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ORIGINAL CONTRIBUTION

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Diffusiophoresis of colloidal spheres in nonelectrolyte gradients at small but finite Péclet numbers

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Abstract The diffusiophoretic motion of a spherical particle in a uniform imposed gradient of a nonionic solute is analyzed for small but finite Péclet numbers. The range of the interaction between the solute molecules and the particle surface is assumed to be small relative to the radius of the particle, but the polarization effect of the mobile solute in the thin diffuse layer surrounding the particle caused by the strong adsorption of the solute is incorporated. A normal flux of the solute and a slip velocity of the fluid at the outer edge of the diffuse layer are used as the boundary conditions for the fluid domain outside the diffuse layer. Through the use of a method of matched asymptotic expansions along with these boundary conditions, a set of transport equations governing this problem is solved in the quasisteady situation and an approximate expression for the diffusiophoretic velocity of the particle good to $O(Pe^2)$ is obtained analytically. The analysis shows that the first correction to the particle velocity is $O(Pe^2)$. The normalized particle velocity is found to decrease monotonically with the Péclet number and to increase monotonically with the dimensionless relaxation coefficient. The stronger the polarization effect in the diffuse layer, the weaker the convective effect on the diffusiophoresis.

Key words Diffusiophoresis in nonelectrolyte gradient · Thin but polarized diffuse layer · Convective transport effect · Spherical particle

Introduction

A colloidal particle, 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 the particle. This migration is termed diffusiophoresis [1] and has been demonstrated experimentally for both ionic [2] and nonionic [3] solutes. In a solution of nonelectrolyte solute with constant concentration gradient $\hat{\nabla} C_\infty$, the diffusiophoretic velocity of a particle is [4]

$$\mathbf{U}^{(0)} = \frac{kT}{\eta} L^* K \, \hat{\nabla} C_\infty \ . \tag{1}$$

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 adsorption of the molecular solute [K and L^* are defined by Eqs. (10) and (11)], 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 three assumptions:

1. 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.
2. 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.
3. The convective transport of momentum and solute is ignored.

By relaxing the second 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 in the limit of zero Reynolds and Péclet numbers (the Péclet number Pe equals the product of the Reynolds number Re and the Schmidt number Sc) when the solution is only slightly nonuniform in solute concentration on the length scale of a. They obtained the diffusiophoretic velocity of the particle as

$$\hat{\mathbf{U}}_0 = \frac{kT}{\eta} L^* K \left(1 + \frac{\hat{\beta}}{a}\right)^{-1} \hat{\nabla} C_\infty \ , \tag{2}$$

where the definition of the relaxation coefficient $\hat{\beta}$ is given by Eqs. (6) and (9). For a strongly adsorbing solute (e.g., a surfactant), the relaxation parameter $\hat{\beta}/a$ (or K/a) can be much greater than unity. If all the adorbed solute is "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 $\hat{\beta}/a \to 0$ (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 velocity of the particle. The reason for this consequence is that the transport of the solute inside the particle–solute interaction layer reduces the local concentration gradient along the particle surface.

For colloidal particles with a radius of several microns undergoing diffusiophoresis in a solute gradient of order 1 M/cm, typical values of the Péclet number would be of the order of 1. Thus, under this situation, the convective transport of the solute can no longer be negligible relative to the solute diffusion. The objective of the present work is to analyze the diffusiophoretic motion of a spherical particle in an unbounded solution of a nonionic solute when the Péclet number is small but nonzero. Although our analysis is restricted to systems for which $Re \ll 1$, it will still include cases with $Pe \le O(1)$ since for many liquid solutions (such as aqueous solutions) the Schmidt number (Pe/Re) can be very large ranging from 10^3 upward. No matter how small the value of Pe is, at sufficiently large distances from the particle, the convective transport terms will become comparable to the diffusive transport terms; therefore, a method of matched asymptotic expansions [6–9] is used to solve the problem. Analytical result in the form of an expansion formula for the diffusiophoretic velocity of the particle up to $O(Pe^2)$ as a function of the relaxation parameter $\hat{\beta}/a$ is given by Eq. (37) together with Eqs. (52) and (62).

