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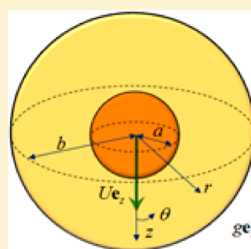
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Sedimentation of a Charged Porous Particle in a Charged Cavity

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ABSTRACT: The sedimentation of a charged porous sphere at the center of a charged spherical cavity filled with an electrolyte solution is analyzed. The thickness of the electric double layers around the particle and cavity wall is arbitrary, and their relaxation effect is considered. Through the use of a set of linearized electrokinetic equations and a perturbation method, the ionic electrochemical potential energy, electric potential, and velocity fields in the fluid are solved with the fixed space charge density of the particle and surface charge density of the cavity as the small perturbation parameters, and an explicit formula for the sedimentation velocity is obtained. Due to the electroosmotic enhancement on the fluid recirculation in the cavity caused by the sedimentation-induced electric field, the presence of the surface charges on the cavity wall increases the sedimentation velocity of the porous particle. For the sedimentation of a porous particle in a cavity with their fixed charges of the same sign, the effect of electric interaction between the particle and cavity wall in general increases the sedimentation velocity. For the case of their fixed charges with opposite signs, the sedimentation velocity is increased/reduced if the magnitude of the fixed charge density of the cavity wall is relatively large/small. The effect of the surface charges at the cavity wall on the sedimentation of the porous particle increases with an increase in the permeability for fluid flow within the particle and with a decrease in the particle-to-cavity radius ratio (i.e., an increase in the surface area of the cavity wall relative to a given size of the particle, which enhances the fluid recirculation effect).


$$U = U_{00} [1 + (\kappa a)^4 H_1 \bar{Q}^2 + (\kappa a)^3 H_2 \bar{Q} \bar{\sigma} + (\kappa a)^2 H_3 \bar{\sigma}^2]$$
$$\bar{Q} = ZeQ / \epsilon \kappa^2 kT$$
$$\bar{\sigma} = Ze\sigma / \epsilon \kappa kT$$

1. INTRODUCTION

The sedimentation of small charged particles in an electrolyte solution is of great fundamental and practical interest in the fields of colloidal science and chemical engineering. This phenomenon is more complicated than that of uncharged particles because the electric double layer surrounding each charged particle is distorted by the ambient fluid flow relative to the settling particle and a sedimentation potential gradient is induced. This potential gradient not only disturbs the ionic fluid flow but also reduces the sedimentation velocity of the charged particle by an electrophoretic driving force in the opposite direction.

Using a perturbation method to solve the basic electrokinetic equations, Booth¹ obtained the sedimentation velocity and potential in a suspension of charged spheres with an arbitrary double-layer thickness as a power series in the small zeta potential of the particles. Later, Stigter² performed numerical calculations for the sedimentation of charged spheres with an arbitrary zeta potential and found the Onsager reciprocal relation between the sedimentation potential and the electrophoretic mobility³ to be satisfied. Ohshima et al.⁴ took the double-layer distortion from equilibrium as a small perturbation and obtained analytical and numerical results of the sedimentation velocity and potential in a suspension of dielectric spheres over a broad range of double-layer thicknesses and zeta potentials. The perturbation analysis was also extended to the determination of the sedimentation velocity and potential in suspensions of interacting dielectric spheres,^{5–9} charged porous spheres,^{10–12} and charged soft

(composite) spheres^{13–15} with low fixed charge densities, and all of these studies manifest the retardation effect of the fixed charges of the particle on its sedimentation.

In real situations of sedimentation, such as in microfluidic and lab-on-a-chip devices, colloidal particles are seldom isolated but usually move near solid boundaries.^{16,17} Although the boundary effects on the sedimentation of uncharged particles have been studied extensively,^{18–21} few investigations about these effects on the sedimentation of charged particles were reported. Using a perturbation expansion in the small zeta potential and the Peclet number, Pujar and Zydney²² calculated the sedimentation velocity of a charged sphere situated at the center of an uncharged spherical cavity. This analysis was extended to a numerical calculation for the case of an arbitrary zeta potential.²³ Recently, the sedimentation of a dielectric sphere in a concentric charged spherical cavity was analyzed with the surface charge densities of the particle and cavity wall as small perturbation parameters.²⁴

The system of a spherical particle settling at the center of a spherical cavity can be an idealized model for the sedimentation in media constructed from connecting spherical pores.^{22–24} In this article, the sedimentation of a charged porous sphere, such as a polyelectrolyte molecule (DNA fragment, peptide, etc.) or an aggregate of fine particles bearing surface charges, in a concentric charged spherical cavity is analyzed. Compared with

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a charged impermeable particle, the distribution of fixed charges and penetration of mobile ions (mostly counterions) as well as the shielding effect of solvent permeation within the porous particle creates differences in electrostatic and hydrodynamic characteristics. The electric double layers of arbitrary thickness around the particle and cavity wall are distorted by the fluid flow accompanying the sedimentation, and the induced electric fields alter the fluid velocity distribution. The linearized electrokinetic equations applicable to the system are solved for the ionic electrochemical potential energy, electric potential, and velocity fields in the fluid, and the double-layer relaxation effect is taken into account appropriately. The spherical symmetry in this system allows an analytical solution of the sedimentation velocity of the confined porous sphere to be obtained in eq 28.

2. ELECTROKINETIC EQUATIONS

We consider the quasi-steady sedimentation of a charged porous spherical particle of radius a located at the center of a charged spherical cavity of radius b filled with a symmetric electrolyte solution, as illustrated in Figure 1. Within the

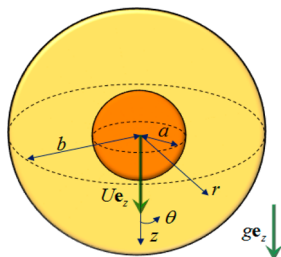


Figure 1. Geometrical sketch for the sedimentation of a porous spherical particle at the center of a spherical cavity.

particle, which is permeable to ions and solvent molecules to some extent, frictional segments with fixed charges are assumed to distribute at a uniform density. The gravitational acceleration equals $g\mathbf{e}_z$, and the sedimentation velocity of the porous particle to be determined is $U\mathbf{e}_z$, where \mathbf{e}_z is the unit vector in the z direction. The spherical coordinate system (r, θ, ϕ) is established with its origin at the center of the particle, and the problem is axially symmetric about the z axis (or the polar axis $\theta = 0$) and independent of the coordinate ϕ .

2.1. Governing Equations. It is assumed that the system is only slightly distorted from equilibrium by the sedimentation of the confined particle. Thus, the ionic concentration distributions $n_{\pm}(r, \theta)$ and electric potential distribution $\psi(r, \theta)$ can be expressed as

$$n_{\pm} = n_{\pm}^{(\text{eq})} + \delta n_{\pm} \quad (1a)$$

$$\psi = \psi^{(\text{eq})} + \delta\psi \quad (1b)$$

where $n_{\pm}^{(\text{eq})}(r)$ and $\psi^{(\text{eq})}(r)$ are the equilibrium ionic concentration and electrostatic potential distributions, respectively, and $\delta n_{\pm}(r, \theta)$ and $\delta\psi(r, \theta)$ are the small perturbations to the corresponding equilibrium distributions. Here, subscripts $+$ and $-$ refer to the cation and anion, respectively. The equilibrium ionic concentrations and electrostatic potential are related by the Boltzmann equation

$$n_{\pm}^{(\text{eq})} = n^{\infty} \exp\left[\mp \frac{Ze\psi^{(\text{eq})}}{kT}\right] \quad (2)$$

where the constants n^{∞} and Z are the bulk concentration and valence, respectively, of the symmetric electrolyte, e is the charge of a proton, k is Boltzmann's constant, and T is the absolute temperature.

