Electrophoresis of a Sphere Normal to a Plane at Arbitrary Electrical Potential and Double Layer Thickness

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INTRODUCTION

The electrophoretic movement of a sphere normal to an uncharged, planar surface is analyzed theoretically, taking the effect of double layer polarization into account. Here, both the surface potential of the particle and the thickness of the double layer surrounding it can be arbitrary. We show that if double layer polarization is neglected, the effect of the surface potential of a particle on its electrophoretic velocity is inappreciable. On the contrary, if the distance between the particle and the surface is sufficiently close, the hydrodynamic effect dominates, the influence of the surface potential and double layer polarization becomes insignificant.

THEORY

Referring to Fig. 1, we consider the electrophoresis of a sphere of radius $a$ normal to an uncharged plane subject to a uniform electric field $E_z$ with strength $E_z$ in the $Z$ direction. Let $h$ be the distance between the center of the particle and the surface. The liquid phase contains $z_1 : z_2$ electrolyte solution, $z_1$ and $z_2$ being respectively the valences of cations and anions, with $n_{20} = n_{10}/\alpha$, $n_{10}$ and $n_{20}$ being respectively the bulk concentrations of cations and anions. Suppose that the velocity of the particle $\mathbf{U}$ is slow so that a quasi-steady state can be assumed. The bispherical coordinates $(\xi, \eta, \phi)$ are adopted with $\eta = 0$ and $\eta = \eta_0$ represent respectively the planar surface and the surface of the particle. The symmetric nature of the problem suggests that only half of the $(\xi, \eta)$ domain needs to be considered. The bispherical coordinates used are related to the cylindrical coordinates $(r, \theta, Z)$ by (25)

$$Z = c \frac{\sinh \eta}{\cosh \eta - \cos \xi}$$

[1]
The governing equations for ion conservation, electrical flow, and physical properties. Assume that the electrical potential in the absence of the applied electric field (16). The distortion of the double layer surrounding the particle can be simulated by

\[ n_j = n_{j0} \exp \left( \frac{-z_j e (\phi_1 + \phi_2 + g_j)}{k_B T} \right), \quad j = 1, 2, \]  \[ \text{[7]} \]

where \( g_j \) is a perturbed function. Suppose that the applied electric field is weak, and \( \phi_2 \) and \( g_j \) are much smaller than \( \phi_1 \). In this case Eq. [7] can be approximated by

\[ n_j = n_{j0} \exp \left( \frac{-z_j e}{k_B T} \phi_1 \right) \left[ 1 - \frac{z_j e}{k_B T} (\phi_2 + g_j) \right], \quad j = 1, 2 \]  \[ \text{[8]} \]

and the space charge density can be approximated by

\[ \rho \approx \sum_{j=1}^{2} z_j e n_{j0} \exp \left( \frac{-z_j e}{k_B T} \phi_1 \right) \left[ 1 - \frac{z_j e}{k_B T} (\phi_2 + g_j) \right]. \]  \[ \text{[9]} \]

For a simpler mathematical manipulation, we define the scaled quantities \( \phi_{1s}^* = \phi_1 / \xi_a, \xi_a^* = g_j / \xi_a, \) and \( n_{1s}^* = n_j / n_{10} \), where \( \xi_a \) is the electrical potential on particle surface. In scaled quantities the equilibrium electrical potential can be expressed as

\[ \nabla^2 \phi_{1s}^* = -\frac{1}{(1 + \alpha)} \frac{(k a)^2}{\phi_r} \left[ \exp(-\phi_{1s}^*) - \exp(\alpha \phi_{1s}^*) \right], \]  \[ \text{[10]} \]

where \( \phi_r = \xi_a / (z_j e / k_B T) \) is the scaled surface potential of the particle, and the reciprocal Debye length \( \kappa \) and the scaled gradient operator \( \nabla^* \) are defined by

\[ \kappa = \left[ \sum_{j=1}^{2} n_{j0} (e z_j)^2 / e k_B T \right]^{1/2} \]  \[ \text{[11]} \]

\[ \nabla^2 = \frac{x^2}{c^*} \left[ \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \xi^2} - \frac{\sinh \eta}{x \sin \xi} \frac{\partial}{\partial \eta} \right]. \]  \[ \text{[12]} \]

In these expression \( c^* = c / a \), and \( x = \cosh \eta - \cos \xi \).

