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Influence of boundary on the effect of double-layer polarization and the electrophoretic behavior of soft biocolloids

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ABSTRACT

The electrophoresis of a soft particle comprising a rigid core and a charged porous membrane layer in a narrow space is modeled. This simulates, for example, the capillary electrophoresis of biocolloids such as cells and microorganisms, and biosensor types of device. We show that, in addition to the boundary effect, the effects of double-layer polarization (DLP) and the electroosmotic retardation flow can be significant, yielding interesting electrophoretic behaviors. For example, if the friction coefficient of the membrane layer and/or the boundary is large, then the DLP effect can be offset by the electroosmotic retardation flow, making the particle mobility to decrease with increasing double layer thickness, which is qualitatively consistent with many experimental observations in the literature, but has not been explained clearly in previous analyses. In addition, depending upon the thickness of double layer, the friction of the membrane layer of a particle can either retard or accelerate its movement, an interesting result which has not been reported previously. This work is the first attempt to show solid evidence for the influence of a boundary on the effect of DLP and the electrophoretic behavior of soft particles. The model proposed is verified by the experimental data in the literature. The results of numerical simulation provide valuable information for the design of bio-analytical apparatus such as nanopore-based sensing applications and for the interpretation of relevant experimental data.

1. Introduction

Electrophoresis has been applied widely in many areas of fundamental and practical significance. Recent advances in fabrication techniques further extend its application to small-scaled operations such as capillary electrophoresis [1,2], lab-on-a-chip devices [3,4], biosensors [5], and nanopore sensing technology [6–8]. In these cases, because the available space for electrophoresis is narrow, the electrophoretic behavior of a particle is influenced inevitably by the boundary of a device. This effect is usually ignored in the early stage of electrophoresis analysis. In fact, the presence of a boundary can have a profound influence on that behavior. For example, if a particle is sufficiently close to a surface, then its electrophoretic velocity can be either raised or reduced, depending upon the neighboring conditions [9–11]. It is also possible that the direction of electrophoresis is altered by a nearby surface [12,13].

Conventional electrophoresis analysis focused mainly on a rigid particle, where its surface is impenetrable to ionic species and fluid medium. Recently, a more general type of particle, namely, soft or fuzzy particle, is proposed to simulate biocolloids such as cells and microorganisms and inorganic particles covered by an artificial membrane layer [14–18]. A soft particle comprises a rigid core and a porous layer, which is penetrable to ionic species and fluid medium. Note that a rigid particle can be viewed as the limiting case of a soft particle where its porous layer is infinitely thin. On the other hand, if the rigid core of a soft particle is infinitely small, then it becomes entirely porous. Polyelectrolytes such as DNA, proteins, and polymer gels, for instance, belong to this category [19,20]. In addition to the charge on the surface of its rigid core, the porous layer of a soft particle is also capable of carrying charge, which comes from, for example, the dissociation/association reactions of function groups. This implies that the electrophoretic behavior of a soft particle can be more complicated than that of the corresponding rigid particle.

Several attempts have been made recently on the modeling of the electrophoresis of soft particles. Ohshima [21–27], for example, conducted a series of theoretical studies on the electrophoretic behaviors of soft particles under the conditions of weak applied electric field and low surface potential. The latter assumption implies that the effect of double-layer polarization (DLP), one of the interesting phenomena in electrophoresis coming from the deformation of double layer when the particle is in motion [28], can be neglected. Under the same conditions, Zhang et al. [29] and Hsu et al. [30,31] investigated further the boundary effect on the electrophoretic behavior of a soft particle by considering the elec-

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trophoresis of a soft toroid [30] and a sphere [29,31] along the axis of a cylindrical pore. Yeh et al. [32] analyzed the electrophoresis of a membrane-coated cylinder positioned eccentrically along the axis of a cylindrical pore for the case of arbitrary double-layer thickness, which is a three-dimensional problem. Taking the effect of DLP, which usually retards the particle motion, into account, Saville [33] and Hill et al. [34] studied the electrophoresis of an isolated soft spherical particle in an unbounded electrolyte solution. It was found that the effect of DLP can be significant when the charge density of a soft particle is high. Those analyses were extended by Lee et al. [35] to take the effect of particle concentration into account. The influence of a boundary on the electrophoretic behavior of a soft sphere for the case of an arbitrary level of surface potential, where applying a nonlinear Poisson–Boltzmann equation to describe the electrical potential is necessary, was analyzed by several investigators through considering various geometries [36–38].

Two types of soft particle have been considered in previous theoretical studies. For convenience, we define type I soft particle as the one with a charged rigid core having a constant surface potential and an ion-penetrable porous layer [25–27,31–38], and type II soft particle as the one with an uncharged rigid core and a polyelectrolyte membrane layer [21–24,29,30]. Note that a Neumann type of boundary condition, imposing a zero charge density on the surface of the rigid core of a particle, is applied in case of type II soft particle. Therefore, the electrical potential on that surface, known as Donnan potential [17,21], varies with the physicochemical properties of the membrane layer of the particle and the electrolyte concentration. This model predicts that the electrophoretic mobility of a particle decreases with decreasing double layer thickness [24]. This is consistent with the behavior of biocolloids such as cells, proteins, microorganisms, and inorganic particle covered by a biological membrane layer [18,20,39,40]. On the other hand, a Dirichlet type of boundary condition, imposing a constant potential on the surface of the rigid core of a particle, is applied in the case of type I soft particle. In this case, the electrophoretic mobility of a particle increases with decreasing double layer thickness, in general [25–27,31–38]. This phenomenon is similar to that of a rigid particle having a constant surface potential [9–13].

