is also given by the form of Eq. (11), but with parameter A defined as

$$A = \left[1 + \frac{\beta}{a} + \left(\frac{1}{2} - \frac{\beta}{a}\right)\varphi\right]^{-1} \ . \tag{14}$$

For the special case of $\beta/a = 1/2$, both Eqs. (12) and (14) give $A = 2/3$, and the concentration gradient in the fluid resulting from Eq. (11) equals the constant imposed value everywhere.

With knowledge of the solution for the solute concentration distribution, we can now proceed to find the flow field in a cell. The fluid surrounding the particle is assumed to be incompressible and Newtonian. Due to the low Reynolds number, the fluid motion caused by the diffusiophoretic migration of the particle is governed by the quasisteady fourth-order differential equation for axisymmetric creeping flows,

$$E^4\Psi = E^2(E^2\Psi) = 0 \ , \tag{15}$$

where $\Psi(r,\theta)$ is the Stokes stream function. In spherical coordinates, the Stokesian operator, E^2, is given by

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right) \ . \tag{16}$$

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

$$v_r = -\frac{1}{r^2 \sin\theta}\frac{\partial\Psi}{\partial\theta} \ , \tag{17}$$

$$v_\theta = \frac{1}{r\sin\theta}\frac{\partial\Psi}{\partial r} \ . \tag{18}$$

The boundary condition for the fluid velocity at the particle surface is [5–7]

$$r = a: \qquad v_r = U\cos\theta \ , \tag{19}$$

$$v_\theta = -U\sin\theta - \frac{kT}{\eta}L^* K\frac{\partial n}{r\partial\theta} \ , \tag{20}$$

where U is the diffusiophoretic velocity of the particle to be determined. The apparent slip velocity given by the second term on the right-hand side of Eq. (20) results from the "diffusio-osmotic" flow caused by the particle–solute interaction energy, $\Phi(y)$, and the tangential gradient, $\partial n/r\partial\theta$, along the particle surface, which can be evaluated from the solute concentration distribution given by Eq. (11). On the outer (virtual) boundary of the cell, the Happel model [8] assumes that the radial velocity and the shear stress are zero, viz.,

$$r = b: \qquad v_r = 0 \ , \tag{21}$$

$$\tau_{r\theta} = \eta\left[r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{1}{r}\frac{\partial v_r}{\partial\theta}\right] = 0 \ . \tag{22}$$

A solution to Eq. (15) suitable for satisfying boundary conditions on the spherical surfaces is [11]

$$\Psi = (Cr^{-1} + Dr + Er^2 + Fr^4)\sin^2\theta \ , \tag{23}$$

where the constants C, D, E, and F are to be determined from Eqs. (19)–(22) using Eqs. (11), (17), and (18). The procedure is straightforward, with the result

$$C = a^3\omega[U - 3A(1 - \varphi^{1/3})V] \ , \tag{24}$$

$$D = -a\omega[(3 + 2\varphi^{5/3})U - 3A(1 - \varphi^{5/3})V] \ , \tag{25}$$

$$E = \omega[(3\varphi^{1/3} + 2\varphi^2)U - 3A(\varphi^{1/3} - \varphi^2)V] \ , \tag{26}$$

$$F = -a^{-2}\omega\left[\varphi^{5/3}U - 3A\left(\varphi^{5/3} - \varphi^2\right)V\right] \ , \tag{27}$$

where $V = kTL^*KE_\infty/\eta$ (a characteristic velocity of the particle) and

$$\omega = (4 - 6\varphi^{1/3} + 6\varphi^{5/3} - 4\varphi^2)^{-1} \ . \tag{28}$$

With this solution, the components of the fluid velocity in this axisymmetric flow (with $v_\phi = 0$) can be calculated using Eqs. (17) and (18).

The drag force (in the z direction) exerted by the fluid on the particle is [11]

$$F_\mathrm{d} = 8\pi\eta D \ . \tag{29}$$

Because the particle (with the thin interfacial 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. (25) yields the diffusiophoretic velocity of the particle,

$$U = 3A(1 - \varphi^{5/3})(3 + 2\varphi^{5/3})^{-1}V \ , \tag{30}$$

where A is given by Eqs. (12) or (14).

