



Diffusiophoresis of a moderately charged cylindrical colloidal particle

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Abstract

We derive an approximate analytic expression for the diffusiophoretic mobility of a cylindrical colloidal particle oriented perpendicularly to an applied electrolyte concentration gradient field in a symmetrical electrolyte solution. This expression, which is correct to the third order of the particle zeta potential, is applicable for particles with low and moderate zeta potentials at arbitrary values of the electrical double layer thickness. This is an improvement of the mobility formula derived by Keh and Wei (2002), which is correct to the second order of the particle zeta potential. We also calculate the average diffusiophoretic mobility of a cylinder oriented at an arbitrary angle between its axis and the applied electrolyte concentration gradient field by combining the obtained mobility expression with the previously obtained mobility expression for a cylinder oriented parallel to the applied electrolyte concentration gradient field.

Keywords Diffusiophoretic mobility · Diffusiophoresis · Cylindrical colloidal particle · Zeta potential

Introduction

There have been a lot of theoretical studies on diffusiophoresis of particles of various types such as rigid spheres [1–15] (see in particular Ref. [6] for weakly charged spheres with arbitrary electrical double layer thickness, Ref. [14] for moderately charged spheres with arbitrary electrical double layer thickness, Ref. [4, 5, 12] for highly charged spheres, and Ref. [8, 11, 13] for spheres in a general electrolyte solution), rigid cylinders [16–18], particles in an electrolyte with finite ion size [19, 20], dielectric liquid drops [21–23], conducting drops or mercury drops [24–26], and soft particles (polymer-coated particles) [27–33]. The diffusiophoresis in fibrous porous media is closely related to the diffusiophoresis of cylindrical particles. Keh and his coworkers have developed the general theory of diffusiophoresis [34–37]. Keh and Wei [34] presented an analytic formula for the transverse diffusiophoretic mobility of a weakly charged cylindrical particle oriented perpendicular to the applied electrolyte concentration gradient field. This expression is correct to the second power of the zeta potential of the particle. In the present paper, we make corrections to the third powers of zeta potentials in

their formula [34] and derive an analytic diffusiophoretic mobility expression for a cylinder in a symmetrical electrolyte solution applicable for low to moderate particle zeta potentials. We also calculate the diffusiophoretic mobility of a cylinder oriented at an arbitrary angle between its axis and the applied electrolyte concentration gradient field by combining the obtained transverse mobility expression with a previously obtained expression for the tangential diffusiophoretic mobility of a cylinder oriented parallel to the applied electrolyte concentration gradient field [18].

Theory

Consider an infinitely long cylinder of radius a and zeta potential ζ moving with a diffusiophoretic velocity \mathbf{U} in an aqueous liquid of relative permittivity ϵ_r and viscosity η containing a symmetrical electrolyte of valence Z under an applied constant electrolyte concentration gradient. The ionic drag coefficient of electrolyte cations λ_+ and that of electrolyte anions λ_- may be different. We take a cylindrical coordinate system (r, θ, z) with its origin fixed at the center of the cylinder, where the z -axis coincides with the cylinder axis (Fig. 1). Let $n_+(\mathbf{r})$ be the concentration (number density) of cations at position \mathbf{r} , $n_-(\mathbf{r})$ be that of anions, and $n(\mathbf{r})$ be their concentrations beyond the electrical double layer around the cylinder, where $n_+(\mathbf{r}) = n_-(\mathbf{r}) = n(\mathbf{r})$. Let the

