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Aggregation of Unequal-sized and Oppositely Charged Colloidal Particles in a Shear Flow

剪断流中における異径・異符号帯電コロイド粒子の凝集

Motoyoshi Kobayashi*
小林幹佳

* Member of JSCE, Dr. (Agr. Sci.), Faculty of Agriculture, Iwate University (Ueda 3-18-8, Morioka, Iwate 020-8550, Japan)

Understanding the rate of aggregation of colloidal particles is very important to consider the transport of substances in water environments. Theoretical investigations on aggregation kinetics have been performed by using trajectory analyses to elucidate the influence of electrochemical and hydrodynamic interactions on aggregation. So far, however, this analysis has not been fully applied to the aggregation between unequal-sized particles with opposite sign of surface electric charge in a shear flow. In this study, the rate of shear heteroaggregation between oppositely charged and unequal-sized particles was evaluated by using the trajectory analysis. The calculated results indicate that the rate of heteroaggregation increases with decreasing salt concentration and that the effect of attractive electric double layer force is more significant at higher shear rates. At low salt concentrations, in addition, the present evaluation reveals that larger values of scaled capture efficiency were found not for the homoaggregation between equal-sized particles but for the heteroaggregation between unequal-sized particles. The calculation also suggests an experimental plan, that is, pure heteroaggregation without electric double layer effect can be obtained by using the binary mixture of oppositely charged and unequal-sized particles in 1-10mM aqueous solutions.

Key Words: *coagulation, flocculation, capture efficiency, trajectory analysis*

1. Introduction

Colloidal particles such as clay minerals and natural organic matter are ubiquitous in water environment. These particles play an essential role in the fate and transport of substances sorbed with the particles[1-4]. One of typical natures of colloidal particles is their aggregation, coagulation, or flocculation. Through aggregation, the size of transport unit increases. And then, increased particle size enhances the sedimentation rate of particles and causes drastic changes of particle transport. Therefore, understanding aggregation process is of vital importance for controlling and predicting transport properties of substances in hydro-environments. Flocculation is also important in water purification[4,5]. For these reasons, many experimental and theoretical works on aggregation or flocculation have been carried out[5-8].

The rate of aggregation is a key to understand the whole aggregation process. Physicochemical and hydrodynamic conditions of colloidal suspensions affect the aggregation rate of colloidal particles[4,7]. A theoretical treatment on the aggregation kinetics in a simple shear flow was started by Smoluchowski[4,9,10], who derived a theoretical equation describing the number of colliding spheres with a radius of R_1 toward a sphere with a radius R_2 per unit time J_{Smol}:

$$J_{Smol} = \frac{4}{3}(R_1 + R_2)^3 G N_1 \qquad (1)$$

where G is velocity gradient of flow and N_1 is the number concentration of particles with a radius R_1. The Smoluchowski expression neglects all the interactions acting between colliding particles. In reality, however, various electrochemical and hydrodynamic interactions act between colliding particles and thus alter the colliding trajectory between particles. As a result, an introduction of correction factor called capture or aggregation efficiency α is needed to modify the expression of aggregation rate J[4,10-18]:

$$J = \alpha J_{Smol} \qquad (2)$$

In order to evaluate the capture efficiency α, a trajectory analysis has been used[11-16]. In doing this analysis, one has to solve trajectory equations describing the relative movement of colliding spheres under the influence of hydrodynamic as well as physicochemical interactions[11-16,19]. The physicochemical interaction is usually given by the sum of electric double layer