The small perturbed quantities δn_{\pm} and $\delta\psi$ together with the fluid velocity field $\mathbf{u}(r, \theta)$, which is also a small perturbed quantity, satisfy a set of linearized electrokinetic equations¹¹

$$\nabla \cdot \mathbf{u} = 0 \quad (3)$$

$$\nabla^2 \nabla \times \mathbf{u} - h(r)\lambda^2 \nabla \times \mathbf{u} = -\frac{\varepsilon}{\eta} \nabla \times [\nabla^2 \psi^{(\text{eq})} \nabla \delta\psi + \nabla^2 \delta\psi \nabla \psi^{(\text{eq})}] \quad (4)$$

$$\nabla^2 \delta\mu_{\pm} = \pm \frac{Ze}{kT} \left\{ \nabla \psi^{(\text{eq})} \cdot \nabla \delta\mu_{\pm} - \frac{kT}{[1 - (1 - \omega_{\pm})h(r)]D_{\pm}} \nabla \psi^{(\text{eq})} \cdot \mathbf{u} \right\} \quad (5)$$

$$\nabla^2 \delta\psi = \frac{Zen^{\infty}}{\varepsilon kT} \left[\exp\left(\frac{Ze\psi^{(\text{eq})}}{kT}\right) (\delta\mu_{-} + Ze\delta\psi) - \exp\left(-\frac{Ze\psi^{(\text{eq})}}{kT}\right) (\delta\mu_{+} - Ze\delta\psi) \right] \quad (6)$$

resulting from the continuity equation for the incompressible fluid, the Stokes/Brinkman equations modified with the electrostatic effect, the conservation equations for the ionic species, and Poisson's equation, respectively. In eqs 4–6, $\delta\mu_{\pm}(r, \theta)$ are the perturbations of the ionic electrochemical potential energies,⁴ defined as a linear combination of δn_{\pm} and $\delta\psi$

$$\delta\mu_{\pm} = kT \frac{\delta n_{\pm}}{n_{\pm}^{(\text{eq})}} \pm Ze\delta\psi \quad (7)$$

η and ε are the viscosity and permittivity of the fluid, respectively; λ is the reciprocal of the Brinkman screening (shielding) length characterizing the extent of flow penetration within the porous particle (λ^{-2} is its permeability dependent on the pore size and porosity); D_{\pm} and $\omega_{\pm}D_{\pm}$ are the diffusion coefficients of the ionic species outside and inside of the particle, respectively ($\omega_{\pm} \leq 1$, depending on the ion-to-pore size ratios and the sign and density of the charge groups of the porous particle); and $h(r)$ is a unit step function that equals unity if $r \leq a$ (inside of the particle) and zero otherwise. The values of η , ε , λ , D_{\pm} , and ω_{\pm} are taken to be constant.

For counterions in polyelectrolyte networks, a theory for the ionic self-diffusion²⁵ and some experimental data²⁶ predict that the parameters ω_{\pm} (which are the normalized diffusion coefficients of the small ions in the porous structure) can have values as low as 0.25–0.31. For model porous particles made of steel wool²⁷ and plastic foam slab,²⁸ experimental data of λ^{-1} can be as high as 0.4 mm, whereas in the surface layers of human erythrocytes,²⁹ rat lymphocytes,³⁰ and grafted polymer microcapsules³¹ in electrolyte solutions, values of λ^{-1} were found to be about 3 nm.

2.2. Boundary Conditions. The boundary conditions for the small perturbed quantities at the surface of the porous sphere are^{11,32–34}

$$\mathbf{u}|_{r=a^+} = \mathbf{u}|_{r=a^-} \quad (8a)$$

$$\mathbf{e}_r \cdot \boldsymbol{\tau}|_{r=a^+} = \mathbf{e}_r \cdot \boldsymbol{\tau}|_{r=a^-} \quad (8b)$$

$$\delta\mu_{\pm}|_{r=a^+} = \delta\mu_{\pm}|_{r=a^-} \quad (9a)$$

$$\nabla\delta\mu_{\pm}|_{r=a^+} = \omega_{\pm}\nabla\delta\mu_{\pm}|_{r=a^-} \quad (9b)$$

$$\delta\psi|_{r=a^+} = \delta\psi|_{r=a^-} \quad (10a)$$

$$\nabla\delta\psi|_{r=a^+} = \nabla\delta\psi|_{r=a^-} \quad (10b)$$

Here, $\boldsymbol{\tau} = \eta[\nabla\mathbf{u} + (\nabla\mathbf{u})^T]$ is the viscous stress of the fluid, \mathbf{e}_r is the unit vector outwardly normal to the particle surface, and the superscripts + and – to a denote the external and internal sides, respectively, to the particle surface. Equations 8–10 are the continuity requirements of the fluid velocity and stress, the ionic concentrations and fluxes, as well as the electric potential and field, respectively, at the particle surface, where the Maxwell stress, the hydrostatic pressure, and thus the total fluid stress are also continuous. The continuity of the electric field in eq 10b is true only if the permittivity of the fluid inside and outside of the porous particle is the same. The various boundary conditions to describe the flow field at the interface between a porous medium and the surrounding fluid (including slip conditions) in relation to both Darcy's law and the Brinkman equation have been discussed in detail in the literature,^{35,36} and eq 8 is physically realistic and mathematically consistent with the Brinkman eq 4 used in the present problem.

The boundary conditions for the perturbed quantities at the cavity wall are

$$\mathbf{u}|_{r=b} = -U\mathbf{e}_z \quad (11)$$

$$\frac{\partial\delta\mu_{\pm}}{\partial r}|_{r=b} = 0 \quad (12)$$

$$\frac{\partial\delta\psi}{\partial r}|_{r=b} = 0 \quad (13)$$

Equation 11 takes a reference frame that the particle is at rest and the fluid velocity at the no-slip cavity wall is the particle velocity in the opposite direction, whereas eqs 12 and 13 state that no ions can penetrate in and the Gauss condition holds at the dielectric cavity wall.

3. SOLUTIONS TO THE ELECTROKINETIC EQUATIONS

3.1. Equilibrium Electrostatic Potential. The equilibrium electrostatic potential for the system of a porous sphere with a uniform fixed charge density Q in a concentric spherical cavity with a constant surface charge density σ filled with a symmetric electrolyte solution, which appears in eqs 4–6, can be obtained as

$$\psi^{(eq)} = \psi_{eq01}(r)\bar{Q} + \psi_{eq10}(r)\bar{\sigma} + O(\bar{Q}^3, \bar{Q}^2\bar{\sigma}, \bar{Q}\bar{\sigma}^2, \bar{\sigma}^3) \quad (14)$$

where $\bar{Q} = ZeQ/\epsilon\kappa^2kT$ and $\bar{\sigma} = Ze\sigma/\epsilon\kappa kT$ are the dimensionless fixed charge densities

$$\psi_{eq01} = \frac{kT}{Ze} \left(1 - B \frac{\sinh \kappa r}{A\kappa r} \right) \quad \text{if } 0 \leq r \leq a \quad (15a)$$

$$\psi_{eq01} = \frac{kT}{Ze} 2C \frac{\kappa b \cosh \kappa(b-r) - \sinh \kappa(b-r)}{A\kappa r} \quad \text{if } a \leq r \leq b \quad (15b)$$

$$\psi_{eq10} = \frac{kT}{Ze} 2(\kappa b)^2 \frac{\sinh \kappa r}{A\kappa r} \quad (16)$$

$$A = e^{\kappa b}(\kappa b - 1) + e^{-\kappa b}(\kappa b + 1) \quad (17a)$$

$$B = e^{\kappa(b-a)}(\kappa a + 1)(\kappa b - 1) - e^{-\kappa(b-a)}(\kappa a - 1)(\kappa b + 1) \quad (17b)$$

$$C = \kappa a \cosh \kappa a - \sinh \kappa a \quad (17c)$$

and $\kappa = (2Z^2e^2n^\infty/\epsilon kT)^{1/2}$ is the reciprocal of the Debye length. Equation 14 for the equilibrium potential as a power expansion in the fixed charge densities of the porous particle and cavity wall up to $O(\bar{Q}\bar{\sigma})$ is the equilibrium solution for the linearized Poisson–Boltzmann equation. Thus, the fixed charge densities must be sufficiently small for electric potentials to remain low (the Debye–Hückel approximation).