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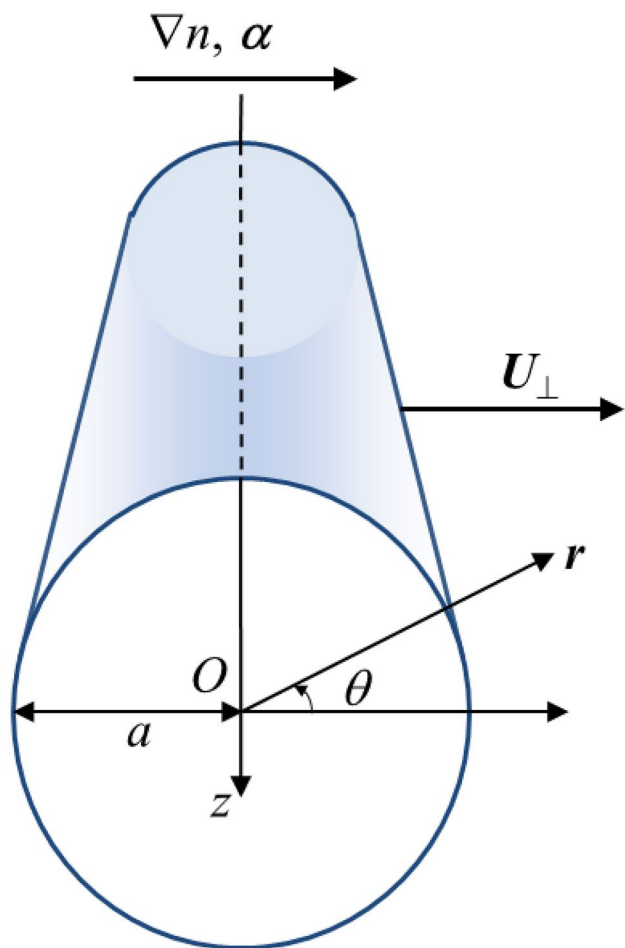


Fig. 1 A cylindrical colloidal particle of radius a moving with a velocity U_{\perp} in a transverse electrolyte concentration gradient field ∇n or α

applied electrolyte concentration gradient be expressed in terms of $n(r)$ as ∇n . We denote by n^{∞} the bulk concentration of electrolytes in the absence of ∇n . The following vector α proportional to ∇n is introduced:

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

where k is the Boltzmann constant, T is the absolute temperature, and e is the elementary electric charge. We assume that the field α is weak so that U is linear in α and the Reynolds number of the liquid flow is low so that inertial terms in the Navier–Stokes equation can be neglected, and the liquid can be regarded as incompressible. We also assume that no electrolyte ions can penetrate the particle surface.

We consider first the cylinder oriented perpendicularly to α and denote the diffusio-phoretic velocity U by U_{\perp} . The z -axis, which coincides with the cylinder axis, is put perpendicular to α (Fig. 1).

It has previously been shown [12] that one can obtain the general expression for the diffusio-phoretic velocity U of a colloidal

particle in an electrolyte concentration gradient field α from the expression for its electrophoretic velocity U_E in an applied electric field E by replacing E with α , since the governing electrokinetic equations take essentially the same form for U and U_E [12]. The only difference is the far-field boundary condition for the deviations $\delta\mu_{\pm}(r)$ of the electrochemical potentials of ions $\mu_{\pm}(r)$ caused by α and E , where $\mu_{+}(r)$ and $\mu_{-}(r)$ are, respectively, the electrochemical potentials of cations and anions. The transverse diffusio-phoretic velocity U_{\perp} in a transverse field α can thus be derived from the corresponding expression for U_E [38, 39], viz.,

$$U_{\perp} = \frac{a^2}{8} \int_a^{\infty} \left[1 - \left(\frac{r}{a}\right)^2 \left\{ 1 - 2 \ln\left(\frac{r}{a}\right) \right\} \right] G(r) dr \alpha \tag{2}$$

with

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

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

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

and

$$\begin{aligned} h(r) = & - \left(\frac{r^3}{16} - \frac{a^2 r}{8} + \frac{a^4}{16r} \right) \int_a^{\infty} G(r) dr \\ & - \left\{ \frac{r}{8} - \frac{a^2}{8r} - \frac{r}{4} \ln\left(\frac{r}{a}\right) \right\} \int_a^{\infty} r^3 G(r) dr \\ & + \int_a^r \left\{ \frac{r^3}{16} - \frac{x^4}{16r} + \frac{rx^2}{4} \ln\left(\frac{x}{r}\right) \right\} G(x) dx \end{aligned} \tag{6}$$

$$\beta = \frac{1/\lambda_{+} - 1/\lambda_{-}}{1/\lambda_{+} + 1/\lambda_{-}} = -\frac{\lambda_{+} - \lambda_{-}}{\lambda_{+} + \lambda_{-}} = -\frac{m_{+} - m_{-}}{m_{+} + m_{-}} \tag{7}$$

where

$$m_{\pm} = \frac{2\epsilon_r \epsilon_0 kT}{3\eta Z^2 e^2} \lambda_{\pm} \tag{8}$$

are the scaled ionic drag coefficients of cations and anions. The equilibrium electric potential $\psi^{(0)}(r)$ is assumed to satisfy the cylindrical Poisson-Boltzmann equation, viz.,

