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SHORT COMMUNICATION

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On the electrophoretic mobility of a cylindrical soft particle

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Abstract A previous theory for the electrophoresis of a cylindrical soft particle (that is, a cylindrical hard particle covered with a layer of polyelectrolytes) [7], which makes use of the condition that the electrical force acting on the polymer segments is balanced with a frictional force exerted by the liquid flow, is modified by replacing this condition with an alternative and more appropriate boundary condition that pressure is continuous at the boundary between the surface layer and the surrounding electrolyte solution. The general mobility expression thus obtained is found to reproduce all of the approximate analytic mobility expressions derived previously.

Key words Electrophoretic mobility · Cylindrical particle · Soft particle

Introduction

We have developed a theory of electrophoresis of spherical [1–6] or cylindrical soft particles [7] (i.e., hard particles coated with a layer of polyelectrolytes) moving in an electrolyte solution. This theory is based on the Debye-Bueche [8] and Hermans-Fujita [9] model for a spherical porous particle, in which polymer segments are regarded as resistance centers distributed within the particle, exerting a frictional force on the liquid flowing inside the particle. In previous papers [1–5], in order to solve electrokinetic equations for electrophoresis of a soft particle, in addition to the condition that the net force acting on the soft particle as a whole (the particle core plus the polyelectrolyte layer) is zero, we employed the condition that the electric and frictional forces acting on the polyelectrolyte layer must be balanced with each other. This condition, however, leads to discontinuity of pressure at the boundary between the surface layer and the surrounding solution. Quite recently it has been shown that for a spherical soft particle replacement of the force balance condition for the polyelectrolyte layer with the condition that the pressure is continuous at the surface layer/solution boundary leads to more consistent results [5, 6]. In the present paper, we make a similar modification of the previous theory [7] of electrophoresis of cylindrical soft particle by using the pressure continuity condition. It will be shown that the obtained general mobility expression reproduces approximate mobility expressions derived in a previous paper [7]. Since the mobility expression for a cylinder in a tangential field remains unchanged with this modification, we confine ourselves to the electrophoretic mobility of a soft cylinder in a transverse field in the following.

General mobility expression for a cylindrical soft particle in a transverse field

Consider an infinitely long cylindrical colloidal particle moving with a velocity **U** in a liquid containing a general electrolyte in an applied electric field **E**. The origin of the cylindrical polar coordinate system (r, θ, φ) is held fixed at the particle. In this section we treat the case where the cylinder axis coincides with the z-axis and the polar axis ($\theta = 0$) is set parallel to **E** so that **E** is perpendicular to the cylinder axis (Fig. 1). We assume that the particle core of radius a is coated with an ion-penetrable layer of

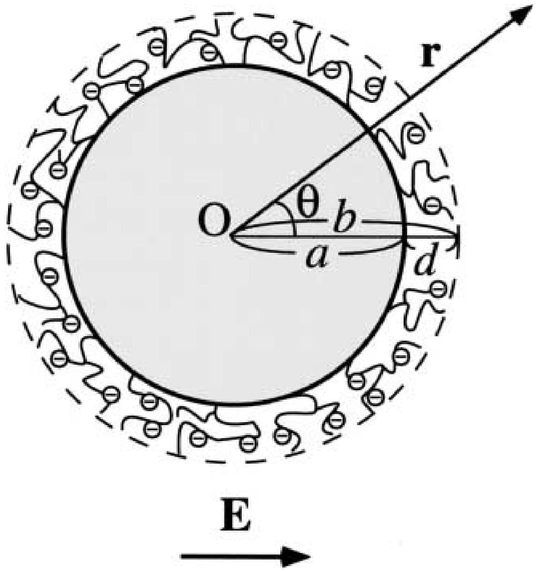

Fig. 1 A cylindrical soft particle moving in a transverse electric field **E**. a = radius of the particle core, d = thickness of the polyelectrolyte layer covering the particle core, $b = a + d$

polyelectrolytes with a thickness d. The polyelectrolyte-coated particle has thus an inner radius a and an outer radius $b \cong a + d$. The relative permittivity ε_r takes the same value both inside and outside the polyelectrolyte layer. Let the electrolyte be composed of M ionic mobile species of valence z_i, bulk concentration (number density) n_i^∞ and drag coefficient λ_i ($i = 1, 2, \ldots, M$). We also assume that fixed charges are distributed with a density of $\rho_{\text{fix}}(r)$, which is a cylindrically-symmetrical function of $r = |\mathbf{r}|$ only. If dissociated groups of valence Z are distributed with a constant density (number density) N within the polyelectrolyte layer, then we have $\rho_{\text{fix}} = ZeN$, where e is the elementary electric charge.