(EDL) and the van der Waals (vdW) forces. The sum of the two forces is referred to as the Derjaguin-Landau and Verwey-Overbeek (DLVO) force[4,20,21]. The EDL force is dependent on the electrostatic potential at particle's surface and the salt concentration of suspension medium. Van de Ven and Mason[12] solved trajectory equations and evaluated the capture efficiency of equal-sized (R_1=R_2=R) spheres α_{11} in a shear flow in the presence of repulsive EDL force; the colliding spheres have the same sign of surface potential. Their results cannot be expressed by a simple correlation equation except for a rapid aggregation, where the EDL force is absent. In the presence of only the vdW force, the capture efficiency $\alpha_{11,0}$ is given by

$$\alpha_{11,0} = c_1 C_A^{0.18} \tag{3}$$

with a dimensionless parameter

$$C_A = \frac{A_{12}}{36\pi\mu G R^3} \tag{4}$$

where μ dynamic viscosity of medium, A_{12} the Hamaker constant reflecting the magnitude of vdW force, c_1=0.79, 0.87, and 0.95 for R=2, 1, and 0.5 μm. Later, trajectory analyses on the rate of shear aggregation were performed for the heteroaggregation between unequal-sized spheres[13-15]. Han and Lawler[5] obtained correlation equations of the capture efficiency for the shear heteroaggregation in the absence of EDL force $\alpha_{12,0}$ written as

$$\alpha_{12,0} = \frac{8}{(1+\lambda)^3} 10^{(a+b\lambda+c\lambda^2+d\lambda^4)} \tag{5}$$

where λ=R_2/R_1 (R_1>R_2) is the ratio of particle radius, a, b, c, and d are constants depending on a dimensionless parameter H_A defined by

$$H_A = \frac{A_{12}}{18\pi\mu G(2R_1)^3}. \tag{6}$$

Both Eqs. (4) and (6) asses the relative importance of van der Waals attractive force to hydrodynamic force. Experimental studies on aggregation in flow fields have been carried out for the homoaggregation of equal-sized spheres with repulsive EDL or without EDL force[10,12,17,18,22]. These investigations have qualitatively supported the validity of the prediction by trajectory analyses.

Recently, the effects of attractive EDL force acting between positively charged and negatively (oppositely) charged particles on aggregation and deposition have been tested[4,23-27]. Previous researches studying the effect of attractive EDL on the aggregation rate by Brownian diffusion[23,24] and the deposition kinetics in porous media[4,25] reported that decreasing salt concentration enhance the rates of particle deposition and aggregation.

As far as the author knows, however, the rate of heteroaggregation between unequal-sized and oppositely charged suspended particles in a shear flow has never been studied. In the natural water, aggregation of colloidal particles proceeds through the collision between unequal-sized particles and/or aggregates[3,6,7] under the influence of flow fields, and both positively and negatively charged particles exist[28,29]. In addition, heteroaggregation of small colloidal particles, which are the cause of turbidity, with oppositely charged large particles, which have large sedimentation velocity, can be used to increase the rate of solid-liquid separation (Fig. 1). Therefore, to study the shear aggregation between unequal-sized and oppositely charged particles is useful from scientific and engineering points of view, because it gives better knowledge on aggregation to us. In this context, this paper describes the results of trajectory analysis for the evaluation of capture efficiency of heteroaggregation with attractive EDL force in a simple shear flow.

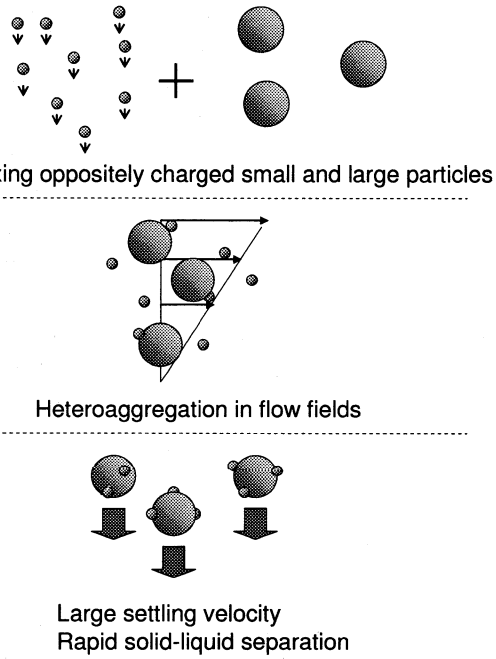

Fig.1 Schematic illustration of heteroaggregation and its application; heteroaggregates enhance solid-liquid separation.

