Rheology and Sedimentation of Aqueous Suspension of Na-montmorillonite in the Very Dilute Domain†

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Abstract
The scheme of DLVO theory and the concept of fractal structure of flocs applied to the suspension of montmorillonite have revealed out the unique nature of this clay dispersion. In this context, two major regimes are recognized. The first is the electrostatically dispersed regime. And the second is the coagulated regime. In the former, the formation of a diffusive electric double layer (EDL) characterized by reciprocal Debye length measured from the surface of the particle is distinctively important. Intrinsic viscosity with electroviscous effects and yield stress are interpreted by the steric presence of EDL. In the latter, the unit of transportation is a coagulated floc with finite cohesive strength. Sedimentation process reflecting these factors is carefully observed to recognize the turbulence generation by the formation of large flocs at the moment of gel collapse. Waiting time prior to gel collapse was found to be determined reflecting the pH-dependent charging behavior. By taking into account the effect pH-dependent charge, the DLVO based two regimes are further categorized into five. The developed tools can be extensively used for the system involved with different ionic species, pH, volume fraction and organic substances.

Keywords: Na-montmorillonite, Debye length, electroviscous effect, floc, cohesive strength, sedimentation turbulence

1. Introduction
In a natural environment, nutrients and chemical pollutants are apt to adsorb on the colloidal particles which are ubiquitously present in soil and water. Clays are major components of environmental colloid. Understanding the behavior of such colloid is critically important to predict the diffusion and fate of chemical substances. In addition to agricultural production, knowledge has been recognized very useful for the design and the development of the technology of environmental remediation. Macroscopic transport properties in soils are determined reflecting microscopic interaction of colloidal phenomena in soils (Adachi Y. and Iwata S., 2003; Adachi Y., 2019). Rheological properties of an aqueous dispersion of clay have also received many attentions with respect to the transportation of cohesive sediment in river and estuary (Winterwerp J.C and Kestern W.G.M.V., 2004), land consolidation (Sudo S. and Yasutomi R., 1961), drilling mud for construction work and petroleum production (Van Olphen H., 1977) and usage in variety of application such as cosmetic, paint, agricultural chemical, cement, ceramics, and so on (Lagaly G. and Ziemer S., 2003).

One of the typical clays with outstanding surface properties is the montmorillonite, which is a pure component of bentonite; a usually used clay industry. Interesting nature of the aquatic system of montmorillonite has classically received scientific attention in the direction to swelling (Norrish K., 1954) and phase separation (Langmuir I., 1938; Michot L.J. et al., 2009). Another interest is also paid for the direct verification of DLVO theory (Callaghan I.C. and Ottewill R.H., 1974). In the present article, we limit our attention to the rheological properties of Na-montmorillonite suspension and sedimentation process of the same clay. Although the choice of Na-montmorillonite seems rather arbitrary, this choice will be turned out to be appropriate to remind typical common features of soil colloid without losing their characteristic factors. The shape and distribution of electric charges in the unit of clay particles will realize the
The accumulation of such clay will bring about a condition of abundant bio-available minerals for crop production. This is very suitable to provide the changeable mineral nutrient near the surface of montmorillonite sheet. This is considered to be suitable for the generation of exchangeable ions at less reversible manner. Such a situation can be considered to be adsorbed onto the surface of montmorillonite when the sheet is immersed in water. Cations are considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible. Such a situation can be considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible. Such a situation can be considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible.

Due to the location of the substitution which taking places at the alumina octahedral sheet sandwiched at the center of two silica layers, direct contact with water molecules or solving cations to the charged part of molecules which will lead to irreversibly strong bond is avoided when the sheet is immersed in water. Cations are considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible. Such a situation can be considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible. Such a situation can be considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible. Such a situation can be considered to be adsorbed onto the surface of montmorillonite sheets with hydrated layer of water molecules more or less reversible.

On the other hand, the broken bonds located at the edge of the layer have a capacity to adsorb H⁺ or OH⁻ resulting in the appearance of pH-dependent charge. Therefore, such charging property causes different types of associations between two sheets which are strongly pH-dependent (Tomczak E. and Szekeres M., 2004; Heath D. and Tadros F., 1983). In the acidic condition, the association between Edge-Face is considered to be dominant and in alkaline condition, Face-Face association will be dominant. A pH-dependent charge at the edge of the sheet is also important when the interaction between natural organic matter most of which has groups with pH-dependent charge is analyzed (Ramos-Tejada M.M. et al., 2001). Unique rheological characteristics and sedimentation behavior of montmorillonite suspension will be influenced by such different associations.