The fundamental electrokinetic equations can be expressed in terms of the liquid velocity $\mathbf{u}(\mathbf{r})$ at position $\mathbf{r}$ relative to the particle ($\mathbf{u}(\mathbf{r}) \to -\mathbf{U}$ as $r \to \infty$) and the deviation $\delta\mu_i(\mathbf{r})$ of the electrochemical potential $\mu_i(\mathbf{r})$ of the i-th ionic species due to the applied field $\mathbf{E}$. These equations are given by [7]

$$\eta\nabla \times \nabla \times \nabla \times \mathbf{u} + \gamma\nabla \times \mathbf{u} = \sum_{i=1}^{M} \nabla\delta n_i \times \nabla n_i^{(0)} \ , \quad a < r < b \ , \tag{1}$$

$$\eta\nabla \times \nabla \times \nabla \times \mathbf{u} = \sum_{i=1}^{M} \nabla\delta n_i \times \nabla n_i^{(0)}, \quad r > b \ , \tag{2}$$

$$\nabla \cdot \left(n_i^{(0)}\mathbf{u} - \frac{1}{\lambda_i} n_i^{(0)} \nabla\delta\mu_i \right) = 0 \ , \tag{3}$$

where η is the viscosity, γ is the frictional coefficient and $n_i^{(0)}$ is the equilibrium concentration (number density) of the i-th ionic species and a function of $r = |\mathbf{r}|$ ($n_i^{(0)} \to n_i^\infty$ as $r \to \infty$)

Further, symmetry considerations permit us to write

$$\mathbf{u}(\mathbf{r}) = (u_r, u_\theta, u_\varphi) = \left(-\frac{h(r)}{r} E\cos\theta, \frac{\mathrm{d}h(r)}{\mathrm{d}r} E\sin\theta, 0 \right) \ , \tag{4}$$

$$\delta\mu_i(\mathbf{r}) = -z_i e\phi_i(r) E\cos\theta \ , \tag{5}$$

with $E = |\mathbf{E}|$. Substituting Eqs. (4) and (5) into Eqs. (1)–(3) gives

$$\mathscr{L}\left(\mathscr{L}h - \lambda^2 h\right) = G(r), \quad a < r < b \ , \tag{6}$$

$$\mathscr{L}(\mathscr{L}h) = G(r), \quad r > b \ , \tag{7}$$

$$\mathscr{L}\phi_i = \frac{\mathrm{d}y}{\mathrm{d}r} \left(z_i \frac{\mathrm{d}\phi_i}{\mathrm{d}r} - \frac{\lambda_i}{e} \frac{h}{r} \right) \tag{8}$$

with

$$\lambda = (\gamma/\eta)^{1/2} \ , \tag{9}$$

$$\mathscr{L} \equiv \frac{\mathrm{d}}{\mathrm{d}r} \frac{1}{r} \frac{\mathrm{d}}{\mathrm{d}r} r = \frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r^2} \tag{10}$$

$$G(r) = -\frac{e}{\eta r} \frac{\mathrm{d}y}{\mathrm{d}r} \sum_{i=1}^{M} z_i^2 n_i^\infty \exp(-z_i y)\phi_i \tag{11}$$

