Kinetics of Shear Coagulation of Oppositely Charged Particles: A Trajectory Analysis

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Transport properties of aqueous colloidal dispersions are controlled by the coagulation of particles in the dispersions. In order to study the coagulation kinetics and stability of colloid in a shear flow, which are practically important, trajectory analyses with electric double layer force have been used. So far, however, this analysis has not been applied to the heterocoagulation between oppositely charged particles in a shear flow. In the present study, the rate of shear coagulation of oppositely charged particle was calculated using the trajectory analysis. The calculated results indicate that the rate of heterocoagulation increases with decreasing ionic strength and increasing the magnitude of surface potential. The increase of the rate is considered to be due to the increases of the thickness of diffuse double layer and the magnitude of attractive double layer force.

1. INTRODUCTION

Colloidal particles have large specific surface area, and therefore, have been pointed out that they work as carriers of substances in natural water environments[1-3]. One of the important properties of colloidal particles is their aggregation, coagulation, or flocculation. These can increase the size of transport unit and then dramatically change the transport and fate of colloidal particles as well as adsorbed substances. Therefore, to understand aggregation process is crucial for the control and prediction of circulation of substances in aqueous systems.

Coagulation of colloidal particles in many industrial and environmental processes is influenced by physicochemical and hydrodynamic conditions of colloidal dispersions. Smoluchowski[4] pioneered theoretical investigations of coagulation kinetics in flow fields and has derived a theoretical expression on the number of colliding spheres with a radius of R toward an equal-sized sphere per unit time in a shear flow J_{Smol}:

$$J_{Smol} = \frac{32}{3} R^3 GN ,$$

(1)

where G shear rate, N the number concentrations of particles. Equation (1) does not include any interactions between colliding particles. In practice, however, colliding particles are subjected to physicochemical and hydrodynamic interactions[1,3,5-8]. These interactions alter the colliding trajectory. Hence, some of colliding particles are able to coagulate and others are not. As a result, a realistic coagulation rate J is modified by introducing a correction factor α called capture efficiency[5-8]:

$$J = \alpha J_{Smol} .$$

(2)

The capture efficiency α has been evaluated by solving trajectory equations describing the relative motion of colliding spheres in the presence of hydrodynamic and physicochemical interactions[1,5-8]. The latter interaction is generally expressed by the Derjaguin-Landau-Verwey-Overbeek (DLVO) force, which is given by the sum of electric double layer (EDL) and van der Waals (vdW) forces[1,5-10]. The EDL force is known to depend on the surface potential of particles and the ionic strength of suspension medium. Using the trajectory analysis, Van de Ven and Mason[6] calculated capture efficiency of equal-sized spheres in a shear flow under the influence of repulsive EDL force. Their results have complicated functional form and thus are not generally expressed by a simple correlation equation except for a rapid coagulation regime, where the EDL force is negligible[1,9,10]. The capture efficiency for the rapid regime α_0 is given by

$$\alpha_0 = c C_A^{0.18}, \quad C_A = \frac{A_{12}}{36\pi\mu GR^3}$$

(3)

where μ dynamic viscosity of medium, A_{12} Hamaker constant, c=0.79, 0.87, and 0.95 for R=2, 1, and 0.5 μm[6]. In the presence of repulsive EDL interaction, the capture efficiency α is expected to behave as follows. That is, critical coagulation concentrations (CCC), above which the rapid regime is achieved, increase with increasing the shear rate of flow. Values of α decrease with decreasing salt concentrations, when salt concentrations are below CCC. Also, more gradual decrease of α with the decrease of salt concentration is expected for higher shear rates. Previous experimental studies have confirmed these trends and qualitatively validated the usefulness of trajectory analysis[6,11-14].

Interests have recently been paid to the effect of attractive EDL force on aggregation and deposition between oppositely charged particles[1,15-17]. There are some studies examining the effect of attractive EDL on the kinetics of aggregation by Brownian motion[16,17] and particle deposition in porous media[1,15]. These studies report that decreasing salt concentration induces the enhancement of the rates of particle deposition and Brownian coagulation. So far, however,

the trajectory analysis has not been applied to the aggregation in a shear flow in the presence of attractive EDL force. To study the shear aggregation of colloidal particles is important because it has many practical applications. To this end, this paper describes the results of trajectory analysis for the evaluation of capture efficiency of shear coagulation with attractive EDL force. The effects of salt concentration, shear rate, surface potential are examined.

