Colloid and Polymer Science (2021) 299:1877–1884
https://doi.org/10.1007/s00396-021-04898-3

ORIGINAL CONTRIBUTION

Diffusiophoretic velocity of a large spherical colloidal particle in a solution of general electrolytes

Hiroyuki Ohshima[1]

Received: 15 July 2021 / Revised: 21 August 2021 / Accepted: 2 September 2021 / Published online: 13 October 2021

Abstract

The general expression is derived for the diffusiophoretic velocity of a large spherical colloidal particle of radius a in a concentration gradient of general electrolytes of Debye-Hückel parameter κ. On the basis of this expression, simple approximate analytic expressions for the diffusiophoretic velocity correct to the order of $(1/\kappa a)^0$ are derived, which can be applied for large particles with $\kappa a \geq 50$ at arbitrary values of the particle zeta potential with negligible errors.

Keywords Diffusiophoretic velocity · Diffusiophoresis · Spherical particle · Zeta potential

Abbreviations

a	Particle radius
$\boldsymbol{a}$	Electrolyte concentration gradient vector
β	Parameter relating to the diffusion potential field defined by Eq. (25)
∇n_i	Concentration gradient of the i th ionic species
e	Elementary electric charge
ε_o	Permittivity of a vacuum
ε_r	Relative permittivity of an electrolyte solution
$\phi_i(r)$	Function relating to the electrochemical potential of the i th ionic species
$h(r)$	Function relating to the liquid flow velocity $\boldsymbol{u}(\boldsymbol{r})$
η	Viscosity of an electrolyte solution
$\boldsymbol{i}$	Electric current density
k	Boltzmann's constant
κ	Debye-Hückel parameter
λ_i	Drag coefficient of the i th ionic species
m_i	Scaled drag coefficient of the i th ionic species
$\mu_i(\boldsymbol{r})$	Electrochemical potential of the i th ionic species at position $\boldsymbol{r}$
$n_i(\boldsymbol{r})$	Concentration (number density) of the i th ionic species at position $\boldsymbol{r}$
n_i^∞	Bulk concentration (number density) of i th ionic species in the absence of the applied electrolyte concentration gradient
$p(\boldsymbol{r})$	Pressure at position r
$\rho_\mathrm{el}(\boldsymbol{r})$	Space charge density at position $\mathbf{r}$
T	Absolute temperature
$\boldsymbol{u}$	Liquid flow velocity
$\boldsymbol{U}$	Diffusiophoretic velocity
U	Magnitude with sign of $\boldsymbol{U}$
U^*	Scaled diffusiophoretic mobility
$\boldsymbol{v}_i(\boldsymbol{r})$	Velocity of the i th ionic species at position $\boldsymbol{r}$
y	Scaled equilibrium electric potential
$\psi(\boldsymbol{r})$	Electric potential at position $\boldsymbol{r}$
$\psi^{(0)}(r)$	Equilibrium electric potential at position r
z_i	Valence of i th ionic species
ζ	Zeta potential
$\tilde{\zeta}$	Scaled zeta potential

Introduction

Our understanding of diffusiophoresis, that is, the motion of charged colloidal particles in an electrolyte concentration gradient, has been advanced by a lot of theoretical studies [1–24]. In particular, the readers should refer to a review article by Keh [8]. Experimentally observed diffusiophoretic mobility of latex particles was in good agreement theoretical results [25]. In a previous paper [24], we derived a general expression for the diffusiophoretic mobility of a spherical particle of radius a in a solution of symmetrical electrolytes of Debye-Hückel parameter κ. On the basis of this general expression, we obtained an approximate diffusiophoretic velocity expression correct to the order of $1/\kappa a$, which is found to be applicable for $\kappa a \geq 20$ at arbitrary values of the particle zeta potential. The obtained expression takes a much

---

✉ Hiroyuki Ohshima
ohshima@rs.noda.tus.ac.jp

[1] Faculty of Pharmaceutical Sciences, Tokyo University of Science, 2641 Yamazaki Noda, Chiba 278-8510, Japan

simpler form than those previously obtained. The leading-order term of the expression is correct to the order of $(1/\kappa a)^0$, which is applicable for $\kappa a \geq 50$ with negligible errors. In the present paper, we extend the previous theory for the case of symmetrical electrolytes to the diffusiophoresis of large spherical particles in a solution of general electrolytes and obtain approximate diffusiophoretic velocity expressions correct to the order of $(1/\kappa a)^0$. Our theory is based on the standard Poisson-Boltzmann theory on the electrical diffuse double layer around a colloidal particle. A comprehensive review of recent advances in the theory of diffuse double layer accounting for the effects of structural details of the ions and the solvent was given by Bohinc et al. [26]. The analytic expressions for the diffusiophoretic velocity of colloidal particles derived in the present paper can thus be applied to the case where the above effects may be neglected.