Basic equations for diffusiophoretic motion

We consider the diffusiophoresis of a spherical particle of radius a in an unbounded solution of an uncharged solute, as illustrated in Fig. 1. The concentration gradient of the solute far away from the particle, $\hat{\nabla} C_\infty$, is a constant equal to $E_\infty \mathbf{e}_z$ and the diffusiophoretic velocity of the particle is $\hat{U}\mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector in the positive z direction. The particle's motion is inherently unsteady because its position depends on time, but a quasisteady solution to this axisymmetric problem exists. The spherical coordinate system $(\hat{r}, \theta, \phi)$, with its origin at the particle center, is chosen to translate with the particle for convenience. It is assumed that the layer of interaction between the solute molecules and the particle surface is thin in comparison with the particle radius. Hence, in the region external to this thin interaction layer, the equations of conservation of the molecular solute and fluid momentum can be expressed as

$$\frac{\partial \hat{C}}{\partial \hat{t}} + \hat{\mathbf{v}} \cdot \hat{\nabla} \hat{C} = D \hat{\nabla}^2 \hat{C} \tag{3}$$

and

$$\eta \hat{\nabla}^2 \hat{\mathbf{v}} - \hat{\nabla} \hat{p} = \mathbf{0} \ , \tag{4}$$

$$\hat{\nabla} \cdot \hat{\mathbf{v}} = 0 \ . \tag{5}$$

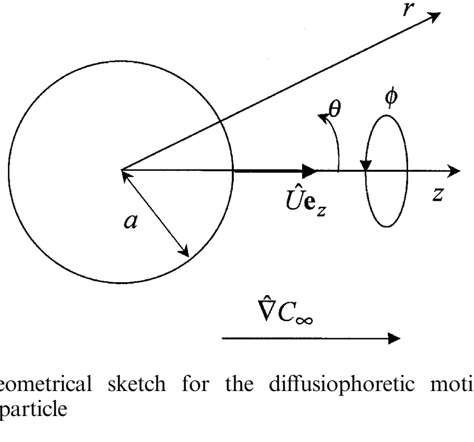

Fig. 1 Geometrical sketch for the diffusiophoretic motion of a spherical particle

Here, $\hat{C}$, $\hat{\mathbf{v}}$, and $\hat{p}$ are the solute concentration, fluid velocity, and dynamic pressure distributions, respectively, D is the solute diffusion coefficient, and $\hat{t}$ is the time. The Stokes equations (Eqs. 4, 5) are employed because of the small Reynolds numbers expected for real situations.

The governing equations (Eqs. 3–5) satisfy the following boundary conditions at the particle surface (outer limit of the thin interfacial layer) obtained by solving for the solute concentration and fluid velocity in the interfacial layer and using a matching procedure to ensure a continuous solution in the whole fluid phase [5, 10, 11]:

$$\hat{r} = a\colon \frac{\partial \hat{C}}{\partial \hat{r}} = -\hat{\beta}\frac{1}{\hat{r}^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\hat{C}}{\partial\theta}\right) \ , \tag{6}$$

$$\hat{v}_r = 0 \ , \tag{7}$$

$$\hat{v}_\theta = -\frac{kT}{\eta}L^* K\frac{1}{\hat{r}}\frac{\partial\hat{C}}{\partial\theta} \ , \tag{8}$$

where $\hat{v}_r$ and $\hat{v}_\theta$ are the $\hat{r}$ and θ components of $\hat{\mathbf{v}}$, and $\hat{\beta}$ is the relaxation coefficient given by

$$\hat{\beta} = (1 + vPe\frac{\hat{C}_0}{E_\infty a})K \ , \tag{9}$$

with

$$K = \int_0^\infty [\exp(-\Phi(y)/kT) - 1]\mathrm{d}y \ , \tag{10}$$

$$L^* = K^{-1}\int_0^\infty y[\exp(-\Phi(y)/kT) - 1]\mathrm{d}y \ , \tag{11}$$

$$v = (L^* K^2)^{-1}\int_0^\infty \left\{\int_y^\infty [\exp(-\Phi(y')/kT) - 1]\mathrm{d}y'\right\}^2 \mathrm{d}y \ , \tag{12}$$