Experimental data for the porous surface layers of human erythrocytes,²⁹ rat lymphocytes,³⁰ and poly(*N*-isopropylacrylamide) hydrogels³⁷ in electrolyte solutions indicate that the magnitude of Q can be as high as 8.7×10^6 C/m³. For the surface charge density σ , an experimental study on the AgI surface in contact with aqueous solutions reported that its value changes from 0 to -0.035 C/m² upon increasing the pAg from 5.6 to 11.³⁸ For a porous particle with $Q = 10^7$ C/m³ and a cavity wall with $\sigma = 0.01$ C/m² around an aqueous solution of a univalent electrolyte with $\kappa^{-1} = 1$ nm, one obtains the dimensionless fixed charge densities $\bar{Q} \cong 0.5$ and $\bar{\sigma} \cong 0.5$, respectively.

3.2. Perturbed Quantities. For solving the perturbed quantities \mathbf{u} , $\delta\mu_{\pm}$, and $\delta\psi$ in terms of the particle velocity U , these variables can be expressed as power series in the small perturbation parameters \bar{Q} and $\bar{\sigma}$

$$\mathbf{u} = \mathbf{u}_{00} + \mathbf{u}_{01}\bar{Q} + \mathbf{u}_{10}\bar{\sigma} + \mathbf{u}_{02}\bar{Q}^2 + \mathbf{u}_{11}\bar{Q}\bar{\sigma} + \mathbf{u}_{20}\bar{\sigma}^2 + \dots \quad (18a)$$

$$\delta\mu_{\pm} = \mu_{01\pm}\bar{Q} + \mu_{10\pm}\bar{\sigma} + \mu_{02\pm}\bar{Q}^2 + \mu_{11\pm}\bar{Q}\bar{\sigma} + \mu_{20\pm}\bar{\sigma}^2 + \dots \quad (18b)$$

$$\delta\psi = \psi_{01}\bar{Q} + \psi_{10}\bar{\sigma} + \psi_{02}\bar{Q}^2 + \psi_{11}\bar{Q}\bar{\sigma} + \psi_{20}\bar{\sigma}^2 + \dots \quad (18c)$$

$$U = U_{00} + U_{01}\bar{Q} + U_{10}\bar{\sigma} + U_{02}\bar{Q}^2 + U_{11}\bar{Q}\bar{\sigma} + U_{20}\bar{\sigma}^2 + \dots \quad (18d)$$

where the perturbation coefficients \mathbf{u}_{ij} , $\mu_{ij\pm}$, ψ_{ij} , and U_{ij} are independent of \bar{Q} and $\bar{\sigma}$. The zeroth-order terms of $\delta\mu_{\pm}$ and $\delta\psi$ vanish because no concentration gradient and electric field are applied.

After substituting eqs 14 and 18 into eqs 3–6 and 8–13 and equating like powers of \bar{Q} and $\bar{\sigma}$ on both sides of the individual equations, a group of linear differential equations and boundary conditions for each set of the coefficient functions \mathbf{u}_{ij} , $\mu_{ij\pm}$, and ψ_{ij} with $i + j$ equal to 0, 1, and 2 resulted. Solving these perturbation equations, we obtain the solutions for the r and θ components of \mathbf{u} (to second order \bar{Q}^2 , $\bar{Q}\bar{\sigma}$, and $\bar{\sigma}^2$), $\delta\mu_{\pm}$, and $\delta\psi$ (to first order \bar{Q} and $\bar{\sigma}$) as

$$u_r = \{F_{00}(r)(U_{00} + U_{01}\bar{Q} + U_{10}\bar{\sigma}) + [U_{02}F_{00}(r) + U_{00}F_{02}(r)]\bar{Q}^2 + [U_{11}F_{00}(r) + U_{00}F_{11}(r)]\bar{Q}\bar{\sigma} + [U_{20}F_{00}(r) + U_{00}F_{20}(r)]\bar{\sigma}^2\} \cos \theta \quad (19a)$$

$$u_\theta = -\frac{\tan \theta}{2r} \frac{d}{dr}(r^2 u_r) \quad (19b)$$

$$\delta\mu_\pm = ZeU_{00}[F_{01\pm}(r)\bar{Q} + F_{10\pm}(r)\bar{\sigma}] \cos \theta \quad (20)$$

$$\delta\psi = U_{00}[F_{\psi 01}(r)\bar{Q} + F_{\psi 10}(r)\bar{\sigma}] \cos \theta \quad (21)$$

where the expressions for the functions $F_{ij}(r)$ (with $i + j = 0$ and 2), $F_{ij\pm}(r)$, and $F_{\psi ij}(r)$ (with $i + j = 1$) are lengthy and given in ref 39. Because $F_{ij\pm}(r)$ and $F_{\psi ij}(r)$ with $i + j = 1$ are affected by the fluid flow via $F_{00}(r)$, the leading order of the relaxation effect of the diffuse ions in the electric double layers around the particle and cavity wall is included in the solution for $\delta\mu_\pm$ and $\delta\psi$ up to first order \bar{Q} and $\bar{\sigma}$ (which will be sufficient for the calculation of the sedimentation velocity to second order \bar{Q}^2 , $\bar{Q}\bar{\sigma}$, and $\bar{\sigma}^2$). Also, $F_{ij}(r)$ with $i + j = 2$ are dependent on $F_{01\pm}(r)$ and $F_{10\pm}(r)$.

3.3. Forces on the Particle. The total force acting on the settling porous sphere is the sum of its gravitational force, electric force, and hydrodynamic force. The gravitational force is

$$\mathbf{F}_g = \frac{4}{3}\pi a^3(1 - \varepsilon_p)\Delta\rho g \mathbf{e}_z \quad (22)$$

where ε_p and $\Delta\rho$ are the porosity and buoyant density of the porous particle, respectively.

