Electrophoresis of a Concentrated Spherical Dispersion at Arbitrary Electrical Potentials

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The electrophoretic behavior of a concentrated spherical dispersion is investigated theoretically. The present analysis extends those in the literature in that both the surface potential of a particle and the strength of the applied electric field are arbitrary and both the effects of double-layer polarization and the overlapping between neighboring double layers are taken into account. Results based on these conditions are highly desirable since they cover essentially all the possible experimental conditions in practice. We show that, for a fixed surface potential and strength of applied electric field, the higher the concentration of particle, the smaller the mobility. Counterions are found to accumulate at the downstream side of a particle. Double-layer polarization is inappreciable if either it is thick or the concentration of the particle is high. © 2002 Elsevier Science (USA)

Key Words: electrophoresis; spherical dispersion; concentrated dispersion; double-layer polarization; double-layer overlapping.

INTRODUCTION

Electrophoresis, one of the most significant electrokinetic phenomena, has various applications in practice. For example, it is widely used to separate proteins, to measure the stability of a colloidal dispersion, and to characterize the surface properties of biological cells such as bacteria and blood cells, to name a few. The mathematical description of electrophoresis involves the governing equations for the flow, the electrical, and the concentration fields. In general, these equations are coupled, nonlinear partial differential equations (1), and solving them simultaneously is nontrivial even if a numerical scheme is adopted. To circumvent this difficulty, assumptions such as low surface potential, thin or thick double layers, and weak applied electric field are often made in previous studies. Under these conditions the governing equations can be decoupled and approximated by linear expressions, which are more readily solvable.

The electrophoretic behavior of a colloidal dispersion depends upon various factors such as the nature of colloidal particle, the bulk concentration of electrolytes (or thickness of double layer), the strength of applied electric field, and the presence of a bound-

ary. The last factor includes, for instance, the existence of a rigid boundary (2–4) and a concentrated dispersion (5–8) in which the interaction between neighboring particles is important. Previous analyses focused mainly on a dilute dispersion where only the behavior of an isolated entity is considered (9–15). Levine and Neale (5) investigated the electrophoresis of a swarm of particles taking the effect of the interaction between neighboring particles into account. Under the assumption of low surface potential, an analytical expression, which is applicable to an arbitrary thickness of double layer, for electrophoretic mobility was derived. Kozak and Davis (6, 7) extended the analysis of Levine and Neale to the case of an arbitrary surface potential and double-layer thickness. The result obtained, however, is limited to the case when the overlapping between neighboring double layers is unimportant. Ohshima (8) was able to derive an approximate expression for the electrophoretic mobility of a concentrated dispersion in which the tedious recursive procedure involved in Levine and Neale can be avoided. The performance of the result obtained was found to be satisfactory with a relative percentage deviation less than 4%. O'Brien and White (14) assumed that the applied electric field is weak and the governing electrokinetic equations could be linearized. The electrical potential was partitioned into two parts and the original problem is divided into two subproblems. They concluded that if the double layer is either very thin or very thick, the effect of its polarization is negligible. Also, the variation of electrophoretic mobility as a function of double-layer thickness may have both a local maximum and a local minimum. Following the same procedure as that employed by O'Brien and White (14), Lee *et al.* (16) considered the case of arbitrary surface potential, double-layer thickness, and concentration of the particle. In addition, the effects of double-layer polarization and relaxation and the overlapping of neighboring double layers were taken into account.

In this study the analysis of Lee *et al.* (16) is further extended to the case where the strength of the applied electric field is arbitrary. This is of practical significance since the general electrokinetic equations are solved and essentially all the significant factors are taken into account. The electric field used by Pikhitsa *et al.* (17) in a study of the drift velocity of particles in water, for example, ranged from 250 to 1000 V/cm. Apparently, previous results based on a weak applied electric field are inapplicable to correlate their data.

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FIG. 1. The cell model adopted. A spherical particle of radius a is enclosed by a concentric liquid shell of radius b . The origin of the spherical coordinates (r, θ, ϕ) is located at the center of the particle. $\mathbf{E}$ is the applied electric field.