$$Pe = \frac{U^{(0)}a}{D} = \frac{kT}{\eta D}L^* K E_\infty a \ . \tag{13}$$

In Eqs. (9), (10), (11), (12), and (13), Φ represents the potential energy resulting from the interaction between a single solute molecule and the particle surface, y or y' is the distance measured normally from the particle surface to the fluid phase, $\hat{C}_0$ is the solute concentration measured at the particle center in the absence of the particle, and we set $U^{(0)} = kTL^* KE_\infty/\eta$ as a characteristic velocity of the diffusiophoretic particle. The physical meaning of Eq. (6) 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. The apparent slip velocity given by Eq. (8) results from the "diffusio-osmotic" flow caused by the particle–solute interaction energy $\Phi(y)$ and the tangential concentration gradient along the particle surface.

The solute concentration far away from the particle approaches the undisturbed values and the fluid is at rest there. Thus, $\hat{C}$ and $\hat{\mathbf{v}}$ must obey

$$\hat{r} \to \infty\colon \ \hat{C} \to \hat{C}_0 + E_\infty(\hat{r}\cos\theta + \hat{U}\hat{t}) \ , \tag{14}$$

$$\hat{\mathbf{v}} \to -\hat{U}\mathbf{e}_z \ . \tag{15}$$

These boundary conditions are consistent with the reference frame traveling with the particle.

For convenience, we use the dimensionless variables defined by

$$r = \frac{\hat{r}}{a}, \ \nabla = a\,\hat{\nabla},$$

$$\mathbf{v} = \frac{\hat{\mathbf{v}}}{U^{(0)}}, \qquad p = \frac{a\hat{p}}{\eta U^{(0)}}, \qquad U = \frac{\hat{U}}{U^{(0)}}, \tag{16}$$

$$C = \frac{\hat{C} - \hat{C}_0}{E_\infty a} - \frac{\hat{U}\hat{t}}{a}, \qquad \beta = \frac{\hat{\beta}}{a} \ .$$

With these definitions, Eqs. (3), (4), (5), (6), (7), (8), (14), and (15) at quasisteady state become

$$Pe(U + \mathbf{v}\cdot\nabla C) = \nabla^2 C \ , \tag{17}$$

$$\nabla^2\mathbf{v} - \nabla p = \mathbf{0} \ , \tag{18}$$

$$\nabla\cdot\mathbf{v} = 0 \ ; \tag{19}$$

$$r = 1\colon \frac{\partial C}{\partial r} = -\beta\frac{1}{r^2}\frac{\partial}{\partial\mu}\left((1-\mu^2)\frac{\partial C}{\partial\mu}\right) \ , \tag{20}$$

$$v_r = 0 \ , \tag{21}$$

$$v_\theta = \frac{(1-\mu^2)^{1/2}}{r}\frac{\partial C}{\partial\mu} \ , \tag{22}$$

$$r \to \infty\colon \ C \to r\mu \ , \tag{23}$$

$$\mathbf{v} \to -U\mathbf{e}_z \ , \tag{24}$$

where $\mu = \cos\theta$. In the following sections, the velocity field $\mathbf{v}(r,\mu)$ and concentration field $C(r,\mu)$ are to be solved from these coupled equations.

Solution for the velocity field

Owing to the axisymmetric nature of the system, it is convenient to introduce the Stokes stream function, Ψ, which satisfies Eq. (19) and is related to the fluid velocity components in spherical coordinates by

$$v_r = \frac{1}{r^2}\frac{\partial\Psi}{\partial\mu} \ , \tag{25}$$

$$v_\theta = \frac{1}{r(1-\mu^2)^{1/2}}\frac{\partial\Psi}{\partial r} \ . \tag{26}$$

Taking the curl of Eq. (18) and applying Eq. (19) as well as the definition of the stream function give a fourth-order linear partial differential equation for Ψ:

$$E^4\Psi = E^2(E^2\Psi) = 0 \ . \tag{27}$$

In spherical coordinates, the operator E^2 is given by

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{1-\mu^2}{r^2}\frac{\partial^2}{\partial\mu^2} \ . \tag{28}$$