The electric force on the porous sphere can be expressed as

$$\mathbf{F}_e = -2\pi Q \int_0^\pi \int_0^a \nabla\psi r^2 \sin \theta \, dr \, d\theta \quad (23)$$

Substituting eqs 1b and 21 into the above equation and applying that the net electrostatic force exerted on the particle at equilibrium is zero, we obtain the leading order of the electric force as

$$\mathbf{F}_e = -\frac{4\pi\epsilon kT}{3Ze}(\kappa a)^2 U_{00}[F_{\psi 01}(a)\bar{Q} + F_{\psi 10}(a)\bar{\sigma}]\bar{Q} \mathbf{e}_z \quad (24)$$

The hydrodynamic force on the porous sphere can be expressed as

$$\mathbf{F}_h = 2\pi\eta\lambda^2 \int_0^\pi \int_0^a \mathbf{u} r^2 \sin \theta \, dr \, d\theta \quad (25)$$

Substitution of eq 19 into eq 25 yields

$$\begin{aligned} \mathbf{F}_h = & \frac{4}{3}\pi\eta\lambda^2 a^3 \{F_{00}(a)(U_{00} + U_{01}\bar{Q} + U_{10}\bar{\sigma}) \\ & + [U_{02}F_{00}(a) + U_{00}F_{02}(a)]\bar{Q}^2 + [U_{11}F_{00}(a) + U_{00}F_{11}(a)]\bar{Q}\bar{\sigma} \\ & + [U_{20}F_{00}(a) + U_{00}F_{20}(a)]\bar{\sigma}^2\} \mathbf{e}_z \end{aligned} \quad (26)$$

3.4. Sedimentation Velocity. Using the constraint that the total force exerted on the settling particle is zero with the summation of eqs 22, 24, and 26, we obtain the sedimentation velocity of the charged porous sphere within the charged cavity as the expansion series in eq 18d with the leading coefficients

$$U_{00} = -\frac{(1 - \varepsilon_p)\Delta\rho g}{\eta\lambda^2 F_{00}(a)} \quad (27a)$$

$$U_{01} = 0 \quad (27b)$$

$$U_{10} = 0 \quad (27c)$$

$$U_{02} = -U_{00} \left[\frac{F_{02}(a)}{F_{00}(a)} - \frac{\epsilon\kappa^2 kT}{\eta\lambda^2 aZe} \frac{F_{\psi 01}(a)}{F_{00}(a)} \right] \quad (27d)$$

$$U_{11} = -U_{00} \left[\frac{F_{11}(a)}{F_{00}(a)} - \frac{\epsilon\kappa^2 kT}{\eta\lambda^2 aZe} \frac{F_{\psi 10}(a)}{F_{00}(a)} \right] \quad (27e)$$

$$U_{20} = -U_{00} \frac{F_{20}(a)}{F_{00}(a)} \quad (27f)$$

Here, U_{00} is the sedimentation velocity of an uncharged porous sphere positioned at the center of an uncharged spherical cavity.⁴⁰

The sedimentation velocity of the charged porous sphere inside of the charged cavity can be written using eqs 18d and 27 as

$$U = U_{00}[1 + (\kappa a)^4 H_1 \bar{Q}^2 + (\kappa a)^3 H_2 \bar{Q}\bar{\sigma} + (\kappa a)^2 H_3 \bar{\sigma}^2 + O(\bar{Q}^3, \bar{Q}^2\bar{\sigma}, \bar{Q}\bar{\sigma}^2, \bar{\sigma}^3)] \quad (28)$$

where the dimensionless second-order coefficients

$$H_1 = \frac{U_{02}}{(\kappa a)^4 U_{00}} \quad (29a)$$

$$H_2 = \frac{U_{11}}{(\kappa a)^3 U_{00}} \quad (29b)$$

$$H_3 = \frac{U_{20}}{(\kappa a)^2 U_{00}} \quad (29c)$$

and $(\kappa a)^4 \bar{Q}^2$, $(\kappa a)^3 \bar{Q}\bar{\sigma}$, and $(\kappa a)^2 \bar{\sigma}^2$ are independent of κ or n^∞ . For a given electrolyte solution, the coefficients H_1 , H_2 , and H_3 are functions of the electrokinetic radius κa , shielding parameter λa , normalized ionic diffusion coefficient within the porous particle ω , and particle-to-cavity radius ratio a/b , and their numerical values for a wide range calculated by using eq 29 will be presented in the next section.

The coefficients H_1 and H_3 can be taken as the dimensionless enhancement or retardation of the sedimentation of a charged porous sphere in an uncharged cavity ($\sigma = 0$) and that of an uncharged porous sphere ($Q = 0$) in a charged cavity, respectively. The charge on the cavity wall alters the sedimentation of the particle through the electroosmotic recirculation flow developing from the interaction of the sedimentation-induced electric field with the electric double layer adjacent to the charged wall (dominant at large κa) and the charged-wall-induced potential over the porous particle. In the limit of $a/b = 0$ and $\sigma = 0$, eq 28 reduces to the formula for the sedimentation velocity of an unconfined charged porous sphere.¹¹

4. RESULTS AND DISCUSSION

The sedimentation velocity of a charged porous sphere situated at the center of a charged spherical cavity filled with a symmetric electrolyte solution in a power series of their fixed charge densities Q and σ is obtained in eqs 28 and 29. The corrections caused by the fixed charges begin with the second order \bar{Q}^2 , $\bar{Q}\bar{\sigma}$, and $\bar{\sigma}^2$ because the interaction between the

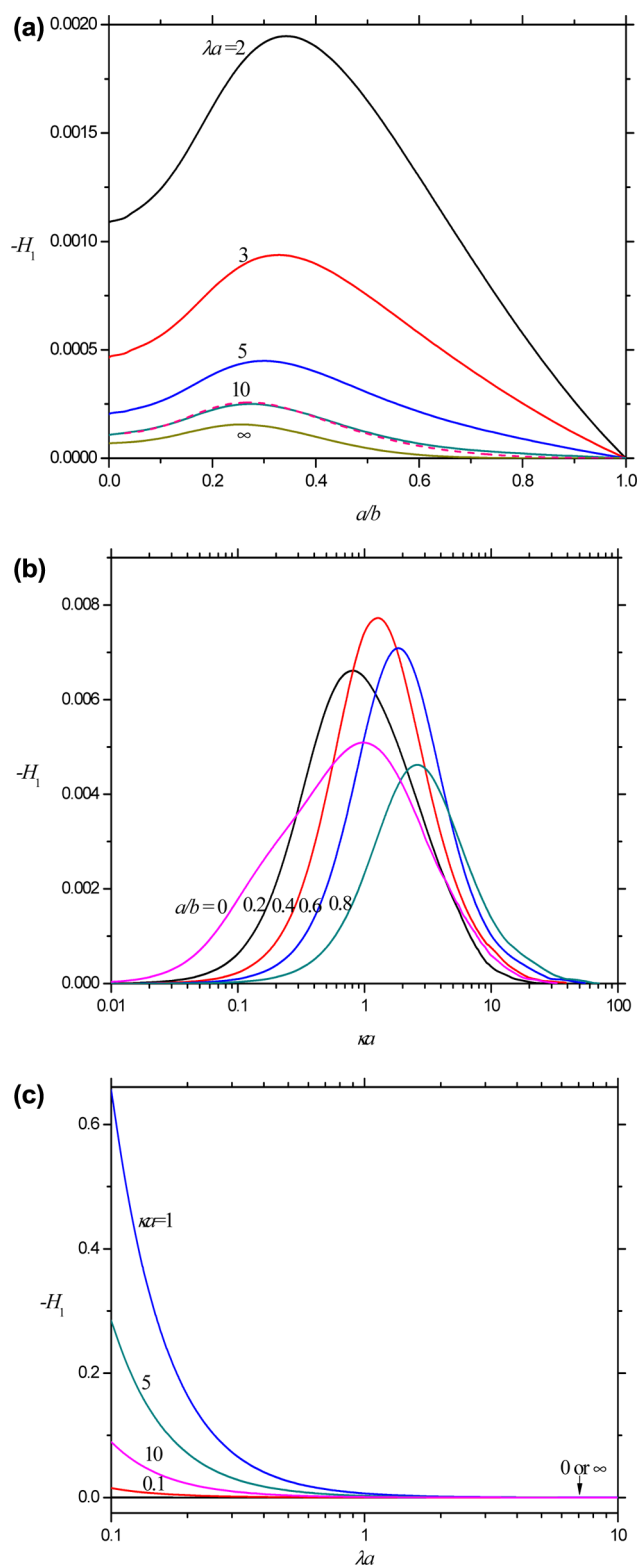


Figure 2. Plots of the dimensionless coefficient H_1 in eq 28 for the sedimentation of a charged porous sphere in a spherical cavity filled with the aqueous KCl solution: (a) $\kappa a = 1$; (b) $\lambda a = 1$; (c) $a/b = 0.5$.

particle or space charges and the sedimentation-induced electric field, both are of first order Q or σ , is of second order.