Suppose that the equilibrium electrical potential vanishes at a point far away from particle surface. Then

\[ \phi_{1s}^* = 0, \quad \eta = 0 \quad \text{and} \quad \xi = 0, \quad \text{or} \quad \eta = 0. \]  \[ \text{[13]} \]

The symmetric nature of the problem implies that

\[ \frac{\partial \phi_{1s}^*}{\partial \xi} = 0, \quad \xi = 0 \quad \text{or} \quad \xi = \pi. \]  \[ \text{[14]} \]

Assuming constant electrical potential on particle surface, we have

\[ \phi_{1s}^* = 1, \quad \eta = \eta_0. \]  \[ \text{[15]} \]
Employing the relation \( \phi = \phi_1 + \phi_2 \), Eqs. [4] and [10] yield

\[
\nabla^2 \phi_2^* - \frac{(k a)^2}{(1 + \alpha^2)} \{ \exp(-\phi, \phi_1^*) + \alpha \exp(\alpha \phi, \phi_1^*) \} \phi_2^* \\

= \frac{(k a)^2}{(1 + \alpha^2)} \{ \exp(-\phi, \phi_1^*) \} g_1^* + \exp(\alpha \phi, \phi_1^*) \alpha g_2^* \}.
\]

The applied electric field is in the \( Z \) direction, therefore, we have, for the scaled perturbed potential \( \phi_2^* \),

\[
\phi_2^* = -E_z^* \cdot r^*, \quad \eta = 0 \quad \text{and} \quad \xi = 0, \quad \text{or} \quad \eta = 0
\]

\[
\frac{\partial \phi_2^*}{\partial \eta} = 0, \quad \eta = \eta_0.
\]

The symmetric nature of the problem suggests that

\[
\frac{\partial \phi_2^*}{\partial \xi} = 0, \quad \xi = 0 \quad \text{or} \quad \xi = \pi.
\]

In these expressions, \( E_z^* \) and \( r = r^* \cdot i_r \) are respectively the scaled electric field and the direction vector where

\[
r^* = c_s \left( \frac{\cos \eta + \cos \xi}{x} \right)^{1/2}.
\]


\[
\nabla^2 g_1^* - \phi_r \nabla^2 \phi_1^* \cdot \nabla^2 g_1^* = \phi_r^2 Pe_1 v^* \cdot \nabla^2 \phi_1^*
\]

\[
\nabla^2 g_2^* + \alpha \phi_r \nabla^2 \phi_1^* \cdot \nabla^2 g_2^* = \phi_r^2 Pe_2 v^* \cdot \nabla^2 \phi_1^*.
\]

In these expressions \( Pe_j = \epsilon (Z_j e / k_B T)^2 / \eta D_j \), \( j = 1, 2 \), is the electric Peclet number of ionic species \( j \), and \( v^* = v / U_E \), \( U_E = (\epsilon \xi / \rho a) \) is the magnitude of the velocity of an isolated particle based on Smoluchowski’s theory when an electric field of strength \( (\xi / a) \) is applied.

Suppose that the perturbed electrical potential arises from the induced electric field vanishes at a point far away from particle and plane surface. Then

\[
g^*_r = -\phi_2^*, \quad \eta = 0 \quad \text{and} \quad \xi = 0, \quad \text{or} \quad \eta = 0.
\]

The surface of particle is impenetrable to ionic species, which implies that

\[
\frac{\partial g_2^*}{\partial \eta} = 0, \quad \eta = \eta_0.
\]

The symmetric nature of the problem requires that

\[
\frac{\partial g_2^*}{\partial \xi} = 0, \quad \xi = 0 \quad \text{or} \quad \xi = \pi.
\]