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

where $\psi^{(0)}(r)$ is the equilibrium electric potential, k is Boltzmann's constant, and T is the absolute temperature. Solving the electrokinetic equations (Eqs. 6–8), we have obtained the following general expression for the electrophoretic mobility $\mu_\perp$ of a cylindrical soft particle in a transverse field:

$$\begin{aligned} \mu_\perp = {} & \frac{H(\lambda b)}{bF(\lambda b)} h(b) + \frac{b^2}{8} \int_b^\infty \left[1 - \frac{r^2}{b^2} \left\{ 1 - 2\ln\left(\frac{r}{b}\right) \right\} \right] G(r)\mathrm{d}r \\ & - \frac{W}{\lambda^2 F(\lambda b)} \int_b^\infty \left(1 - \frac{r^2}{b^2} \right) G(r)\mathrm{d}r \\ & + \frac{1}{2\lambda^2} \int_a^b H(\lambda b) G(r)\mathrm{d}r \\ & + \frac{H(\lambda b)}{2\lambda^2 F(\lambda b)} \int_a^b \left[1 - \frac{r^2}{b^2} - F(\lambda r) \right] G(r)\mathrm{d}r \end{aligned} \tag{13}$$

with

$$H(x) = x\{I_0(\lambda a)K_1(x) + K_0(\lambda a)I_1(x)\} - 1 \ , \tag{14}$$

$$F(x) = xI_1(x)\left\{K_0(\lambda a) - \frac{a^2}{b^2}K_2(\lambda a)\right\} + xK_1(x)\left\{I_0(\lambda a) - \frac{a^2}{b^2}I_2(\lambda a)\right\} \ , \tag{15}$$

$$W = 1 + \frac{(\lambda b)^2}{4}\Big[I_2(\lambda b)K_0(\lambda a) - K_2(\lambda b)I_0(\lambda a) - \frac{a^2}{b^2}\Big\{I_0(\lambda b)K_2(\lambda a) - K_0(\lambda b)I_2(\lambda a)\Big\}\Big] \ , \tag{16}$$

where $I_n(z)$ and $K_n(z)$ are, respectively, the n-th order modified Bessel functions of the first and second kinds. In order to calculate the mobility of a cylindrical soft particle via Eq. (13) one needs the value $h(b)$. To this end, in addition to the force balance condition for the soft cylinder as a whole, we previously employed the following force balance condition for the polyelectrolyte layer [7]:

$$\mathbf{F}_\mathrm{e} + \mathbf{F}_\mathrm{f} = 0 \ , \tag{17}$$

with

$$\mathbf{F}_\mathrm{e} = -\int_{\mathrm{V_p}} \rho_\mathrm{fix}(r)\nabla\psi(\mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{18}$$

$$\mathbf{F}_\mathrm{f} = \int_{\mathrm{V_p}} \gamma\mathbf{u}(\mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{19}$$

where $\psi(\mathbf{r})$ is the electric potential and the integral is carried out over the volume V_p of the polyelectrolyte layer. As stated in the introduction, this leads to the discontinuity of pressure at $r = b$.

In the present paper, in order to calculate $h(b)$ in Eq. (13), instead of the force balance condition for the polyelectrolyte layer (Eq. 17), we use an alternative and more appropriate boundary condition, i.e., the condition of continuity of pressure at $r = b$, which can be expressed by

$$\frac{\mathrm{d}}{\mathrm{d}r}\left[(L - \lambda^2)h\right]\Big|_{r=b^-} = \frac{\mathrm{d}}{\mathrm{d}r}(Lh)\Big|_{r=b^+} \ . \tag{20}$$

Then, Eq. (13) becomes

$$\begin{aligned}\mu_\perp = {} & \frac{b^2}{8}\int_b^\infty \left[\left\{1 + \frac{2L_3}{\lambda b L_2(\lambda b)}\right\}\left(1 - \frac{r^2}{b^2}\right) + \frac{2r^2}{b^2}\ln\left(\frac{r}{b}\right)\right]G(r)\mathrm{d}r \\ & + \frac{L_1(\lambda b)}{2\lambda^2 L_2(\lambda b)}\int_a^\infty \left(1 + \frac{r^2}{b^2}\right)G(r)\mathrm{d}r \\ & + \frac{1}{2\lambda^2}\int_a^b \lambda r\left[L_1(\lambda r) - \frac{L_1(\lambda b)}{L_2(\lambda b)}L_2(\lambda r)\right]G(r)\mathrm{d}r \ ,\end{aligned} \tag{21}$$