The general solution of Eq. (27) in spherical coordinates is well known [12]. The result of the stream function which satisfies the boundary conditions (Eqs. 21, 22, 24) and the requirement of zero hydrodynamic drag force on the freely suspended particle is

$$\Psi = -\frac{2}{3}B_2(r^2 - r^{-1})G_2^{-1/2}(\mu) + \sum_{n=3}^{\infty} B_n(r^{-n+1} - r^{-n+3})G_n^{-1/2}(\mu) \ . \tag{29}$$

Here, $G_n^{-1/2}(\mu)$ is the Gegenbauer polynomial of the first kind of order n and degree $-1/2$, and coefficients B_n with $n \geq 2$ are integrals related to the solute concentration field on the particle surface,

$$B_n = -\frac{1}{4}n(n-1)(2n-1)\int_{-1}^{1} C(1,\mu)P_{n-1}(\mu)\mathrm{d}\mu \ , \tag{30}$$

where $P_n(\mu)$ is the Legendre polynomial of order n. The dimensionless diffusiophoretic velocity of the particle is

$$U = -\frac{2}{3}B_2 = \int_{-1}^{1} C(1,\mu)\mu \,\mathrm{d}\mu \ . \tag{31}$$

Thus, both the fluid velocity field and the particle velocity depend on the solute concentration distribution on the particle surface.

Solutions for the concentration field and particle velocity

To solve for the solute concentration field, the method of matched asymptotic expansions must be employed. In this method, the inner concentration field is required to satisfy only the boundary condition at the particle surface and to match to the outer concentration field, which takes care of the condition at infinity.

We retain the symbol $C(r,\mu)$ for the inner solution and use $\Gamma(\rho,\mu)$ for the outer solution, where $\rho = Per$ and $\Gamma = PeC$. Thus, the equations to be solved for the inner field are given by Eqs. (17) and (20), while the equations satisfied by the outer field are obtained from Eqs. (17) and (23),

$$U + \mathbf{V}\cdot\nabla\Gamma = \nabla^2\Gamma \ , \tag{32}$$

$$\rho \to \infty: \ \Gamma \to \rho\mu \ , \tag{33}$$

where $\mathbf{V}$ is the fluid velocity field expressed in terms of the outer variable with $\mathbf{V}(\rho,\mu) = \mathbf{v}(r,\mu)$. The solutions for the inner and outer fields are expressed in regular expansions,

$$C = C_0 + PeC_1 + Pe^2C_2 + \cdots \ , \tag{34}$$

$$\Gamma = \Gamma_0 + Pe\Gamma_1 + Pe^2\Gamma_2 + \cdots \ . \tag{35}$$

The unknown constants in functions $C_i(r,\mu)$ and $\Gamma_i(\rho,\mu)$ with $i = 0, 1, 2, ...$, which are independent of Pe, are to be determined by matching Eqs. (34) and (35) at equivalent orders in Pe,

$$\lim_{r\to\infty}(PeC) = \lim_{\rho\to 0}\Gamma \ . \tag{36}$$

From Eqs. (31) and (34), the particle velocity can be expressed as an expansion in powers of Pe,

$$U = U_0(1 + \alpha_1 Pe + \alpha_2 Pe^2 + \cdots) \ , \tag{37}$$

where coefficients α_i should be functions of β only. In order to transform Eqs. (17), (20), (32), and (33) into equations for the expansion functions $C_i(r,\mu)$ and $\Gamma_i(\rho,\mu)$, the velocity fields $\mathbf{v}(r,\mu)$ and $\mathbf{V}(\rho,\mu)$ are also expanded as

$$\mathbf{v} = \mathbf{v}_0 + Pe\mathbf{v}_1 + Pe^2\mathbf{v}_2 + \cdots \ , \tag{38}$$

$$\mathbf{V} = \mathbf{V}_0 + Pe\mathbf{V}_1 + Pe^2\mathbf{V}_2 + \cdots \ . \tag{39}$$

