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ORIGINAL CONTRIBUTION

Hsiu-Yu Yu
Shih-Hsing Hung
Jyh-Ping Hsu

Electrophoresis of a charge-regulated particle at an arbitrary position in a spherical cavity

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H.-Y. Yu · S.-H. Hung
Department of Chemical Engineering,
National Taiwan University,
10617 Taipei, Taiwan

J.-P. Hsu (✉)
Department of Chemical and Materials
Engineering, National I-Lan University,
26041 I-Lan, Taiwan
E-mail: jphsu@ccms.ntu.edu.tw
Tel.: +886-3-9357400 ext. 285
Fax: +886-3-9353731

Abstract The boundary effect on the electrophoretic behavior of a particle is examined by considering a sphere at an arbitrary position in a spherical cavity for the case of low electrical potential and weak applied electric field. Here, a charge-regulated model is used to describe the charge conditions on the particle surface. This model finds practical applications where the behavior of biocolloids such as cells or microorganisms and entities covered by an artificial membrane need to be simulated. The two idealized models often used in relevant studies can be recovered as the limiting cases of the present model.

Keywords Electrophoresis · Boundary effect · Sphere in spherical cavity · Arbitrary position · Charge-regulated particle

Introduction

Electrophoresis, one of the most important electrokinetic phenomena, has wide applications in practice. The estimation of the surface properties of entities of colloidal size, for example, is often based on this technique. It is applicable to both biocolloids such as microorganisms and cells, and inorganic entities such as sols and aerosols. Owing to the difficulty involved in solving the governing equations, the available results are usually based on drastic assumptions such as simple geometry, isolated entity, thin double layer, and low surface potential. Nevertheless, information thus retrieved provides useful reference both for design of electrophoresis instruments and for interpretation of experimental observations.

The boundary effect can play a key role in the application of electrophoresis. In electrophoretic separations, for example, electrophoresis is conducted in a porous medium where the movement of charged entities is influenced by the presence of walls. Microelectrophoresis is another example where electrophoresis is conducted in a narrow space, and the wall effect is important. The electrophoresis of a concentrated dispersion leads to another type of boundary effect where the interaction between neighboring entities should be considered. In these cases the classic electrophoresis theory of Smoluchowski [1], which is based on an isolated entity in an infinite medium, needs to be modified accordingly so that the results derived are more realistic. Various types of problems have been discussed in the literature [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20].

In a recent study, Hsu et al. [21] considered the electrophoresis of a sphere at an arbitrary position in a spherical cavity; both are maintained at either constant surface potential or constant surface charge density. Several interesting phenomena were observed such as if both particle and cavity are maintained at constant surface potential, the closer the particle to the cavity surface, the greater its mobility. It should be pointed out that both constant surface potential and constant surface charge density are idealized conditions which represent two limiting cases [22]. In practice, the charge condition on a surface is somewhere between these two limiting cases. For example, in the case of biocolloids or particles covered by an artificial membrane layer, the degree of dissociation of the functional groups depends on the environment, and usually leads to a complicated charge condition, the so-called charge-regulation model. Previous efforts regarding this are ample in the literature [23, 24, 25, 26, 27, 28, 29]. Hsu et al. [30], for instance, analyzed the electrophoresis of concentrated spherical particles with a charge-regulated surface. In mathematical language, constant surface potential and constant surface charge density models correspond, respectively, to Dirichlet-type and Neumann-type problems, and the charge-regulation model may lead to a mixed-type problem. In this study, the analysis of Hsu et al. [21] is extended to the case when the surface of a particle is of charge-regulated nature.

Theory

Referring to Fig. 1, a charged, nonconducting spherical particle of radius a is placed at an arbitrary position in a spherical cavity of radius b filled with an aqueous z_1:z_2 electrolyte solution, $z_1$and z_2 being, respectively, the valences of cations and anions. The center of the cavity is at $z=0$, and that of the particle at $z=m$. An external electric field, **E**, which is parallel to the z-direction, is applied. Suppose that the liquid phase is incompressible and has constant physical properties. Also, the system under consideration is at quasi-steady state. If we assume that **E** is weak and the deformation of the double layer surrounding the particle is negligible, then the spatial variation in the electrical potential, Ψ, can be described by

$$\nabla^2\Psi = -\frac{\rho}{\varepsilon} = -\sum_{j=1}^{2}\frac{z_j e n_j^0 \exp\left(-z_j e\Psi/k_\mathrm{B}T\right)}{\varepsilon}, \tag{1}$$

where ∇^2 is the Laplace operator, ϵ is the permittivity of the liquid phase, ρ is the space charge density, n_j^0 and z_j are, respectively, the bulk number concentration and the valence of ionic species j, and e, k_B , and T are, respectively, the elementary charge, the Boltzmann constant, and the absolute temperature. Following the treatment of Hsu et al. [21], Ψ is decomposed as the electrical potential in the absence of **E**, Ψ_1, and that outside the particle which arises from **E**, Ψ_2, i.e., $\Psi=\Psi_1+\Psi_2$.