Theory

Consider a spherical particle of radius a moving with diffusiophoretic velocity $\boldsymbol{U}$ in an aqueous liquid of viscosity η and relative permittivity ε_r containing a general electrolyte under a constant applied gradient of electrolyte concentration. We suppose that the electrolyte consists of N ionic species with valence z_i and drag coefficient λ_i ($i = 1, 2, \ldots, N$). Let n_i^∞ be the bulk concentration (number density) of the i th ionic species in the absence of the applied electrolyte concentration gradient. The electroneutrality condition is given by $\sum_{i=1}^{N} z_i n_i^\infty = 0$. Let $n_i(\boldsymbol{r})$ be the concentration (number density) of the i th ionic species at position $\boldsymbol{r}$. The concentration gradient for the i th ionic species is expressed as ∇n_i in the region beyond the electrical double layer around the particle. We treat the case where all the ionic species have the same relative concentration gradient $\nabla n_i / n_i^\infty$ and introduce a constant vector $\boldsymbol{\alpha}$ proportional to ∇n_{oi}:

$$\boldsymbol{\alpha} = \frac{kT}{en_1^\infty}\nabla n_1 = \frac{kT}{en_2^\infty}\nabla n_2 = \cdots = \frac{kT}{en_N^\infty}\nabla n_N \tag{1}$$

where e is the elementary electric charge, k is the Boltzmann constant, and T is the absolute temperature. 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 $\boldsymbol{a}$. For a spherical particle, $\boldsymbol{U}$ is parallel to $\boldsymbol{a}$. We treat the case where the following conditions are satisfied: (i) The electrolyte concentration gradient field $\boldsymbol{a}$ is weak so that U is linear in a, where $a = |\boldsymbol{a}|$ and U is the magnitude with sign of $\boldsymbol{U}$ (positive (negative) values of U correspond to migration toward higher (lower) electrolyte concentration). (ii) In the absence of $\boldsymbol{a}$, the particle has a uniform surface potential, which is regarded as the particle zeta potential z at $r = a$, where $r = |\boldsymbol{r}|$. (iii) 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. (iv) Electrolyte ions cannot penetrate the particle surface. (v) The liquid flow velocity relative to the particle is zero at the particle surface.

The Navier-Stoke equation for a steady incompressible liquid flow velocity $\boldsymbol{u}(\boldsymbol{r}) = (u_r(\boldsymbol{r}), u_\theta(\boldsymbol{r}), 0)$ at low Reynolds numbers and the continuity equation for $\boldsymbol{u}(\boldsymbol{r})$ are given by

$$\eta\Delta\boldsymbol{u}(\boldsymbol{r}) - \nabla p(\boldsymbol{r}) - \rho_{\mathrm{el}}(\boldsymbol{r})\nabla\psi(\boldsymbol{r}) = \boldsymbol{0} \tag{2}$$

$$\nabla \cdot \boldsymbol{u}(\boldsymbol{r}) = 0 \tag{3}$$

where $p(\boldsymbol{r})$ is the pressure, $\psi(\boldsymbol{r})$ is the electric potential, and $\rho_{\mathrm{el}}(\boldsymbol{r})$ is the charge density given by

$$\rho_{\mathrm{el}}(\boldsymbol{r}) = \sum_{i=1}^{N} z_i e n_i(\boldsymbol{r}) \tag{4}$$

The velocity $\boldsymbol{v}_i(\boldsymbol{r}) = (v_{ir}(\boldsymbol{r}), v_{i\theta}(\boldsymbol{r}), 0)$ of the i th ionic species, which is given by

$$\boldsymbol{v}_i(\boldsymbol{r}) = \boldsymbol{u}(\boldsymbol{r}) - \frac{1}{\lambda_i}\nabla\mu_i(\boldsymbol{r}) \tag{5}$$

satisfies the following continuity condition:

$$\nabla \cdot (n_i \boldsymbol{v}_i(\boldsymbol{r})) = 0 \tag{6}$$

where

$$\mu_i(\boldsymbol{r}) = \mu_o^i + z_i e\psi(\boldsymbol{r}) + kT\ln n_i(\boldsymbol{r}) \tag{7}$$

is the electrochemical potential of the i th ionic species and μ_o^i is a constant terms of $\mu_i(\boldsymbol{r})$.

The deviations of $n_i(\boldsymbol{r})$, $\psi(\boldsymbol{r})$, $\mu_i(\boldsymbol{r})$, and $\rho_{\mathrm{el}}(\boldsymbol{r})$ from their equilibrium values are small for a weak field $\boldsymbol{a}$, so that we may write

$$n_i(\boldsymbol{r}) = n_i^{(0)}(r) + \delta n_i(\boldsymbol{r}) \tag{8}$$

$$\psi(\boldsymbol{r}) = \psi^{(0)}(r) + \delta\psi(\boldsymbol{r}) \tag{9}$$

$$\mu_i(\boldsymbol{r}) = \mu_i^{(0)} + \delta\mu_i(\boldsymbol{r}) \tag{10}$$

$$\rho_{\mathrm{el}}(\boldsymbol{r}) = \rho_{\mathrm{el}}^{(0)}(r) + \delta\rho_{\mathrm{el}}(\boldsymbol{r}) \tag{11}$$

where the quantities with superscript (0) refer to those at equilibrium in the absence of $\boldsymbol{a}$.