2. METHOD

Let us consider that two spheres, sphere 1 and sphere 2, have the same radius R and have different surface potentials Ψ_1 and Ψ_2, respectively. These particles are placed in a simple shear flow with a shear rate of G as shown in Fig. 1.

Capture efficiency can be obtained by solving trajectory equations. By taking the center of sphere 1 as the origin of spherical coordinate, one can write the relative position of the center of sphere 2 as (r, θ, ϕ). The evolution of the relative position with time t is governed by the following trajectory equations[7,8]:

$$\frac{dr*}{dt*} = r*(1-A)\sin^2\theta\sin\phi\cos\phi + \frac{C}{6\pi\mu GR^2}(F_{el}+F_{vdW}), \qquad (4)$$

$$\frac{d\theta}{dt*} = (1-B)\sin\theta\cos\theta\sin\phi\cos\phi, \qquad (5)$$

$$\frac{d\phi}{dt*} = \cos^2\phi - \frac{B}{2}\cos 2\phi, \qquad (6)$$

where $r* = r/R$ dimensionless distance between particles' centers, $t* = Gt$ dimensionless time, A, B, and C are hydrodynamic interaction functions depending on $r*$. When two spheres are very close to each other, hydrodynamic functions are given as follows[7,8]:

$$A = 1 - 4.077h*, \qquad (7)$$

$$B = 0.4060 + \frac{0.78}{\ln h*}, \qquad (8)$$

$$C = 4h*(1+1.34h*\ln h*), \qquad (9)$$

where $h* = r*-2$ dimensionless surface separation. When the spheres are far apart, on the other hand, these functions are written by[7,8]

$$A = \frac{5}{r*^3} - \frac{8}{r*^5} + \frac{25}{r*^6}, \qquad (10)$$

$$B = \frac{16}{3r*^5}, \qquad (11)$$

$$C = 2. \qquad (12)$$

For moderate separation, approximate expressions proposed by Wang[8] are available and are used in this study.

The last two terms in Eq. (4), F_{el} and F_{vdW}, are electric double layer (EDL) and van der Waals (vdW) forces, respectively. The sum of these forces gives so-called DLVO force[1,9,10]. In a salt solution of 1:1 electrolyte (such as KCl and NaCl) with a number concentration of $n=1000N_AC_s$, where N_A Avogadro's number and C_s salt concentration in M(=mol/L), the EDL force is given by[1,9,10]

$$F_{el} = \pi R \frac{64\gamma_1\gamma_2 n k_B T}{\kappa}\exp(-\kappa h), \gamma_i = \tanh\left(\frac{e\psi_i}{4k_B T}\right), i = 1, 2 \qquad (13)$$

where k_B Boltzmann constant, T absolute temperature, $\kappa = \sqrt{2ne^2/(\varepsilon_r\varepsilon_0 k_B T)}$ the reciprocal Debye length, ε_r relative dielectric permittivity, ε_0 vacuum dielectric permittivity, h distance between particle surfaces, e elementary charge. The Debye length $1/\kappa$ has a dimension of length and is regarded as a measure of the thickness of diffuse double layer around colloidal particles[1,9,10]. Equation (13) is derived on the basis of linear superposition approximation (LSA), which is valid at large surface separation. In the LSA, potential between two interaction surfaces is given by adding contributions from each surface[1,9,10]. For lower values of surface potential, F_{el} is also given by[1,8,9,10]

$$F_{el} = \frac{\pi R\kappa\varepsilon_r\varepsilon_0}{2}\left[\frac{2\Psi_1\Psi_2 - (\Psi_1^2 + \Psi_2^2)\exp(-\kappa h)}{\sinh(\kappa h)}\right], \qquad (14)$$

which assumes constant low surface potential (CP) when two surfaces interact. In the CP mode, the linearized Poisson-Boltzmann equation is solved to evaluate the interaction energy between surfaces. The difference between LSA

and CP modes appears at close separation distance between particles' surfaces[1]. The both expressions indicate that EDL force is attractive when the interacting surfaces are oppositely charged.