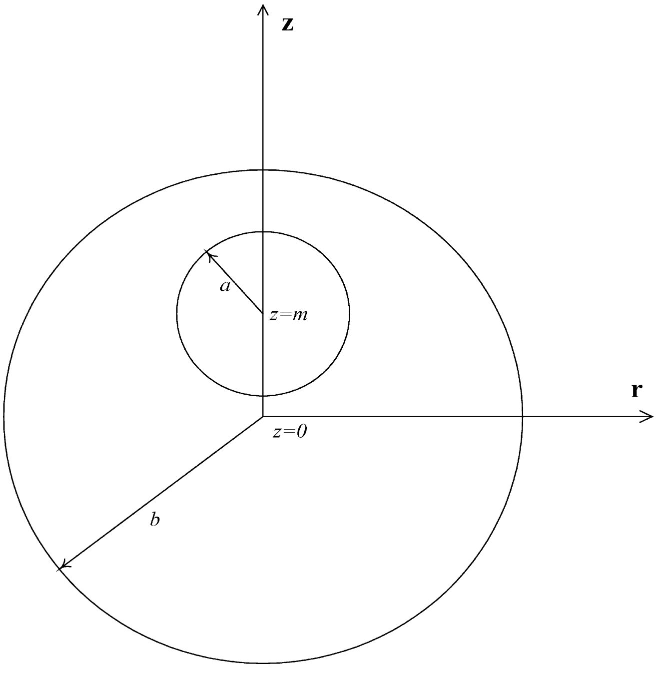

Fig. 1 Schematic representation of the problem considered. A charged, nonconducting spherical particle of radius a is placed at an arbitrary position in a spherical cavity of radius b. The centers of the cavity and the particle are at $z=0$ and $z=m$, respectively. An external electric field, **E**, parallel to the z-direction is applied

Under the Debye–Hückel condition, Ψ_1 and Ψ_2 can be described approximately by

$$\nabla^2\Psi_1 = \kappa^2\Psi_1 \tag{2}$$

and

$$\nabla^2\Psi_2 = 0 \tag{3}$$

where $\kappa = \left(e^2\sum_j z_j^2 n_j^0 \Big/ \varepsilon k_\mathrm{B}T\right)^{1/2}$ is the reciprocal Debye length.

Suppose that the surface of a particle carries acidic functional groups AH, the dissociation of which can be represented by [31]

$$A\mathrm{H} \Leftrightarrow A^- + \mathrm{H}^+. \tag{4}$$

Then it can be shown that the surface charge density of the particle, s, can be expressed as

$$\sigma = -eC_{A^-}^\mathrm{s} = \frac{-eN_\mathrm{s}}{1+\left(C_{\mathrm{H}^+}^0 \Big/ K_\mathrm{d}\right)\exp\left(-\frac{e\Psi}{k_\mathrm{B}T}\right)}, \tag{5}$$

where $K_\mathrm{d} = C_{A^-}^\mathrm{S} C_{\mathrm{H}^+}^\mathrm{s} / C_{A\mathrm{H}}^\mathrm{s}$ is the equilibrium constant for the dissociation reaction represent by Eq. (4),N_s is the concentration of AH, C represents the concentration of a species, and the superscript s denotes a surface property. The boundary conditions associated with Eqs. (2) and (3) can be expressed as

$$\mathbf{n}\cdot\nabla\Psi_1 = \frac{eN_S}{\varepsilon\left[1+\left(C^0_{\mathrm{H}^+}\Big/K_\mathrm{d}\right)\exp\left(-\frac{e\Psi}{k_\mathrm{B}T}\right)\right]} \quad \text{and}$$

$$\mathbf{n}\cdot\nabla\Psi_2 = 0, \text{ on the particle surface} \tag{6}$$

and

$$\mathbf{n}\cdot\nabla\Psi_1 = 0 \quad \text{and } \boldsymbol{n}\cdot\nabla\Psi_2 = -E_z\cos\theta, \text{ on the cavity surface,} \tag{7}$$

where **n** is the unit normal vector, and E_z is the z-component of **E**.