The r and θ components of the expansion functions $\mathbf{v}_i(r,\mu)$ can be derived by using Eqs. (25), (26), (29), (30), (31), (34), (37), and (38),

$$v_{r,i} = -U_0\alpha_i(1 - r^{-3})\mu + \sum_{n=3}^{\infty} B_{n,i}(r^{-n+1} - r^{-n-1})P_{n-1}(\mu) \ , \tag{40}$$

$$v_{\theta,i} = U_0\alpha_i\left(1 + \frac{1}{2}r^{-3}\right)\left(1-\mu^2\right)^{1/2} + \left(1-\mu^2\right)^{-1/2}\sum_{n=3}^{\infty} B_{n,i} \times \left[(n-3)r^{-n+1} - (n-1)r^{-n-1}\right]G_n^{-1/2}(\mu) \ . \tag{41}$$

Here, the coefficients α_i and $B_{n,i}$ should be calculated from Eqs. (30) and (31) with $C(1,\mu)$ being replaced by $C_i(1,\mu)$. The components of the expansion functions $\mathbf{V}_i(\rho,\mu)$ can be determined from Eqs. (38), (39), (40), and (41) after substituting ρ/Pe for r. The first four functions, which will be sufficient for the calculation of the particle velocity up to U_2, are

$$
\begin{aligned}
&V_{r,0} = -U_0\mu, \quad V_{\theta,0} = U_0\left(1-\mu^2\right)^{1/2},\\
&V_{r,1} = -U_0\alpha_1\mu, \quad V_{\theta,1} = U_0\alpha_1\left(1-\mu^2\right)^{1/2},\\
&V_{r,2} = -U_0\alpha_2\mu + B_{3,0}\rho^{-2}P_2(\mu), \quad V_{\theta,2} = U_0\alpha_2\left(1-\mu^2\right)^{1/2},\\
&V_{r,3} = -U_0\left(\alpha_3-\rho^{-3}\right)\mu + B_{3,1}\rho^{-2}P_2(\mu) + B_{4,0}\rho^{-3}P_3(\mu),\\
&V_{\theta,3} = U_0\left(\alpha_3+\frac{1}{2}\rho^{-3}\right)\left(1-\mu^2\right)^{1/2}\\
&\qquad + B_{4,0}\rho^{-3}\left(1-\mu^2\right)^{-1/2}G_4^{-1/2}(\mu) \ . \qquad (42)
\end{aligned}
$$

The zeroth-order functions $C_0(r,\mu)$ and $\Gamma_0(\rho,\mu)$ obtained from solving Eqs. (17), (20), (32), and (33) after the substitution of Eqs. (34), (35), (39), and (42) and matching according to Eq. (36) are

$$C_0 = A_0 + \left(r + \frac{1-2\beta}{2(1+\beta)}r^{-2}\right)\mu \ , \qquad (43)$$

$$\Gamma_0 = \rho\mu \ . \qquad (44)$$

Here the constant A_0 is to be determined by matching C_0 and Γ_1. The zeroth-order velocity coefficients computed using Eqs. (30), (31), and (43) are

$$U_0 = (1+\beta)^{-1} \ , \qquad (45)$$

$$B_{n,0} = 0 \quad \text{for } n \geq 3 \ . \qquad (46)$$

The result of Eq. (45) agrees with Eq. (2), which is the diffusiophoretic velocity when convective transport is completely neglected.

The general expressions for the first-order functions $C_1(r,\mu)$ and $\Gamma_1(\rho,\mu)$ can be obtained by solving the appropriate equations. Matching $Pe(C_0 + PeC_1)$ with $(\Gamma_0 + Pe\Gamma_1)$ according to Eq. (36) results in $A_0 = 0$ and

$$
\begin{aligned}
C_1 &= A_1 + d_1(4r^{-1} - r^{-4})\\
&\quad + (d_2r^{-1} + d_3r^{-3} - 2d_1r^{-4})P_2(\mu) \ , \qquad (47)
\end{aligned}
$$