In the present article, our attentions are limited to dilute suspension to clarify the relationship between the macroscopic interaction at the level of colloidal surface and the macroscopic behavior such as mechanical properties and hydrological transportation. Our purpose here is to introduce the variety of resulted behaviors which appears reflecting just microscopically different conditions around the clay particles. For this purpose, the framework of the classical theory of electric double layer (EDL) (Gouy M., 1910; Chapman, 1913) and DLVO (Derjaguin B.V. and Landau L.D., 1941; Verwaay E.J.W. and Overbeek J.Th.G., 1948) are confirmed to be very useful. In this respect, we regard the Debye reciprocal length which can be the index of the thickness of EDL is one of the most important parameters. The value is expressed as,

$$\kappa^{-1} = \frac{1}{\sqrt{\varepsilon_0 \sum \varepsilon_i^2 \eta_i kT}}$$

(1)

By the analysis of dielectric spectroscopy and electrokinetic spectroscopy, we recognized $\kappa^{-1}$ is also an important parameter (Tsujimoto Y. et al., 2013; Ishida T. et al., 1999).

However, this is not sufficient from two points. One is that the colloidal stability is influenced by the above-mentioned variety of pH-dependent associations. The other is the lack of description of flocculated material. That is, the geometrical structure (Adachi Y. and Ooi S., 1990) and the strength of formed floc (Kobayashi M. et al., 1999; Kobayashi M., 2004) need to be considered (Adachi Y. et al., 2019). These two factors will be explained by the concept of fractal nature of flocculated montmorillonite and the concept of cohesive strength of floc. These aspects can be understood by referring our recent result on the basis of hydrodynamic analysis. We will also add our recent result of the sedimentation of flocculated montmorillonite which also demonstrates the significant
finding of the generation of turbulent flow when the material is strongly cohesive. The waiting time for gel collapse prior to the onset of sedimentation turbulence is affected also by the pH-dependent charge (Wu M. and Adachi Y., 2017). That is, microscopic pH-dependent charge also affects the macroscopic behavior.

2. Scheme of rheological data

2.1 Three regimes

The behavior of relative viscosity of dilute suspension or the yield stress of slightly higher concentration of Na-montmorillonite is summarized as a function of ionic strength in the monograph of clay colloid chemistry (Van Olphen H., 1977). The most typical pattern obtained for the dilute suspension (0.23%) using the rheometer taken from the text is shown in Fig. 2.

As shown in the figure, in the limit of low ionic strength, relatively high value of viscosity is observed. But the value of viscosity decreases dramatically with the increase of ionic strength and after passing through the minimum value, it will increase again monotonously with an increase of ionic strength (Abend S. and Lagaly G., 2000; Ali S. and Bandyopadhyay R., 2016). Similar behavior of the yield stress against ionic strength is also reported (Van Olphen H., 1977). The development of diffusive electric double layer formed around the montmorillonite sheet induces the electro viscous effect, thus resulting in the high resistance against flowing motion. On the other side, the increase of ionic strength will result in the depression of diffusive part of electric double layer. And in the extreme case, as predicted by the DLVO theory, flocculation is induced by the effect of van der Waals attractive force. With these pictures, in the system of slightly high concentration of montmorillonite: 1) Repulsive gel, 2) Intermediate dispersion and 3) Attractive gel, arc recognized.

2.2 Capillary viscometer

It should be noted that in the flocculation region, the viscosity increases more gradually than that of the steep slope observed for the limit of low ionic strength. By carrying out the additional experiment against pH change and also with some observation of thixotropy, Van Olphen H. (1977) proposed various types of association between clay sheets such as Edge-Edge, Edge-Face and Face-Face. As a result, microscopic card house structure and layered stuck have been considered. However, it is not easy to quantify these effects. Now the question arises, how to quantify these pictures. This question was the starting point of our long trip of study. Since it is known that the measurement of intrinsic viscosity polymer solution using capillary viscometer (Fig. 3) will provide information of polymer conformation, we decided to apply the same method to the analysis of montmorillonite suspension.