4.1. Coefficients H_1 , H_2 , and H_3 . The dimensionless coefficients H_1 , H_2 , and H_3 for the sedimentation velocity of a porous sphere in a spherical cavity filled with aqueous KCl

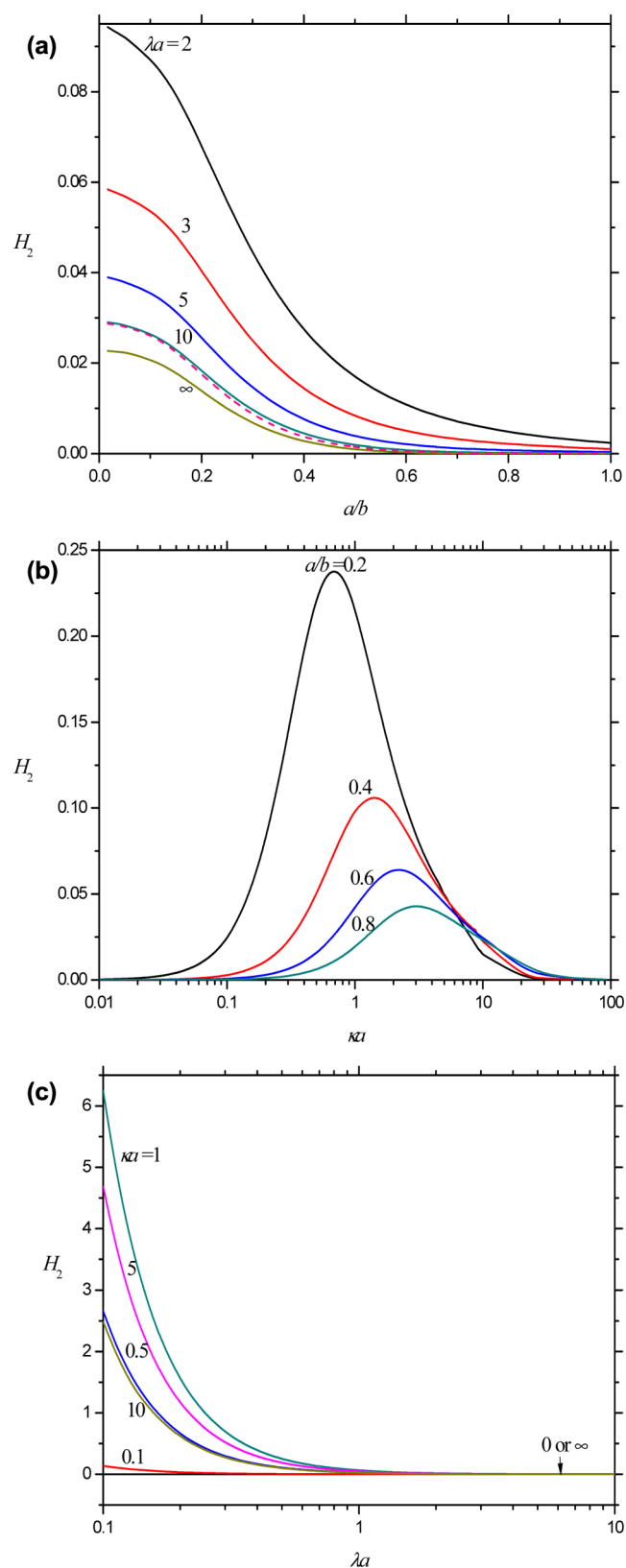


Figure 3. Plots of the dimensionless coefficient H_2 in eq 28 for the sedimentation of a charged porous sphere in a charged spherical cavity filled with the aqueous KCl solution: (a) $\kappa a = 1$; (b) $\lambda a = 1$; (c) $a/b = 0.5$.

solutions at room temperature (with $\epsilon k^2 T^2 / \eta D_{\pm} Z^2 e^2 = 0.26$), as calculated from eq 29, are plotted versus the electrokinetic

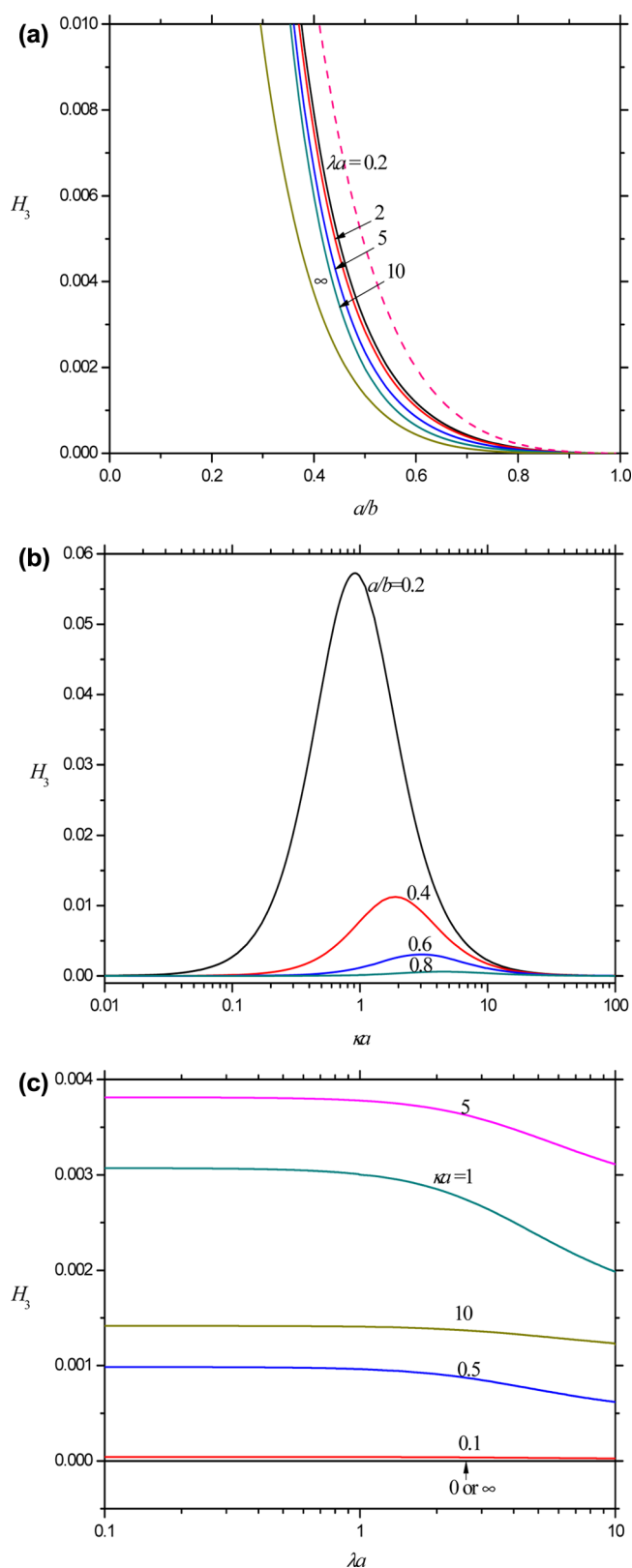


Figure 4. Plots of the dimensionless coefficient H_3 in eq 28 for the sedimentation of a porous sphere in a charged spherical cavity filled with the aqueous KCl solution: (a) $\kappa a = 1$; (b) $\lambda a = 1$; (c) $a/b = 0.5$.

radius κa , friction parameter λa , and particle-to-cavity radius ratio a/b in Figures 2–4 for a wide range. For conciseness, ω_{\pm}

$= 1$ (the same diffusion coefficient for each ionic species inside and outside of the porous particle) is taken in the calculations.