$$\Gamma_1 = 0 \ , \qquad (48)$$

where

$$d_1 = \frac{1-2\beta}{24(1+\beta)^2} \ , \qquad (49)$$

$$d_2 = -\frac{2-\beta}{6(1+\beta)^2} \ , \qquad (50)$$

$$d_3 = \frac{2+5\beta-6\beta^2}{9(1+\beta)^2(1+2\beta)} \ , \qquad (51)$$

and the constant A_1 will be determined by matching at the next order. The substitution of Eq. (47) into Eqs. (30) and (31) leads to the first-order velocity coefficients,

$$\alpha_1 = 0 \ , \qquad (52)$$

$$B_{3,1} = \frac{7+10\beta+24\beta^2}{90(1+\beta)^2(1+2\beta)} \ , \qquad (53)$$

$$B_{n,1} = 0 \quad \text{for } n \geq 4 \ . \qquad (54)$$

Equation (52) indicates that the first correction for the convective transport effect is identically zero.

By solving for the second-order function $\Gamma_2(\rho,\mu)$ and matching it to $O(Pe^2)$ with $Pe(C_0 + PeC_1)$, one obtains $A_1 = 0$ and

$$\Gamma_2 = 0 \ . \qquad (55)$$

The equations to be solved for the third-order function $\Gamma_3(\rho,\mu)$ are derived from Eqs. (32) and (33) using the lower-order results,

$$
\begin{aligned}
&\nabla^2\Gamma_3 + (1+\beta)^{-1}\left(\mu\frac{\partial\Gamma_3}{\partial\rho} + \frac{1-\mu^2}{\rho}\frac{\partial\Gamma_3}{\partial\mu}\right)\\
&\quad = \frac{3}{2}B_{3,1}\rho^{-2}[2\mu + 3P_3(\mu)] + (1+\beta)^{-1}\rho^{-3}P_2(\mu) \ , \qquad (56)
\end{aligned}
$$

$$\rho \to \infty: \ \Gamma_3 \to 0 \ . \qquad (57)$$

The solution of these equations after matching it to $O(Pe^3)$ with $Pe(C_0 + PeC_1)$ is

$$
\begin{aligned}
\Gamma_3 &= -5(1+\beta)B_{3,1}\rho^{-1}\left[1 + \frac{1}{2}P_2(\mu)\right]\\
&\quad + \frac{1}{12}(1+2\beta)^{-1}(1-2\beta+24\beta^2)\rho^{-2}P_1(\mu)\\
&\quad + \frac{1}{24}(1+\beta)^{-2}(1+2\beta)^{-1}\rho^{-1}\{15+23\beta+14\beta^2\\
&\quad + 24\beta^3 + (5+\beta-46\beta^2-24\beta^3)[1+2(1+\beta)\rho^{-1}]\mu\}\\
&\quad \times \exp\left[-\frac{1}{2}(1+\beta)^{-1}\rho(1+\mu)\right] \ . \qquad (58)
\end{aligned}
$$

The equations for the second-order function $C_2(r,\mu)$ derived from Eqs. (17) and (20) using the results of C_0 and C_1 are

$$
\begin{aligned}
\nabla^2 C_2 &= \frac{1}{60}(1+\beta)^{-3}(1+2\beta)^{-1}\\
&\quad \times \{[2(20+29\beta+6\beta^2+24\beta^3)r^{-2}\\
&\qquad + 2(-8+19\beta+30\beta^2+48\beta^3)r^{-5}\\
&\qquad + 3(-1-24\beta+28\beta^2-48\beta^3)r^{-7}\\
&\qquad + 21(1+2\beta)(1-2\beta)r^{-8}]\mu\\
&\qquad + [3(-5-\beta+46\beta^2+24\beta^3)r^{-2}\\
&\qquad + 5(1+3\beta-58\beta^2-24\beta^3)r^{-4}\\
&\qquad + 3(-13+4\beta+20\beta^2+48\beta^3)r^{-5}\\
&\qquad + 2(-1-24\beta+28\beta^2-48\beta^3)r^{-7}\\
&\qquad + 9(1+2\beta)(1-2\beta)r^{-8}]P_3(\mu)\} \ , \qquad (59)
\end{aligned}
$$

$$r = 1: \ \frac{\partial C_2}{\partial r} = -\beta r^{-2} \frac{\partial}{\partial \mu}\left[(1-\mu^2)\frac{\partial C_2}{\partial \mu}\right] \ . \tag{60}$$