Attractive London-van der Waals force F_{vdW} is described by[7,8]

$$F_{vdW} = -\frac{A_{12}R}{12h^2}\frac{1+3.54p}{(1+1.77p)^2} \qquad \text{(for } p<1) \qquad (15)$$

$$F_{vdW} = -\frac{A_{12}R}{12h^2}\left(\frac{0.98}{p} - \frac{0.434}{p^2} + \frac{0.067429}{p^3}\right) \quad \text{(for } 1 \leq p) \qquad (16)$$

where A_{12} Hamaker constant, p dimentionless distance defined by $p = 2\pi h/\lambda_L$ using the London wave length $\lambda_L = 100$nm. Equations (15) and (16) take into account the retardation effect that reduces the magnitude of the van der Waals force.

Equations (2)-(4) were numerically solved by the Runge-Kutta method[18] to obtain relative colliding trajectories. Sphere 2 was released from the initial conditions, a fixed y ($y^* = y/R = -20$) and various trial positions of $x^* = x/R$ and $z^* = z/R$ [6,8], and was then moving toward sphere 1 according to the trajectory equations. The calculation was stopped once the position of sphere 2 reached (a) $r^*-2 < \delta^* = \delta/R$, where δ is the minimum separation, (b) $\phi > \pi/2$, or (c) $y^* = 10^6$ [6,7]. The cases (a) and (b) correspond to the occurrence of aggregation, while no aggregation occurs in the case (c). This study employed $\delta = 0.1$nm to avoid numerical divergence. By trial and error scheme, one can obtain the boundary of the capture cross-section $x_c^*(z^*)$ at $y^* = -20$ (Figs. 1 and 2); all the spheres 2 released within the boundary are able to coagulate with sphere 1. From the shape of the capture cross-section, the capture efficiency α can be calculated by using the following equation[7,8]:

$$\alpha = \frac{3}{16}\int_0^{z_m^*}\left[x_c^*(z^*)\right]^2 dz^* \qquad (17)$$

With the procedure described above, in the present study, α was computed as a function of salt concentration, surface potential, and shear rate with $R = 1\mu$m and $A_{12} = 0.967 \times 10^{-20}$J[7]. The following section discusses obtained results.
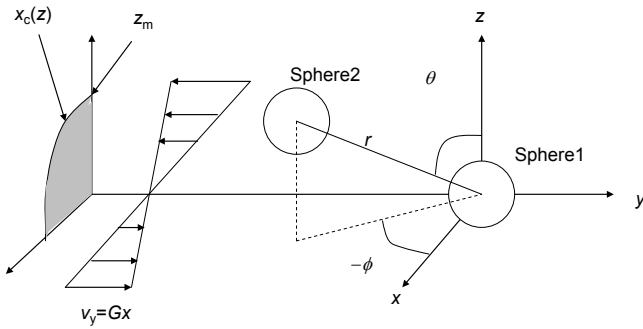

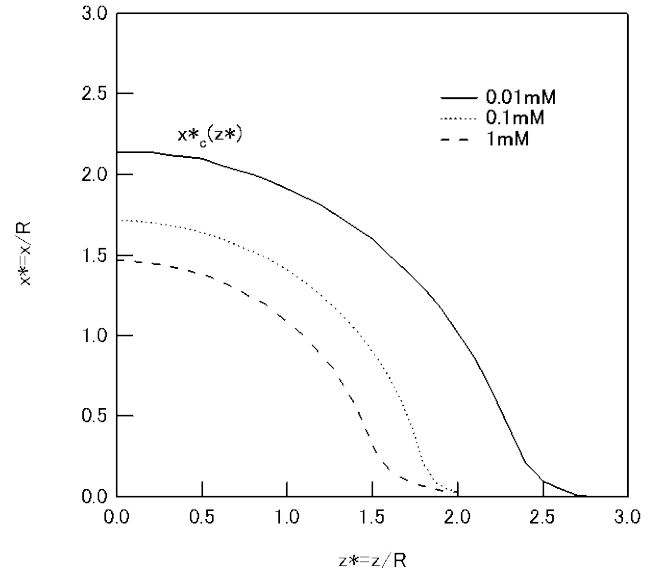**Figure 1** Coordinate for the trajectory analysis of two spheres in a shear flow.

Figure 2 Calculated capture cross sections with attractive electrical double layer force. $G=10$ s^{-1}, $\psi_1 = -\psi_2 = 10$ mV.