For the present problem, the flow field can be described by

$$\eta\nabla^2\boldsymbol{u} - \nabla p = \rho\nabla\Psi \tag{8}$$

and

$$\nabla\cdot\boldsymbol{u} = 0. \tag{9}$$

In these expressions, $\boldsymbol{u}$ is the fluid velocity, η is the liquid viscosity, and p is the pressure. We assume that both the surface of the particle and that of the cavity are nonslip.

The electrophoretic mobility of a particle can be evaluated based on the fact that the total force acting on it, which includes the electrostatic force and the hydrodynamic force, vanishes at steady state.

Results and discussion

The influences of the key parameters of the system under consideration on the electrophoretic behavior of a particle are examined through numerical simulation. To this end, the equations governing the electrical and the flow fields are solved numerically subject to the associated boundary conditions by FlexPDE [32]. The applicability of this software was justified by Hsu et al. [21]. For convenience, we define $\omega = e\eta U/\epsilon k_\mathrm{B}TE_z$, $\lambda = a/b$, $u^* = u/U$, and $P = 100m/(b\text{-}a)\%$. ω is the electrophoretic mobility of a particle, λ is the relative magnitude of the particle and the cavity, u^* is the scaled particle velocity, U is the z-component of particle velocity, and P is a position parameter. Note that if a particle is at the center of a cavity, $P = 0\%$, and $P = 100\%$ if the former touches the latter.

The influence of the cavity, measured by λ, on the electrophoretic behavior of a particle is illustrated in Fig. 2a, and that of the thickness of the double layer surrounding the particle, measured byκa, is presented in Fig. 2b. Figure 2a reveals that, for a fixed λ, the absolute value of the scaled mobility, $|\omega|$, decreases with the increase in P, and for a fixed P, $|\omega|$ decreases with the increase in λ. These are expected because both a large λ and a large P imply that the presence of a cavity is significant, and has a negative effect on the movement of a particle. As can be seen in Fig. 2b, for a fixed κa, $|\omega|$ decreases with the increase in P, and for a fixed P, $|\omega|$ increases with the increase in κ. This is because if P is large, the viscous retardation due to the presence of a cavity is important, and a large κa (thin double layer) means that the absolute value of the electrical potential gradient near the particle surface is large, which implies a high surface charge density.

The effects of N_s and K_d on the electrophoretic behavior of a particle are shown in Fig. 3. This figure reveals that for a fixed P, $|\omega|$ increases both with the increase in N_s and with the increase in K_d. This is expected because both a large N_s and a large K_d lead to a high surface charge density. As in the case of Fig. 2b, for fixed $N_\mathrm{s}$and K_d, $|\omega|$ decreases with the increase in P.

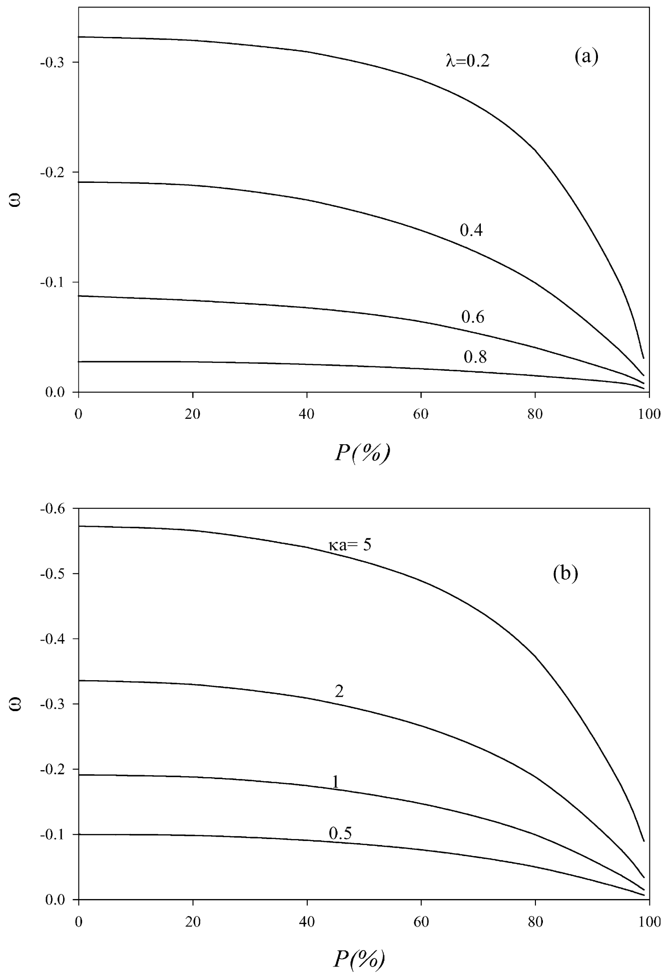

Fig. 2 Variation of scaled mobility, ω, as a function of P at **a** various λ ($=a/b$) and **b** various κa, for the case when K_d= 10^{-2} M, $N_\mathrm{s}=2\times10^{-9}$ M, and $C^0_{\mathrm{H}^+} = 10^{-7}$ M . κa = 1 in **a** and $\lambda = 0.4$ in **b**

