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SHORT COMMUNICATION

Diffusiophoretic velocity of a spherical soft particle

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Abstract
The general expression is derived for the diffusiophoretic velocity of a spherical soft particle (that is, a spherical hard particle consisting of the particle core covered with an ion-penetrable surface layer of polyelectrolytes) in an electrolyte concentration gradient. For a weakly charged soft particle, the obtained general expression for the diffusiophoretic velocity is shown to reproduce the results derived by Huang and Keh (J Phys Chem B (2012) 116: 7575–7589). A simple approximate analytic expression is obtained for the diffusiophoretic velocity applicable for the case where the particle core radius and the thickness of the polyelectrolyte layer are much larger than the Debye length and the Brinkman screening length.

Keywords Diffusiophoretic velocity · Diffusiophoresis · Soft particle

Introduction

Diffusiophoresis, that is, the motion of charged colloidal particles in an electrolyte concentration gradient, is one of the electrokinetic phenomena in suspensions of colloidal particles and has been experimentally observed (e.g., Refs. [1, 2]). There are a lot of theoretical studies on diffusiophoresis of hard and soft particles, the latter of which are hard particles covered with an ion-penetrable surface layer of polyelectrolytes [2–28]. In particular, the readers should refer to a review article covering both hard and soft particles by Keh [11]. In previous papers [27, 28], we derived general expressions for the diffusiophoretic mobility of a spherical hard particle and obtained approximate diffusiophoretic velocity expressions. In the present paper, we derive the general expression for the diffusiophoretic velocity of a spherical soft particle and its approximate formula applicable for a weakly charged spherical soft particle. We then derive a simple approximate analytic expression for the diffusiophoretic velocity applicable for the case where the particle core radius and the thickness of the polyelectrolyte layer are much larger than the Debye length and the Brinkman screening length.

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Theory

Consider a spherical soft particle, moving with diffusiophoretic velocity $\boldsymbol{U}$ in an aqueous liquid of viscosity η and relative permittivity ε_r containing a symmetrical electrolyte under a constant applied gradient of electrolyte concentration ∇n. The soft particle consists of a spherical hard core of radius a covered with an ion-penetrable surface layer of polyelectrolytes of thickness b–a so that the particle has an inner radius a and an outer radius b (Fig. 1). The electrolyte is of the z:z symmetrical type with valence z but may have different ionic drag coefficients λ_+ and λ_- for cations and anions, respectively. Let n^∞ be the bulk concentration of electrolytes in the absence of the applied electrolyte concentration gradient. We treat the case where the particle core and the surface polyelectrolyte layer are uniformly charged in the absence of the applied field ∇n. We denote the surface charge density of the particle core by σ and the volume density of the fixed charges in the surface layer by ρ_{fix}. We assume that the surface layer can be described by the Brinkman-Debye-Bueche model [29, 30]. In this model polymer segments in the surface layer are regarded as resistance centers, exerting frictional forces on the liquid flowing in the surface layer. The frictional force is characterized by the Brinkman parameter λ, which is defined $\lambda = \sqrt{\gamma/\eta}$ (see Eq. (10)), where γ is the frictional coefficient of each polymer segment times the polymer segment number of the per unit volume (that is, γ is the frictional coefficient per unit volume). We introduce a constant vector $\boldsymbol{\alpha}$ proportional to ∇n, viz.