2. Method

A method to evaluate capture efficiency α from trajectory analysis is given below.

Consider two spheres, sphere 1 with a radius R_1 and a surface potential Ψ_1, and sphere 2 with a radius R_2 and a surface potential Ψ_2, in a simple shear flow with a shear rate of G. As shown in Fig. 2, the relative position of sphere 2 is given by rectangular coordinates (x, y, z) or by spherical coordinates (r, θ, ϕ).

Evaluation of capture efficiency α can be done by solving trajectory equations describing the relative motion of

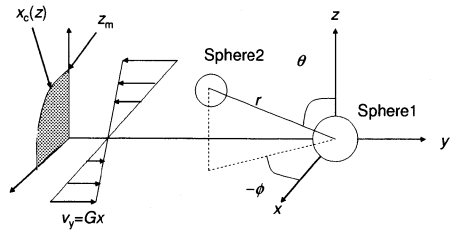

Fig.2 Coordinates for trajectory analysis.

aggregating spheres. The relative motion of colliding sphere is governed by the following trajectory equations[13,14]:

$$\frac{dr^*}{dt^*} = r^*(1-A)\sin^2\theta\sin\phi\cos\phi + \frac{C}{6\pi\mu G R_1^2}(F_{el}+F_{vdW}) \quad (7)$$

$$\frac{d\theta}{dt^*} = (1-B)\sin\theta\cos\theta\sin\phi\cos\phi \quad (8)$$

$$\frac{d\phi}{dt^*} = \cos^2\phi - \frac{B}{2}\cos 2\phi \quad (9)$$

where t time, $r^* = r/R_1$ dimensionless distance between particles' centers, $t^* = Gt$ dimensionless time, A, B, and C are hydrodynamic interaction functions[4,19] that depend on r^* and the radius ratio $\lambda = R_2/R_1$ ($R_1 > R_2$). At the large separation distance between particles, the functions A, B, and C are shown as[13,14]

$$A = \frac{\frac{5}{2}(1+\lambda^3)}{r^{*3}} - \frac{\frac{3}{2}(1+\lambda^5)+\frac{5}{2}\lambda^2(1+\lambda)}{r^{*5}} + \frac{25\lambda^3}{r^{*6}} \quad (10)$$

$$B = \frac{1+\lambda^5+\frac{5}{3}\lambda^2(1+\lambda)}{r^{*5}} \quad (11)$$

$$C = 1+\frac{1}{\lambda} \quad (12)$$

At very small distances, on the other hand, hydrodynamic functions are written as follows[13,14]:

$$A = 1-4.077h^* \quad (13)$$

$$B = 0.4060 + \frac{0.78}{\ln h^*} \quad (14)$$

$$C = 4h^*(1+1.34h^*\ln h^*) \quad (15)$$

for $\lambda=1$. Similar expressions, not shown here, are available for λ=0.1, 0.2, and 0.5[13,14]. In the above equations, $h^* = r^* - \lambda - 1$ is the dimensionless separation distance between surfaces. For intermediate separation, interpolated approximate expressions by Wang[14] are adopted in the present study.

The attractive van der Waals (vdW) force and electric double layer (EDL) force are introduced in Eq. (7) as F_{vdW} and F_{el}, respectively. The electrochemical force known as DLVO force is expressed by the sum of F_{vdW} and F_{el}. The vdW force is described by[13,14]

$$F_{vdW} = -\frac{A_{12}R_2}{(1+\lambda)6h^2}\frac{1+3.54p}{(1+1.77p)^2} \quad (16)$$

for $p<1$ and

$$F_{vdW} = -\frac{A_{12}R_2}{(1+\lambda)h^2}\left(\frac{2.45}{15p} - \frac{2.17}{30p^2} + \frac{1.18}{105p^3}\right) \quad (17)$$

for $1 \leq p$, where h distance between particles' surfaces, A_{12} Hamaker constant, p dimensionless distance defined by $p=2\pi h/\lambda_L$ using the London wave length λ_L (typically 100nm).