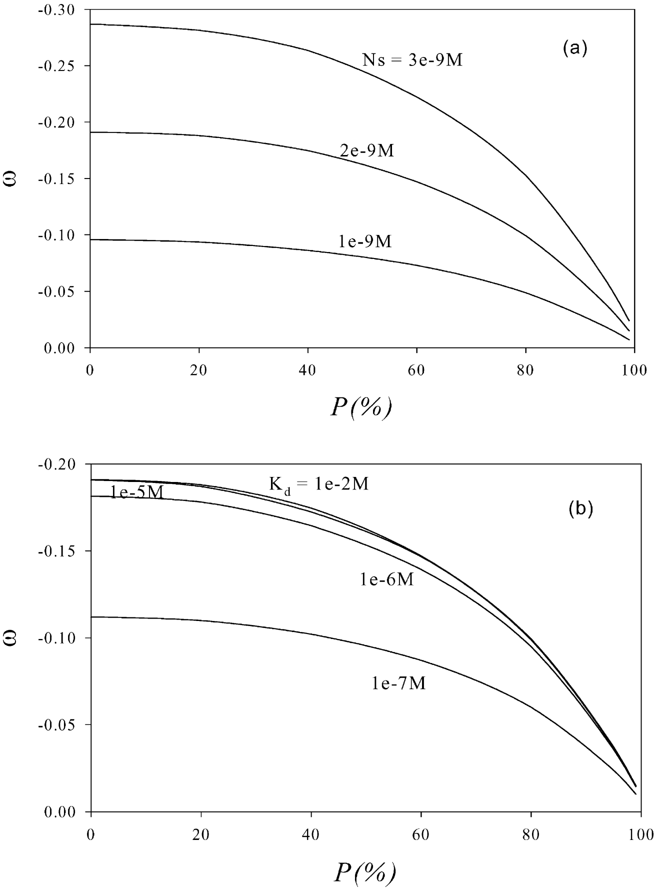

Fig. 3 Variation ofωas a function$_s$ of Pat **a** various N and **b** various K_d, for the case when $\lambda=0.4$, $\kappa a=1$, and $C^0_{H^+}=10^{-7}$ M.$K_d=10^{-2}$ M in **a** and $N_s=2\times10^{-9}$ M in **b**

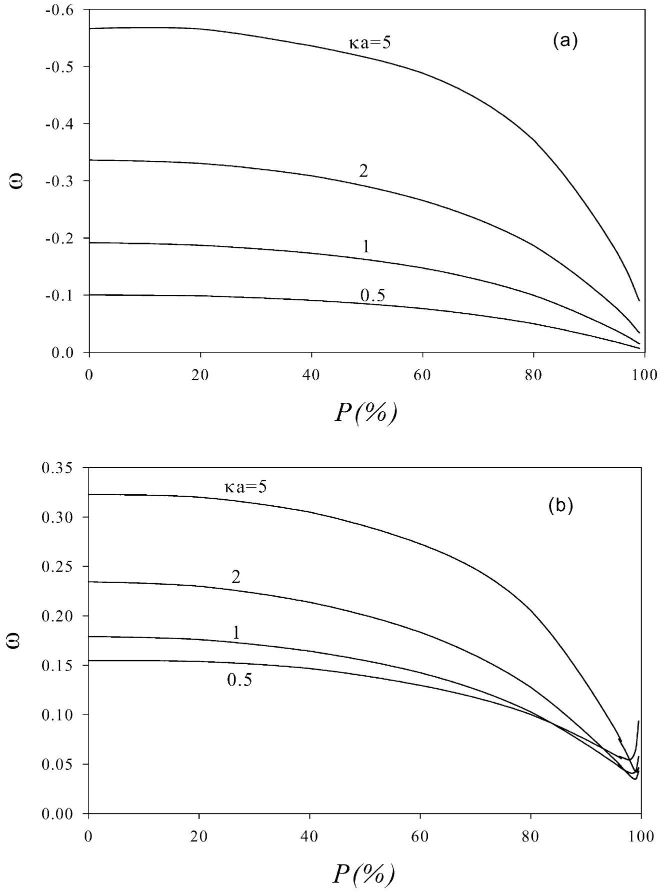

Fig. 4 Variation of ω as a function of P for the case when **a** $K_d\rightarrow\infty$ and **b** $K_d\rightarrow0$, for the case when $\lambda=0.4$,$N_s=2\times10^{-9}$ M, and $C^0_{H^+}=10^{-7}$ M

