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Sedimentation and electrophoresis of a porous floc and a colloidal particle coated with polyelectrolytes

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ABSTRACT

Sedimentation and electrophoresis of porous colloid complex; a colloidal floc and a colloidal particle covered with adsorbed polyelectrolytes are visited to examine the characteristic length of the transport phenomena. In the sedimentation, the overall size of a floc is dominative in the determination of Stokes drag, while the permeability is determined by the largest pore in the floc. This picture is important when break-up of flocs in a turbulent flow is considered. When a colloidal particles is coated with polyelectrolytes, the characteristic length for diffusion is that of the diameter of colloidal particle plus protruding part of polymer chain adsorbed onto the particle. On the other hand, when the porous colloid complex is placed in the electric field, fluid surrounding the complex can easily penetrate into the complex by means of electro-osmosis. The diffusive part of electric double layer located inside of the complex is the source of strong driving force of this osmotic flow. Flow generated in this regime can be treated as a sort of shear driven. The characteristic length scale for transport phenomena is the Debye length or the distance between charged segments. These lengths are much shorter than the case of sedimentation and Brownian diffusion.

1. Introduction

Motion of Colloidal particels immersed in water is usually treated as a hydrodynamic problem on the basis of Stokes equation where the linear relation between stress and rate of strain is assumed [1–3]. An elementary analysis is carried out assuming simple geometry such as a sphere [4] or a flat plate [5–8] as a boundary condition. However, the majority of colloid in nature or engineered system; suspended solid in water environment, organic substances and microbiology in soil are found as a complex of highly porous structure such as a floc [9] or a particle coated with adsorbing polymers or polyelectrolytes [10•]. In the geometry of highly porous structure, the associated permeability will play a significant role in the determination of the boudary condition. That is, there appears slipping flow or penetration of outer flow into the porous domain. These effects are nontrivial on the estimation of mass transfer between inside and outside of the porous structure or the analysis of collision process between colloidal complexes [11–14•]. On the other hand, most of the surface of colloidal particles are charged srrounded by electric double layer [15,16]. The diffusive part of electric double layer can easily migrate subject to electric field. This phenomenon is known as electroosmosis [17]. The characteristic length of this motion is the tickness of electric double layer, usually denoted as Debye reciprocal length, which is usually much shorter than the characteristic length of pore size or the size of flocs. In this situation, essentially, the slip boundary contidtion at the solid wall can be applied [18–20•]. Consequently, considerable hydrodynamic differences can be found for the problem of the transport phenomena of a porous floc and a polymer coated colloidal particle placed in electric field [21•] from the problem of gravitational sedimentation and Brownian diffusion observed under the condition without an effect of surface charge. The different situation is illustrated in the graphical abstract. In the present opinion article, I summarize experimental aspects of the hydrodynamic behavior of a floc and a colloidal sphere coated with polyelectrolytes moving under gravity, Brownian diffusion and electric field placing an emphasis on the difference in the characteristic length of transport phenomina.

2. Sedimentation of a coagulated floc

The rate ofsedimentation of a coagulated floc is one of the most important factors not only for the rational design and the effective operation of water and waste water treatment plant but also for the prediction of the diffusion of cohesive sediment and suspended matter in coast and estuaries [22•–25]. In their pionieering work of pysical properties of flocs, Tambo and Watanabe [22•] intensively measured the settling velocity of kaolinite alminium floc as a function of floc diameter. They demonstrated that the density of floc decreases with an increase of floc size by a power law. Using the obtained results, they

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established the methodology to design the settling tank for water treatment.

The equation of the terminal settling velocity of a floc can be derived from the force balance of settling floc assuming that a floc is an impermeable sphere. When the hydrodynamic drag is equal to the sum of gravity and buoyancy, the following equation for the settling floc can be derived.

$$3\pi D_f \eta V_f = \frac{\pi}{6} {D_f}^3 \Delta\rho_f g \tag{1}$$

where D_f is the diameter of a floc , V_f the settling velocity of the floc , η fluid viscosity and g the gravitational constant. $\Delta\rho_f$ is the density difference between the mean value of the spherical domain containing the floc (ρ_f) and the density of solvent (ρ_w). This value can be expressed by the following equation,

$$\Delta\rho_f = \rho_f - \rho_w = (1-\varepsilon)(\rho_s - \rho_w) \tag{2}$$

where ρ_s is the density of solid composing the floc and ε average porosity of the spherical domain. If we can assume that the floc is an fractal aggregate composed of identical spheres, the number of primary particles, *i*, composing the floc can be written,