We assume that the equilibrium concentration $n_i^{(0)}(r)$ obeys the Boltzmann distribution and the equilibrium electric potential $y^{(0)}(r)$ satisfies the Poisson-Boltzmann equation, viz.,

$$n_i^{(0)}(r) = n_i^{\infty}(r)e^{-z_i y(r)} \tag{12}$$

$$\Delta y(r) = -\kappa^2 \frac{\sum_{i=1}^{N} z_i n_i^{\infty} e^{-z_i y(r)}}{\sum_{i=1}^{N} z_i^2 n_i^{\infty}} \tag{13}$$

with

$$y(r) = \frac{e\psi^{(0)}(r)}{kT} \tag{14}$$

$$\kappa = \sqrt{\frac{\sum_{i=1}^{N} z_i^2 e^2 n_i^{\infty}}{\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}} kT}} \tag{15}$$

where $y(r)$ is the scaled equilibrium electric potential, κ is the Debye-Hückel parameter, and ε_{o} is the permittivity of a vacuum.

The boundary conditions for $n_i^{(0)}(r)$, $\psi^{(0)}(r)$,$\boldsymbol{u}(\boldsymbol{r})$, and $\delta n_i(\boldsymbol{r})$ are given by

$$n_i^{(0)}(r) \to n_i^{\infty} \text{ as } r \to \infty \tag{16}$$

$$\psi^{(0)}(r) \to 0 \text{ as } r \to \infty \tag{17}$$

$$\psi^{(0)}(a) = \zeta \tag{18}$$

$$\boldsymbol{u}(\boldsymbol{r}) \to -\boldsymbol{U} \text{ as } r \to \infty \tag{19}$$

$$\boldsymbol{u}(\boldsymbol{r}) = 0 \text{ at } r = a \tag{20}$$

$$\delta n_i(\boldsymbol{r}) \to \left|\nabla n_i\right| r\cos\theta = \frac{e n_i^{\infty}}{kT}\alpha r\cos\theta \text{ as } r \to \infty \tag{21}$$

The ionic flows $\boldsymbol{v}_i(\boldsymbol{r})$ induce the diffusion potential field, which nullifies the net electric current. The electric current density $\boldsymbol{i}(\boldsymbol{r})$ is given by

$$\boldsymbol{i}(\boldsymbol{r}) = \sum_{i=1}^{N} z_i e n_i(\boldsymbol{r})\boldsymbol{v}_i(\boldsymbol{r}) \tag{22}$$

By substituting Eqs. (5), (8), and (10) into Eq. (22) and neglecting the products of the small quantities $\boldsymbol{u}$, δn_i, and $\delta\mu_i$, we obtain

$$\boldsymbol{i}(\boldsymbol{r}) = \rho_{\mathrm{el}}^{(0)}(r)\boldsymbol{u}(\boldsymbol{r}) - \sum_{i=1}^{N} \frac{z_i e}{\lambda_i} n_i^{(0)}(r)\nabla\delta\mu_i(\boldsymbol{r}) \tag{23}$$

which must be zero beyond the particle double layer. We thus find that (see Appendix)

$$\delta\psi(\boldsymbol{r}) \to -\beta\alpha r\cos\theta \text{ as } r \to \infty \tag{24}$$

with

$$\beta = \frac{\sum_{i=1}^{N} \frac{z_i n_i^{\infty}}{\lambda_i}}{\sum_{i=1}^{N} \frac{z_i^2 n_i^{\infty}}{\lambda_i}} = \frac{\sum_{i=1}^{N} \frac{n_i^{\infty}}{z_i m_i}}{\sum_{i=1}^{N} \frac{n_i^{\infty}}{m_i}} \tag{25}$$

where

$$m_i = \frac{2\varepsilon_{\mathrm{r}}\varepsilon_{\mathrm{o}} kT}{3\eta z_i^2 e^2}\lambda_i \tag{26}$$

is the scaled drag coefficient of i th ionic species. It follows from Eqs. (21) and (24) that the boundary condition for $\delta\mu_i(\boldsymbol{r})$ is given by

$$\delta\mu_i(\boldsymbol{r}) = z_i e\delta\psi(\boldsymbol{r}) + kT\frac{\delta n_i(\boldsymbol{r})}{n_i^{\infty}} \to z_i e\left(\frac{1}{z_i} - \beta\right)\alpha r\cos\theta \text{ as } r \to \infty \tag{27}$$

Finally, the boundary condition for $\boldsymbol{v}_i(\boldsymbol{r})$ is given by

$$v_{ir}(\boldsymbol{r}) = 0 \text{ at } r = a \tag{28}$$

which follows from the condition (iv). In addition, we have the constraint that the net force acting on the particle must be zero.

By symmetry, we may write

$$\delta\mu_i(\boldsymbol{r}) = -z_i e\alpha\phi_i(r)\cos\theta \tag{29}$$

$$\boldsymbol{u}(\boldsymbol{r}) = \left(-\frac{2}{r}h(r)\alpha\cos\theta, \frac{1}{r}\frac{d}{dr}[rh(r)]\alpha\sin\theta, 0\right) \tag{30}$$

where $\phi_i(r)$ and $h(r)$ are functions of r. By substituting Eqs. (29) and (30) into Eqs. (2)–(6), the following equations for $\phi_i(r)$ and $h(r)$ are obtained:

$$L\phi_i(r) = g_i(r) \tag{31}$$

$$L(Lh(r)) = G(r) \tag{32}$$

with

$$L = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} \tag{33}$$

$$g_i(r) = \frac{dy}{dr}\left(z_i\frac{d\phi_i}{dr} - \frac{2\lambda_i}{e}\frac{h}{r}\right) \tag{34}$$

$$G(r) = -\frac{e}{\eta r}\frac{dy}{dr}\sum_{i=1}^{N} z_i^2 n_i^{\infty} e^{-z_i y}\phi_i(r) \tag{35}$$