If the Kuwabara model [9] 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. (22) is replaced by

$$r = b: \qquad (\nabla\times\mathbf{v})_\phi = \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} - \frac{1}{r}\frac{\partial v_r}{\partial\theta} = 0 \ . \tag{31}$$

With this change, Ψ can still be expressed in the form of Eq. (23), and the coefficients C, D, E, and F should be determined by the boundary conditions expressed by Eqs. (19)–(21) and (31). The result is

$$C = a^3\omega'[(5 - 2\varphi)U - 3A(5 - 6\varphi^{1/3} + \varphi)V] \ , \tag{32}$$

$$D = -15a\omega'[U - A(1 - \varphi)V] \ , \tag{33}$$

$$\begin{aligned} E = \omega'[&(18\varphi^{1/3} - 5\varphi + 2\varphi^2)U \\ &- 3A(6\varphi^{1/3} - 5\varphi - \varphi^2)V] \ , \end{aligned} \tag{34}$$

$$F = -3a^{-2}\omega'[\varphi U - A(\varphi - \varphi^2)V] \ , \tag{35}$$

where

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

The fact that there is no drag force exerted on the particle requires $D = 0$, and Eq. (33) gives the particle velocity as

$$U = A(1 - \varphi)V \ . \tag{37}$$

For the sedimentation of a suspension of identical spherical particles, both the Happel and the Kuwabara models give qualitatively the same flow fields and approximately comparable drag forces; however, the Happel model has a significant advantage in that it does not require an exchange of mechanical energy between the cell and the environment [11].

Results and discussion

Due to the differences in the boundary conditions for the solute concentration 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 concentration gradient at the virtual surface (the boundary conditions at $r = b$ are described by Eqs. 10, 21, 22.
- Case II: the Happel model with a specified concentration profile at the virtual surface (the boundary conditions at $r = b$ are described by Eqs. 13, 21, 22.
- Case III: the Kuwabara model with a specified concentration gradient at the virtual surface (the

boundary conditions at $r = b$ are described by Eqs. 10, 21, 31.

Case IV: the Kuwabara model with a specified concentration profile at the virtual surface (the boundary conditions at $r = b$ are described by Eqs. 13, 21, 31.

The analytical solutions of the concentration and flow fields in the unit cell and the diffusiophoretic velocity of the particle with a thin, but polarized, interfacial layer were obtained in the previous section for all four cases.

In case I, the particle velocity is given by Eq. (30) with A defined by Eq. (12). This migration velocity can be expressed as

$$U = U^{(0)}(1-\varphi^{5/3})\left(1+\frac{\beta}{a}\right)\left[1+\frac{\beta}{a}-\left(1-2\frac{\beta}{a}\right)\varphi\right]^{-1} \times\left(1+\frac{2}{3}\varphi^{5/3}\right)^{-1} , \tag{38}$$

where

$$U^{(0)} = \left(1+\frac{\beta}{a}\right)^{-1}\frac{kT}{\eta}L^{*}KE_{\infty} , \tag{39}$$

which is the diffusiophoretic velocity of the particle given by Eq. (2) in the limit $\varphi = 0$. U can also be written as the following power expansion in φ:

$$U = U^{(0)}[1+\alpha\varphi+\gamma\varphi^{5/3}+O(\varphi^2)] . \tag{40}$$

A comparison between Eqs. (38) and (40) leads to the coefficients α and γ:

$$\alpha = \left(1-2\frac{\beta}{a}\right)\left(1+\frac{\beta}{a}\right)^{-1} , \tag{41}$$

$$\gamma = -\frac{5}{3} . \tag{42}$$

Note that α is a function of the parameter β/a, but γ is a constant not related to this parameter. One can find $\alpha = 0$ if $\beta/a = 1/2$, $0 < \alpha \le 1$ for $0 \le \beta/a < 1/2$, and $-2 < \alpha < 0$ for $\beta/a > 1/2$ (α is a monotonically decreasing function of β/a).