3. RESULTS AND DISCUSSION

Values of capture efficiency calculated without electrical double layer (EDL) force α_0 are plotted against the dimensionless quantity C_A in Fig. 3. The line in the figure is drawn by Eq. (3) with $c=0.87$ obtained by van de Ven and Mason[6]. Figure 4 shows the values of capture efficiency α calculated with the constant potential (CP) mode of repulsive EDL force as a function of shear rate. The curve in the Fig. 4 is taken from the report by Vanni and Baldi[7]. In both figures, symbols denote the computed results of this study. A minimum around $G=10$ s^{-1} seen in Fig. 4 arises from a secondary minimum coagulation[6,7]. As we see from the graphs, the values of α_0 and α obtained by this work are in good

agreement with previously published data. This agreement proves the validity of calculation of this work. Hence, we are ready to focus on the effects of attractive EDL force on capture efficiency α.
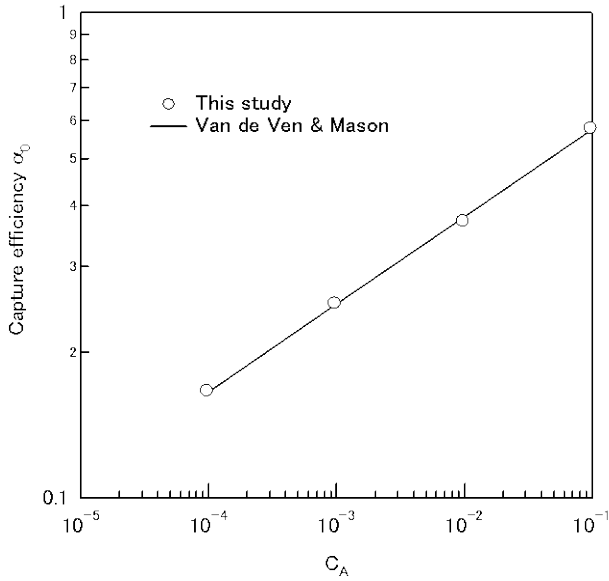

Figure 3 Capture efficiency in the absence of electrical double layer force.
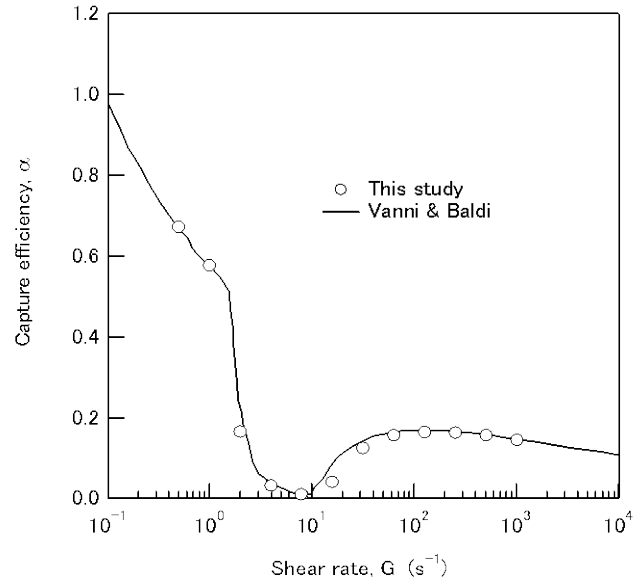

Figure 4 Capture efficiency calculated with repulsive electrical double layer force with $\kappa=10^8\,\text{m}^{-1}$ and $\psi_1=\psi_2=5$ mV.

