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Sedimentation velocity and potential in a concentrated suspension of charged soft spheres

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HIGHLIGHTS

- ► The sedimentation in a suspension of charged soft spheres is analytical studied.
- ► A unit cell model allowing the overlap of the adjacent double layers is used.
- ► The sedimentation velocity and potential are obtained with the relaxation effect.
- ► The particle concentration effects are significant, even in dilute suspensions.
- ► Charged but neutral soft spheres can produce sedimentation potential.

GRAPHICAL ABSTRACT

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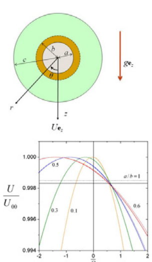

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ABSTRACT

An analytical study of sedimentation in a suspension of charged spherical soft particles, each with the structure of a rigid core surrounded by a porous shell, in an electrolyte solution is presented. The porous shell of the particle is treated as a solvent-permeable and ion-penetrable surface layer of finite thickness, in which hydrodynamic frictional segments with fixed charges distribute uniformly. A unit cell model that allows the overlap of the electric double layers of adjacent particles is employed to account for the effect of particle interactions. When the system is slightly distorted from equilibrium, the electrokinetic equations governing the electric potential, ion concentration, and fluid velocity distributions are linearized and solved using a perturbation method with the fixed charge densities of the core surface and porous layer of each soft sphere as the small parameters. Explicit formulas for the sedimentation velocity and potential in the suspension are obtained to the second orders of these fixed charge densities with the relaxation effect of the double layers included. The sedimentation velocity and potential are not necessarily monotonic functions of the volume fraction of the particles; the particle concentration effects are significant, even in dilute suspensions. In the limiting cases, the analytical solutions of the sedimentation velocity and potential for charged soft spheres reduce to those for charged rigid spheres and charged porous spheres. It is shown that a suspension of charged but neutral soft spheres can produce sedimentation potential, and their sedimentation velocity differs from that of the uncharged soft spheres.

1. Introduction

The movement of small charged particles suspended in an electrolyte solution is of great fundamental and practical interest in the fields of chemical, biomedical, and environmental engineering and colloidal science. This motion is more complicated than that of uncharged ones because the electric double layer surrounding each

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charged particle is distorted by the ambient fluid flow relative to the particle and a sedimentation/migration potential is induced in the suspension. The sedimentation potential gradient not only disturbs the ionic fluid flow but also affects the sedimentation velocity of the charged particles.

Using a perturbation method to solve the basic electrokinetic equations, Booth [1] obtained the sedimentation velocity and potential in a dilute suspension of charged spheres with an arbitrary double-layer thickness as power series in the small zeta potential of the particles. Numerical results relieving the restriction of low zeta potential were reported by Stigter [2] using the theory of electrophoresis of a charged sphere [3], and the Onsager reciprocal relation between the sedimentation potential and the electrophoretic mobility [4] was found to be satisfied. Taking the double-layer distortion from equilibrium as a small perturbation, Ohshima et al. [5] obtained analytical and numerical results of the sedimentation velocity and potential in a dilute suspension of dielectric spheres over a broad range of double-layer thickness and zeta potential. Later, the perturbation analysis was extended to the derivation of the sedimentation velocity and potential in a dilute suspension of charged soft spheres, having a central rigid core and an outer porous shell for each particle [6–10], and again the Onsager relation is satisfied between sedimentation and electrophoresis [11]. In the limiting cases, the analytical formulas describing the sedimentation velocity and potential for charged soft spheres reduce to those for charged impermeable spheres [5] and charged porous spheres [12,13].

In some practical applications of sedimentation of charged soft particles [14–16], relatively concentrated suspensions are encountered and effects of particle interactions will be important. The unit cell models, which involve the concept that a swarm of particles can be divided into a number of identical cells and one particle occupies each cell at its center, have been widely employed to estimate the effects of particle interactions on the mean sedimentation velocity [17–23], electrophoretic mobility [24–30], and diffusiophoretic mobility [31,32] in a bounded suspension of identical hard or soft spheres. Among these models with various boundary conditions for the fluid flow at the virtual surface of the cell, the most acceptable ones are the Happel “free-surface” model [33] and Kuwabara “zero-vorticity” model [34].