The boundary conditions, Eqs. (19), (20), (27), and (28) reduce to

$$\frac{d\phi_i}{dr} = 0 \text{ at } r = a \tag{36}$$

$$\phi_i(r) \to \left(-\frac{1}{z_i} + \beta\right) r \text{ as } r \to \infty \tag{37}$$

$$h = \frac{dh}{dr} = 0 \text{ at } r = a \tag{38}$$

$$h(r) \to \frac{U}{2\alpha} r + O\left(\frac{1}{r}\right) \text{as } \ r \to \infty \tag{39}$$

Equations (31) and (32) subject to Eqs. (36)–(39) can be solved to give

$$\phi_i(r) = \left(-\frac{1}{z_i} + \beta\right)\left(r + \frac{a^3}{2r^2}\right) - \frac{1}{3}\left(r + \frac{a^3}{2r^2}\right)\int_a^\infty g_i(r)dr + \frac{1}{3}\int_a^r \left(r - \frac{x^3}{r^2}\right) g_i(x)dx \tag{40}$$

and

$$h(r) = -\left(\frac{r^3}{30} - \frac{a^2 r}{18} + \frac{a^5}{45r^2}\right)\int_a^\infty G(x)dx + \left(\frac{r}{9a} - \frac{1}{6} + \frac{a^2}{18r^2}\right)\int_a^\infty x^3 G(x)dx - \int_a^r \left(-\frac{r^3}{30} + \frac{rx^2}{6} - \frac{x^3}{6} + \frac{x^5}{30r^2}\right) G(x)dx \tag{41}$$

By using Eq. (39), the magnitude (with sign) U of the diffusiophoretic velocity $\boldsymbol{U}$ is given by

$$U = 2\alpha \lim_{r\to\infty} \frac{h(r)}{r} \tag{42}$$

From Eqs. (41) and (42), we find that

$$U = \frac{\alpha a^2}{9}\int_a^\infty \left(1 - \frac{3r^2}{a^2} + \frac{2r^3}{a^3}\right) G(r)dr \tag{43}$$

We note that the fundamental electrokinetic equations for the electrophoresis and diffusiophoresis problems are the same except for the boundary condition for $\phi_i(r)$ for $r \to \infty$. Indeed, Eq. (43) is obtained from the expression for the electrophoretic velocity of a spherical particle in an applied electric field $\boldsymbol{E}$ [27–29] by replacing $\boldsymbol{E}$ with $\boldsymbol{\alpha}$. Thus, by applying the same approximation method as in Ref. [28], we can derive similar approximate formulas for the diffusiophoretic velocity U correct to order $(1/\kappa a)^0$ with the same accuracy as those derived for the electrophoresis problem [28]. We define the scaled diffusiophoretic mobility U^* as

$$U^* = \frac{3\eta e}{2\varepsilon_r \varepsilon_o kT}\frac{U}{\alpha} \tag{44}$$

We give the results applicable for large particles with $\kappa a \geq 50$ at arbitrary values of ζ as follows.

$$U^* = -\frac{1}{2a}\sum_{i=1}^{N} z_i n_i^\infty \phi_i(a) \int_0^{\tilde{\zeta}} \left\{ \int_0^y \frac{e^{-z_i y'} - 1}{K(y')} dy' \right\} \frac{dy}{K(y)} \tag{45}$$

with

$$\phi_i(a) = -\frac{3}{2}\left(\frac{1}{z_i} - \beta\right) a + sgn(\zeta)\frac{\phi_i(a)}{\kappa a} W \int_0^{\tilde{\zeta}} \frac{e^{-z_i y} - 1}{K(y)} dy + sgn(\zeta)\frac{3 z_i m_i}{4\kappa a} W \int_0^{\tilde{\zeta}} \left[(e^{-z_i y} - 1) \sum_{i=1}^{N} z_i n_i^\infty \phi_i(a) \int_{\tilde{\zeta}}^{y} \left\{ \int_0^{y'} \frac{e^{-z_j y''} - 1}{K(y'')} dy'' \right\} \frac{dy'}{K(y')} \right] \frac{dy}{K(y)} \tag{46}$$

$$\tilde{\zeta} = \frac{e\zeta}{kT} \tag{47}$$

and

$$W = \sqrt{\frac{1}{2}\sum_{i=1}^{N} z_i^2 n_i^\infty}, \quad K(y) = \sqrt{\sum_{i=1}^{N} n_i^\infty (e^{-z_i y} - 1)} \tag{48}$$

where $\tilde{\zeta}$ is the scale zeta potential and $sgn(\zeta)$ is + 1(-1) if $\zeta > 0$ ($\zeta < 0$).

Results and discussion

We have derived the general expression (45) for the scaled diffusiophoretic mobility U^*. We give below explicit expressions for U^* for the case of binary electrolytes.