$$\frac{d^2 y(r)}{dr^2} + \frac{1}{r} \frac{dy(r)}{dr} = \kappa^2 \sinh y(r) \tag{9}$$

with

$$y(r) = \frac{Ze\psi^{(0)}(r)}{kT} \tag{10}$$

$$\kappa = \sqrt{\frac{2Z^2e^2n^\infty}{\epsilon_r\epsilon_0kT}} \tag{11}$$

where $y(r)$ is the scaled equilibrium electric potential, κ is the Debye-Hückel parameter, and ϵ_0 is the permittivity of a vacuum. Equation (9) is subject to the following boundary conditions:

$$\psi^{(0)}(r) \rightarrow 0 \text{ as } r \rightarrow \infty \tag{12}$$

$$\psi^{(0)}(a) = \zeta \tag{13}$$

The liquid fluid velocity $\mathbf{u}(r)$ and the deviations $\delta\mu_{\pm}(r)$ of the ionic electrochemical potentials $\mu_{\pm}(r)$ due to α are related to $h(r)$ and $\phi_{\pm}(r)$, respectively, as

$$\mathbf{u}(r) = \left(-\frac{1}{r}h(r)\alpha\cos\theta, \frac{dh(r)}{dr}\alpha\sin\theta, 0 \right) \tag{14}$$

$$\delta\mu_{\pm}(r) = \mp Ze\alpha\phi_{\pm}(r)\cos\theta \tag{15}$$

where α is $|\alpha|$. Let us define the scaled diffusiophoretic mobility U_{\perp}^* as

$$U_{\perp} = \frac{2\epsilon_r\epsilon_0kT}{3\eta Ze}U_{\perp}^*\alpha \tag{16}$$

We expand $y(r)$ in powers of ζ , which is the solution to Eq. (9) [39], viz.,

$$y(r) = \tilde{\zeta}y_1(r) + \tilde{\zeta}^3y_3(r) \tag{17}$$

with

$$y_1(r) = \frac{K_0(\kappa r)}{K_0(\kappa a)} \tag{18}$$

$$y_3(r) = \frac{1}{6K_0^3(\kappa a)} \left[K_0(\kappa r) \left\{ \frac{I_0(\kappa a)}{K_0(\kappa a)} \right\} \int_{\kappa a}^{\infty} K_0^4(t)tdt - I_0(\kappa r) \int_{\kappa r}^{\infty} K_0^4(t)tdt - K_0(\kappa r) \int_{\kappa a}^{\kappa r} I_0(t)K_0^3(t)tdt \right] \tag{19}$$

where

$$\tilde{\zeta} = \frac{Ze\zeta}{kT} \tag{20}$$

is the scaled zeta potential and $I_n(\kappa a)$ and $K_n(\kappa a)$ are, respectively, the n th order modified Bessel functions of the first and second kinds.

We first derive an expression for U_{\perp}^* correct to the order of ζ^2 . It follows from Eqs. (3), (4), (6), and (17) that the following approximate form for $G(r)$ correct to the order of ζ^2 , which involves only $y_1(r)$, can be obtained:

$$G(r) = -\frac{2Zen^\infty}{\eta} \frac{d(\tilde{\zeta}y_1)}{dr} \left(1 + \frac{a^2}{r^2} \right) \left\{ \beta + \tilde{\zeta}y_1 + \frac{1}{2} \int_a^\infty \frac{d(\tilde{\zeta}y_1)}{dr} \left(1 - \frac{a^2}{r^2} \right) dr \right\} + \frac{Zen^\infty}{\eta} \frac{d(\tilde{\zeta}y_1)}{dr} \int_a^r \frac{d(\tilde{\zeta}y_1)}{dx} \left(1 - \frac{x^2}{r^2} \right) \left(1 - \frac{a^2}{x^2} \right) dx \tag{21}$$