The coefficient H_1 is negative, and thus, the presence of the fixed charges within the particle always reduces the sedimentation velocity of the particle. This retardation effect reflects the electrophoretic driving force in the opposite direction caused by the electric potential gradient induced by the particle sedimentation. For given values of κa and λa , H_1 is not a monotonic function of a/b (therefore, it is not the sedimentation-induced potential gradient around the particle given by eq 21) and has a maximum magnitude. Both U_{00} and $-U_{02}$ given by eqs 27a and 27d decrease monotonically with an increase in a/b due to the effect of the cavity wall on the viscous and electrophoretic retardations to the settling particle. The rate of the decrease of $-U_{02}$ is slower for small values of a/b and faster for large values of a/b than that of U_{00} , thereby causing the maximum in $-H_1$ according to eq 29a. The location of this maximum shifts to greater a/b as κa increases or λa decreases.

The coefficients H_2 and H_3 are both positive. Thus, the contribution from H_3 for the surface charges on the cavity wall increases the sedimentation velocity of an uncharged particle in a charged cavity. The concentration of the counterions adjoining the charged cavity wall near the front end of the settling particle is increased due to the squeeze of fluid, and that near the rear end of the particle is decreased due to the compensation of fluid, resulting in a sedimentation-induced electric field and electroosmotic flow along the cavity wall to enhance the fluid recirculation and particle migration. The contribution from the coefficient H_2 for the fixed charge interaction between the particle and the cavity wall increases the particle velocity if the fixed charges have the same sign ($Q\sigma > 0$, where the reduction of the counterions in the electric double layers around the particle and cavity wall due to mutual competition reduces the sedimentation-induced potential gradient and the electrophoretic retardation of the particle) and decreases this velocity if the fixed charges have the opposite signs ($Q\sigma < 0$, where the enrichment of these counterions enhances the induced electric field and electrophoretic retardation). For fixed values of κa and λa , the coefficients H_2 and H_3 increase monotonically with a decrease in a/b , and this outcome will be explained in the next subsection.

For specified values of a/b and λa , the magnitudes of the coefficients H_1 , H_2 , and H_3 have maxima at some finite values of κa and fade out when κa becomes small or large. In general, the locations of these maxima shift to greater κa as a/b increases but are insensitive to the variation of λa . In the limit of $\kappa a \rightarrow 0$ (infinitely thick double layers), the accumulation of the counterions in the double layers is negligible, and the particle migration is not influenced by the fixed charge interactions, whereas in the limit of $\kappa a \rightarrow \infty$ (infinitely thin double layers), the charge density is zero everywhere, and the fixed charge interactions also disappear.

For given values of κa and a/b , the coefficients H_1 , H_2 , and H_3 increase monotonically with decreasing λa (decreasing friction or increasing permeability for the fluid flow inside of the particle). H_1 and H_2 depend on λa impressively, but H_3 is not a sensitive function of λa . These coefficients for an impermeable sphere²⁴ having a surface charge density of $\sigma_p = Qa/3$ (the same total fixed charge as a porous sphere of equal radius) in a concentric spherical cavity as a function of a/b are also drawn by dashed curves in Figures 2a, 3a, and 4a for comparison. It can be seen that the values of H_1 and H_2 for the

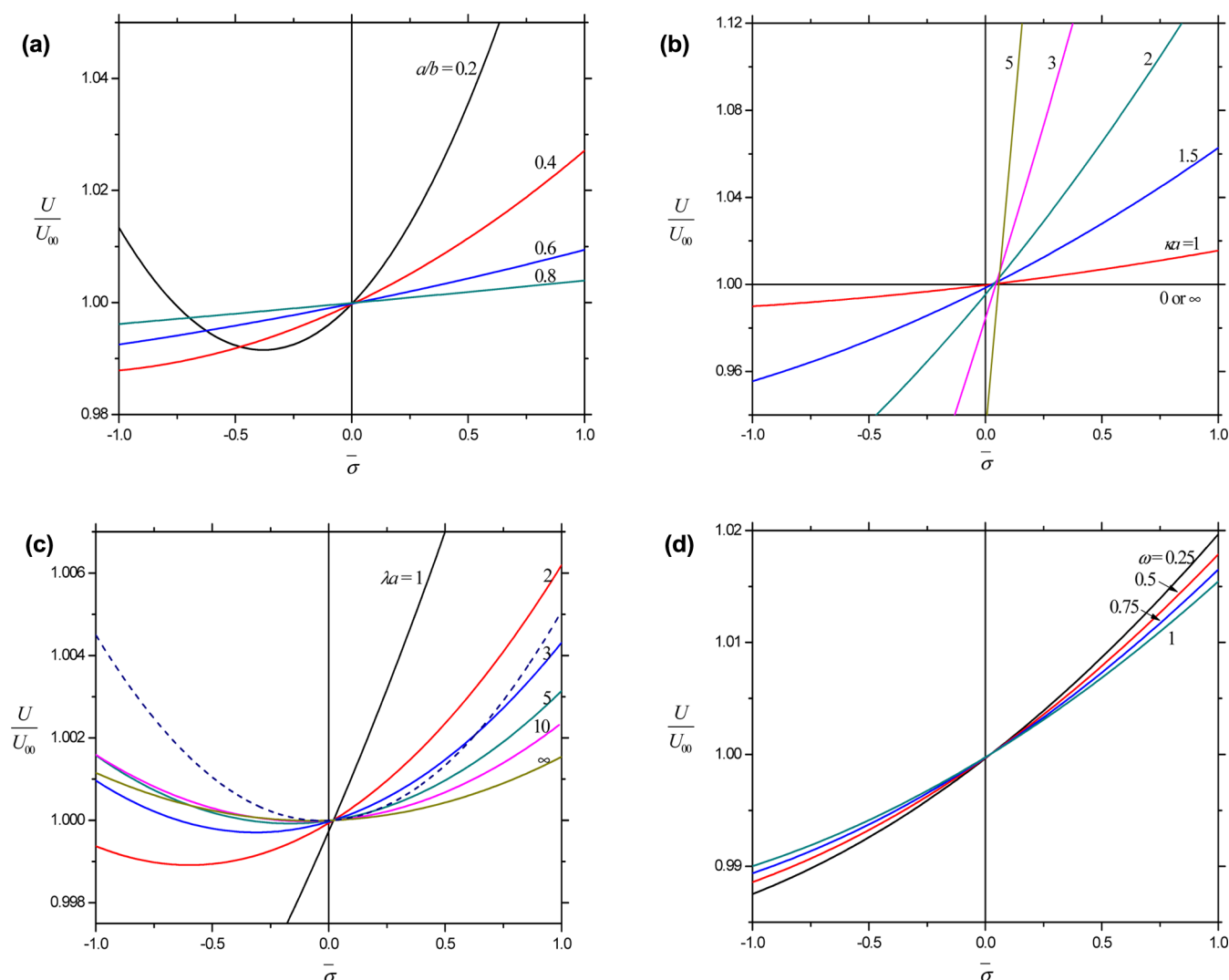


Figure 5. Plots of the normalized sedimentation velocity U/U_{00} of a charged porous sphere with $\bar{Q} = 0.2$ in a charged spherical cavity filled with the aqueous KCl solution versus the parameter $\bar{\sigma}$: (a) $\kappa a = 1$, $\lambda a = 1$, $\omega = 1$; (b) $\lambda a = 1$, $a/b = 0.5$, $\omega = 1$; (c) $\kappa a = 1$, $a/b = 0.5$, $\omega = 1$; (d) $\kappa a = 1$, $\lambda a = 1$, $a/b = 0.5$.