(i) z_+:z_- binary electrolytes ($z_+ > 0$ and $z_- < 0$)

$$U^* = -\frac{1}{2a}\int_0^{\tilde{\zeta}} \left\{ \int_0^y \frac{\phi_+(a)\left(e^{-z_+ y'} - 1\right) - \phi_-(a)\left(e^{-z_- y'} - 1\right)}{M(y')} dy' \right\} \frac{dy}{M(y)} \tag{49}$$

with

$$M(y) = \sqrt{(e^{-z_+ y} - 1)/z_+ - (e^{-z_- y} - 1)/z_-} \tag{50}$$

$$\frac{\phi_+(a)}{a} = -\frac{3}{2}\left(\frac{1}{z_+} - \beta\right), \ \frac{\phi_-(a)}{a} = -\frac{3}{2}\left(\frac{1}{z_-} - \beta\right)\frac{1}{(1+F)} \text{ for } \ \tilde{\zeta} > 0 \tag{51}$$

$$\frac{\phi_+(a)}{a} = -\frac{3}{2}\left(\frac{1}{z_+} - \beta\right)\frac{1}{(1+F)}, \ \frac{\phi_-(a)}{a} = -\frac{3}{2}\left(\frac{1}{z_-} - \beta\right) \text{for } \ \tilde{\zeta} < 0 \tag{52}$$

$$F = \frac{1}{\kappa a}\sqrt{2\left(1 - \frac{z_+}{z_-}\right)}\left(1 + 3m_-\right)\left(e^{-z_-\tilde{\zeta}/2} - 1\right)\text{for } \tilde{\zeta} > 0 \tag{53}$$

$$F = \frac{1}{\kappa a}\sqrt{2\left(1 - \frac{z_-}{z_+}\right)}\left(1 + 3m_+\right)\left(e^{-z_+\tilde{\zeta}/2} - 1\right)\text{for } \tilde{\zeta} < 0 \tag{54}$$

$$\beta = \frac{(z_+/z_-)m_+ - (z_-/z_+)m_-}{z_+m_+ - z_-m_-},\ m_+ = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta z_+^2 e^2}\lambda_+,\ m_- = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta z_-^2 e^2}\lambda_- \tag{55}$$

(ii) z:z symmetrical electrolytes ($z_+ = -z_- = z > 0$)

$$U^* = \frac{6}{z^2(m_+ + m_-)}\left\{m_+\ln\left(\frac{1 + e^{-z\tilde{\zeta}/2}}{2}\right) + \frac{m_-}{(1+F)}\ln\left(\frac{1 + e^{z\tilde{\zeta}/2}}{2}\right)\right\}\text{ for } \zeta > 0 \tag{56}$$

$$U^* = \frac{6}{z^2(m_+ + m_-)}\left\{\frac{m_+}{(1+F)}\ln\left(\frac{1 + e^{-z\tilde{\zeta}/2}}{2}\right) + m_-\ln\left(\frac{1 + e^{z\tilde{\zeta}/2}}{2}\right)\right\}\text{ for } \zeta > 0 \tag{57}$$

with

$$F = \frac{2}{\kappa a}\left(1 + 3m_-\right)\left(e^{z\tilde{\zeta}/2} - 1\right)\text{for } \tilde{\zeta} > 0 \tag{58}$$

$$F = \frac{2}{\kappa a}\left(1 + 3m_+\right)\left(e^{-z\tilde{\zeta}/2} - 1\right)\text{ for } \tilde{\zeta} < 0 \tag{59}$$

$$m_+ = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta z^2 e^2}\lambda_+,\ m_- = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta z^2 e^2}\lambda_- \tag{60}$$

Note that Eqs. (56) and (57) differ from Eq. (54) in Ref. [23] by a factor of $1/z^2$, because of the different definitions of U^* and $\boldsymbol{a}$.

In the limit of $\kappa a \to \infty$, Eqs. (56) and (57) reduce to

$$U^* = \frac{3}{2z^2}\left\{4\ln\left(\cosh\left(\frac{z\tilde{\zeta}}{4}\right)\right) - \left(\frac{m_+ - m_-}{m_+ + m_-}\right)z\tilde{\zeta}\right\} \tag{61}$$

which agrees with previously derived well-known expression [1–3]

(iii) 2:1 electrolytes

$$U^* = -\frac{3}{2}\left(\frac{1}{2} - \beta\right)\tilde{\zeta} + \frac{3\{3 + (1 - 2\beta)F\}}{2(1+F)}\ln\left(\frac{1}{2} + \frac{1}{2}\sqrt{\frac{2}{3}e^{\tilde{\zeta}} + \frac{1}{3}}\right)\text{ for } \tilde{\zeta} > 0 \tag{62}$$

$$U^* = \frac{3}{2}(1 + \beta)\tilde{\zeta} + \frac{3\{3 + 2(1 + \beta)F\}}{2(1+F)}\ln\left(\frac{e^{-\tilde{\zeta}/2}}{2} + \frac{1}{2}\sqrt{\frac{1}{3}e^{-\tilde{\zeta}} + \frac{2}{3}}\right)\text{ for } \tilde{\zeta} < 0 \tag{63}$$

with

$$F = \frac{\sqrt{6}}{\kappa a}\left(1 + 3m_-\right)\left(e^{\tilde{\zeta}/2} - 1\right)\text{ for } \tilde{\zeta} > 0 \tag{64}$$

$$F = \frac{\sqrt{3}}{\kappa a}\left(1 + 3m_+\right)\left(e^{-\tilde{\zeta}} - 1\right)\text{ for } \tilde{\zeta} < 0 \tag{65}$$

$$\beta = -\frac{4m_+ - m_-}{2\left(2m_+ + m_-\right)},\ m_+ = \frac{\varepsilon_r\varepsilon_o kT}{6\eta e^2}\lambda_+,\ m_- = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta e^2}\lambda_-, \tag{66}$$