In case II, the diffusiophoretic velocity of the particle can be evaluated by Eq. (30) with A given by Eq. (14), and its expression parallel to Eq. (38) for case I is

$$U = U^{(0)}(1-\varphi^{5/3})\left(1+\frac{\beta}{a}\right)\left[1+\frac{\beta}{a}+\left(\frac{1}{2}-\frac{\beta}{a}\right)\varphi\right]^{-1} \times\left(1+\frac{2}{3}\varphi^{5/3}\right)^{-1} . \tag{43}$$

This particle velocity can also be expressed in the expansion form of Eq. (40), with the coefficients α and γ given by

$$\alpha = -\left(\frac{1}{2}-\frac{\beta}{a}\right)\left(1+\frac{\beta}{a}\right)^{-1} , \tag{44}$$

$$\gamma = -\frac{5}{3} . \tag{45}$$

Here, γ is the same as that in case I, and again, Eq. (44) yields $\alpha = 0$ if $\beta/a = 1/2$; however, in this case, $-1/2 \le \alpha < 0$ for $0 \le \beta/a < 1/2$ and $0 < \alpha < 1$ for $\beta/a > 1/2$ (α is a monotonically increasing function of β/a), which is opposite to the corresponding tendency in case I (α in this case equals the value of α in case I multiplied by $-1/2$).

In case III, the diffusiophoretic velocity of the particle can be obtained by the substitution of Eq. (12) into Eq. (37), with the result

$$U = U^{(0)}(1-\varphi)\left(1+\frac{\beta}{a}\right)\left[1+\frac{\beta}{a}-\left(1-2\frac{\beta}{a}\right)\varphi\right]^{-1} . \tag{46}$$

When this velocity is expressed in the expansion form of Eq. (40), one has

$$\alpha = -3\frac{\beta}{a}\left(1+\frac{\beta}{a}\right)^{-1} , \tag{47}$$

$$\gamma = 0 . \tag{48}$$

Equation (47) indicates $\alpha = 0$ if $\beta/a = 0$, $\alpha = -1$ if $\beta/a = 1/2$, and $-3 < \alpha < 0$ for $\beta/a > 0$ (α in this case equals the value of α in case I minus 1).

In case IV, the particle velocity is given by Eq. (37) with A defined by Eq. (14), and it can be expressed as

$$U = U^{(0)}(1-\varphi)\left(1+\frac{\beta}{a}\right)\left[1+\frac{\beta}{a}+\left(\frac{1}{2}-\frac{\beta}{a}\right)\varphi\right]^{-1} . \tag{49}$$

When this formula is written in the form of Eq. (40), one has

$$\alpha = -\frac{3}{2}\left(1+\frac{\beta}{a}\right)^{-1} , \tag{50}$$

$$\gamma = 0 . \tag{51}$$

As in case III, $\alpha = -1$ if $\beta/a = 1/2$ and $\gamma = 0$; however, here, $\alpha = -3/2$ if $\beta/a = 0$ and $-3/2 < \alpha < 0$ for $\beta/a > 0$ (α in this case equals the value of α in case II minus 1).

It can be found from Eqs. (38)–(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 solute concentration at the virtual surface, $r = b$, determines the dependence of the normalized particle velocity (or mobility), $U/U^{(0)}$, as a function of β/a, while the boundary condition for the fluid velocity at $r = b$ controls the connection of $U/U^{(0)}$ with the remainder part. For given values of β/a and φ, the mean particle velocities obtained from cases III and IV are always smaller than those obtained from cases I and II, respectively.

Based on the analytical (approximate) solution of the hydrodynamic interaction between pairs of diffusiophoretic spheres in a uniformly prescribed solute concentration gradient obtained by the method of reflections correct to $O(r_{12}^{-7})$, Keh and Luo [7] also derived a formula for the mean diffusiophoretic velocity in a dilute suspension of particles (say, $\varphi < 0.1$) in the expansion form of Eq. (40) with $\gamma = 0$ by using the concept of statistical mechanics. This ensemble-averaged result gives the coefficient α approximately as

$$\alpha = -\frac{3}{2}\left(1+\frac{\beta}{a}\right)^{-1} - \frac{\beta}{a}\left[\frac{3}{16}\left(1-2\frac{\beta}{a}\right)\left(1+\frac{\beta}{a}\right)^{-2} + \frac{5}{4}\left(1+2\frac{\beta}{a}\right)^{-1}\right] . \tag{52}$$

In this statistical model γ vanishes, which is similar to that in the Kuwabara cell model (cases III, IV). Equation (52) indicates that the value of α (which is always negative) increases with an increase in β/a. As examples of limiting situations, Eq. (52) yields $\alpha = -3/2$ if $\beta/a = 0$ and $\alpha = -1/4$ if $\beta/a \to \infty$.