The EDL force in a simple salt solution of 1:1 electrolyte such as KCl and NaCl is given by[4,21]

$$F_{el} = \frac{2\pi R_2}{1+\lambda}\frac{64\gamma_1\gamma_2 nk_BT}{\kappa}\exp(-\kappa h) \quad (18)$$

with

$$\gamma_i = \tanh\left(\frac{e\psi_i}{4k_BT}\right), i = 1, 2 \quad (19)$$

where k_B the Boltzmann constant, T absolute temperature, $\kappa = \sqrt{2ne^2/(\varepsilon_r\varepsilon_0 k_BT)}$ the reciprocal Debye length, ε_r relative dielectric permittivity, ε_0 vacuum dielectric permittivity, e elementary charge, $n=1000N_AC_s$ the number concentration of salt, N_A Avogadro's number and C_s salt concentration in M (=mol/L). The dimension of $1/\kappa$ is length and is thus referred to as the Debye length. The Debye length $1/\kappa$ is regarded as a measure of the thickness of the diffuse part of EDL around colloidal particles and increases with decreasing salt concentration. It is clear from Eq. (18) that the EDL force is attractive when Ψ_1 and Ψ_2 have different sign, that is, the surfaces are oppositely charged.

In order to calculate colliding trajectories with hydrodynamic and physicochemical interactions, Eqs (7)-(9) were numerically solved by the Runge-Kutta method[30]. Calculations were started from $y^*=y/R_1$= -20 and trial ($x^*=x/R_1$, $z^*=z/R_1$). Each calculation was stopped when the position of sphere 2 resulted in one of the following three fates; (i) $r^*-\lambda-1<\delta^*=\delta/R_1$, where δ is the minimum separation, (ii) $\phi>\pi/2$, or (iii) y^*=10. The cases (i) and (ii) mean that sphere 2 is captured by sphere 1, that is, aggregation occurs. The case (iii), on the other hand, indicates that spheres 2 is separated and no aggregation happens. In the present work, δ=0.1nm was used to avoid numerical divergence. The shape of boundary of the capture cross-section $x_c^*(z^*)$ at y^*= -20 can be found by calculating trajectories from trial starting points (Fig. 2). All calculations started from points (x^*, z^*) within the boundary result in aggregation. From the shape of the capture cross-section, the capture efficiency α was evaluated from the following equation[13,14]:

$$\alpha = \frac{3}{2(1+\lambda)^3}\int_0^{z_m^*}[x_c^*(z^*)]^2 dz^* \quad (20)$$

In this study, the procedure described above was applied to compute capture efficiency α. Evaluated results are plotted as a function of dimensionless parameters[8,11,12]; the ratio of the vdW force to hydrodynamic force C_A (or H_A), the ratio of the EDL to the vdW forces $N_{el}= \varepsilon_r\varepsilon_0 R_1|\Psi_1||\Psi_2|/A_{12}$, and the relative thickness of diffuse part of EDL $\tau=\kappa R_1$, in order to make the results universal and meaningful.

3. Results and Discussion

3.1. Capture Efficiency without Electric Double Layer Force

Values of capture efficiency for homoaggregation between equal-sized particles calculated without electrical double layer (EDL) force $\alpha_{11,0}$ are plotted against the dimensionless quantity C_A in Fig. 3. Circles and triangles are calculations by this work and by Eq. (5), respectively. The line in the figure is drawn by Eq. (3) obtained by van de Ven and Mason[12]. The symbols in Fig. 4 are evaluated values by this study for the capture efficiency of heteroaggregation between unequal-sized particles calculated without EDL force $\alpha_{12,0}$. The calculations were made for three values of H_A. The curves in Fig. 4 are drawn by Eq. (5). As seen from the graphs, the values of $\alpha_{11,0}$ and $\alpha_{12,0}$ evaluated by this work show good agreement with previous calculations. This agreement confirms the calculation by the present work.