(iv) 1:2 electrolytes

$$U^* = -\frac{3}{2}(1 - \beta)\tilde{\zeta} + \frac{3\{3 + 2(1 - \beta)F\}}{2(1+F)}\ln\left(\frac{e^{\tilde{\zeta}/2}}{2} + \frac{1}{2}\sqrt{\frac{1}{3}e^{\tilde{\zeta}} + \frac{2}{3}}\right)\text{for } \tilde{\zeta} > 0 \tag{67}$$

$$U^* = \frac{3}{2}\left(\frac{1}{2} + \beta\right)\tilde{\zeta} + \frac{3\{3 + (1 + 2\beta)F\}}{2(1+F)}\ln\left(\frac{1}{2} + \frac{1}{2}\sqrt{\frac{2}{3}e^{-\tilde{\zeta}} + \frac{1}{3}}\right)\text{for } \tilde{\zeta} < 0 \tag{68}$$

with

$$F = \frac{\sqrt{3}}{\kappa a}\left(1 + 3m_-\right)\left(e^{\tilde{\zeta}} - 1\right)\text{ for } \tilde{\zeta} > 0 \tag{69}$$

$$F = \frac{\sqrt{6}}{\kappa a}\left(1 + 3m_+\right)\left(e^{-\tilde{\zeta}/2} - 1\right)\text{ for } \tilde{\zeta} < 0 \tag{70}$$

$$\beta = -\frac{m_+ - 4m_-}{2\left(m_+ + 2m_-\right)},\ m_+ = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta e^2}\lambda_+,\ m_- = \frac{2\varepsilon_r\varepsilon_o kT}{6\eta e^2}\lambda_- \tag{71}$$

Note that F corresponds to Dukhin's number.

Figure 1 shows examples of the results of the calculation of the reduced diffusiophoretic velocity U^* of a charged spherical particle of radius a calculated with Eqs. (56) and (57) as a function of the particle zeta potential ζ for $m_+ = 0.176$ and $m_- = 0.169$, which are, respectively, the values of m_+ for K$^+$ ions and m_- for Cl$^-$ ions in an aqueous KCl solution at 25 °C. Figures 2, 3, respectively, show the results for MgCl$_2$ with $m_+ = 0.122$ and $m_- = 0.169$ at 25 °C and those for LaCl$_3$ with $m_+ = 0.0618$ and $m_- = 0.169$ at 25 °C. It is seen that there are maxima in the mobility curves plotted as a function of the particle zeta potential ζ. This is caused by the relaxation effect, which becomes appreciable for higher zeta potential values as in the electrophoresis problem. We also note that U^* reaches a nonzero finite value as the magnitude of the zeta potential tends to infinity. This is a kind of counterion condensation effect, as in the case of electrophoresis [30, 31]. The limiting values for several types of electrolytes can be obtained from the above expressions for U^* with the result that.

(i) z:z symmetrical electrolytes

$$U^* \to -\frac{6m_+}{z^2\left(m_+ + m_-\right)}\ln 2 \text{ as } \tilde{\zeta} \to +\infty \tag{72}$$

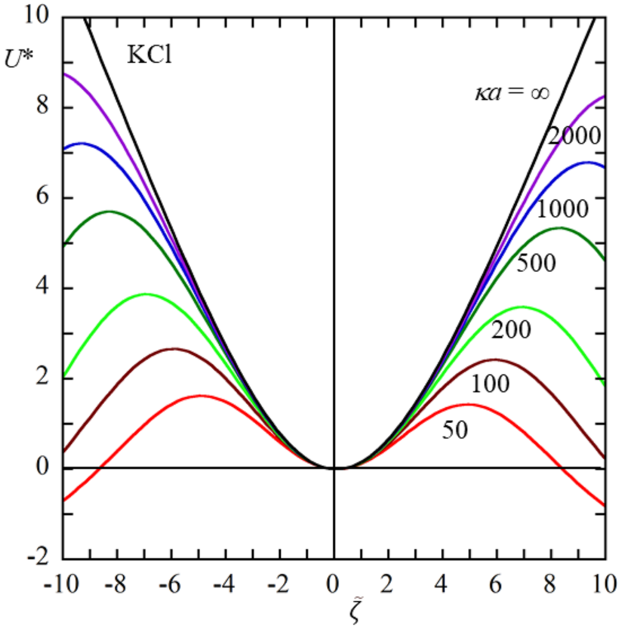

Fig. 1 Scaled diffusiophoretic mobility U^* of a spherical particle of radius a as a function of scaled zeta potential ζ for various values of κa in an aqueous KCl solution at 25 °C. Calculated with Eqs. (56) and (57)