The normalized diffusiophoretic velocity in a homogeneous suspension of identical spherical particles, $U/U^{(0)}$, as calculated from Eqs. (38), (43), (46), and (49) for the four cases of the cell model, is plotted versus the volume fraction of the particles, φ, in Figs. 2–4 for various values of β/a. 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 [10]. 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 Fig. 2, the normalized diffusiophoretic mobility, $U/U^{(0)}$, for a suspension of identical spherical particles with $\beta/a = 1/2$ is plotted as a function of φ for the Happel cell model (cases I, II, which are the same with $\beta/a = 1/2$) and for the Kuwabara cell model (cases III, IV, which are also the same with $\beta/a = 1/2$). In this special situation, the Kuwabara model predicts a smaller diffusiophoretic velocity than the Happel model does.

The results of $U/U^{(0)}$ as a function of φ for a suspension of identical particles with $\beta/a = 0$ are shown in Fig. 3a. The results obtained from Eq. (40) for the statistical model (with $\alpha = -3/2$ and $\gamma = 0$) are also exhibited in this figure to compare them 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. $U/U^{(0)}$ is greater than unity for case I, is a monotonically decreasing function of φ for cases II and IV, and is independent of φ for case III. Note that the result for case IV is consistent with that for the statistical model in dilute suspensions ($\varphi \to 0$).

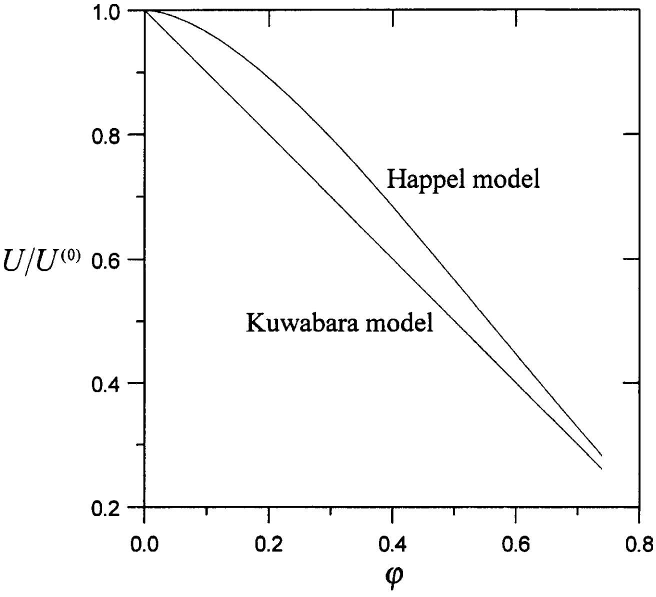

Fig. 2 Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles with $\beta/a = 1/2$ versus the volume fraction of the particles for the Happel cell model (cases I, II, Eq. 38 or Eq. 43) and the Kuwabara cell model (cases III, IV, Eq. 46 or Eq. 49)

The results of $U/U^{(0)}$ as a function of φ for a monodisperse suspension of particles with $\beta/a \to \infty$ are plotted in Fig. 3b for both cases of the statistical model (Eq. 40 with $\alpha = -1/4$ and $\gamma = 0$) and the cell model. Now, $U/U^{(0)}$ is greater than unity for case II, is a monotonically decreasing function of φ for cases I and III, and is independent of φ for case IV. Again, the result for case IV is quite close to that for the statistical model in dilute systems. It can be found from Eqs. (38), (43), (46), and (49) that, for the situations with $\beta/a > 1/2$, the diffusiophoretic velocity predicted by cases I and III is smaller than that predicted by cases II and IV (as illustrated in Fig. 3b), which is opposite to the situations with $\beta/a < 1/2$ (as illustrated in Fig. 3a).

$U/U^{(0)}$ for a suspension of identical particles is plotted in Fig. 4 as a function of φ for the four cases of the cell model with β/a as a parameter. For a fixed value of φ, $U/U^{(0)}$ decreases monotonically with an increase in β/a in cases I and III (opposite to the trend of the ensemble-averaged results), but is a monotonically increasing function of β/a in cases II and IV. For case I with $\beta/a < 1/2$ or case II with $\beta/a > 1/2$, $U/U^{(0)}$