The results of constant surface potential and constant surface charge density on both the particle and the cavity surface can be recovered as the limiting cases of the present model. The simulated results for these cases are presented in Fig. 4. Note that as $K_d\rightarrow\infty$, Eq. (5) reduces to $\sigma=-eN_s$ and Eq. (7) becomes $\mathbf{n}\cdot\nabla\Psi_1=eN_s/\epsilon$ and $\mathbf{n}\cdot\nabla\Psi_2=0$, i.e., both the charge density on the particle surface and that on the cavity surface remain constant. In this case, the general trends of ω as P and κa vary are similar to those illustrated in Fig. 2b. Those for the case when $K_d\rightarrow0$, however, become different. In this case, Eq. (7) gives $\Psi_1=$constant and $\mathbf{n}\cdot\nabla\Psi_2=0$, and Eq. (8) yields $\Psi_1=0$ and $\mathbf{n}\cdot\Psi_2=E_z\cos\theta$. That is, both the surface of the particle and that of the cavity remain at constant potential (the cavity surface remains at zero surface potential). Figure 4b shows that if P is not large, then $|\omega|$ increases with the increase in κa, but if P is sufficiently large, i.e., a particle is sufficiently close to the cavity, $|\omega|$ decreases with the increase in κa. Also, the variation of $|\omega|$ as a function of P exhibits a local minimum, and the thicker the double layer the smaller the value of P at which the local minimum occurs. These are similar to the observations of Hsu et al. [21], and can be explained by a charge reversal occurring on the cavity surface.

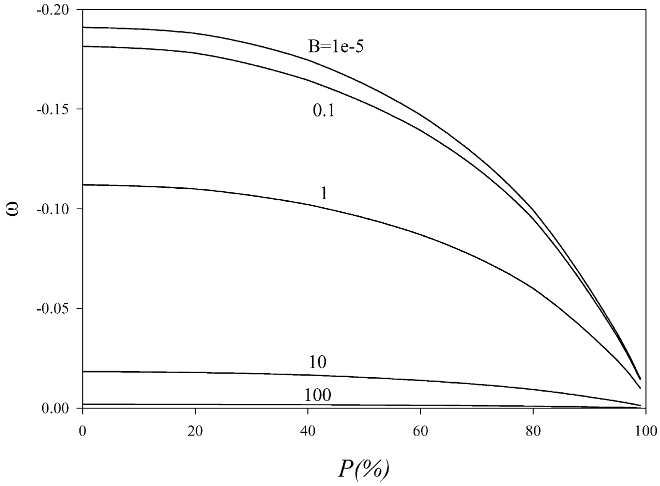

Fig. 5 Variation ofω as a function of P at various $B(=C^0_{H^+}/K_d)$ for the case when $\lambda=0.4$, $\kappa a=1$, $K_d=10^{-2}$ M, and $N_s=2\times10^{-9}$ M

The influence of pH on the electrophoretic mobility of a particle is illustrated in Fig. 5, where ω is plotted as a function of P at various values of $B(= C^0_{H^+}/K_d)$. This figure suggests that the higher the $C^0_{H^+}$ the smaller the $|\omega|$ is. This is because a large B implies a low pH, and the bulk conditions are disadvantageous to the dissociation of AH, and, therefore, the charge density on particle surface is low.

Conclusion

In summary, the boundary effect of electrophoresis was investigated by considering a charge-regulated sphere at an arbitrary position in a spherical cavity. The present analysis extends previous ones in that the particle surface is assumed to be a mixed-type boundary condition; previous results can be recovered as the limiting cases of the present model. Numerical simulations reveal that both the charge conditions and the presence of a boundary can play a significant role in determining the electrophoretic behavior of a particle. In general, the presence of a boundary exhibits a negative effect on the movement of a particle, and the thinner the double layer surrounding a particle the larger its mobility. However, the reverse becomes true if the particle is sufficiently close to the boundary, which can be explained by a charge reversal occurring on the latter.

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