Computed values of α with attractive EDL force are shown in Figs. 5, 7, and 8. In Fig 5, valued of α calculated with the constant potential (CP) and the linear superposition approximation (LSA), are shown as a function of salt concentration with a shear rate G of 10 s^{-1} and a absolute surface potential ($\psi_1 = -\psi_2$) of 10mV. The figure indicates that α increases with decreasing salt concentration and that CP and LSA modes provide almost the same values. These trends are similar to the results of kinetics of particle deposition[1,15] and Brownian aggregation[16,17] and can be regarded as general natures of aggregation and deposition in the presence of attractive EDL force. The enhanced coagulation at lower salt concentrations is considered to be due to the extension of the thickness of diffuse double layer, the Debeye length, surrounding particle. The increment of the Debye length extends the range of interaction force and thus increases the rate of coagulation. The increased range of attractive force is clearly seen in the force profile between particles (Fig. 6). At higher salt concentrations, the reduced Debye length induces the screening of EDL interaction; in this case, coagulation is not enhanced by attractive EDL force because the van der Waals force dominates the coagulation rate. As for the modes of EDL, relatively insignificant effect of the type of EDL expressions is obtained. This result contradicts the calculation with repulsive EDL, where the CP mode provides less repulsive force and thus higher values of capture or collector efficiency[1,5]. The result suggests that aggregation and deposition kinetics with attractive EDL are mainly controlled by the interaction at larger particle-particle distance, where the difference between CP and LSA modes disappears. Since the both EDL expressions give comparable data, the results calculated with the LSA mode are shown in Figs. 7 and 8.

In Fig. 7, the ratio of capture efficiency with attractive EDL to that without EDL α/α_0 is plotted against salt concentration for three different values of G. By using this plot, we see the influence of EDL more clearly. The figure demonstrates that α/α_0 decreases and reaches unity as salt concentration increases, indicating the existence of critical concentration, above which EDL force does not contribute to the kinetics of coagulation. Two effects of G are also seen in Fig. 7. That is, the higher the value of G is, the larger the value of α/α_0 is. This means that the enhancement of aggregation rate due to attractive EDL is more effective at higher G. Another effect of G is the shift of the critical coagulation (CC). The CC moves to higher values as G increases. The shift also implies that the enhancement of capture efficiency is more effective for higher G.

Figure 8 shows a plot of α/α_0 versus magnitude of surface potentials of two spheres (ψ_1 and ψ_2), which are oppositely charged. The figure shows that increasing the magnitude of ψ_1 and ψ_2 enhances α/α_0 because of the increase of magnitude of attractive EDL force indicated by Eq. (13). The value of α/α_0 rapidly rises even at lower values of ψ_1 and ψ_2 in very low salt concentrations. In higher salt concentrations, however, the degree of enhancement by increased surface potential weakens. At the condition where salt concentration and shear rate are 1mM and 1 s^{-1}, respectively, no significant elevation of α/α_0 is observed even at very high surface potentials. Insignificant effect of the magnitude of surface potentials is also seen in previous studies on the kinetic of deposition and Brownian coagulation[1,17]. This weak

surface potential dependence means that sufficient length of the Debye length is prerequisite to enhance α/α_0 by attractive EDL force, although both decreasing salt concentration and increasing surface potential are effective to increase capture efficiency of shear coagulation in the presence of attractive EDL interaction.

Throughout this study, the DLVO force based on the classical picture of EDL was employed. That is, dynamic behaviors of EDL such as retardation and relaxation of double layer[10] was neglected. While the dynamic effects of EDL are not necessarily to describe the kinetics of heteroaggregation by Brownian motion[17], its influence on the rate of shear aggregation is still unknown. In order to discuss this point, we need further experimental studies on the kinetics of heteroaggregation in flow fields.
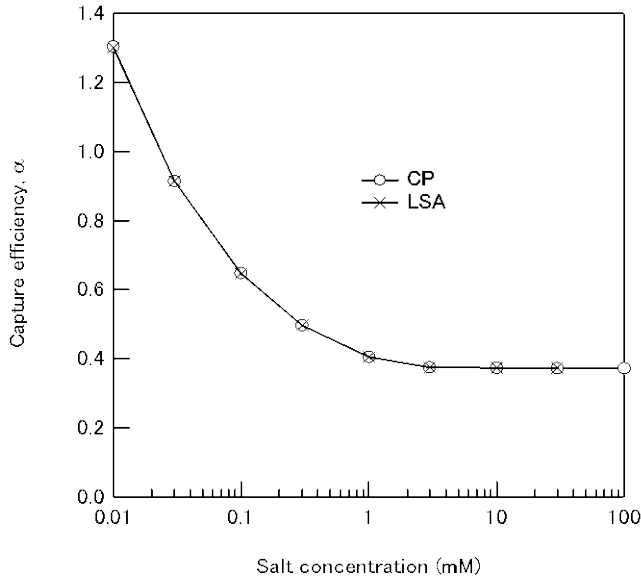