By combining Eq. (2) with Eq. (21) for $G(r)$ and Eq. (18) for $y_1(r)$, we obtain an approximate expression for U_{\perp}^* which is correct to the order of ζ^2 , viz.,

$$U_{\perp}^* = \frac{3}{2}\beta\tilde{\zeta}f_1(\kappa a) + \frac{3}{16}\tilde{\zeta}^2f_2(\kappa a) \tag{22}$$

where

$$f_1(\kappa a) = 1 - \frac{4(\kappa a)^4}{K_0(\kappa a)} \int_{\kappa a}^{\infty} \frac{K_0(t)}{t^5} dt + \frac{(\kappa a)^2}{K_0(\kappa a)} \int_{\kappa a}^{\infty} \frac{K_0(t)}{t^3} dt \tag{23}$$

and

$$f_2(\kappa a) = -(\kappa a)^2 \int_a^\infty \left[1 - \left(\frac{r}{a} \right)^2 \left\{ 1 - 2 \ln \left(\frac{r}{a} \right) \right\} \right] \times \left[\frac{dy_1}{dr} \left(1 + \frac{a^2}{r^2} \right) \left\{ y_1 + \frac{1}{2} \int_a^\infty \frac{dy_1}{dr} \left(1 - \frac{a^2}{r^2} \right) dr \right\} - \frac{1}{2} \frac{dy_1}{dr} \int_a^r \frac{dy_1}{dx} \left(1 - \frac{x^2}{r^2} \right) \left(1 - \frac{a^2}{x^2} \right) dx \right] dr \tag{24}$$

Equation (22) agrees with the result of Keh and Wei [34]. Note that $f_1(\kappa a)$ and $f_2(\kappa a)$ are equivalent to $\Theta_1(\kappa a)$ and $\Theta_2(\kappa a)$, respectively, in their paper (Eqs. (35a) and (35b) in Ref. [34]). Equation (22) for U_{\perp}^* consists of two terms. The first term is the electrophoresis component and the second term is the chemiphoresis component. Note also that $f_1(\kappa a)$ given by Eq. (23) corresponds to Henry’s function for the transverse electrophoretic mobility of a cylinder oriented perpendicular to an applied electric field [38, 39].

Next let us derive an expression for U_{\perp}^* correct to the order of ζ^3 . This term is related to the electrophoresis component, and thus, it is proportional to β . By using the same method employed to obtain the transverse electrophoretic mobility of a cylinder of radius a correct to the order of ζ^3 [39], by using Eq. (17), we finally obtain the following expression for U_{\perp}^* correct to the order of ζ^3 :

$$U_{\perp}^* = \frac{3}{2}\beta\tilde{\zeta}f_1(\kappa a) + \frac{3}{16}\tilde{\zeta}^2f_2(\kappa a) - \frac{3}{2}\beta\tilde{\zeta}^3 \left\{ f_3(\kappa a) + \left(\frac{m_+ + m_-}{2} \right) f_4(\kappa a) \right\} \quad (25)$$

with

$$f_3(\kappa a) = \frac{3(\kappa a)^2}{64} \int_a^{\infty} \left[1 - \frac{r^2}{a^2} \left\{ 1 - 2 \ln \left(\frac{r}{a} \right) \right\} \right] \frac{dy_1}{dr} \times \left\{ \left(1 + \frac{a^2}{r^2} \right) \int_a^{\infty} H_1(x) \frac{dy_1}{dx} dx - \int_a^r \left(1 - \frac{x^2}{r^2} \right) H_1(x) \frac{dy_1}{dx} dx \right\} dr + \frac{(\kappa a)^2}{32} \int_a^{\infty} \left[1 - \frac{r^2}{a^2} \left\{ 1 - 2 \ln \left(\frac{r}{a} \right) \right\} \right] \frac{dy_1^2}{dr} \times \left\{ \left(1 + \frac{a^2}{r^2} \right) \int_a^{\infty} \left(1 - \frac{a^2}{x^2} \right) \frac{dy_1}{dx} dx - \int_a^r \left(1 - \frac{x^2}{r^2} \right) \left(1 - \frac{a^2}{x^2} \right) \frac{dy_1}{dx} dx \right\} dr + \frac{(\kappa a)^2}{8} \int_a^{\infty} \left[1 - \frac{r^2}{a^2} \left\{ 1 - 2 \ln \left(\frac{r}{a} \right) \right\} \right] \left(1 + \frac{a^2}{r^2} \right) \left(\frac{dy_3}{dr} + \frac{1}{6} \frac{dy_1^3}{dr} \right) dr \quad (26)$$

and

$$f_4(\kappa a) = \frac{3(\kappa a)^2}{64} \int_a^{\infty} \left[1 - \frac{r^2}{a^2} \left\{ 1 - 2 \ln \left(\frac{r}{a} \right) \right\} \right] \frac{dy_1}{dr} \times \left\{ \left(1 + \frac{a^2}{r^2} \right) \int_a^{\infty} H_2(x) \frac{dy_1}{dx} dx - \int_a^r \left(1 - \frac{x^2}{r^2} \right) H_2(x) \frac{dy_1}{dx} dx \right\} dr \quad (27)$$