Taking the effect of DLP into account, the influence of a boundary on the electrophoretic behavior of a soft biocolloid (type II soft particle) is investigated in this study by considering the electrophoresis of a soft sphere in a spherical cavity. This geometry was adopted by Zydney [41] to simulate the electrophoresis of a rigid sphere in a porous medium, and by others to model that of a concentrated dispersion [42,43]. As pointed out by Lee et al. [44], although the sphere-in-spherical cavity model is an idealized one, it is relatively simple in mathematical representation and can be used to predict the behavior of a sphere in a cylindrical pore. The electrophoretic mobility of the particle under various conditions is examined in detail through varying the thickness of double layer, the position of the particle in the cavity, the properties of the membrane layer of the particle, and the size of the cavity. Since the position of the particle is arbitrary, the geometry considered is capable of simulating more realistically the experiments in practice, such as the characterization of biocolloids by capillary electrophoresis [18,39,40] and the electrophoretic translocation of protein [45,46] and DNA [6–8], through a nanopore. This study is also aimed to provide theoretical background for the interpretation of the dependence of the electrophoretic mobility of biocolloids on salt concentration usually observed in experiments.

2. Theory

The problem under consideration is illustrated in Fig. S1 of Supplementary Material, where a soft sphere of radius a comprising a rigid core of radius $(a–c)$ and an ion-penetrable membrane layer of thickness c at an arbitrary position in a spherical cavity of radius b is driven by an applied uniform electric field $\mathbf{E}$ of strength E in the z-direction. The cylindrical coordinate (r,θ,z) is adopted with the origin located at the center of the cavity, and the center of the particle is at $z = m$. Let $\Lambda = a/b$ and $M = 100\% \times [m/(b-a)]$ be the relative size of the cavity and the relative position of the particle, respectively. Note that the larger the Λ or M the more important the boundary effect is. The cavity is filled with an aqueous, incompressible Newtonian fluid containing z_1:z_2 electrolytes with z_1 and z_2 being the valences of cations and of anions, respectively.

If we let ϕ, n_j, p, and $\mathbf{v}$ be the electrical potential, the number concentration of ionic species j, the pressure, and the fluid velocity relative to the particle, respectively, then, because the present problem is θ-symmetric, the electric, the concentration, and the flow fields of the present problem can be described by [17,47]

$$\nabla^2\phi = -\frac{\rho + h(r,z)\rho_{fix}}{\varepsilon}, \tag{1}$$

$$\nabla \cdot \left[-D_j(\nabla n_j + \frac{z_j e}{k_B T} n_j \nabla\phi) + n_j \mathbf{v}\right] = 0 \tag{2}$$

$$\nabla \cdot \mathbf{v} = 0 \tag{3}$$

$$-\nabla p + \eta\nabla^2\mathbf{v} - \rho\nabla\phi - h(r,z)\gamma\mathbf{v} = 0 \tag{4}$$

Here, ∇^2 and $\nabla$are the Laplace operator and the gradient operator, respectively; ε, ρ $(=\sum_{j=1}^{2} z_j e n_j)$, and ρ_{fix} are the permittivity of the fluid phase, the space charge density of mobile ions, and the fixed charged density of the membrane layer, respectively; D_j and z_j are the diffusivity and the valance of ionic species j, respectively; e, k_B, and T are the elementary charge, the Boltzmann constant, and the absolute temperature, respectively; η is the fluid viscosity; γ is the hydrodynamic frictional coefficient of the membrane layer per unit volume; $h(r,z) = 0$ for the region outside the particle, and $h(r,z) = 1$ for the region inside the membrane layer. Eq. (2), which implies that the mobile ions can be driven by the flow of fluid, the ionic concentration gradient, and the electric field, is a statement of the conversation of ionic species j. Eqs. (3) and (4) are the continuity equation and a modified Navier–Stokes equation, respectively, with $-\rho\nabla\phi$ and $-\gamma\mathbf{v}$ being respectively the electric body force acting on the fluid and the frictional force exerted on the fluid by the composing material of the porous layer [17]. Note that because the flow field in electrophoresis is in the creeping flow regime, there is no inertial term in Eq. (4). For simplicity, we assume that the values of ε, D_j, and η inside the membrane layer are the same as those outside the particle, and ρ_{fix} is independent of the position inside the membrane layer [17]. Duval et al. [48] verified experimentally that if the water content within the membrane layer is sufficiently high, then the ε inside the membrane layer and that outside it can be assumed equal.

We assume that the strength of $\mathbf{E}$ is much weaker than that of the equilibrium electric field established by the particle and/or the boundary [49]. Similar to the treatments of Yeh and Hsu [47], each dependent variable is partitioned into an equilibrium term coming from the particle in the absence of $\mathbf{E}$, and a perturbed term from the application of $\mathbf{E}$. Because both the electrical potential and the thickness of double layer are arbitrary, the effect of DLP can be significant, implying that the double layer surrounding the particle can be asymmetric. Under these conditions, the equations governing the present problem can be summarized as following [47]:

$$\nabla^{*2}\phi_e^* = -\frac{(\kappa a)^2}{1+\alpha}[\exp(-\phi_e^*) - \exp(\alpha\phi_e^*)] - h(r,z)Q^* \tag{5}$$