impermeable sphere are comparable with those for the porous sphere with $\lambda a = 10$, but the value of H_3 is greater for the impermeable sphere than that for the porous sphere with even a very low value of λa (because the sedimentation-induced electric field around an uncharged particle impermeable to the electrolyte ions in the charged cavity is greater than that around a permeable one). Because the fixed charges are distributed uniformly within a porous particle but on the surface of an impermeable particle, the limits of H_1 and H_2 at infinite λa for the porous sphere do not coincide with their values for the impermeable sphere.

4.2. Normalized Sedimentation Velocity. Figures 2–4 indicate that the magnitude of the coefficient H_2 is generally about one order greater than that of the coefficients H_1 and H_3 . Therefore, for a porous particle undergoing sedimentation in a cavity with fixed charges with the same sign ($Q\sigma > 0$), their net effect in general increases the particle velocity (unless the magnitude of $\bar{\sigma}$ is very small relative to that of \bar{Q}). For the case of fixed charges with opposite signs ($Q\sigma < 0$), their net effect enhances/reduces the particle velocity if the fixed charge density of the cavity has a sufficiently great/small magnitude relative to that of the particle. This tendency is shown in Figure

5, where the normalized sedimentation velocity U/U_{00} of a charged porous sphere with its dimensionless fixed charge density $\bar{Q} = 0.2$ in a charged cavity filled with aqueous KCl solutions (the normalized diffusion coefficients of the cations and anions within the porous particle are assumed to be the same, i.e., $\omega_+ = \omega_- = \omega$) calculated using eq 28 is plotted as a function of the dimensionless surface charge density $\bar{\sigma}$ of the cavity. The enhancement effect of the surface charges at the cavity wall on the particle sedimentation can be significant as the magnitude of $\bar{\sigma}$ becomes large (e.g., for the case of small a/b and λa with $2 \leq \kappa a \leq 5$).

Figures 3a and b, 4a and b, and 5a illustrate that the effect of the surface charges at the cavity wall on the sedimentation (the coefficients H_2 and H_3 and thus the normalized sedimentation velocity U/U_{00}) of the porous particle increases with a decrease in the particle-to-cavity radius ratio a/b , keeping the other factors unchanged. This outcome is understood as a decrease in a/b increases the surface area of the cavity for a fixed size of the particle and thus enhances the effect caused by the cavity surface charges on the particle. Under an otherwise specified condition, the effect of surface charges at the cavity wall on the particle sedimentation increases with an increase in the

electrokinetic radius κa in the range of small to intermediate κa , with a decrease in κa in the range of intermediate to large κa (as shown in Figure 5b) and with a decrease in the friction parameter λa (as shown in Figure 5c).

For given values of κa , λa , and a/b , the effect of surface charges at the cavity wall on the sedimentation of a charged porous sphere increases with a decrease in the value of ω (i.e., the value of U/U_0 in general deviates more from unity as the hindrance to the diffusive transport of the electrolyte ions within the particle becomes more significant), as illustrated in Figure 5d. The dependence of U/U_0 on ω can be strong as $\kappa a > 1$ but becomes quite weak as $\kappa a < 0.1$ (or as λa is large). At small κa , the porous particle behaves electrically like a point charge; therefore, the detail of what happens (such as the diffusion of ions) inside of the particle is unimportant for the determination of U/U_0 by a force balance.

The corresponding results of U/U_0 for an impermeable dielectric sphere,²⁴ having the same total fixed charge on its surface as that within a porous sphere of equal radius, settling in a concentric charged cavity as a function of $\bar{\sigma}$ are also displayed in Figure 5c for comparison. The values of U/U_0 for the impermeable sphere are comparable with those for the porous sphere (taking $\omega = 1$) with $\lambda a = 3$ if $\sigma_p \sigma > 0$ (analogous to the values of its coefficients H_1 and H_2) but can be greater than those for the porous sphere with any value of λa if $\sigma_p \sigma < 0$ (analogous to its values of H_3).

5. CONCLUSIONS

In this article, the sedimentation of a charged porous sphere located at the center of a charged spherical cavity is analyzed at arbitrary values of the electrokinetic radius κa , shielding parameter λa , normalized ionic diffusion coefficients within the particle ω_{\pm} , and particle-to-cavity radius ratio a/b . Solving a set of linearized electrokinetic equations by a perturbation method, we have obtained the ionic electrochemical potential energy, electric potential, and fluid velocity fields, with the consideration of the double-layer relaxation effect. The requirement that the net force acting on the particle vanishes results in eq 28 for the sedimentation velocity. The corrections due to the effects of the fixed charges in the porous particle and at the cavity wall to the sedimentation velocity start at second order Q^2 , $Q\sigma$, and σ^2 of their densities. For given values of λa , ω_{\pm} , and a/b , these effects are maximum at some finite values of κa and vanish as κa approaches zero and infinity. The effect of the surface charges at the cavity wall on the sedimentation of a porous particle increases with a decrease in λa , a/b , and ω_{\pm} .