THEORY

We consider a concentrated dispersion of nonconducting, monodispersed, positively charged spherical particles in a $z_1 : z_2$ electrolyte solution, z_1 and z_2 being the valences of cations and anions, respectively. The cell model of Kuwabara (18) is adopted to simulate the system under consideration. As shown in Fig. 1, it is modeled by a representative cell, which comprises a spherical particle of radius a surrounded by a concentric spherical liquid shell of radius b . A uniform electric field $\mathbf{E}$ is applied in the Z -direction, and the particle moves in the same direction with velocity $\mathbf{U}$. The spherical coordinates (r, θ, ϕ) are adopted in the following analysis. The conservation of ions leads to

$$\frac{\partial n_j}{\partial t} = \nabla \cdot \left[D_j \left[\nabla n_j + \frac{z_j e n_j}{k_B T} \nabla \phi \right] - n_j \mathbf{v} \right], \quad [1]$$

where ∇ is the gradient operator, n_j is the number density of ionic species j ($j = 1$, cations, 2 , anions), D_j and $z_j e$ are the diffusivity and the charge of ionic species j , ϕ is the electric potential, k_B and T are, respectively, the Boltzmann constant and the absolute temperature, and $\mathbf{v}$ is the fluid velocity. We assume that the electrical potential is described by the Poisson equation

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon} = -\sum_{j=1}^2 \frac{z_j e n_j}{\varepsilon}, \quad [2]$$

where ε is the permittivity of the liquid phase and ρ is the space charge density.

Suppose that the flow field around the particle in the representative cell can be described by the Navier–Stokes equations in the creeping flow regime with electrical body forces considered. We have

$$\nabla \cdot \mathbf{v} = 0 \quad [3]$$

$$\rho_f \frac{\partial \mathbf{v}}{\partial t} = \eta \nabla^2 \mathbf{v} - \nabla p - \rho \nabla \phi, \quad [4]$$

where p is the pressure and ρ_f and η are the density and the viscosity of the liquid phase, respectively. Here, we assume that the liquid phase is incompressible and has constant physical properties.

For convenience, the electrical potential ϕ is decomposed into the electrical potential that would exist in the absence of the applied field, ϕ_1 , and that outside the particle which arises from the applied electrical field, ϕ_2 , that is,

$$\phi = \phi_1 + \phi_2. \quad [5]$$

The effect of double-layer relaxation is taken into account by defining the potential g_j through

$$n_j = n_{j0} \exp \left[-\frac{z_j e (\phi_1 + \phi_2 + g_j)}{k_B T} \right], \quad [6]$$

where n_{j0} is the bulk concentration of ionic species j .

For a more concise presentation, the governing equations are rewritten in scaled forms. In the discussion below, a symbol with an asterisk denotes a scaled quantity. For example, the scaled number concentration of ions, n_1^* and n_2^* are

$$n_1^* = \exp[-\phi_r (\phi_1^* + \phi_2^* + g_1^*)] \quad [7a]$$

$$n_2^* = \exp[\alpha \phi_r (\phi_1^* + \phi_2^* + g_2^*)]. \quad [7b]$$

The scaled governing equation for ϕ_1 is

$$\nabla^{*2} \phi_1^* = -\frac{1}{(1 + \alpha)} \frac{(\kappa a)^2}{\phi_r} [\exp(-\phi_r \phi_1) - \exp(\alpha \phi_r \phi_1)], \quad [8]$$

where $\phi_r = \zeta_a z_1 e / k_B T$ is the scaled surface potential, $\alpha = -z_2 / z_1$, and $\kappa = [\sum_{j=1}^2 n_{j0} (e z_j)^2 / \varepsilon k_B T]^{1/2}$ is the reciprocal Debye length. The scaled boundary conditions associated with Eq. [8] are

$$\phi_1^* = 1, \quad r^* = 1 \quad [8a]$$

$$\frac{\partial \phi_1^*}{\partial r^*} = 0, \quad r^* = 1/\lambda, \quad [8b]$$

where $r^* = r/a$ and $\lambda = a/b$.

The scaled governing equation for ϕ_2^* is

$$\nabla^{*2} \phi_2^* = -\frac{1}{(1+\alpha)} \frac{(\kappa a)^2}{\phi_r} \{(n_1^* - n_2^*) - [\exp(-\phi_r \phi_1^*) - \exp(\alpha \phi_r \phi_1^*)]\}. \quad [9]$$