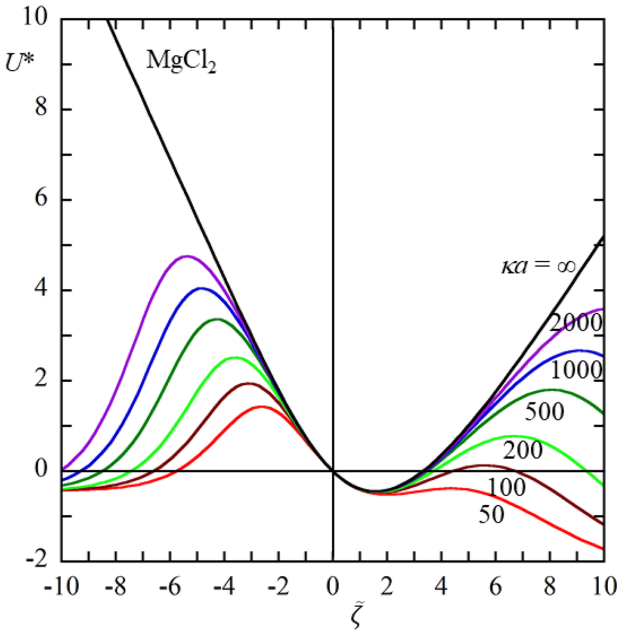

Fig. 2 Same as Fig. 1 but for MgCl$_2$. Calculated with Eqs. (62) and (63)

$$U^* \to -\frac{6m_-}{z^2\left(m_+ + m_-\right)}\ln 2 \text{ as } \tilde{\zeta} \to -\infty \tag{73}$$

(ii) 2:1 electrolytes

$$U^* \to -\frac{3}{4}(1 - 2\beta)\ln 6 \text{ as } \tilde{\zeta} \to +\infty \tag{74}$$

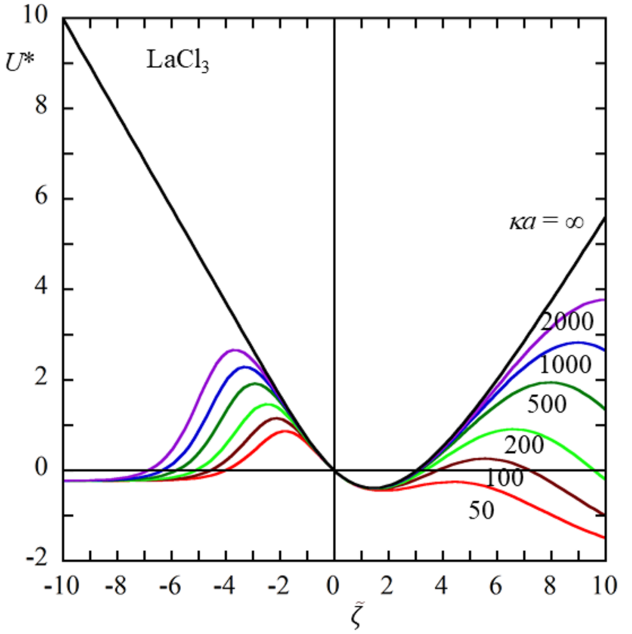

Fig. 3 Same as Fig. 1 but LaCl$_3$. Calculated with Eq. (49)

$$U^* \to -3(1+\beta)\ln\left(3-\sqrt{3}\right) \text{as } \tilde{\zeta} \to -\infty \tag{75}$$

(iii) 1:2 electrolytes

$$U^* \to -3(1-\beta)\ln\left(3-\sqrt{3}\right) \text{ as } \tilde{\zeta} \to +\infty \tag{76}$$

$$U^* \to -\frac{3}{4}(1+2\beta)\ln 6 \text{ as } \tilde{\zeta} \to -\infty \tag{77}$$

Concluding remarks

We have derived the general expression for the diffusiophoretic mobility U^* of a spherical colloidal particle of radius a in a concentration gradient of general electrolyte (Eq. (43)). On the basis of this expression, we have derived simple approximate analytic expressions for U correct up to the order of $(1/\kappa a)^0$ (Eq. (45)) applicable for large particles with $\kappa a \geq 50$ at arbitrary zeta potential with negligible errors. Explicit expressions for U^* for particles in z_+:z_-, z:z, 2:1, and 1:2 electrolyte solutions are given (Eqs. (49), (56), (57), (62), (63), (67), and (68)).

Appendix

Equation (24) can be derived from Eq. (23) as follows. Since beyond the particle double layer, $\rho_{\mathrm{el}}^{(0)}(r) \to 0$ and $n_i^{(0)}(r) \to n_i^\infty$, we obtain from Eq. (23)

$$\sum_{i=1}^{N} \frac{z_i e n_i^\infty}{\lambda_i} \nabla \delta\mu_i(\boldsymbol{r}) \to 0 \text{ as } r \to \infty \tag{78}$$

From Eqs. (7) and (10), we have

$$\nabla \delta\mu_i(\boldsymbol{r}) = z_i e \nabla \delta\psi(\boldsymbol{r}) + kT\frac{\nabla \delta n_i}{n_i^\infty} \tag{79}$$

By substituting Eq. (79) into Eq. (78) and using Eq. (21), we obtain Eq. (24). Here, it must be noted that unlike the electrophoresis problem, in the diffusiophoresis problem dn_i does not tend to zero but to a nonzero value given by Eq. (21).

Declarations

Conflict of interest The author declares no competing interests.