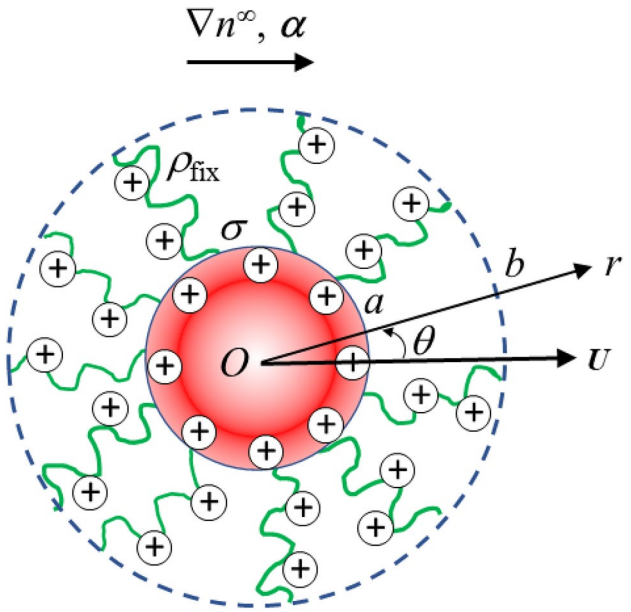

Fig. 1 Spherical soft particle consisting of the particle core of radius a covered with an ion-penetrable surface layer of polyelectrolytes of thickness b–a so that the particle has an inner radius a and an outer radius b. The particle moves with diffusiophoretic velocity $\boldsymbol{U}$ in an electrolyte concentration gradient ∇n or the corresponding vector field $\boldsymbol{\alpha}$. U is parallel to ∇n and $\boldsymbol{\alpha}$

$$\boldsymbol{\alpha} = \frac{kT}{zen^{\infty}}\nabla n \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, and e is the elementary electric charge.

The origin of the spherical polar coordinate system (r, θ, ϕ) is held fixed at the center of the particle, and the polar axis ($\theta = 0$) is put parallel to ∇n. For a spherical particle $\boldsymbol{U}$ is parallel to ∇n. The concentration gradient field ∇n is assumed to be weak so that $\boldsymbol{U}$ is linear in ∇n. The main assumptions are as follows. (i) The Reynolds number of the liquid flow is small enough to ignore inertial terms in the Navier–Stokes equation, and the liquid can be regarded as incompressible. (ii) The equilibrium electric potential in the absence of the field $\boldsymbol{\alpha}$ satisfies the Poisson-Boltzmann equation. (iii) No electrolyte ions can penetrate the particle core surface.

In a previous paper [27], we have shown that the general expression for the diffusiophoretic velocity $\boldsymbol{U}$ of a colloidal particle in an electrolyte concentration gradient field $\boldsymbol{\alpha}$ is obtained from the expression for its electrophoretic velocity $\boldsymbol{U}_{\mathrm{E}}$ in an applied electric field $\boldsymbol{E}$ by replacing $\boldsymbol{E}$ with $\boldsymbol{\alpha}$. Indeed, the fundamental equations take the same form for these two velocities [31–34]. The only difference is the far-field boundary condition for the deviation $\phi_{\pm}(r)$ of the electrochemical potential of ions. The diffusiophoretic velocity $\boldsymbol{U}$ of a spherical soft particle can thus be derived from the corresponding expression for the electrophoretic mobility [33, 34] with the result that:

$$\begin{aligned}\boldsymbol{U} =& \frac{b^2}{9}\int_b^{\infty}\left\{3\left(1-\frac{r^2}{b^2}\right)-\frac{2L_2}{L_1}\left(1-\frac{r^3}{b^3}\right)\right\}G(r)dr\boldsymbol{\alpha}\\ &+\frac{2L_3}{3\lambda^2 L_1}\int_a^{\infty}\left(1+\frac{r^3}{2b^3}\right)G(r)dr\boldsymbol{\alpha}\\ &-\frac{2}{3\lambda^2}\int_a^{b}\left[1-\frac{3a}{2\lambda^2 b^3 L_1}\{(L_3+L_4\lambda r)\cosh[\lambda(r-a)]\right.\\ &\left.-(L_4+L_3\lambda r)\sinh[\lambda(r-a)]\}\right]G(r)dr\boldsymbol{\alpha}\end{aligned} \tag{2}$$