The presence of the surface charges on the cavity wall increases the sedimentation velocity of the confined porous particle (owing to the electroosmotic enhancement on the fluid recirculation along the cavity wall caused by the sedimentation-induced electric field), whereas the presence of the fixed charges in the particle reduces the sedimentation velocity (due to the electrophoretic retardation on the particle caused by the induced electric field). For the sedimentation of a porous particle in a cavity with their fixed charges of the same sign, their net effect in general increases the sedimentation velocity. For the case of the fixed charges with opposite signs, their net effect increases/reduces the sedimentation velocity if the magnitude of the fixed charge density of the cavity wall is sufficiently great/small relative to that of the particle. On typical conditions, the effect of the surface charges at the cavity wall on the sedimentation of a porous particle can be significant.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Booth, F. Sedimentation Potential and Velocity of Solid Spherical Particles. *J. Chem. Phys.* **1954**, *22*, 1956–1968.
- (2) Stigter, D. Sedimentation of Highly Charged Colloidal Spheres. *J. Phys. Chem.* **1980**, *84*, 2758–2762.
- (3) De Groot, S. R.; Mazur, P.; Overbeek, J. Th. G. Nonequilibrium Thermodynamics of the Sedimentation Potential and Electrophoresis. *J. Chem. Phys.* **1952**, *20*, 1825–1829.
- (4) Ohshima, H.; Healy, T. W.; White, L. R.; O'Brien, R. W. Sedimentation Velocity and Potential in a Dilute Suspension of Charged Spherical Colloidal Particles. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1299–1317.
- (5) Levine, S.; Neale, G.; Epstein, N. The Prediction of Electrokinetic Phenomena within Multiparticle Systems II. Sedimentation Potential. *J. Colloid Interface Sci.* **1976**, *57*, 424–437.
- (6) Ohshima, H. Sedimentation Potential in a Concentrated Suspension of Spherical Colloidal Particles. *J. Colloid Interface Sci.* **1998**, *208*, 295–301.
- (7) Keh, H. J.; Ding, J. M. Sedimentation Velocity and Potential in Concentrated Suspensions of Charged Spheres with Arbitrary Double-Layer Thickness. *J. Colloid Interface Sci.* **2000**, *227*, 540–552.
- (8) Carrique, F.; Arroyo, F. J.; Delgado, A. V. Sedimentation Velocity and Potential in a Concentrated Colloidal Suspension: Effect of a Dynamic Stern Layer. *Colloids Surf., A* **2001**, *195*, 157–169.
- (9) Zholkovskiy, E. K.; Masliyah, J. H.; Shilov, V. N.; Bhattacharjee, S. Electrokinetic Phenomena in Concentrated Disperse Systems: General Problem Formulation and Spherical Cell Approach. *Adv. Colloid Interface Sci.* **2007**, *134–135*, 279–321.
- (10) Hermans, J. J. Sedimentation and Electrophoresis of Porous Spheres. *J. Polym. Sci.* **1955**, *18*, 527–533.
- (11) Liu, Y. C.; Keh, H. J. Sedimentation Velocity and Potential in a Dilute Suspension of Charged Porous Spheres. *Colloids Surf., A* **1998**, *140*, 245–259.
- (12) Keh, H. J.; Chen, W. C. Sedimentation Velocity and Potential in Concentrated Suspensions of Charged Porous Spheres. *J. Colloid Interface Sci.* **2006**, *296*, 710–720.
- (13) Keh, H. J.; Liu, Y. C. Sedimentation Velocity and Potential in a Dilute Suspension of Charged Composite Spheres. *J. Colloid Interface Sci.* **1997**, *195*, 169–191.
- (14) Ohshima, H. Sedimentation Potential and Velocity in a Concentrated Suspension of Soft Particles. *J. Colloid Interface Sci.* **2000**, *229*, 140–147.
- (15) Chiu, Y. S.; Keh, H. J. Sedimentation Velocity and Potential in a Concentrated Suspension of Charged Soft Spheres. *Colloids Surf., A* **2013**, DOI: 10.1016/j.colsurfa.2012.08.069.
- (16) Lee, S. Y.; Yalcin, S. E.; Joo, S. W.; Sharma, A.; Baysal, O.; Qian, S. The Effect of Axial Concentration Gradient on Electrophoretic Motion of a Charged Spherical Particle in a Nanopore. *Microgravity Sci. Technol.* **2010**, *22*, 329–338.
- (17) Jiemvarangkula, P.; Zhang, W.; Lien, H.-L. Enhanced Transport of Polyelectrolyte Stabilized Nanoscale Zero-Valent Iron (nZVI) in Porous Media. *Chem. Eng. J.* **2011**, *170*, 482–491.
- (18) Happel, J.; Brenner, H. *Low Reynolds Number Hydrodynamics*; Nijhoff: Dordrecht, The Netherlands, 1983.
- (19) Kim, S.; Karrila, S. J. *Microhydrodynamics: Principles and Selected Applications*; Dover: Mineola, NY, 2005.

- (20) Yeh, H. Y.; Keh, H. J. Axisymmetric Creeping Motion of a Prolate Particle in a Cylindrical Pore. *Eur. J. Mech., B: Fluids* **2013**, *39*, 52–58.
- (21) Lee, T. C.; Keh, H. J. Slow Motion of a Spherical Particle in a Spherical Cavity with Slip Surfaces. *Int. J. Eng. Sci.* **2013**, *69*, 1–15.
- (22) Pujar, N. S.; Zydney, A. L. Boundary Effects on the Sedimentation and Hindered Diffusion of Charged Particles. *AIChE J.* **1996**, *42*, 2101–2111.
- (23) Lee, E.; Yen, C.-B.; Hsu, J.-P. Sedimentation of a Non-conducting Sphere in a Spherical Cavity. *J. Phys. Chem. B* **2000**, *104*, 6815–6820.
- (24) Keh, H. J.; Cheng, T. F. Sedimentation of a Charged Colloidal Sphere in a Charged Cavity. *J. Chem. Phys.* **2011**, *135*, 214706/1–214706/10.
- (25) Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions II. Self-Diffusion of the Small Ions. *J. Chem. Phys.* **1969**, *51*, 934–938.
- (26) Hyk, W.; Ciszewska, M. Studies of Transport Phenomena and Electrostatic Interactions in Polyacrylate Gels. *J. Phys. Chem. B* **1999**, *103*, 6466–6474.
- (27) Matsumoto, K.; Suganuma, A. Settling Velocity of a Permeable Model Floc. *Chem. Eng. Sci.* **1977**, *32*, 445–447.
- (28) Masliyah, J. H.; Polikar, M. Terminal Velocity of Porous Spheres. *Can. J. Chem. Eng.* **1980**, *58*, 299–302.
- (29) Kawahata, S.; Ohshima, H.; Muramatsu, N.; Kondo, T. Charge Distribution in the Surface Region of Human Erythrocytes as Estimated from Electrophoretic Mobility Data. *J. Colloid Interface Sci.* **1990**, *138*, 182–186.
- (30) Morita, K.; Muramatsu, N.; Ohshima, H.; Kondo, T. Electrophoretic Behavior of Rat Lymphocyte Subpopulations. *J. Colloid Interface Sci.* **1991**, *147*, 457–461.
- (31) Aoyanagi, O.; Muramatsu, N.; Ohshima, H.; Kondo, T. Electrophoretic Behavior of PolyA-Graft-PolyB-Type Microcapsules. *J. Colloid Interface Sci.* **1994**, *162*, 222–226.
- (32) Lopez-Garcia, J. J.; Grosse, C.; Horno, J. Numerical Calculation of the Electrophoretic Mobility of Concentrated Suspensions of Soft Particles. *J. Colloid Interface Sci.* **2006**, *301*, 651–659.
- (33) Ahualli, S.; Jimenez, M. L.; Carrique, F.; Delgado, A. V. AC Electrokinetics of Concentrated Suspensions of Soft Particles. *Langmuir* **2009**, *25*, 1986–1997.
- (34) Zhang, X.; Hsu, W.-L.; Hsu, J.-P.; Tseng, S. Diffusiophoresis of a Soft Spherical Particle in a Spherical Cavity. *J. Phys. Chem. B* **2009**, *113*, 8646–8656.
- (35) Neale, G.; Epstein, N.; Nader, W. Creeping Flow Relative to Permeable Spheres. *Chem. Eng. Sci.* **1973**, *28*, 1865–1874.
- (36) Koplik, J.; Levine, H.; Zee, A. Velocity Renormalization in the Brinkman Equation. *Phys. Fluids* **1983**, *26*, 2864–2870.
- (37) Makino, K.; Yamamoto, S.; Fujimoto, K.; Kawaguchi, H.; Ohshima, H. Surface Structure of Latex Particles Covered with Temperature-Sensitive Hydrogel Layers. *J. Colloid Interface Sci.* **1994**, *166*, 251–258.
- (38) Blaakmeer, J.; Bohmer, M. R.; Cohen Stuart, M. A.; Fleer, G. J. Adsorption of Weak Polyelectrolytes on Highly Charged Surfaces. Poly(acrylic acid) on Polystyrene Latex with Strong Cationic Groups. *Macromolecules* **1990**, *23*, 2301–2309.
- (39) Chang, Y. J. *Sedimentation of a Charged Porous Particle in a Charged Cavity*. M. S. Thesis, National Taiwan University, 2013.
- (40) Keh, H. J.; Chou, J. Creeping Motions of a Composite Sphere in a Concentric Spherical Cavity. *Chem. Eng. Sci.* **2004**, *59*, 407–415.