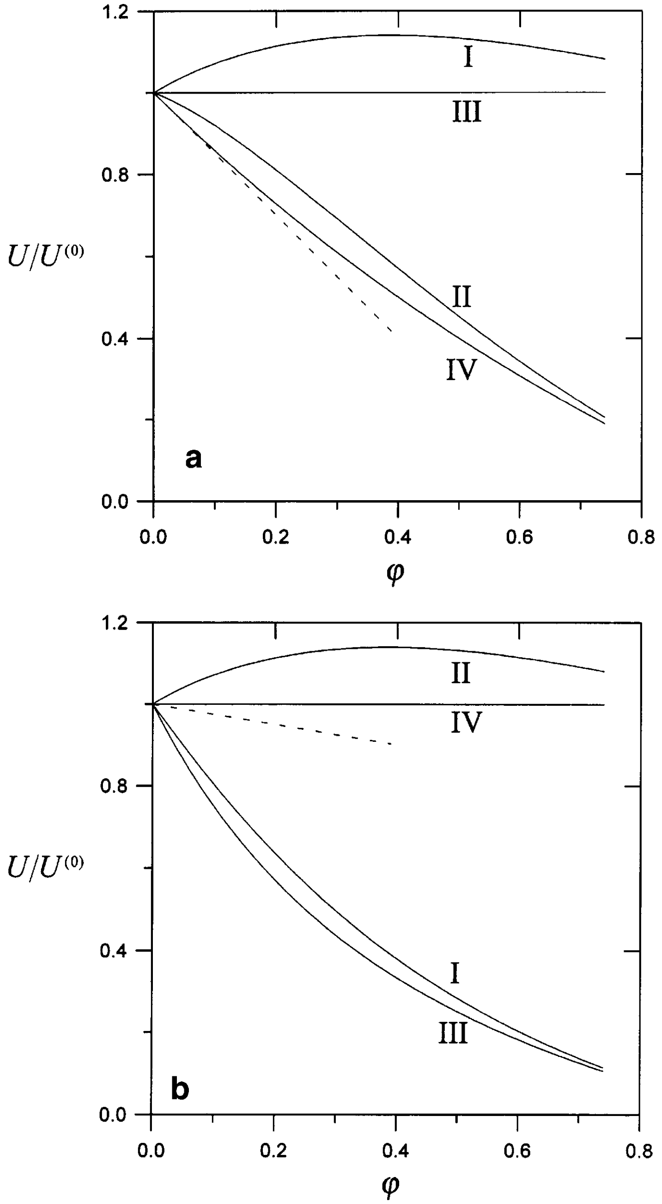

Fig. 3 Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus the volume fraction of the particles: **a** $\beta/a = 0$; **b** $\beta/a \to \infty$. The solid curves with labels *I*, *II*, *III*, and *IV* represent the cell model calculations from Eqs. (38), (43), (46), and (49), respectively, and the *dashed curves* are the statistical model results calculated from Eqs. (40) and (52) with $\gamma = 0$

increases with an increase in φ in a dilute suspension, while this normalized velocity is a monotonically decreasing function of φ for case I with $\beta/a \geq 1/2$ or for case II with $\beta/a \leq 1/2$. For the special situations of case III with $\beta/a = 0$ and case IV with $\beta/a \to \infty$, $U/U^{(0)}$ is not a function of φ; however, this normalized velocity decreases monotonically with an increase in φ in all the other situations of cases III and IV.