With

$$G(r) = -\frac{zen^{\infty}}{\eta r}\frac{dy}{dr}\left\{e^{-y}\phi_{+}(r)+e^{y}\phi_{-}(r)\right\} \tag{3}$$

$$\begin{aligned}\phi_{\pm}(r) =& (\mp 1+\beta)\left(r+\frac{a^3}{2r^2}\right)-\frac{1}{3}\left(r+\frac{a^3}{2r^2}\right)\int_a^{\infty}g_{\pm}(r)dr\\ &+\frac{1}{3}\int_a^{r}\left(r-\frac{x^3}{r^2}\right)g_{\pm}(x)dx\end{aligned} \tag{4}$$

$$g_{\pm}(r) = \pm\frac{dy}{dr}\left(\frac{d\phi_{\pm}}{dr}\mp\frac{2\lambda_{\pm}}{ze}\frac{h}{r}\right) \tag{5}$$

$$\begin{aligned}L_1 =& \left(1+\frac{a^3}{2b^3}+\frac{3a}{2\lambda^2 b^3}-\frac{3a^2}{2\lambda^2 b^4}\right)\cosh[\lambda(b-a)]\\ &-\left(1-\frac{3a^2}{2b^2}+\frac{a^3}{2b^3}+\frac{3a}{2\lambda^2 b^3}\right)\frac{\sinh[\lambda(b-a)]}{\lambda b}\end{aligned} \tag{6}$$

$$\begin{aligned}L_2 =& \left(1+\frac{a^3}{2b^3}+\frac{3a}{2\lambda^2 b^3}\right)\cosh[\lambda(b-a)]\\ &+\frac{3a^2}{2b^2}\frac{\sinh[\lambda(b-a)]}{\lambda b}-\frac{3a}{2\lambda^2 b^3}\end{aligned} \tag{7}$$

$$L_3 = \cosh[\lambda(b-a)]-\frac{\sinh[\lambda(b-a)]}{\lambda b}-\frac{a}{b} \tag{8}$$

$$L_4 = \sinh[\lambda(b-a)]-\frac{\cosh[\lambda(b-a)]}{\lambda b}+\frac{\lambda a^2}{3b}+\frac{2\lambda b^2}{3a}+\frac{1}{\lambda b} \tag{9}$$

$$\lambda = \sqrt{\gamma/\eta} \tag{10}$$

$$\beta = \frac{1/\lambda_+ - 1/\lambda_-}{1/\lambda_+ + 1/\lambda_-} = -\frac{\lambda_+ - \lambda_-}{\lambda_+ + \lambda_-} \tag{11}$$

$$y(r) = \frac{ze}{kT}\psi^{(0)}(r) \tag{12}$$

where $r = |\boldsymbol{r}|$ is the radial distance from the particle core center, λ is the Brinkman parameter, the reciprocal of which $1/\lambda$ is the Brinkman screening length, $\psi^{(0)}(r)$ is the equilibrium electric potential at position r in the absence of the field $\boldsymbol{\alpha}$, $y(r)$ is its scaled quantity, and $h(r)$, which relates to the radial function of the liquid fluid velocity, satisfies

$$L(Lh - \lambda^2 h) = G(r) \; for \; a < r < b \tag{13}$$

$$L(Lh) = G(r) \; for \; r > b \tag{14}$$

subject to suitable boundary conditions, and L is defined by

$$L = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} \tag{15}$$

Results and discussion

Equation (2) is the required general expression for the diffusiophoretic velocity $\boldsymbol{U}$ of a spherical particle of radius a in an electrolyte concentration gradient field $\boldsymbol{\alpha}$. In the limit of $\lambda \to \infty$ or $a \to b$, Eq. (2) tends to the result for a hard spherical particle [27].

For a weakly charged soft particle, $G(r)$ is given by:

$$G(r) = -\frac{2zen^{\infty}}{\eta}\frac{dy}{dr}\left(1 + \frac{a^3}{2r^3}\right)\left\{\beta + y + \frac{1}{3}\int_a^{\infty}\frac{dy}{dr}\left(1 - \frac{a^3}{r^3}\right)dr\right\}$$

$$+\frac{2zen^{\infty}}{3\eta}\frac{dy}{dr}\int_a^{r}\frac{dy}{dx}\left(1 - \frac{x^3}{r^3}\right)\left(1 - \frac{a^3}{x^3}\right)dx \tag{16}$$

with

$$\psi^{(0)}(r) = \frac{\sigma}{\varepsilon_r\varepsilon_o\kappa(1 + 1/\kappa a)} \cdot \frac{a}{r}e^{-\kappa(r-a)}$$