In terms of stream function, Eq. [5] becomes, after taking curl,

\[
\mu \frac{1}{\omega} E^4 \psi - \nabla \times (\rho \nabla \phi) = 0,
\]

where \( \omega = c \sin \xi / x \) is the distance from the plane \( \xi = \pi \). If we let \( v_\eta \) and \( v_\xi \) be the \( \eta \) and \( \xi \) components of velocity \( v \), then

\[
v_\eta = \frac{x^2}{c^2 \sin \xi} \frac{\partial \psi}{\partial \xi}
\]

\[
v_\xi = -\frac{x^2}{c^2 \sin \xi} \frac{\partial \psi}{\partial \eta}.
\]

Substituting Eq. [9] into Eq. [26] and rewriting the resultant expression in scaled form, we obtain

\[
E^4 \psi^* = -(k a)^2 \frac{x \sin \xi}{c^2} \left( \frac{\partial \phi_1^*}{\partial \xi} \frac{\partial \phi_2^*}{\partial \eta} - \frac{\partial \phi_1^*}{\partial \eta} \frac{\partial \phi_2^*}{\partial \xi} \right).
\]

Here, \( \psi^* = \psi / U_E a \) is the scaled stream function, and \( E^4 = E^2 E^2 \), with \( E^2 \) defined by

\[
E^2 = \frac{x^2}{c^2} \left[ \frac{\partial^2}{\partial \eta^2} + \frac{\partial^2}{\partial \xi^2} + \frac{\sin \eta}{x} \frac{\partial}{\partial \eta} + \frac{1 - \cos \xi}{x \sin \xi} \frac{\partial}{\partial \xi} \right].
\]

The following boundary conditions are assumed for the flow field:

\[
\psi^* = -\frac{1}{2} \omega^2 U^* \quad \text{and} \quad \frac{\partial \psi^*}{\partial \eta} = \frac{c^2}{x^3} \sin \xi \sinh \eta U^*, \quad \eta = \eta_0
\]

\[
\psi^* = 0 \quad \text{and} \quad \frac{\partial \psi^*}{\partial \xi} = 0, \quad \xi = 0 \quad \text{or} \quad \xi = \pi
\]

\[
\psi^* = 0 \quad \text{and} \quad \frac{\partial \psi^*}{\partial \eta} = 0, \quad \eta = 0
\]

\[
\psi^* \to 0, \quad \eta = 0 \quad \text{and} \quad \xi = 0.
\]

In these expressions, \( \omega = c \sin \xi / x \) and \( U^* = U / U_E \). Equations [31]–[34] imply that the velocity of the particle is \( U \), and the fluid at infinity is stationary.

The forces acting on the particle include the electric force \( F_{E_z} \) and the hydrodynamic force \( F_{D_z} \), which can be evaluated respectively by

\[
F_{E_z} = 2 \pi \int_0^\pi \sigma (-\nabla \phi) \delta s
\]

\[
F_{D_z} = 2 \pi \int_0^\pi \sigma (-\nabla \phi) \delta s
\]
Variation of scaled mobility ($U^*/E^*$) as a function of $\kappa a$ at various scaled surface potential $\phi_r$ without considering DLP for the case $\alpha = 1.0$ and $\eta_0 = 2.0$. The dashed line represents the result based on the linearized Eq. [4].

and

$$F_{Dz} = \mu \pi \int_0^\pi \omega^3 \frac{\partial}{\partial n} \frac{E^2 \psi}{\omega^2} \delta s - \pi \int_0^\pi \omega^2 \rho_e \frac{\partial \phi}{\partial s} \delta s. \quad [36]$$

In these expressions $s$ represents the tangential surface, and the charge density on particle surface $\sigma$ can be evaluated by

$$\sigma = \varepsilon \frac{\chi}{c} \frac{\partial \phi}{\partial \eta}. \quad [37]$$

Substituting Eq. [37] into Eq. [35] yields

$$F_{Ez}^* = 2\pi \int_0^\pi \sin \xi \frac{\partial \phi^*}{\partial \eta} \left[ (1 - \cosh \eta \cos \xi) \frac{\partial \phi^*}{\partial \eta} - \sinh \eta \sin \xi \frac{\partial \phi^*}{\partial \xi} \right] d\xi. \quad [38]$$