where

$$H_1(x) = \frac{2}{3} \left(1 - \frac{a^2}{x^2} \right) \int_a^{\infty} \left(1 - \frac{a^2}{t^2} \right) \frac{dy_1}{dt} dt - \frac{2}{3} \int_a^x \left(1 + \frac{t^2}{x^2} \right) \left(1 - \frac{a^2}{t^2} \right) \frac{dy_1}{dt} dt \quad (28)$$

and

$$H_2(x) = -\frac{\kappa^2}{8} \int_a^x \left\{ x^2 - \frac{t^4}{x^2} + 4t^2 \ln \left(\frac{t}{x} \right) \right\} \left(1 + \frac{a^2}{t^2} \right) \frac{dy_1}{dt} dt + \frac{\kappa^2}{8} \int_a^{\infty} \left\{ x^2 + \frac{a^4}{x^2} - 2a^2 + 2 \left(1 - \frac{a^2}{x^2} \right) t^2 - 4t^2 \ln \left(\frac{x}{a} \right) \right\} \left(1 + \frac{a^2}{t^2} \right) \frac{dy_1}{dt} dt \quad (29)$$

The first and second terms on the right-hand side of Eq. (25) are equivalent to Eq. (22), and the last term is the correction term of the order of ζ^3 to Eq. (22). The above

functions $f_1(\kappa a)$, $f_2(\kappa a)$, $f_3(\kappa a)$, and $f_4(\kappa a)$ defined by Eqs. (23), (24), (26), and (27) in the present paper, respectively, correspond to the functions $f_1(\kappa a)$ – $f_4(\kappa a)$ defined in the previous paper [39] but they differ from each other by a factor of 2/3 due to different definitions in the present paper and the previous paper [39].

In the large κa limit ($\kappa a \rightarrow \infty$), Eq. (25) becomes

$$U_{\perp}^* = \frac{3}{2} \left(\beta\tilde{\zeta} + \frac{1}{8}\tilde{\zeta}^2 \right) \quad (30)$$

which agrees with the result for a particle with a planar surface [1, 2]. In the small κa limit ($\kappa a \rightarrow 0$), on the other hand, Eq. (25) becomes

$$U_{\perp}^* = \frac{3}{4}\beta\tilde{\zeta} \quad (31)$$

It is thus seen that there are no contributions of $f_3(\kappa a)$ and $f_4(\kappa a)$ in the limits of $\kappa a \rightarrow \infty$ and $\kappa a \rightarrow 0$.

We next consider the tangential diffusiophoretic mobility U_{\parallel}^* of a cylindrical particle oriented parallel to α . It can be shown [18] that U_{\parallel}^* can be expressed as

$$U_{\parallel}^* = \frac{3}{2} \left\{ \beta\tilde{\zeta} + \frac{1}{8}\tilde{\zeta}^2 f(\kappa a) \right\} \quad (32)$$

where

$$f(\kappa a) = (\kappa a)^2 \left[1 + \frac{K_2(\kappa a)}{K_0(\kappa a)} - 2 \left\{ \frac{K_1(\kappa a)}{K_0(\kappa a)} \right\}^2 \right] \quad (33)$$

Note that Eq. (32) is already correct to the order of $\tilde{\zeta}^3$, since the next-order correction term to Eq. (32) is of the order of $\tilde{\zeta}^4$. It is to be noted that U_{\parallel}^* depends on κa unlike the case of electrophoresis, where the tangential electrophoretic mobility of a cylinder does not depend on κa [38, 39].

In the limit of $\kappa a \rightarrow \infty$, $f(\kappa a)$ tends to 1 so that Eq. (32) tends to Eq. (30), viz.,

$$U_{\parallel}^* = \frac{3}{2} \left(\beta\tilde{\zeta} + \frac{1}{8}\tilde{\zeta}^2 \right) \quad (34)$$

In the opposite limit of $\kappa a \rightarrow 0$, $f(\kappa a)$ tends to 0 so that Eq. (32) tends to

$$U_{\parallel}^* = \frac{3}{2}\beta\tilde{\zeta} \quad (35)$$

It is thus seen that in the limit of $\kappa a \rightarrow \infty$, U_{\perp}^* and U_{\parallel}^* tend to the same limiting value (Eqs. (30) and (34)), while in the opposite limit of $\kappa a \rightarrow 0$, the limiting value of U_{\parallel}^* (Eq. (35)) is twice that of U_{\perp}^* (Eq. (31)).