In Fig. 5, previous experimental data[18] of capture efficiency of homoaggregation ($R_1=R_2=R$) in a shear flow without EDL force, denoted by symbols, are compared with the present calculations shown as lines. In the plotting, in order to obtain the best fit between theory and experiment, values of the Hamaker constant A_{12} are assumed to be 3×10^{-21} J and 1×10^{-21} J for R=1μm and 1.4μm, respectively. The figure demonstrates that trajectory analysis reasonably describes experimental behavior; the trajectory analysis is found to be practically useful for the evaluation of aggregation kinetics in flow fields. While the values of A_{12} are lower than that by theoretical predictions, they are comparable to the values suggested in previous studies[10,22], which concluded that A_{12} should be 1×10^{-21} J. The reduction of A_{12} in the experiment is probably due to surface roughness or accumulation of salt adjacent to surface[22].

3.2. Capture Efficiency in the Presence of Attractive Electric Double Layer Force

In Figs. 6 and 7, values of capture efficiency between unequal-sized spheres are plotted against $\tau=\kappa R_1$ for four values of radius ratio λ. Values of H_A, reflecting the relative effect of shear rates of flow, were written in Figs. 6 and 7, respectively. In these figures, the capture efficiency with attractive EDL α_{12} is normalized by that without EDL $\alpha_{12,0}$. By using this expression, we can see the effect of EDL force clearly.

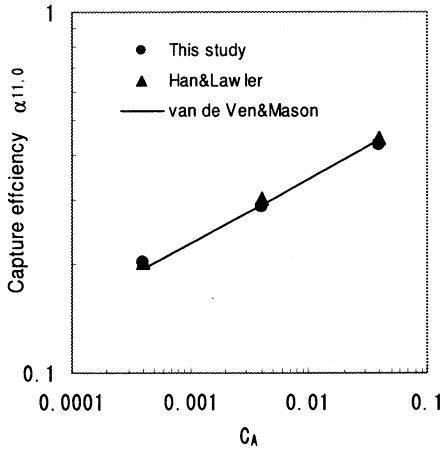

Fig.3 Capture efficiency of homoaggregation without EDL force.

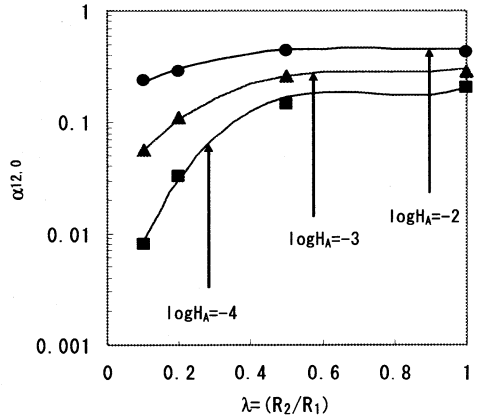

Fig.4 Capture efficiency of heteroaggregation without EDL force: Symbols and lines are evaluated by this work and by Eq. (5), respectively

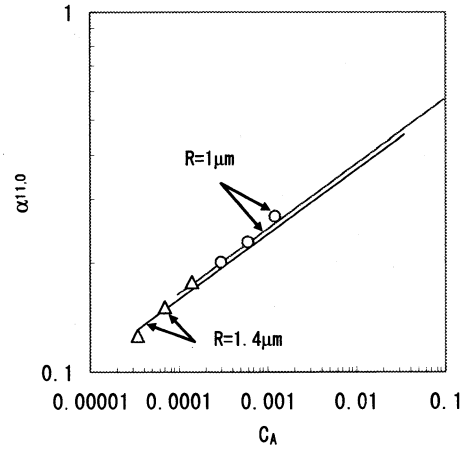

Fig.5 Capture efficiency of homoaggregation ($R_1=R_2=R$) without EDL force. Experiments (symbols) are compared with calculations (Lines). To obtain better fits, A_{12} (10^{-21}J) =3 and 1 are assumed for R=1 and 1.4 μm, respectively.