The solution to Eqs. (59) and (60) after matching according to Eq. (36) is

$$\begin{aligned} C_2 = {} & \frac{1}{2880}(1+\beta)^{-3}(1+2\beta)^{-1} \\ & \times \{-60(15+23\beta+14\beta^2+24\beta^3) \\ & +4[-12(20+29\beta+60\beta^2+24\beta^3) \\ & +2(1+\beta)^{-1}(25+115\beta-10\beta^2-160\beta^3+48\beta^4)r^{-2} \\ & +6(-8+19\beta+30\beta^2+48\beta^3)r^{-3} \\ & +2(-1-24\beta+28\beta^2-48\beta^3)r^{-5} \\ & +9(1+2\beta)(1-2\beta)r^{-6}]\mu \\ & +3[4(5+\beta-46\beta^2-24\beta^3) \\ & +8(-1-3\beta+58\beta^2+24\beta^3)r^{-2} \\ & +8(13-4\beta-20\beta^2-48\beta^3)r^{-3} \\ & +3(1+3\beta)^{-1}(-27-68\beta+80\beta^2-56\beta^3+48\beta^4)r^{-4} \\ & +4(-1-24\beta+28\beta^2-48\beta^3)r^{-5} \\ & +8(1+2\beta)(1-2\beta)r^{-6}]P_3(\mu)\} \ . \end{aligned} \tag{61}$$

On substituting this into Eqs. (30) and (31), we obtain

$$\alpha_2 = -\frac{(77+111\beta+274\beta^2+312\beta^3)(1+\beta)}{360(1+\beta^4)(1+2\beta)} \ , \tag{62}$$

$$B_{4,2} = \frac{-39+1828\beta+4\beta^2+48\beta^3+1296\beta^4}{3360(1+\beta)^3(1+2\beta)(1+3\beta)} \ , \tag{63}$$

$$B_{n,2} = 0 \quad \text{for } n = 3 \text{ and } n \geq 5 \ . \tag{64}$$

Discussion

The problem of diffusiophoresis of a spherical particle, in which the inertial terms in the equation of motion can be ignored but the convective transport terms in the continuity equation are not negligible, has been solved analytically. Through the use of a matched asymptotic expansion procedure, the dimensionless diffusiophoretic velocity of the particle is expressed by Eq. (37) correct to $O(Pe^2)$ with U_0 given by Eq. (45). Equation (52) gives that the first correction of $O(Pe)$ vanishes. This is a consequence of the fact that only even-order Legendre polynomials appear in Eq. (47) for $C_1(r,\mu)$ and only the $P_1(\mu)$ component of the surface concentration field contributes to the particle velocity shown by Eq. (31). It can be shown that the expression for $C_3(r,\mu)$ also consists only of even-order harmonics, and, therefore, the contribution of $O(Pe^3)$ to the diffusiophoretic velocity in Eq. (37) will be zero (i.e., $\alpha_3 = 0$).

Some values of α_2 as a function of the relaxation parameter $\beta(=\hat{\beta}/a)$ computed from Eq. (62) are listed in Table 1. The negative nature of α_2 indicates that the convective transport retards the particle's movement. This behavior may be expected knowing that the convective transport of solute in the vicinity of the particle brings fluid from the regions of higher concentration to the regions of lower concentration and acts to reduce the concentration gradient along the particle surface.