For a cylindrical particle oriented at an arbitrary angle between its axis and the applied electrolyte concentration gradient field \mathbf{a} , its diffusiophoretic mobility U_{av}^* averaged over a random distribution of orientation is given by [40]:

$$U_{av}^* = \frac{1}{3}U_{\parallel}^* + \frac{2}{3}U_{\perp}^* \tag{36}$$

Results and discussion

The main result of this paper is Eq. (25) for the transverse diffusiophoretic mobility U_{\perp}^* of a cylinder oriented perpendicular to an applied electrolyte concentration gradient, which is correct to the order of ζ^3 . Equation (25) is an improvement of Eq. (22) correct to the order of ζ^2 .

Since Eqs. (23), (24), (26), (27), and (33) for $f_1(\kappa a)$ – $f_4(\kappa a)$ and $f(\kappa a)$ are not very convenient for the practical use, since they involve modified Bessel functions and numerical integrations, we derive simpler approximate formula for $f_1(\kappa a)$, $f_3(\kappa a)$, and $f_4(\kappa a)$ without involving modified Bessel functions and numerical integrations on the basis of the same approximation method as used in the electrophoresis problem [38, 39]. As for $f_2(\kappa a)$, Keh and Wei [34] derived an excellent approximate expression (Eq. (38)). Thus, we find that

$$f_1(\kappa a) = \frac{1}{2} \left[1 + \frac{1}{\left\{ 1 + \frac{2.55}{\kappa a(1+e^{-\kappa a})} \right\}^2} \right] \tag{37}$$

$$f_2(\kappa a) = 1 - \frac{1.15}{1 + 0.066(\kappa a)^{1.15} - 0.02(\kappa a)^{0.2}} + \frac{0.15}{[1 + 15(\kappa a)^{1.7}]^{0.8}} \tag{38}$$

$$f_3(\kappa a) = \frac{\kappa a(\kappa a + 0.162)}{3\{(\kappa a)^3 + 9.94(\kappa a)^2 + 18.7\kappa a + 0.147 \exp(-9.41\kappa a)\}} \tag{39}$$

$$f_4(\kappa a) = \frac{3\kappa a\{\kappa a + 0.361 \exp(-0.475\kappa a) + 0.0878\}}{4\{(\kappa a)^3 + 10.8(\kappa a)^2 + 18.2\kappa a + 0.0633\}} \tag{40}$$

Also, we find that $f(\kappa a)$ given by Eq. (33) can be approximated with negligible errors as

$$f(\kappa a) = \frac{\kappa a(\kappa a + 2.5)}{(\kappa a)^2 + 3\kappa a + 0.91 \exp(-0.59\kappa a)} + \frac{2 \exp(-5.7\kappa a)}{1.62 - \ln(\kappa a)} \tag{41}$$