Assuming that the overlap of the electric double layers of adjacent particles is negligible and neglecting the polarization/relaxation effect of the double layers, Ohshima [35] used the Kuwabara cell model to obtain expressions for the sedimentation velocity and potential in a suspension of charged soft spheres for the case of small electric potentials. The sedimentation velocity and potential for a suspension of charged soft spheres were also calculated numerically on the basis of the Kuwabara model and nonoverlapping double layers [36]. On the other hand, the sedimentation phenomena in suspensions of charged impermeable spheres [19] and porous spheres [22] with low electric potentials were analyzed with using the cell models and allowing the overlap of adjacent double layers; the results of the sedimentation velocity and potential demonstrate that, even for the case of thin double layers, the effects of the double-layer relaxation and overlap are significant.

In this paper, the unit cell model is used to analyze the sedimentation in a suspension of charged soft spheres, and both the Happel model and the Kuwabara model are considered. The overlap of adjacent double layers is allowed and the relaxation effect in the double layers is included. A set of electrokinetic equations are linearized assuming that the double layers are only slightly distorted from the equilibrium state. Through the use of a perturbation method with the fixed charge densities of the soft particles as the small perturbation parameters, the ion concentration, electric potential, and fluid velocity profiles are determined by solving these linearized electrokinetic equations subject to appropriate boundary conditions. Closed-form formulas for the sedimentation velocity and potential in the suspension are obtained.

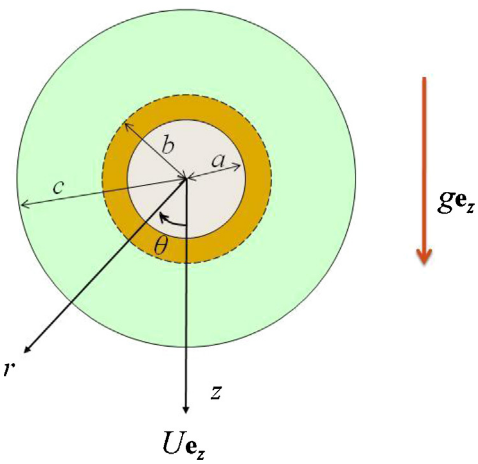

Fig. 1. Geometrical sketch for the sedimentation of a soft sphere at the center of a spherical cell.

2. Electrokinetic equations

Consider the steady sedimentation of a homogeneous distribution of identical charged soft particles with a structure of spherical symmetry in a bounded fluid solution containing M ionic species. Each soft particle of radius b is composed of a rigid-sphere core of radius a and an adsorbed surface layer of porous substance or polyelectrolytes of thickness $b-a$. The porous surface layer is treated as a solvent-permeable and ion-penetrable homogeneous shell in which fixed charges distribute uniformly. The sedimentation velocity of the particle is $U\mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector in the z direction. As illustrated in Fig. 1, we employ a unit cell model in which each soft particle is surrounded by a concentric spherical envelope of suspending solution having an outer radius c such that the particle/cell volume ratio equals the particle volume fraction φ of the suspension; i.e., $\varphi=(b/c)^3$. The origin of the spherical coordinate system (r, θ, ϕ) is set at the particle center and the axis $\theta=0$ points toward the z direction. Evidently, the problem for each cell is axially symmetric about the z-axis and does not depend on ϕ.

2.1. Governing equations

We assume that the system is only slightly distorted from equilibrium and the concentration distribution $n_m(r,\theta)$ of species m, the electric potential distribution $\psi(r,\theta)$, and the pressure distribution $p(r,\theta)$ can be expressed as

$$n_m = n_m^{(\mathrm{eq})} + \delta n_m \tag{1a}$$

$$\psi = \psi^{(\mathrm{eq})} + \delta\psi \tag{1b}$$

$$p = p^{(\mathrm{eq})} + \delta p \tag{1c}$$

Here, $n_m^{(\mathrm{eq})}(r)$, $\psi^{(\mathrm{eq})}(r)$, and $p^{(\mathrm{eq})}(r, \theta)$ are the equilibrium distributions of the concentration of species m, electric potential, and pressure, respectively, and $\delta n_m(r, \theta)$, $\delta\psi(r, \theta)$, and $\delta p(r, \theta)$ are the corresponding deviations from the equilibrium state. The equilibrium ion concentrations are related to the equilibrium potential by the Boltzmann equation.

A previous study [11] shows that the small perturbed quantities δn_m, $\delta\psi$, and δp as well as the fluid velocity field $\mathbf{u}(r, \theta)$, which is also a small quantity, satisfy the following linearized equations:

$$\nabla\cdot\mathbf{u} = 0 \tag{2}$$