Figure 5 Capture efficiency calculated with attractive electrical double layer force with $G=10$ s^{-1} and $\psi_1=-\psi_2=10$ mV.
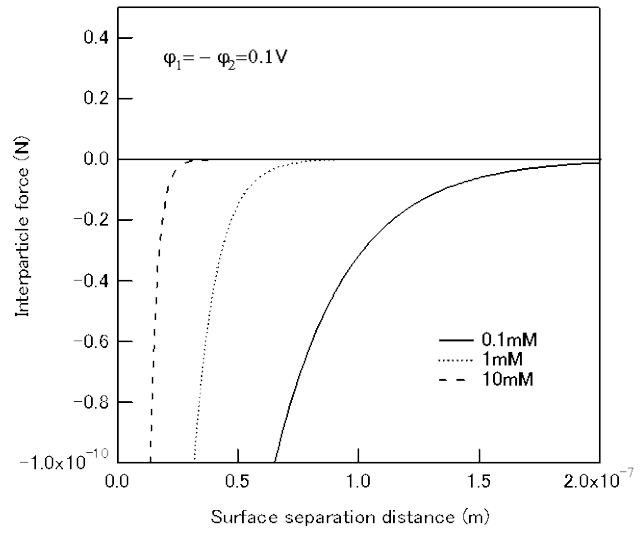

Figure 6 Interaction force profile between two spheres with attractive electrical double layer.
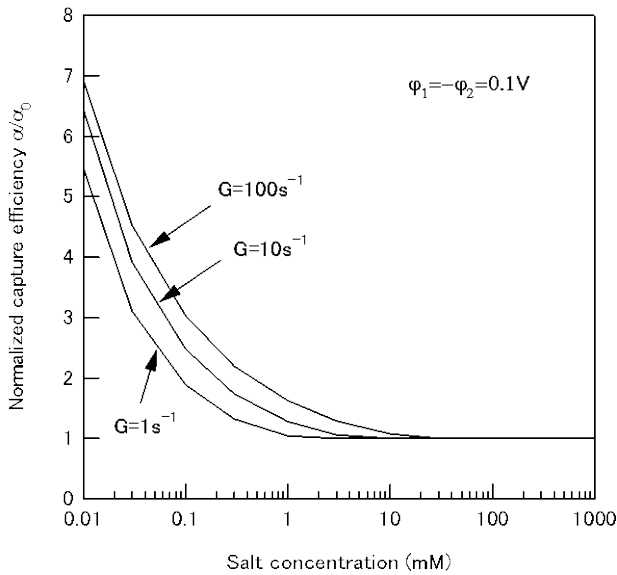

Figure 7 Effect of salt concentration on normalized capture efficiency.
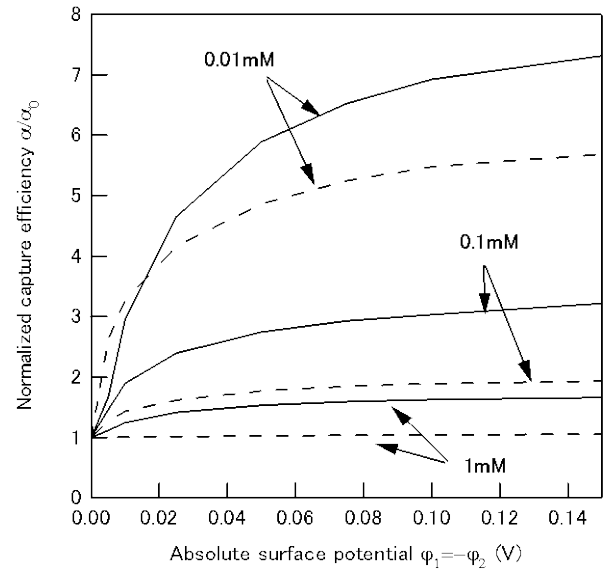

Figure 8 Effect of surface potential on normalized capture efficiency. Solid and dashed lines are drawn for $G=100$ and 1 s^{-1}, respectively.

4. CONCLUSIONS

The rate of shear coagulation with attractive double layer force was investigated by using trajectory analysis. The results of trajectory analysis demonstrated that capture efficiency of shear heteroaggregation increases with decreasing

ionic strength. The enhanced aggregation is likely due to the increases of Debye length as well as the magnitude of attractive double layer force. The effect of surface potential is significant only at low salt concentration.

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