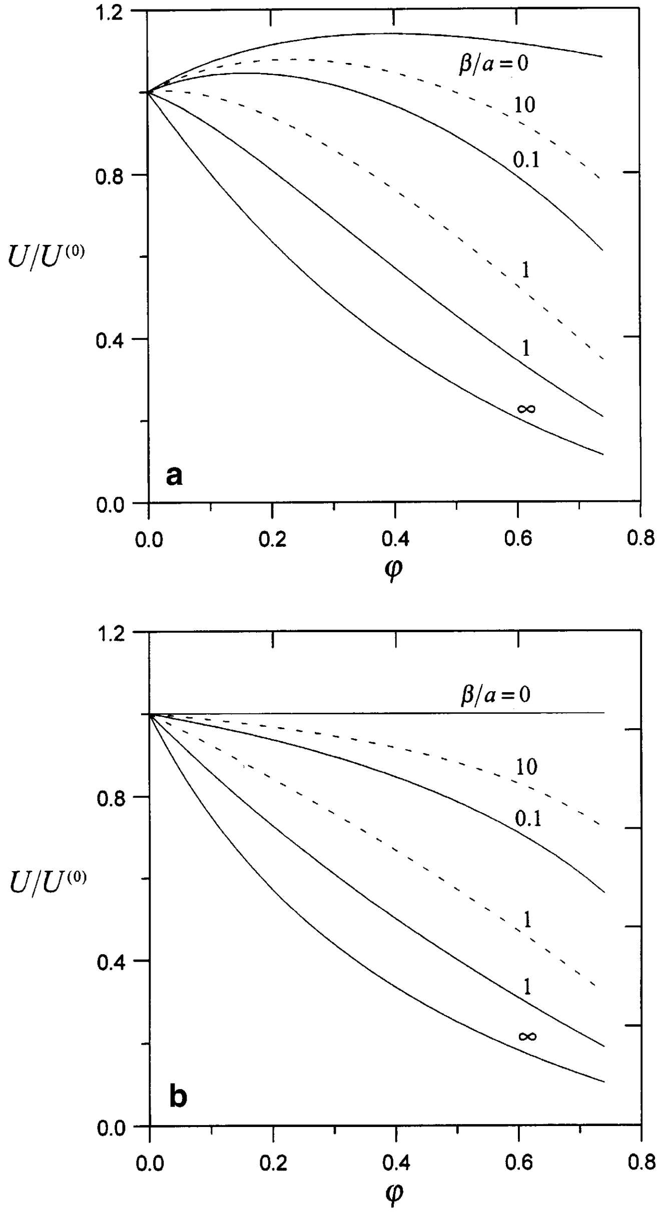

Fig. 4 Plots of the normalized diffusiophoretic velocity in a monodisperse suspension of spherical particles versus the volume fraction of the particles with β/a as a parameter: **a** case I (Eq. 38, *solid curves*) and case II (Eq. 43, *dashed curves*); **b** case III (Eq. 46, *solid curves*) and case IV (Eq. 49, *dashed curves*). The dashed curves of $\beta/a \to \infty$ and $\beta/a = 0$ coincide with the solid curves of $\beta/a = 0$ and $\beta/a = 1$, respectively

Concluding remarks

In this article, the diffusiophoresis of a swarm of identical spherical particles with thin, but polarized, interfacial layers suspended uniformly in a fluid with a constant solute concentration gradient has been analyzed using the unit cell models with various boundary conditions at the outer (virtual) surface of the cell. On the basis of the assumption of small Peclet and Reynolds numbers, the solute concentration and fluid flow fields in the cell were solved analytically and the particle velocities as functions of the volume fraction of the particles were obtained in the closed-form expressions of Eqs. (38), (43), (46), and (49). Comparisons of the results among the cell models and between the statistical model for dilute suspensions and the cell models have also been provided.

We note that the four cases of the cell model defined in the previous section lead to somewhat different results for the particle velocity. The unit cell models with various boundary conditions at the virtual surface of the cell have also been used in the literature to study the electrophoresis of charged spherical particles, a force-free "phoretic" motion similar to the diffusiophoretic motion considered here. For example, Levine and Neale [10] used cases I and III, Zharkikh and Shilov [12] used cases II and IV, Kozak and Davis [13] used case III, and Ohshima [14] used case IV (the solute concentration was replaced by the electric potential in these studies) to obtain the electrophoretic mobility of a well-mixed suspension of identical charged spheres. None of these boundary conditions is rigorously correct on the virtual surface of the unit cell, for the surrounding spheres affect the concentration (potential) and velocity at this surface. Mathematically, the concentration and flow fields in the surrounding matrix should be coupled to the corresponding fields in the unit cell through appropriate compatibility conditions (as opposed to boundary conditions), and specification of boundary conditions at the virtual surface is, at best, an approximation. Nonetheless, the analysis presented here provides meaningful information for the volume fraction effects on the diffusiophoretic mobility in concentrated suspensions of particles and for the extension of the cell-model analysis to other "phoretic" motions, such as thermocapillary migration of fluid droplets [15] and osmophoresis of vesicles [16]. Our results indicate that the tendency of the dependence of $U/U^{(0)}$ on β/a in cases I and III is not correct, in comparison with the ensemble-averaged results. So, the boundary condition represented by Eq. (10) is not as accurate as that represented by Eq. (13), probably due to the fact that the angular component of the solute concentration gradient at the virtual surface of the cell is not specified in Eq. (10). It has been shown that the diffusiophoretic velocity predicted by case IV of the cell model agrees quite well with that calculated from the statistical model for dilute suspensions of particles. The relevant experimental data, which are not available in the literature, would be needed to confirm the validity of each case of the cell model at various ranges of β/a and φ.

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