The associated scaled boundary conditions are

$$\frac{\partial \phi_2^*}{\partial r^*} = 0, \quad r^* = 1 \quad [9a]$$

$$\frac{\partial \phi_2^*}{\partial r^*} = -E_z^* \cos \theta, \quad r^* = 1/\lambda, \quad [9b]$$

where $E_z^* = E_z a / \zeta_a$. At steady state, the left-hand side of Eq. [1] vanishes. In this case, substituting Eqs. [5] and [6] into Eq. [1] yields the following scaled equations for g_j^* ($g_j^* = g_j / \zeta_a$):

$$\begin{aligned} & \nabla^{*2} g_1^* - \phi_r \nabla^* \phi_1^* \cdot \nabla^* g_1^* \\ &= Pe_1 u^* \cdot \nabla^* \phi_1^* + Pe_1 u^* \cdot \nabla^* \phi_2^* + Pe_1 u^* \cdot \nabla^* g_1^* \\ &+ \phi_r \nabla^* \phi_2^* \cdot \nabla^* g_1^* + \phi_r \nabla^* g_1^* \cdot \nabla^* g_1^* \end{aligned} \quad [10]$$

$$\begin{aligned} & \nabla^{*2} g_2^* + \alpha \phi_r \nabla^* \phi_1^* \cdot \nabla^* g_2^* \\ &= Pe_2 u^* \cdot \nabla^* \phi_1^* + Pe_2 u^* \cdot \nabla^* \phi_2^* + Pe_2 u^* \cdot \nabla^* g_2^* \\ &- \alpha \phi_r \nabla^* \phi_2^* \cdot \nabla^* g_2^* - \alpha \phi_r \nabla^* g_2^* \cdot \nabla^* g_2^*. \end{aligned} \quad [11]$$

The associated scaled boundary conditions are

$$\frac{\partial g_1^*}{\partial r^*} = 0, \quad r^* = 1 \quad [11a]$$

$$g_1^* = -\phi_2^*, \quad r^* = 1/\lambda \quad [11b]$$

$$\frac{\partial g_2^*}{\partial r^*} = 0, \quad r^* = 1 \quad [11c]$$

$$g_2^* = -\phi_2^*, \quad r^* = 1/\lambda. \quad [11d]$$

In these expressions $Pe_j = U_E a / D_j$ is the electric Peclet numbers for ionic species j , $U_E = \varepsilon(z_1 e / k_B T)^2 / \eta a$ being the electrophoretic velocity based on Smoluchowski's result for an isolated particle in an electric field of strength ζ_a / a .

The scaled Navier–Stokes equation, in terms of scaled stream function, and the associated scaled boundary conditions are

$$\begin{aligned} E^{*4} \psi^* &= -\frac{(\kappa a)^2}{(1+\alpha)} \left\{ \left[\frac{\partial g_1^*}{\partial r^*} n_1^* + \frac{\partial g_2^*}{\partial r^*} \alpha n_2^* \right] \frac{\partial \phi^*}{\partial \theta} \right. \\ &\quad \left. - \left[\frac{\partial g_1^*}{\partial \theta} n_1^* + \frac{\partial g_2^*}{\partial \theta} \alpha n_2^* \right] \frac{\partial \phi^*}{\partial r^*} \right\} \sin \theta \end{aligned} \quad [12]$$

$$\psi^* = -\frac{1}{2} U^* r^{*2} \sin^2 \theta, \quad r^* = 1 \quad [12a]$$

$$\frac{\partial \psi^*}{\partial r^*} = -U^* r^* \sin^2 \theta, \quad r^* = 1 \quad [12b]$$

$$\psi^* = 0, \quad r^* = 1/\lambda \quad [12c]$$

$$\left(\frac{1}{r^* \sin \theta} \frac{\partial^2}{\partial r^{*2}} - \frac{\cos \theta}{r^{*3} \sin^2 \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^{*3} \sin \theta} \frac{\partial^2}{\partial \theta^2} \right) \psi^* = 0, \quad r^* = 1/\lambda. \quad [12d]$$

In these expressions, $\psi^* = \psi / U_E a^2$, $U^* = U / U_E$, and $E^{*4} = E^{*2} E^{*2}$, where

$$E^{*2} = \frac{\partial^2}{\partial r^{*2}} + \frac{\sin \theta}{r^{*2}} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right). \quad [12e]$$

The physical meaning of each boundary condition can be found in Lee *et al.* (16).

The external force acting on a particle in the Z-direction includes the electrical force and the hydrodynamic force. The scaled form of the former, F_{Ez} , is

$$\begin{aligned} F_{Ez} &= 2\pi \varepsilon \zeta_a^2 \int_0^\pi \left(\frac{\partial \phi_1^*}{\partial r^*} \right)_{r^*=1} \left(\frac{\partial(\phi_1^* + \phi_2^*)}{\partial r^*} \cos \theta \right. \\ &\quad \left. - \frac{1}{r^*} \frac{\partial(\phi_1^* + \phi_2^*)}{\partial \theta} \sin \theta \right)_{r^*=1} r^{*2} \sin \theta d\theta \\ &= 2\pi \varepsilon \zeta_a^2 E_z^* K_E, \end{aligned} \quad [13]$$

where

$$\begin{aligned} E_z^* K_E &= \int_0^\pi \left(\frac{\partial \phi_1^*}{\partial r^*} \right)_{r^*=1} \left(\frac{\partial(\phi_1^* + \phi_2^*)}{\partial r^*} \cos \theta \right. \\ &\quad \left. - \frac{1}{r^*} \frac{\partial(\phi_1^* + \phi_2^*)}{\partial \theta} \sin \theta \right)_{r^*=1} r^{*2} \sin \theta d\theta. \end{aligned} \quad [13a]$$