where

$$L_1(x) = I_0(\lambda a)K_1(x) + K_0(\lambda a)I_1(x) - 1/x \tag{22}$$

$$L_2(x) = \left\{I_0(\lambda a) + \frac{a^2}{b^2}I_2(\lambda a)\right\}K_1(x) + \left\{K_0(\lambda a) + \frac{a^2}{b^2}K_2(\lambda a)\right\}I_1(x) \tag{23}$$

$$L_3 = \left\{I_0(\lambda a) + \frac{a^2}{b^2}I_2(\lambda a)\right\}K_0(\lambda b) - \left\{K_0(\lambda a) + \frac{a^2}{b^2}K_2(\lambda a)\right\}I_0(\lambda b) + \frac{2}{(\lambda b)^2} \tag{24}$$

Equation (21) is the required general expression for the electrophoretic mobility $\mu_\perp$ of a cylindrical soft particle in a transverse field.

Results and discussion

In the present paper we have derived the general mobility expression (Eq. 21) for the electrophoretic mobility $\mu_\perp$ of a soft cylinder in a transverse field. Consider limiting cases of the general mobility expression. In the limit $a \to b$, the polyelectrolyte layer vanishes and the particle becomes a rigid particle of radius $a = b$. In this limit Eq. (21) tends to

$$\mu_\perp = \frac{b^2}{8}\int_b^\infty \left[1 - \frac{r^2}{b^2}\left\{1 - 2\ln\left(\frac{r}{b}\right)\right\}\right]G(r)\mathrm{d}r \ . \tag{25}$$

Equation (25) agrees with the general mobility expression for a cylindrical hard particle with a radius b in a transverse field obtained in the previous paper [10]. Also, in the limit $\lambda \to \infty$, the polyelectrolyte-coated particle becomes a rigid particle with a radius of b and Eq. (21) again tends to Eq. (25). The above results all agree with the previous results [7]. We thus found that general mobility expression (Eq. 21) reproduces all of the previous results [7]. In addition it can be shown that if the frictional coefficient tends to zero and the particle core is charged with a surface charge density σ (the polyelectrolyte layer vanishes), i.e., $\lambda \to 0$ and $\rho_\mathrm{fix}(r) = \sigma\delta(r\text{–}a)$ ($\delta(x)$ is Dirac's delta function), then Eq. (21) tends to

$$\mu_\perp = \frac{a^2}{8}\int_a^\infty \left[1 - \frac{r^2}{a^2}\left\{1 - 2\ln\left(\frac{r}{a}\right)\right\}\right]G(r)\mathrm{d}r \ , \tag{26}$$

as expected. Note that the force balance condition for the polyelectrolyte layer does not give this result. In this respect, the pressure continuity condition (Eq. 20) is more appropriate than Eq. (17).

In the limit $a \to 0$, the particle core vanishes and the particle becomes a cylindrical polyelectrolyte (a porous charged cylinder) of radius b. For the case where $a \to 0$ and the polyelectrolyte is uniformly charged, i.e., $\rho_\mathrm{fix}(r) = \rho_\mathrm{fix}$ (= constant), we obtain, for low potentials,

$$\mu_\perp = \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2} + \frac{\rho_{\mathrm{fix}} b}{2\eta\kappa}\left[I_1(\kappa b)K_0(\kappa b) + \frac{\kappa}{\kappa^2-\lambda^2} \times \left\{ \kappa I_0(\kappa b) - \lambda \frac{I_0(\lambda b)}{I_1(\lambda b)} I_1(\kappa b) \right\} K_1(\kappa b) \right] , \qquad (27)$$

where κ is the Debye-Hückel parameter. Equation (27) agrees with the previous result [7].