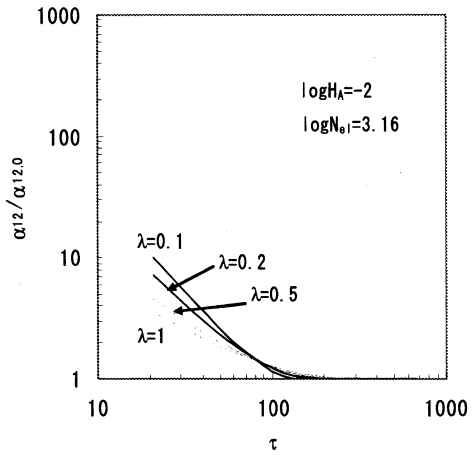

Fig.6 Capture efficiency of heteroaggregation between unequal-sized spheres with attractive EDL force.

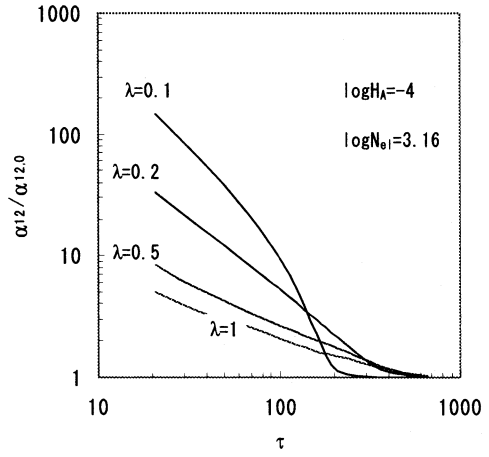

Fig.7 Capture efficiency of heteroaggregation between unequal-sized spheres with attractive EDL force.

These figures demonstrate that $\alpha_{12}/\alpha_{12,0}$ increases with decreasing τ, namely, with decreasing salt concentration. The tendency is similar to previous studies on the kinetics of particle deposition in porous media[4,25] and the rate of aggregation by Brownian diffusion[23,24] in the presence of attractive EDL force. At lower salt concentrations, as deduced from the Debye length $1/\kappa$, the range and the magnitude of EDL force become large[4]. The increased range and magnitude of EDL force enhance the capture of colliding particles and thus result in the increase of aggregation rates. At higher τ, the effect of EDL force disappears; the van der Waals force becomes dominant in physicochemical interaction forces. In this case, the aggregation rates are not raised by attractive EDL force.

By comparing Fig. 6 with Fig. 7, we see the influence of shear rates H_A on the normalized capture efficiency $\alpha_{12}/\alpha_{12,0}$. That is, higher values of $\alpha_{12}/\alpha_{12,0}$ are found for lower values of H_A, that is, for higher shear rates, with the same radius ratio λ. Decreasing the value of H_A increases the hydrodynamic retardation force, which pushes away colliding particles and prevents aggregation[31,32]. This effect is clear in the calculation with only the van der Waals force (Fig. 3). The attractive EDL force effectively overcomes the hydrodynamic retardation force and gains $\alpha_{12}/\alpha_{12,0}$.

Effects of the radius ratio λ on $\alpha_{12}/\alpha_{12,0}$ are found in Figs. 6 and 7. It is clear from the figures that the sharper reduction of $\alpha_{12}/\alpha_{12,0}$ against τ (salt concentration) is obtained for smaller λ. This means that the attractive EDL enhances the aggregation rate more effectively for smaller λ, i.e., for heteroaggregation. The prevention of aggregation by the hydrodynamic retardation force is more significant for heteroaggregation of unequal-sized spheres than that of equal-sized particles[32]. This is also indicated by the trend of $\alpha_{12,0}$ (Fig. 4). Increasing range and magnitude of attractive EDL force by decreasing τ increases the number of captured particles and therefore raises the capture efficiency compared with the system where only the van der Waals force works.

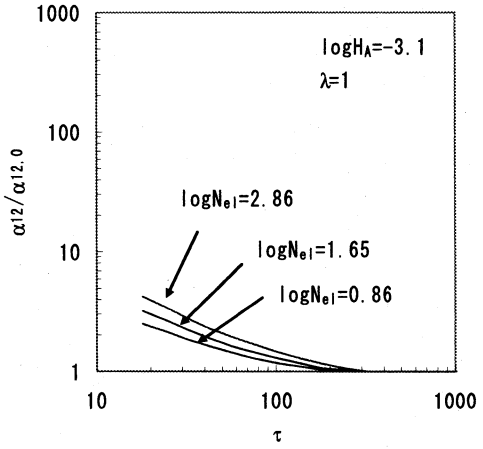

Fig.8 Capture efficiency of heteroaggregation between unequal-sized spheres with attractive EDL force.