The scaled form of the hydrodynamic force, F_{Dz} , can be expressed by

$$\begin{aligned} F_{Dz} &= \pi \varepsilon \zeta_a^2 \int_0^\pi \left(r^{*4} \sin^3 \theta \frac{\partial}{\partial r^*} \frac{E^{*2} \psi^*}{r^{*2} \sin^2 \theta} \right)_{r^*=1} d\theta \\ &\quad - \pi \varepsilon \zeta_a^2 \frac{(\kappa a)^2}{(1+\alpha) \phi_r} \int_0^\pi \left(r^{*2} \sin^2 \theta (n_1^* - n_2^*) \frac{\partial \phi_2^*}{\partial \theta} \right)_{r^*=1} d\theta \\ &= \pi \varepsilon \zeta_a^2 \left(U^* K_{Df} - \frac{(\kappa a)^2}{(1+\alpha) \phi_r} E_z^* K_{De} \right) = F_{Df}^* + F_{De}^*, \end{aligned} \quad [14]$$

where

$$U^* K_{Df} = \int_0^\pi \left(r^{*2} \sin^3 \theta \frac{\partial}{\partial r^*} \frac{E^{*2} \psi^*}{r^{*2} \sin^2 \theta} \right)_{r^*=1} d\theta \quad [14a]$$

$$E_z^* K_{De} = \int_0^\pi \left(r^{*2} \sin^2 \theta (n_1^* - n_2^*) \frac{\partial \phi_2^*}{\partial \theta} \right)_{r^*=1} d\theta. \quad [14b]$$

F_{Df}^* and F_{De}^* are the scaled viscous force and the scaled electric body force exerted on the particle. At steady state the net force acting on the particle vanishes, that is,

$$F_{Dz} + F_{Ez} = 0 \quad [15]$$

It can be shown that the scaled electrophoretic mobility of the particle, U_m^* , is

$$U_m^* = \frac{\eta U}{\varepsilon \xi_a E} = \frac{U^*}{E_z^*} = \frac{(\kappa a)^2 [K_{De}/(1 + \alpha)\phi_r] - 2K_E}{K_{Df}} \quad [16]$$

Note that since K_E , K_{De} , and K_{Df} are all functions of the applied electric field and the terminal velocity of the particle, U_m^* needed to be calculated through an iterative procedure.

RESULTS AND DISCUSSION

The governing equations and the associated boundary conditions are solved by the pseudo-spectral method based on the Chebyshev polynomials (4). Although this method is appropriate for κa smaller than about 10, it is sufficient for our purpose since we are mainly interested in the behavior of the system under consideration for the case of medium to thick double layers.

Figure 2 shows the variation of the scaled mobility U_m^* as a function of κa at various scaled applied field E_z^* for two different levels of scaled surface potential. For comparison, the results of Lee *et al.* (16) in which the applied electric field is weak and the governing equations, Eqs. [9]–[12], are linearized are also presented. Figure 2 reveals that if κa is small (thick double-layer), both models lead to essentially the same result. However, if κa has a medium value, the linear result of Lee *et al.* (16) is appropriate for $E_z^* \cong 1$ at $\phi_r = 3$ and for $E_z^* \ll 1$ at $\phi_r = 5$. A comparison between Fig. 2 suggests that, for κa in the range [1, 10], the behavior of U_m^* against κa curve at a higher ϕ_r is more complicated than that at a lower ϕ_r . As pointed out by Lee *et al.* (16), this is due to the fact that as κa increases (double layer becomes thin), the electric field induced by a charged particle, which is in the opposite direction as the applied electric field, becomes more important. Therefore, if the applied electric field is weak, it will be dominated by the electric field induced by the particle. Apparently, for a fixed surface potential, the weaker the applied electric field, the more complicated the behavior of the U_m^* against κa curve, as is justified in Fig. 2b. On the other hand, if the applied electric field is sufficiently strong, it will dominate the electric field induced by a particle and the U_m^* against κa curve is more smooth.