The normalized diffusiophoretic velocity of the particle U/U_0 $(=\hat{U}/\hat{U}_0$, where $\hat{U}_0$ is the particle velocity in the limit of $Pe = 0$ given by Eq. 2), as calculated from Eqs. (37), (52), and (62), is plotted versus the Péclet number in the range $0 < Pe < 1$ in Fig. 2 with β as a parameter and is plotted versus β in a broad range in Fig. 3 with Pe as a parameter. It can be seen that U/U_0 is a monotonic increasing function of β for a given Péclet

Table 1 The coefficient α_2 defined by Eq. (37) calculated from Eq. (62) for various values of β

β	$-\alpha_2$
0	0.2139
0.01	0.2045
0.1	0.1441
1	0.0448
10	0.0031
∞	0

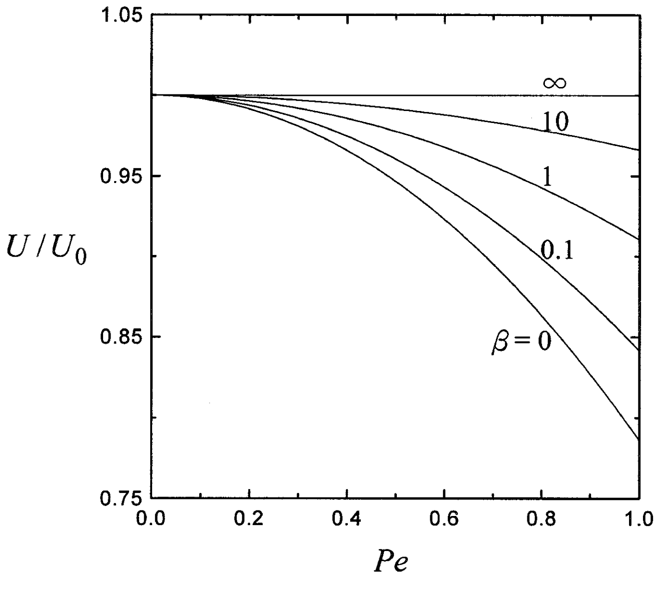

Fig. 2 Plots of the normalized diffusiophoretic velocity, U/U_0, of a spherical particle versus the Péclet number, Pe, for various values of the relaxation parameter $\beta(=\hat{\beta}/a)$

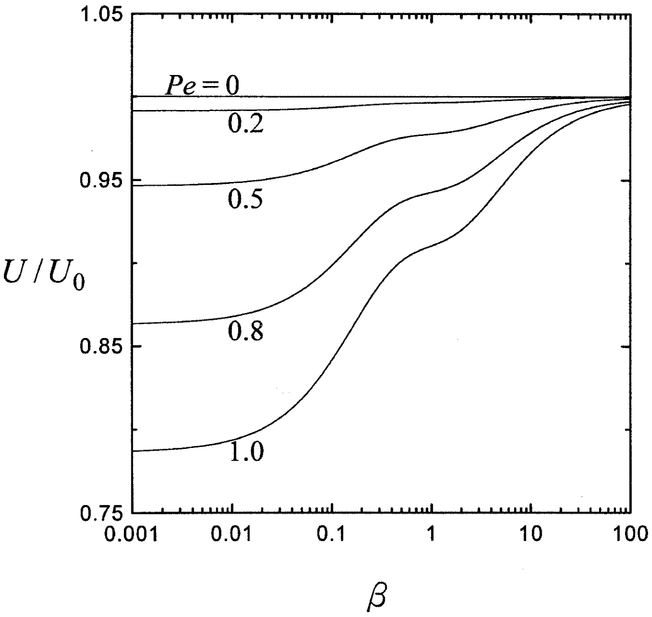

Fig. 3 Plots of U/U_0 of a spherical particle versus the relaxation parameter, β, with Pe as a parameter

number (although U_0 is a monotonic decreasing function of β), and $U/U_0 \to 1$ as $\beta \to \infty$ (irrespective of the value of Pe). Namely, as the polarization effect in the diffuse layer adjacent to the diffusiophoretic particle is stronger (or the value of β is larger), the effect of the fluid convection on the diffusiophoresis will be weaker. When $\beta = 0$, the diffusiophoretic velocity of the particle in the case of $Pe = 1$ is approximately 21.4% smaller than that in the case of $Pe = 0$. As the Péclet number is increased above unity, the correction will increase rapidly. The actual value of Pe to which Eq. (37) can be used safely with the $O(Pe^2)$ correction can be established only by comparison with an independent solution or experimental data.

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