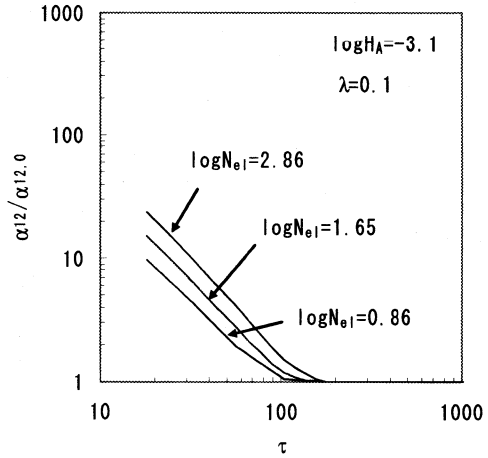

Fig.9 Capture efficiency of heteroaggregation between unequal-sized spheres with attractive EDL force.

Figures 8 and 9 examine the effects of N_{el} (= $\varepsilon_r\varepsilon_0 R_1|\Psi_1||\Psi_2|/A_{12}$), ie., the magnitude of electric surface potential, on $\alpha_{12}/\alpha_{12,0}$. The figures demonstrate that $\alpha_{12}/\alpha_{12,0}$ increases with increasing N_{el} due to the increase of the attractive EDL force. As for the degree of enhancement, the increment of N_{el} has minor effect compared to the influence of τ; two orders of magnitude increase of N_{el} results in about twice increase in $\alpha_{12}/\alpha_{12,0}$. Thus, we can say that the range of EDL force, reflected by τ, is more important than the magnitude of EDL force to enhance the rate of aggregation.

3.3. Suggestion for Experimental Approach

Equation (5), the correlation equation of calculated values of capture efficiency in the absence of EDL effect $\alpha_{12,0}$, has been used to compute aggregation kinetics between aggregates, which are regarded as fractal objects, in marine waters[3]. So far, however, no systematic experiment has been carried out to validate the numerical prediction by Eq. (5); decrease of $\alpha_{12,0}$ with decreasing λ. The reason is probably due to the difficulty of experiment. That is, if we perform experimental study on the rapid heteroaggregation between larger and smaller particles with the same sign of surface electric charge, we generally need to raise salt concentration of suspension medium to 100-1000 mM to induce aggregation. Such high concentration gives rise to simultaneous homo and heteroaggregation of particles[17,18], and causes data interpretation of heteroaggregation difficult.

The present calculation indicates that the enhancement of heterocoagulation by attractive EDL force becomes weak with increasing τ and disappears around τ=200-500, namely in C_s=1-10 mM solution for micrometer sized particles, where α_{12} coincides with $\alpha_{12,0}$. In 1-10 mM solutions, homoaggregation is negligible because of the presence of repulsive EDL force[17,18]. Thus, from the present results, we can conclude that pure heteroaggregation without EDL effects can be realized by using the binary mixture of oppositely charged and unequal-sized particles in 1-10 mM solutions. The finding of this work allows us to use the binary mixture of oppositely charged particles when doing experiments to test the behavior of $\alpha_{12,0}$ in future.

4. Conclusion

The capture efficiency of heteroaggregation between oppositely charged and unequal-sized particles in a shear flow was evaluated by the trajectory analysis. The results indicate that the rate of heteroaggregation increases with decreasing salt concentration. The effect of attractive electric double layer force on the capture efficiency is more profound at higher shear rates and for heteroaggrgation between unequal-sized particles. The calculated results also suggests an experimental approach, that is, pure heterocoagulation without EDL effect can be accomplished by using the binary mixture of oppositely charged and unequal-sized particles in solutions with concentrations of 1-10 mM.

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