Figure 3 illustrates the variation of the scaled mobility U_m^* as a function of κa at various λ ($=a/b$), for the case $\phi_r = 1$, and that for the case $\phi_r = 5$ is presented in Fig. 4. Note that λ is a measure for the concentration of the particle; the larger its value, the higher the concentration. These figures reveal that, for a fixed surface potential and applied electric strength, the higher the concentration of the particle, the smaller the mobility. This

FIG. 2. Variation of scaled mobility U_m^* as a function of κa at various scaled applied field E_z^* . $\phi_r = 2$ (a), $\phi_r = 5$ (b). The linear case is based on Lee *et al.* (16). Key: $\lambda = 0.5$, $\alpha = 1$, and $Pe_1 = Pe_2 = 0.01$.

is mainly due to the electrical interaction between neighboring particles. Figure 5 shows the variation of $2K_E$ as a function of κa at various λ for the case of Fig. 3. It can be shown that the K_E in Eq. [16] can be rewritten as

$$K_E E_z^* = - \int_0^\pi \left(\frac{\partial \phi_1^*}{\partial r^*} \right)_{r^*=1} \left(\frac{\partial \phi_2^*}{\partial \theta} \right)_{r^*=1} \sin^2 \theta d\theta. \quad [17]$$

According to Eq. [16], the larger the K_E , the smaller the mobility. If E_z^* is constant, then $-(\partial \phi_1^*/\partial r^*)_{r^*=1}$ increases with the increase in κa . Due to the interaction between neighboring particles, this effect is pronounced if the concentration of the

$$\phi_r = 1.0, E_z^* = 3.0$$

FIG. 3. Variation of scaled mobility U_m^* as a function of κa at various λ ($=a/b$) for the case $\phi_r = 1$, $E_z^* = 3$, $Pe_1 = Pe_2 = 0.01$, and $\alpha = 1$.

$$\phi_r = 1.0, E_z^* = 3.0$$

FIG. 5. Variation of $2K_E$ as a function of κa at various λ for the case of Fig. 3.

particle is high. If κa is large, this leads to a drastic increase in K_E .

Figures 6–9 show the contours of the scaled net ion concentrations CD ($=n_1^* - n_2^*$) at various conditions. In our case since a particle is positively charged, the concentration of anions near it is higher than that of cations and CD is negative. Also, the applied electric field is in the positive Z direction, and the particle moves in this direction too. In Fig. 6, the applied electric field is weak, and the polarization of the double layer is inappreciable. As the strength of the applied electric field increases, the distortion of the double layer surrounding a particle becomes significant, as illustrated in Fig. 7. This figure shows that an-

ions will accumulate at the rear of a particle. If the double layer surrounding a particle is thin, its polarization becomes inappreciable, as can be seen in Fig. 8. This is because that for a fixed surface potential the thinner the double layer (larger κa), the stronger the electric field induced by a particle, which is proportional to $(\partial\phi_1^*/\partial r^*)_{r^*=1}$. Since this induced electric field is in the opposite direction as that of the applied electric field, the

$$\phi_r = 5.0, E_z^* = 3.0$$

FIG. 4. Variation of scaled mobility U_m^* as a function of κa at various λ ($=a/b$) for the case of Fig. 3 except that $\phi_r = 5$.

$$\phi_r = 3.0, E_z^* = 0.1, \kappa a = 0.1$$

FIG. 6. Contours of net scaled ion concentrations CD ($=n_1^* - n_2^*$) for the case $\phi_r = 3$, $E_z^* = 0.1$, $\kappa a = 0.1$. Key: $\lambda = 0.5$, $Pe_1 = Pe_2 = 0.01$, and $\alpha = 1$.

FIG. 7. Contours of net scaled ion concentrations $CD (=n_1^* - n_2^*)$ for the case $\phi_r = 3, E_z^* = 3, \kappa a = 0.1$. Key: same as Fig. 8.

extent of double-layer polarization is lowered. A comparison between Figs. 7 and 9 reveals that double-layer polarization is less significant if the concentration of the particle is high. This is because the interaction between neighboring particles becomes significant, which has the effect of compressing the double layer surrounding a particle.

FIG. 8. Contours of net scaled ion concentrations $CD (=n_1^* - n_2^*)$ for the case $\phi_r = 3, E_z^* = 3, \kappa a = 5.6$. Key: same as Fig. 8.

FIG. 9. Contours of net scaled ion concentrations $CD (=n_1^* - n_2^*)$ for the case $\phi_r = 3, E_z^* = 3, \kappa a = 0.1, \lambda = 0.8, Pe_1 = Pe_2 = 0.01$, and $\alpha = 1$.

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