Substituting Eq. [7a] into Eq. [41] gives

$$F_{Dz} = \pi \int_0^\pi -\omega^3 \frac{\partial}{\partial n} \frac{E^2 \psi^*}{\omega^2} \delta \xi - \frac{(\kappa a)^2}{(1 + \alpha)\phi_r} \pi \int_0^\pi \omega^2 \exp(-\alpha \phi_r \psi^*) (1 - \phi_r (\phi^*_2 + g^*_1)) \frac{\partial \phi^*}{\partial \xi} d\xi. \quad [39]$$

The problem under consideration can be decomposed into two subproblems (6). In the first, the particle moves at constant velocity in the absence of the applied electric field, and in the second it is held constant under the external electric field. Let $f_1$ and $f_2$ be respectively the net forces acting on the particle in the first and second problems. We have $f_1 = \chi U^*$ and $f_2 = \beta E^*$. At steady state the net force acting on the particle vanishes, and, therefore, its mobility can be expressed as $U^*/E^* = -\beta/\chi$.

RESULTS AND DISCUSSION

The behavior of the system under consideration is examined through numerical simulation. A pseudo-spectral method based on Chebyshev polynomial (26), which is readily applicable to the present problem, is adopted for the resolution of the governing equations subject to the boundary conditions assumed.

FIG. 2. Variation of scaled mobility ($U^*/E^*$) as a function of $\kappa a$ at various scaled surface potential $\phi_r$ without considering DLP for the case $\alpha = 1.0$ and $\eta_0 = 2.0$. The dashed line represents the result based on the linearized Eq. [4].

FIG. 3. Variation of scaled mobility ($U^*/E^*$) as function of $\kappa a$ at various scaled surface potential $\phi_r$ for the case when DLP is considered with $Pr_1 = 0.01$, $Pr_2 = 0.01$, and $\alpha = 1.0$: (a) $\eta_0 = 2.0$; (b) $\eta_0 = 1.5$. 
The numerical procedure is introduced briefly in the Appendix. The method adopted has a fast rate of convergence, and the convergent properties are independent of the associated boundary conditions. Also, the mini-max property typically associated with the Chebyshev polynomial is maintained.

Figure 2 shows the variations of the scaled mobility \((U^* / E^*)\) as a function of \(\kappa a\) at various scaled surface potential \(\phi_0\), without considering DLP, which can be obtained by letting \(g_j = 0\) in Eq. [7], and the corresponding result when DLP is taken into account is illustrated in Fig. 3. For comparison, the results based on linearized Eq. [4], that is, those at low electrical potentials, are also presented in these figures. Figure 2 reveals that if \(\kappa a\) is small (i.e., thick double layer), \((U^* / E^*)\) becomes independent of the surface potential of particle. This is because if the double layer is sufficiently thick, it will reach the planar surface. In this case, the movement of the particle is dominated by hydrodynamic conditions, and the effect of the electric field is less significant. As \(\kappa a\) increases, the presence of the planar surface on the movement of the particle becomes less significant, and \((U^* / E^*)\) increases accordingly. Figure 2 also suggests that \((U^* / E^*)\) increases with the increase in the surface potential of particle, but the degree of increase is inappreciable. As can be seen in Fig. 3, the behavior of \((U^* / E^*)\) at small \(\kappa a\) when the effect of DLP is taken into account is similar to that when it is neglected. The situation is different, however, if \(\kappa a\) becomes large. This figure reveals that \((U^* / E^*)\) decreases with the increase in the surface potential of particle, and the degree of increase is appreciable. This is because the polarization of the double layer has the effect of inducing an internal electric field, which is in the inverse direction as that of the applied electric field. Since the strength of the induced electric field increases with the surface potential of the particle, \((U^* / E^*)\) decreases with the increase in \(\phi_0\). This phenomenon can also be explained by the variation of \(\beta\) as a function of \(\kappa a\), as illustrated in Fig. 4. According to its definition, \(\beta\) is a measure for the net force acting on a particle in problem 2. Figure 4 shows that if \(\phi_0\) is fixed, \(\beta\) increases with the increase in \(\kappa a\). This is because the thinner the double layer, the smaller the resistant force experienced by a particle. Again, the presence of DLP has the effect of reducing the electric force arising from the applied electric field, and the larger the \(\phi_0\) the more significant the effect DLP.