By using the above equations, Eq. (25) becomes

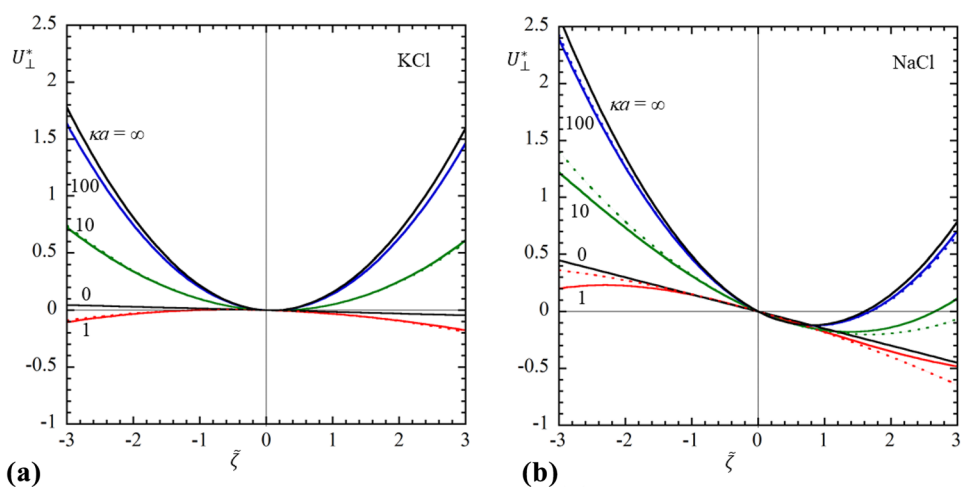
$$U_{\perp}^* = \frac{3}{4}\beta\tilde{\zeta}^2 \left[1 + \frac{1}{\left\{ 1 + \frac{2.55}{\kappa a(1+e^{-\kappa a})} \right\}^2} \right] + \frac{3}{16}\tilde{\zeta}^2 \left\{ 1 - \frac{1.15}{1 + 0.066(\kappa a)^{1.15} - 0.02(\kappa a)^{0.2}} + \frac{0.15}{[1 + 15(\kappa a)^{1.7}]^{0.8}} \right\} - \beta\tilde{\zeta}^3 \frac{\kappa a(\kappa a + 0.162)}{2\{(\kappa a)^3 + 9.94(\kappa a)^2 + 18.7\kappa a + 0.147 \exp(-9.41\kappa a)\}} - \beta\tilde{\zeta}^3 \left(\frac{m_+ + m_-}{2} \right) \frac{9\kappa a\{\kappa a + 0.361 \exp(-0.475\kappa a) + 0.0878\}}{8\{(\kappa a)^3 + 10.8(\kappa a)^2 + 18.2\kappa a + 0.0633\}} \tag{42}$$

and Eq. (32) becomes

$$U_{\parallel}^* = \frac{3}{2}\beta\tilde{\zeta}^2 + \frac{3}{16}\tilde{\zeta}^2 \left\{ \frac{\kappa a(\kappa a + 2.5)}{(\kappa a)^2 + 3\kappa a + 0.91 \exp(-0.59\kappa a)} + \frac{2 \exp(-5.7\kappa a)}{1.62 - \ln(\kappa a)} \right\} \tag{43}$$

Figure 2a, b shows some results of U_{\perp}^* calculated via Eq. (25) (or Eq. (42) with negligible errors) for a cylinder of radius a in an aqueous KCl solution ($m_+ = 0.176, m_- = 0.169, \beta = -0.02$) (Fig. 2a) and NaCl solution ($m_+ = 0.258, m_- = 0.169, \beta = -0.2$) (Fig. 2b) at 25 °C (solid curves) in comparison with those obtained via Eq. (22) (dotted curves, Keh and Wei [34]). The contribution of the correction term of order ζ^3 is related to the electrophoresis component of diffusiophoresis and becomes more significant as β becomes larger. Indeed, it is seen from Fig. 2a, b that this correction contribution is larger for NaCl

Fig. 2 Scaled diffusiophoretic mobility U_{\perp}^* of a cylindrical colloidal particle of radius a in an aqueous electrolyte solution at 25 °C as a function of the scaled zeta potential $\tilde{\zeta}$ at several values of κa . Calculated via Eq. (25) (or Eq. (42) with negligible errors) (solid curves) in comparison with the results for U_{\perp}^* correct to the order of ζ^2 obtained from Eq. (22) (Keh and Wei [8]) (dotted curves). Results for KCl ($m_+ = 0.176, m_- = 0.169, \beta = -0.02$) (a) and NaCl ($m_+ = 0.258, m_- = 0.169, \beta = -0.2$) (b)



