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Approximate expression for the electrophoretic mobility of a spherical colloidal particle in a solution of general electrolytes

Hiroyuki Ohshima*

Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

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Abstract

An approximate analytic expression is derived for the electrophoretic mobility of a charged spherical colloidal particle in a solution of general electrolytes on the basis of an approximation method by [Ohshima et al., J. Chem. Soc. Faraday Trans. 2, 79 (1983) 1613]. This expression, which takes into account the relaxation effects, is applicable for all values of zeta potential at large κa ($\kappa a \geq$ ca. 30), where κ is the Debye–Hückel parameter and a is the radius of the particle core.

Keywords: Electrophoretic mobility; Spherical colloidal particle; Zeta potential

1. Introduction

Theories of the electrophoretic mobility μ of a spherical particle of radius a carrying zeta potential ζ in an electrolyte solution of the Debye–Hückel parameter κ were presented by Smoluchowski [1], Hückel [2], and Henry [3]. These theories are applicable for limiting cases of large κa [1], small κa [2], or low ζ [3] (see also [4] and [5]). Full electrokinetic equations determining μ of spherical particles with arbitrary values of κa and ζ were given independently by Overbeek [6] and Booth [7]. Wiersema et al. [8] solved these equations numerically. The computer calculation of the electrophoretic mobility was considerably improved by O'Brien and White [9].

Approximate analytic mobility expressions other than those in [1–3] were proposed by several authors [6,7,10–13]. Two types of approximation methods have been devised to obtain the electrophoretic mobility. In the first method, the electrophoretic mobility is expressed in powers of zeta potential [6,7,13], while in the second method it is expressed in powers of $1/\kappa a$ [10–12]. In particular, Ohshima et al. [12] derived a mobility formula correct to order $1/\kappa a$ applicable for all values of ζ. This expression, however, is applicable only for a particle in a symmetrical electrolyte solution. In the present paper we extend Ohshima et al's method [12] to the case of a particle in a solution of general electrolytes.

2. Fundamental electrokinetic equations

Consider a spherical particle of radius a and zeta potential ζ moving with a velocity $\boldsymbol{U}$ in a liquid containing a general electrolyte composed of N ionic species with valence z_i and bulk concentration (number density) n_i^∞, and drag coefficient λ_i ($i = 1, 2, \ldots, N$). The origin of the spherical polar coordinate system (r, θ, ϕ) is held fixed at the center of the particle. From the electroneutrality condition, we have

$$\sum_{i=1}^{N} z_i n_i^\infty = 0. \tag{1}$$

The main assumptions in our analysis 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 applied field $\boldsymbol{E}$ is weak so that the particle velocity $\boldsymbol{U}$ is proportional to $\boldsymbol{E}$ and terms of higher order in $\boldsymbol{E}$ may be neglected; (iii) the

* Tel.: +81 4 7121 3661; fax: +81 4 7121 3661.
E-mail address: ohshima@rs.noda.tus.ac.jp.

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slipping plane is located on the particle surface (at $r=a$); and (iv) no electrolyte ions can penetrate the particle surface.

The fundamental electrokinetic equations are given by

$$\eta\nabla\times\nabla\times\boldsymbol{u}+\nabla p+\rho_{el}\,\nabla\psi=0, \tag{2}$$

$$\nabla\cdot\boldsymbol{u}=0, \tag{3}$$

$$\boldsymbol{v}_i=\boldsymbol{u}-\frac{1}{\lambda_i}\nabla\mu_i, \tag{4}$$

$$\nabla(n_i\boldsymbol{v}_i)=0, \tag{5}$$

$$\rho(\boldsymbol{r})=\sum_{i=1}^{N}z_ien_i(\boldsymbol{r}) \tag{6}$$

$$\mu_i(\boldsymbol{r})=\mu_i^{\mathrm{o}}+z_ie\psi(\boldsymbol{r})+kT\,\ln n_i(\boldsymbol{r}), \tag{7}$$

$$\Delta\psi(\boldsymbol{r})=-\frac{\rho(\boldsymbol{r})}{\varepsilon_r\varepsilon_{\mathrm{o}}}, \tag{8}$$

where ε_{r} is the relative permittivity of the electrolyte solution, ε_{o} is the permittivity of a vacuum, e is the elementary electric charge, $\boldsymbol{u}(\boldsymbol{r})$ is the liquid velocity at position $\boldsymbol{r}$, $\boldsymbol{v}_i$ is the velocity of the ith ionic species, $p(\boldsymbol{r})$ is the pressure, $\rho(\boldsymbol{r})$ is the charge density resulting from the mobile charged ionic species given by Eq. (6), $\psi(\boldsymbol{r})$ is the electric potential, $\mu_i(\boldsymbol{r})$ and $n_i(\boldsymbol{r})$ are, respectively, the electrochemical potential and the concentration (the number density) of the ith ionic species, and μ_i^{o} is a constant term in $\mu_i(\boldsymbol{r})$. Eqs. (2) and (3) are the Navier–Stokes equation and the equation of continuity for an incompressible flow. Eq. (4) expresses that the flow $\boldsymbol{v}_i(\boldsymbol{r})$ of the ith ionic species is caused by the liquid flow $\boldsymbol{u}(\boldsymbol{r})$ and the gradient of the electrochemical potential $\mu_i(\boldsymbol{r})$, given by Eq. (7). Eq. (5) is the continuity equation for the ith ionic species, and Eq. (8) is Poisson's equation. The drag coefficient λ_i of the ith ionic species is further related to the limiting conductance Λ_i^{o} of that ionic species by