Figure 5 illustrates the variation of the scaled mobility \((U^* / E^*)\) as a function of \(\eta_0\) at various scaled surface potential \(\phi_0\) for the case when DLP is considered. According to its definition \((h/a = \cosh \eta_0)\), \(\eta_0\) is a measure for the distance between particle and surface, the smaller the \(\eta_0\) the closer the distance. As can be seen from Fig. 5, \((U^* / E^*)\) decreases with the decrease in \(\eta_0\). This is expected since the closer the distance between the particle and the surface the more significant the hydrodynamic hindrance of the movement of the former by the latter. Figure 5 suggests that if \(\eta_0 < 1.0\), the mobility of a particle becomes insensitive to its surface potential. This is because if the distance between the particle and the surface is sufficiently close, the hydrodynamic effect dominates the electrical effect.

**CONCLUSION**

We conclude that under the condition in which a particle and a planar surface are not close, the surface potential of the farmer on its electrophoretic mobility is negligible when double layer polarization is neglected, but it becomes crucial if double layer polarization is taken into account. However, if the distance between the particle and the planar surface is sufficiently close, the hydrodynamic effect dominates, and the electric effects are insignificant.

**APPENDIX**

In the present case, the computational domain is two dimensional, and the pseudo-spectral method is applied in both the
\( \eta \) and \( \xi \) directions. For instance, the \( N \)th-order \( \times \) \( M \)th-order approximation to the function \( f_{NM}(\eta, \xi) \) is expressed by

\[
f_{NM}(\eta, \xi) = \sum_{i=0}^{N} \sum_{j=0}^{M} f_{i,j} h_i(\eta) h_j(\xi). \tag{A-1}
\]

where \( f_{NM}(\eta_j, \xi_k) \) is the value of \( f_{NM} \) at the \( k \)th collocation point, where \( k = [(N-1)\eta + j] \). The interpolation polynomials \( h_i(\eta) \) and \( h_j(\xi) \) depend on the collocation points and these points are determined by mapping the computational domain onto the square \([-1, 1] \times [-1, 1]\) through

\[
\eta = \frac{\eta_0}{2} y + \frac{\eta_0}{2} \tag{A-2}
\]

\[
\xi = \frac{\pi}{2} (x + 1). \tag{A-3}
\]

The \( N + 1 \) interpolation points in the interval \([-1, 1]\) are chosen to be the extreme values of an \( N \)th-order Chebyshev polynomial \( T_N(y) \)

\[
y_j = \cos\left(\frac{\pi j}{N}\right), \quad j = 0, 1, \ldots, N. \tag{A-4}
\]

The corresponding interpolation polynomial \( h_j(y) \) is

\[
h_j(y) = \frac{(-1)^{j+1}(1 - y^2)(d T_N(y)/dy)}{c_j N^2(y - y_j)} \quad j = 0, 1, \ldots, N, \tag{A-5}
\]

where \( c_j \) is defined by

\[
c_j = \begin{cases} 2, & j = 0, N \\ 1, & 1 \leq j \leq N - 1. \end{cases} \tag{A-6}
\]

Both the partial derivatives and the integration of \( f_{NM}(\eta, \xi) \) are evaluated based on Eq. [A-1]. The corresponding nonlinear system is then solved with a Newton–Raphson iteration scheme.

Double precision is used throughout the computation, and grid independence is checked to ensure that the mesh used is fine enough. For each \( \kappa a \) the calculations consist of 41 \( \times \) 41 nodal points for \((N_\eta \times M_\xi)\).

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**REFERENCES**