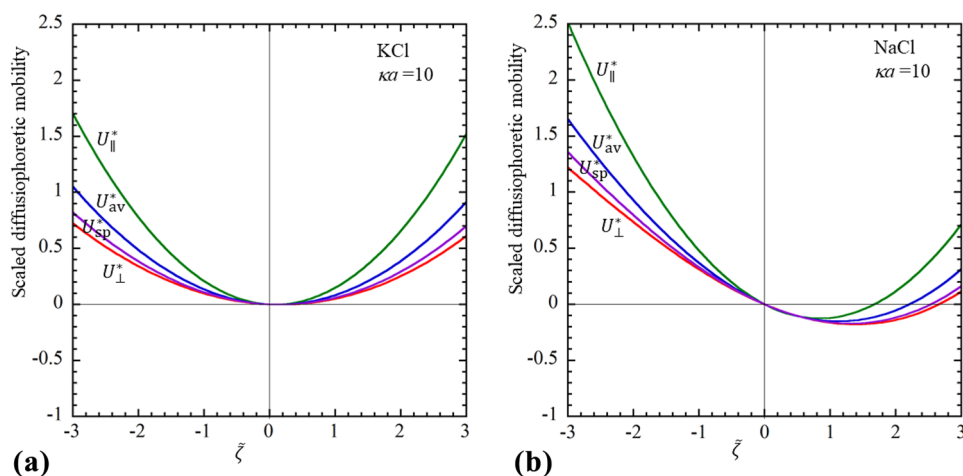


Fig. 3 Scaled average diffusiophoretic mobility U_{av}^* of a cylindrical colloidal particle of radius a in an aqueous electrolyte solution at 25 °C as a function of the scaled zeta potential $\tilde{\zeta}$ at $\kappa a = 10$. Calculated via Eqs. (25) and (32) (or Eqs. (42) and (43) with negligible errors) (solid curves) in com-

parison with the results for the diffusiophoretic mobility U_{sp}^* for a spherical particle [14] (dotted curves). Results for KCl ($m_+ = 0.176$, $m_- = 0.169$, $\beta = -0.02$) (a) and NaCl ($m_+ = 0.258$, $m_- = 0.169$, $\beta = -0.2$) (b)

($\beta = -0.2$) than for KCl ($\beta = -0.02$). We also see that this contribution is large for moderate values of κa ($0.1 < \kappa a < 100$) and becomes small for large κa (> 100) or small κa (< 0.1), vanishing in the limit of $\kappa a \rightarrow \infty$ (thin double layer limit) or $\kappa a \rightarrow 0$ (thick double layer limit). Note that in these two limiting cases the solid and dotted curves coincide with each other.

In Fig. 3a, b, we plot the scaled average electrophoretic mobility given by Eq. (36) of a cylinder of radius a and zeta potential ζ as a function of scaled zeta potential $\tilde{\zeta}$ (solid curves) in comparison with the scaled diffusiophoretic mobility U_{sp}^* of a sphere of the same radius a and zeta potential ζ as the cylinder, which is correct to the order of ζ^3 (dotted curves) [14]. It is seen that the curve for U_{sp}^* lies between those for U_{\parallel}^* and U_{\perp}^* and is close to that of U_{av}^* .

It has been shown [1, 2] that in the case of diffusiophoresis of a sphere, the chemiphoresis component causes the particle to move toward higher electrolyte concentrations, while the electrophoresis component moves the particle toward higher or lower electrolyte concentrations depending on the sign of the particle zeta potential, which may cause a sign reversal of the diffusiophoretic mobility in some cases. Figures 2 and 3 demonstrate that a cylinder exhibits the same diffusiophoretic behavior as a sphere. That is, for electrolytes with almost equal ion mobilities such as KCl ($\beta = -0.02$, Figs. 2a and 3a), the electrophoretic contribution becomes negligible relative to chemiphoresis and almost only chemiphoresis component moves the cylinder toward higher electrolyte concentrations (positive diffusiophoretic mobility). In the case of a cylinder with large κa in NaCl ($\beta = -0.2$, Figs. 2b and 3b), however, a particle of low to moderate positive zeta potential migrates toward lower

electrolyte concentrations, while a particle of high positive zeta potential can migrate toward higher electrolyte concentrations.

Evel and others [41] measured the diffusiophoretic mobility of spherical latex particles. As for cylindrical particles, McMullen and others [42] recently performed diffusiophoresis measurement of DNA cylinders. The present theory is thus expected to apply for such systems.

Concluding remarks

Keh and Wei [34] derived an analytic expression for the transverse diffusiophoretic mobility of a cylinder in a symmetrical electrolyte solution correct to the order of ζ^2 . In the present paper, we have provided the next-order correction terms to the mobility expression by Keh and Wei [34] and derived Eq. (25) as well as its simpler approximate expression (Eq. (42)). These equations, which are correct to the order of ζ^3 , are applicable for any values of κa at low to moderate values of ζ . The contribution of the correction terms becomes larger as the magnitude of β becomes larger and becomes zero in the limits of $\kappa a \rightarrow \infty$ and $\kappa a \rightarrow 0$. We also present an approximate expression (Eq. (43)) for the tangential diffusiophoretic mobility and calculate the average diffusiophoretic mobility of a cylinder oriented at an arbitrary angle between its axis and the applied electrolyte concentration gradient field using Eq. (36).

Declarations

Conflict of interest The author declares no competing interests.

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