References

1. Derjaguin BV, Dukhin SS, Korotkova AA (1961) Diffusiophoresis in electrolyte solutions and its role in the mechanism of film formation of cationic latex by ionic deposition. Kolloidyni Zh 23:53–58
2. Prieve DC (1982) Migration of a colloidal particle in a gradient of electrolyte concentration. Adv Colloid Interface Sci 16:321–335
3. Prieve DC, Anderson JL, Ebel JP, Lowell ME (1984) Motion of a particle generated by chemical gradients. Part 2. Electrolytes J Fluid Mech 148:247–269
4. Prieve DC, Roman R (1987) Diffusiophoresis of a rigid sphere through a viscous electrolyte solution. J Chem Soc Faraday Trans II 83:1287–1306
5. Anderson JL (1989) Colloid transport by interfacial forces. Ann Rev Fluid Mech 21:61–99
6. Pawar Y, Solomentsev YE, Anderson JL (1993) Polarization effects on diffusiophoresis in electrolyte gradients. J Colloid Interface Sci 155:488–498
7. Keh HJ, Chen SB (1993) Diffusiophoresis and electrophoresis of colloidal cylinders. Langmuir 9:1142–1149
8. Keh HJ (2016) Diffusiophoresis of charged particles and diffusioosmosis of electrolyte solutions. Curr Opin Colloid Interface Sci 24:13–22
9. Keh HJ, Wei YK (2000) Diffusiophoretic mobility of spherical particles at low potential and arbitrary double-layer thickness. Langmuir 16:5289–5294
10. Tseng S, Su C-Y, Hsu J-P (2016) Diffusiophoresis of a charged, rigid sphere in a Carreau fluid. J Colloid Interface Sci 465:54–57
11. Hsu J-P, Hsieh S-H, Tseng S (2017) Diffusiophoresis of a pH-regulated polyelectrolyte in a pH-regulated nanochannel. Sensors Actuators B: Chemical 252:1132–1139
12. Chiu HC, Keh HJ (2017) Diffusiophoresis of a charged particle in a microtube. Electrophoresis 38:2468–2478
13. Chiu HC, Keh HJ (2017) Electrophoresis and diffusiophoresis of a colloidal sphere with double-layer polarization in a concentric charged cavity. Microfluid Nanofluid 21:45
14. Chiu YC, Keh HJ (2018) Diffusiophoresis of a charged porous particle in a charged cavity. J Phys Chem B 122:9803–9814
15. Chiu YC, Keh HJ (2018) Diffusiophoresis of a charged particle in a charged cavity with arbitrary electric double layer thickness. Microfluidics Nanofluidics 22:84
16. Yeh YZ, Keh HJ (2018) Diffusiophoresis of a charged porous shell in electrolyte gradients. Colloid Polym Sci 296:451–459
17. Gupta A, Rallabandi B, Howard A, Stone HA (2019) Diffusiophoretic and diffusioosmotic velocities for mixtures of valence-asymmetric electrolytes. Phys Rev Fluids 4:043702
18. Gupta A, Shim S, Stone HA (2020) Diffusiophoresis: from dilute to concentrated electrolytes. Soft Matter 16:6975–6984
19. Lin WC, Keh HJ (2020) Diffusiophoresis in suspensions of charged soft particles. Colloids Interfaces 4:30
20. Sin S (2020) Diffusiophoretic separation of colloids in microfluidic flows. Phys Fluids 32:101302
21. Wu Y, Chang W-C, Fan L, Jian E, Tseng J, Lee E (2021) Diffusiophoresis of a highly charged soft particle in electrolyte solutions induced by diffusion potential Phys. Fluids 33:012014
22. Wu Y, Lee E (2021) Diffusiophoresis of a highly charged soft particle normal to a conducting plane. Electrophoresis. https://doi.org/10.1002/elps.202100052
23. Majee PS, Bhattacharyya S (2021) Impact of ion partitioning and double layer polarization on diffusiophoresis of a pH-regulated nanogel. Meccanica 56:1989–2004

24. Ohshima H (2021) Approximate analytic expressions for the diffusiophoretic velocity of a spherical colloidal particle. Electrophoresis. https://doi.org/10.1002/elps.202100178
25. Ebel JP, Anderson JL, Prieve DC (1988) Diffusiophoresis of latex particles in electrolyte gradients. Langmuir 4:396–406
26. Bohinc K, Bossa GV, May S (2017) Incorporation of ion and solvent structure into mean-field modeling of the electric double layer. Adv Colloid Interface Sci 249:220–233
27. Ohshima H, Healy TW, White LR (1983) Approximate analytic expressions for the electrophoretic mobility of spherical colloidal particles and the conductivity of their dilute suspensions. J Chem Soc Faraday Trans II 79:1613–1628
28. Ohshima H (2005) Approximate expression for the electrophoretic mobility of a spherical colloidal particle in a solution of general electrolytes. Colloids Surf A: Physicochem Eng Asp 267:50–55
29. Ohshima H (2006) Theory of colloid and interfacial electric phenomena. Elsevier, Amsterdam
30. Ohshima H (2003) On the limiting electrophoretic mobility of a highly charged colloidal particle in an electrolyte solution. J Colloid Interface Sci 263:337–340
31. Ohshima H (2016) On the maximum of the magnitude of the electrophoretic mobility of a spherical colloidal particle in an electrolyte solution. Colloid Polym Sci 294:13–17