Consider next the case where $\lambda a \gg 1$, $\kappa a \gg 1$ (and thus $\lambda b \gg 1$, $\kappa b \gg 1$) and $\lambda d = \lambda(b–a) > > 1$, $\kappa d = \kappa(b–a) \gg 1$ and the relaxation effect is negligible and where the electrolyte is symmetrical with a valence z and bulk concentration n^∞, and $\rho_{\mathrm{fix}}(r) = \rho_{\mathrm{fix}}$ (=constant). By using an approximation method developed previously [7], we obtain from Eq. (21)

$$\mu_\perp = \frac{\varepsilon_r\varepsilon_o}{\eta} \frac{\psi_o/\kappa_m + \psi_{\mathrm{DON}}/\lambda}{1/\kappa_m + 1/\lambda} f\left(\frac{d}{a}\right) + \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2} , \qquad (28)$$

with

$$f\left(\frac{d}{a}\right) = \frac{1}{2}\left[1 + \left(\frac{a}{b}\right)^2\right] = \frac{1}{2}\left[1 + \frac{1}{(1+d/a)^2}\right] \qquad (29)$$

$$\psi_{\mathrm{DON}} = \frac{kT}{ze} \ln\left[\frac{\rho_{\mathrm{fix}}}{2zen^\infty} + \left\{\left(\frac{\rho_{\mathrm{fix}}}{2zen^\infty}\right)^2 + 1\right\}^{1/2}\right] \qquad (30)$$

$$\psi_o = \frac{kT}{ze}\left(\ln\left[\frac{\rho_{\mathrm{fix}}}{2zen^\infty} + \left\{\left(\frac{\rho_{\mathrm{fix}}}{2zen^\infty}\right)^2 + 1\right\}^{1/2}\right] + \frac{2zen^\infty}{\rho_{\mathrm{fix}}}\left[1 - \left\{\left(\frac{\rho_{\mathrm{fix}}}{2zen^\infty}\right)^2 + 1\right\}^{1/2}\right] \right) , \qquad (31)$$

where ψ_{DON} is the Donnan potential in the polyelectrolyte layer, ψ_o is the potential at the boundary $r = b$ between the polyelectrolyte layer and the surrounding solution, which we call the surface potential of the soft particle, and

$$\kappa_m = \kappa\left[1 + \left(\frac{\rho_{\mathrm{fix}}}{2zen^\infty}\right)^2\right]^{1/4} \qquad (32)$$

is the Debye-Hückel parameter of the polyelectrolyte layer. The limiting forms of Eq. (28) for the two cases $d/a \ll 1$ and $d/a \gg 1$ are given by

$$\mu_\perp = \frac{\varepsilon_r\varepsilon_o}{\eta} \frac{\psi_o/\kappa_m + \psi_{\mathrm{DON}}/\lambda}{1/\kappa_m + 1/\lambda} + \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2}, \quad d \ll a , \qquad (33)$$

$$\mu_\perp = \frac{\varepsilon_r\varepsilon_o}{2\eta} \frac{\psi_o/\kappa_m + \psi_{\mathrm{DON}}/\lambda}{1/\kappa_m + 1/\lambda} + \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2}, \quad d \gg a . \qquad (34)$$

The above results again agree with the previous results [7].

The electrophoretic mobility $\mu_{//}$ of an infinitely long cylindrical soft particle in a tangential field is independent of the cylinder radius and is equal to that for a plate-like particle with the applied field being parallel to the particle surface, as in the case of a cylindrical hard particle [11]. For the case where $\lambda a \gg 1$, $\kappa a \gg 1$, $\lambda d \gg 1$, $\kappa d \gg 1$ and $\rho_{\mathrm{fix}}(r) = \rho_{\mathrm{fix}}$, this is given by Eq. (33), viz.,

$$\mu_\parallel = \frac{\varepsilon_r\varepsilon_o}{\eta} \frac{\psi_o/\kappa_m + \psi_{\mathrm{DON}}/\lambda}{1/\kappa_m + 1/\lambda} + \frac{\rho_{\mathrm{fix}}}{\eta\lambda^2} . \qquad (35)$$

For a cylindrical soft particle oriented at an arbitrary angle between its axis and the applied electric field, its electrophoretic mobility averaged over a random distribution of orientation is given by, as in the case of hard cylinders [12, 13],

$$\mu_{\mathrm{av}} = \frac{1}{3}\mu_\parallel + \frac{2}{3}\mu_\perp . \qquad (36)$$

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