$$\lambda_i=\frac{N_{\mathrm{A}}e^2\,|z_i|}{\Lambda_i^{\mathrm{o}}}, \tag{9}$$

where N_{A} is Avogadro's number.

We assume that the slipping plane, at which the liquid velocity $\boldsymbol{u}$ relative to the particle is zero coincides with the particle surface at $r=a$ (assumption (iii)). Then the above electrokinetic equations must be solved under the following boundary conditions.

$$\boldsymbol{u}=0\ \text{ at }\ r=a, \tag{10}$$

$$\boldsymbol{u}\to-\boldsymbol{U}\ \text{ as }\ r\to\infty. \tag{11}$$

In the stationary state the net force acting on the particle or an arbitrary volume enclosing the particle must be zero. Consider a large sphere S of radius r containing the particle (plus the electrical double layer around the particle) at its center. The radius r of S is taken to be sufficiently large so that the net electric charge within S is zero. There is then no electric force acting on S, and we need consider only hydrodynamic force $\boldsymbol{F}_{\mathrm{H}}$, which must be zero, i.e.,

$$\boldsymbol{F}_{\mathrm{H}}=\int_S\boldsymbol{\sigma}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}S\to0\ \text{ as }\ r\to\infty, \tag{12}$$

where the integration is carried out over the surface of S, $\boldsymbol{\sigma}$ is the hydrodynamic stress tensor and $\hat{\boldsymbol{n}}$ is the outward normal to S. Finally, the boundary condition for the velocity of the ionic flow $\boldsymbol{v}_i$ is given by

$$\boldsymbol{v}_i\cdot\hat{\boldsymbol{n}}|_{r=a}=0. \tag{13}$$

which states that no electrolyte ions can penetrate the particle surface (assumption (iv)).

3. Linearized equations

Under assumption (ii), we may write

$$n_i(\boldsymbol{r})=n_i^{(0)}(r)+\delta n_i(\boldsymbol{r}) \tag{14}$$

$$\psi(\boldsymbol{r})=\psi^{(0)}(r)+\delta\psi(\boldsymbol{r}) \tag{15}$$

$$\mu_i(\boldsymbol{r})=\mu_i^{(0)}+\delta\mu_i(\boldsymbol{r}) \tag{16}$$

$$\rho(\boldsymbol{r})=\rho^{(0)}(r)+\delta\rho(\boldsymbol{r}) \tag{17}$$

where the quantities with superscript (0) refer to those at equilibrium, i.e., in the absence of $\boldsymbol{E}$, and $\mu_i^{(0)}$ is a constant independent of $\boldsymbol{r}$.

We assume that the distribution of electrolyte ions at equilibrium $n^{(0)}(r)$ obeys the Boltzmann equation and the equilibrium potential $\psi^{(0)}(r)$ outside the particle satisfies the Poisson–Boltzmann equation, both being functions of r ($=|\boldsymbol{r}|$) only, viz.,

$$n_i^{(0)}=n_i^{\infty}\exp\left(-\frac{z_ie\psi^{(0)}}{kT}\right), \tag{18}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi^{(0)}}{\mathrm{d}r}\right)=-\frac{\rho_{\mathrm{el}}^{(0)}(r)}{\varepsilon_r\varepsilon_{\mathrm{o}}}, \tag{19}$$

with

$$\rho_{\mathrm{el}}^{(0)}(r)=\sum_{i=1}^{N}z_ien_i^{(0)}(r)=\sum_{i=1}^{N}z_ien_i^{\infty}\exp\left(-\frac{z_ie\psi^{(0)}}{kT}\right), \tag{20}$$

where k is Boltzmann's constant and T is the absolute temperature. The boundary conditions for $\psi^{(0)}(r)$ are

$$\psi^{(0)}(a)=\zeta, \tag{21}$$

$$\psi^{(0)}(r)\to0\ \text{ as }\ r\to\infty. \tag{22}$$

Further, symmetry considerations permit us to write

$$\boldsymbol{u}(\boldsymbol{r})=\left(-\frac{2}{r}h(r)E\cos\theta,\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}(rh(r))E\sin\theta,0\right), \tag{23}$$

$$\delta\mu_i(\boldsymbol{r})=-z_ie\phi_i(r)E\cos\theta \tag{24}$$