$$+\frac{\rho_{fix}}{\varepsilon_r\varepsilon_o\kappa^2}\left[1 - \left(\frac{1 + \kappa b}{1 + \kappa a}\right)e^{-\kappa(b-a)} \times\left\{\frac{\sinh[\kappa(r-a)]}{\kappa r} + \frac{a\cosh[\kappa(r-a)]}{r}\right\}\right], a \le r \le b \tag{17}$$

$$\psi^{(0)}(r) = \psi^{(0)}(b)\frac{b}{r}e^{-\kappa(r-b)}, r \ge b \tag{18}$$

where

$$\kappa = \left(\frac{2z^2e^2n^{\infty}}{\varepsilon_r\varepsilon_o kT}\right)^{1/2} \tag{19}$$

is the Debye-Hückel parameter and ε_o is the permittivity of a vacuum. Equations (17)–(18) are obtained by solving the linearized Poisson-Boltzmann equation [10].

Equation (2) as combined with Eqs. (16)–(18) for $G(r)$ and $y^{(0)}(r)$ gives an approximate expression for $\boldsymbol{U}$ correct to the order of σ^2, ${\rho_{fix}}^2$, and $\sigma\rho_{fix}$, which is found to reproduce the result obtained by Huang and Keh [10].

We now introduce the diffusiophoretic mobility U^* defined by

$$\boldsymbol{U} = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta ze}U^*\boldsymbol{\alpha} \tag{20}$$

We derive a simple approximate expression for U^* without involving numerical integrations for the case where $\kappa a \gg 1$ and $\lambda a \gg 1, \kappa(b-a) \gg 1$, and $\lambda(b-a) \gg 1$. This condition is satisfied for most practical cases, since the size of typical soft particles such as biological cells is of the order of μm, and their surfaces are covered by a polyelectrolyte layer of the thickness of the order of 10 nm, while $1/\lambda$ and $1/\kappa$ under the physiological condition are of the order of 1 nm [35, 36]. In such a case, where the contribution of σ (which is proportional to $e^{-\kappa(b-a)}$) can be neglected, Eq. (2) as combined with Eqs. (16)–(18) further yields

$$U^* = \left\{\left(1 + \frac{a^3}{2b^3}\right)\left(\frac{\kappa + \lambda/2}{\kappa + \lambda}\right) + \frac{3\kappa^2}{2\lambda^2}\right\} \times\left\{\beta - \frac{1}{3}\left(1 - \frac{a^3}{b^3}\right)y_{DON}\right\}y_{DON}$$

$$+\frac{1}{32}\left(1 + \frac{a^3}{2b^3}\right)\left\{1 + \frac{2\kappa}{\lambda} - \frac{16\kappa^2}{\lambda(\kappa + \lambda)} + \frac{2\kappa^2}{\lambda(\kappa + \lambda/2)}\right\}y_{DON}^2 + \left(\frac{3\kappa^2}{4\lambda^2}\right)y_{DON}^2 \tag{21}$$

with

$$\psi_{DON} = \frac{\rho_{fix}}{\varepsilon_r\varepsilon_o\kappa^2} \quad \text{and} \quad y_{DON} = \frac{ze\psi_{DON}}{kT} \tag{22}$$

where ψ_{DON} is the low-potential form of the Donnan potential in the surface polyelectrolyte layer, and y_{DON} is its scaled quantity [31–34].

In the limit of $\kappa \to \infty$, U^* tends to a non-zero constant value independent of the electrolyte concentration, viz.,

$$U^* = \frac{3\rho_{fix}\beta}{2\varepsilon_r\varepsilon_o\lambda^2}\left(\frac{ze}{kT}\right) \tag{23}$$