$$i = \alpha \left(\frac{D_f}{d_0}\right)^D. \tag{3}$$

Where d_0 and *D*, denotes the diameter of primary particle and fractal dimension respectively. α is the fractal pre-factor. Strictly, this value is dependent on the method of measurement, the value of fractal dimension and range of . However, for the sufficiently large flocs, this value can be treated as unity [28•]. Substituting the relation,

$$1-\varepsilon = \left(\frac{D_f}{d_0}\right)^{D-3} \tag{4}$$

into Eq. (1) yields [26],

$$V_f = \frac{(\rho_s - \rho_w)}{18\eta} g {d_0}^{3-D} {D_f}^{D-1}. \tag{5}$$

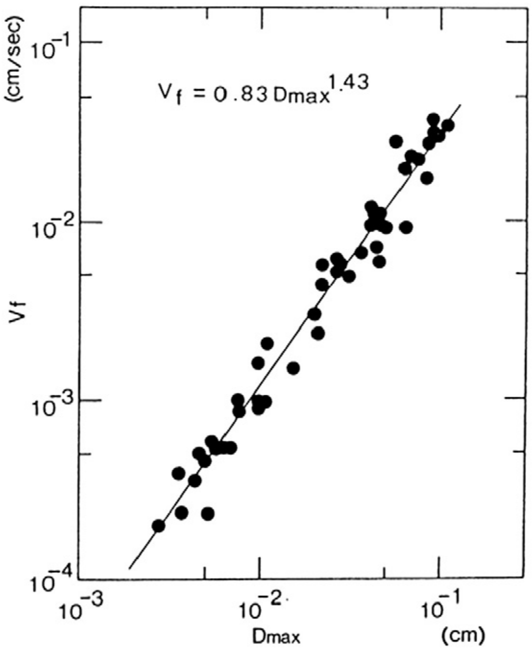

Fig. 1. The settling velocity of a floc as a function of maximum distance in the projected floc. Flocs are made of monodispersed polystyrene latex particles with diameter of 0.93μm coagulated in KCl solution [28•].

Therefore, if we measure the settling velocity of single floc as a function of the diameter of the floc, we can easily obtain the information of d_0 and fractal dimension *D*. Intensive measurement of the settling velocity of a floc and the analysis of effects of the chemical and mechanical condition of the formation process is reported by many researchers. And by these efforts, we can confirm the universe fractal nature of coagulated flocs in many situations. However, the assumption of the impermeable sphere adopted in the previous investigation should be examined more carefully in the further analysis [27]. In Fig. 1, the settling velocity of a floc made of polystyrene latex particles is demonstrated as a function of the maximum distance in the projected floc image [28•]. The value of fractal dimension can be obtained from the slope of the plot, however, the obtained value is slightly larger by 0.1-0.2, than the value obtained by other direct method e.g. direct particle number counting [29]. This slight increase is suggesting the effect of permeability which will reduce the hydrodynamic drag estimated on the basis of Stokes law as discussed Eq. (1).

The physical meaning of permeability which is used in Darcy law can be analogically interpreted by the so-called capillary model [30]. If the porous media is filled with water with pressure gradient, the volume flux of flow by osmotic flow induced by the pressure gradient per unit cross section, *q*, is expressed,

$$q = -\frac{k}{\eta}\frac{dP}{dx}. \tag{6}$$

Where, *P*, *k* and η denotes the pressure, permeability and the viscosity of water, respectively. If we assume the porous media is represented by the bundle of capillaries each of which satisfies Hagen-Poiseullie law, *q* can be expressed as,

$$q = -n\frac{\pi a^4}{8\eta}\frac{dP}{dx}, \tag{7}$$

Where *a* and *n* denotes the radius of capillary and the number of capillaries in unit cross section, respectively. If one remind the relation,

$$\varepsilon = n\pi a^2, \tag{8}$$

the value of *k* can be expressed as,

$$k = \frac{\varepsilon}{8} a^2. \tag{9}$$

Obviously, the porous media is different from the bundle of capillaries, however, Eq. (9) gives a geometrical picture of *k*. Carman generalized the relation expressed in Eq. (9) by introducing the concept of the hydraulic radius, r_H. That is,

$$k \approx \varepsilon {r_H}^2. \tag{10}$$

Where,

$$r_H = \frac{\varepsilon}{S}. \tag{11}$$

(See Fig. 2) S is the specific surface area of material which forms porous structure. The value of , more or less, represents the scale of channel as illustrated in Fig. 2. The velocity of fluid in the pore changes from zero to certain mean value with the length scale of. It is rather crude,