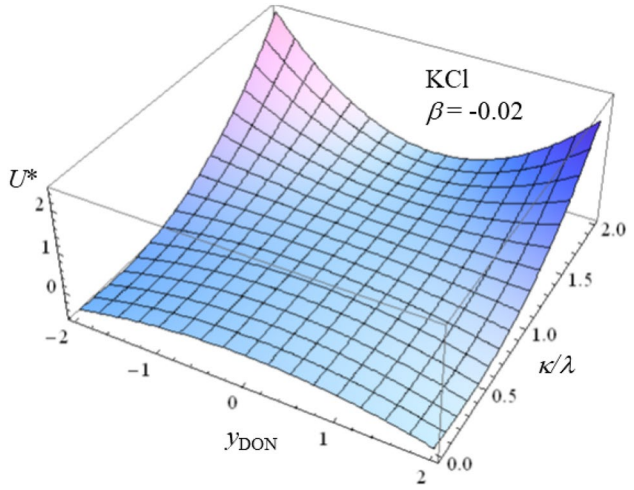

Fig. 2 Scaled diffusiophoretic mobility U^* of a soft particle in an aqueous KCl solution ($\beta = -0.02$) as a function of the scaled Donnan potential y_{DON} in the surface polyelectrolyte layer (Eq. (22)) and the ratio κ/λ of the Brinkman screening length $1/\lambda$ to the Debye length $1/\kappa$ at a/b=0.5. Calculated with Eq. (21)

which is a characteristic of the electrokinetics of soft particles, as in the case of electrophoresis [31–34].

For the case of $b–a \ll a$ (thin surface polyelectrolyte layer), Eq. (21) tends to

$$U^* = \frac{3}{2}\beta\left(\frac{\kappa+\lambda/2}{\kappa+\lambda}+\frac{\kappa^2}{\lambda^2}\right)y_{DON} + \frac{3}{64}\left\{1+\frac{2\kappa}{\lambda}+\frac{16\kappa^3}{\lambda^2(\kappa+\lambda)}+\frac{2\kappa^2}{\lambda(\kappa+\lambda/2)}\right\}y_{DON}^2 \quad (24)$$

which, for $\lambda \to \infty$, reduces to the result for a spherical hard particle [2–4], viz.,

$$U^* = \frac{3}{2}\left(\beta y_o + \frac{y_o^2}{8}\right) \quad (25)$$

where

$$\psi_o = \frac{\psi_{DON}}{2} = \frac{\rho_{fix}}{2\varepsilon_r\varepsilon_o\kappa^2} \quad \text{and} \quad y_o = \frac{ze\psi_o}{kT} \quad (26)$$

where ψ_0 ($=\psi_{DON}/2$) is the low-potential form of the surface potential of the soft spherical particle, i.e., the potential at the front edge of the surface polyelectrolyte layer at $r=b$, and y_0 is its scaled quantity.

In the opposite limit of $a \to 0$, Eq. (21) tends to the result for a spherical polyelectrolyte of radius b, viz.,

$$U^* = \left(\frac{\kappa+\lambda/2}{\kappa+\lambda}+\frac{3\kappa^2}{2\lambda^2}\right)\left(\beta-\frac{y_{DON}}{3}\right)y_{DON} + \frac{1}{32}\left\{1+\frac{2\kappa}{\lambda}+\frac{24\kappa^2}{\lambda^2}-\frac{16\kappa^2}{\lambda(\kappa+\lambda)}+\frac{2\kappa^2}{\lambda(\kappa+\lambda/2)}\right\}y_{DON}^2 \quad (27)$$

Figure 2 shows some examples of the results of the calculation of U^* of a soft particle in an aqueous KCl solution ($\beta = -0.02$) as a function of y_{DON} and κ/λ at a/b=0.5, showing how U^* strongly depends on λ/κ.

Concluding remarks

Equation (2) is the general expression for the diffusiophoretic velocity of a soft particle applicable for any values of κa, λa, σ, ρ_{fix}. For the case of a weakly charged sot particle, in particular, Eq. (2) as combined with Eqs. (16)–(18), which is correct to the order of σ^2 and ${\rho_{fix}}^2$, and $\sigma\rho_{fix}$, is found to reproduce the results obtained by Huang and Keh [10]. In addition, we have derived a simple analytic expression, which does not involve numerical integrations, for the diffusiophoretic mobility for the case where the particle core radius a and the thickness of the polyelectrolyte layer $b–a$ are much larger than the Debye length $1/\kappa$ and the Brinkman screening length $1/\lambda$.

Declarations

Conflict of interest The author declares no competing interests.

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