Usually, the viscosity of colloidal suspension is expressed as a function of the volume fraction of solid. The most basic expression for the relative viscosity can be written as a power series. That is,

\[ \eta_r = \frac{\eta}{\eta_0} = 1 + K_1 \phi + K_2 \phi^2 + \ldots \]  

(2)

Where \( \eta_r \) denotes the relative viscosity. \( K_1 \) is usually referred as intrinsic viscosity which represents the increment of energy dissipation due to the interaction of a particle and surrounding fluid and \( K_2 \) is termed as the Huggins’ coefficient representing the factor due to the interaction between two particles. Theoretical values of \( K_1 \) and \( K_2 \) for a suspension of rigid sphere were obtained 2.5 (Einstein A., 1905) and 6.7 (Batchelor G., 1976), respectively. These values will increase reflecting the shape, the degree of flocculation by means of the increase of

![Fig. 2 Relative viscosity of a 0.23 percent (weight) Na-montmorillonite sol as a function of the amount of NaCl added.](image)

![Fig. 3 Schematic illustration of capillary viscometer.](image)
immobile water. It should be noted that the square of $K_1$ is close to $K_2$.

In practice, we use the value of reduced viscosity defined as,

$$\eta_{\text{red}} = \frac{\eta - 1}{\eta_0} = K_1 + K_2 \phi$$

If we plot $\eta_{\text{red}}$ against $\phi$, we can obtain $K_1$ and $K_2$, from the intercept and slope of the plot, respectively. Our data of reduced viscosity of montmorillonite suspensions are plotted against volume fraction for various ionic strength in Figs. 4 and 5. The former is the case of high ionic strength. And the latter is the case of low ionic strength.

As for the data plotted in Fig. 4, we can immediately draw the following conclusions: (1) $K_1$ is significantly larger than 2.5 reflecting the shape of montmorillonite. The value is roughly a few hundred. (2) The considerable value of the slope of all plot demonstrates significant effect of the interaction between clay sheets. (3) $K_2$ increases monotonously with an increase of ionic strength. It should be noted that this tendency will continue in the region of rapid coagulation; the tendency is still much enhanced in the region where the concentration of NaCl is higher than 1.0 M. The reason for their results will be described in section five.

In the meantime, from the data plotted in Fig. 5 for the region of low ionic strength; much lower than CCC (critical coagulation concentration), we can conclude as follows. (1) $K_1$ is smaller than the value demonstrated in Fig. 4. It is due to the reflection of smaller size of flowing unit under the condition of electrostatically dispersed state. (2) Small increase of $K_1$ and $K_2$ by decreasing ionic strength is confirmed. This result is an implication of electroviscous effects. That is, the decrease of ionic strength means the increase of the thickness of electric double layer. The increment of $K_1$ denotes a primary electroviscous effect due to the interaction between the charged sheet and ambient fluid containing ionic atmosphere. The increment of $K_2$ denotes a secondary electroviscous effect which can be ascribed to the additional interaction of the two EDLs surrounding the two charged sheets.

As demonstrated so far, schema of the rheological data proposed by Van Olphen H. (1977) was confirmed systematically to be reproduced by the simplest measurement of viscosity of dilute suspension. However, it is obvious that the formed flocs are much bigger than the diameter of commercially available capillary viscometer, and the analysis of zero shear limit behavior to correlate with yield stress desirable. This was the motivation to continue further investigation on the flowing behavior of the suspension in extremely low shear rate, the yield stress and strength of coagulated flocs.

2.3 Spiral viscometer

Spiral type viscometer is a home-made capillary viscometer which we developed in order to analyze zero shear and dilute limit (Kobayashi S. and Adachi Y., 2005; Tsujimoto Y. and Adachi Y., 2011). As depicted in Fig. 6, this viscometer is composed of two graduated cylinders connected by a long capillary tube. This system enables to measure viscosity at low-pressure gradient, which is more than one thousand times smaller than the normal capillary viscometer. The difference of the water levels in the cylinders changes over time will eventually approach zero pressure gradients. The temporal variation of the difference of water level provides the information on the...
rheological behavior of suspension in the zero shear limits.

Assuming the law of Poiseuille flow, the volumetric flow rate in the tube, $Q$, is given as functions of scale of the viscometer by,

$$Q = \frac{\pi}{128\eta} \frac{gh}{L} D^4$$

(4)

Where $h$ indicates the difference of the levels. In our investigation, we used the viscometer with the length, $L$, and the inner diameter, $D$, of the tube is one m and 2.40 mm, respectively.

Based on the conservation of mass, the flow rate in the tube is equal to the half of the temporal change of the difference level times cross section of cylinder, $A$. That is

$$Q = -\frac{1}{2} A \frac{dh}{dt}$$

(5)

From the substitution of the relation of Eqn. (4) into Eqn. (5), the functional form of $h(t)$ is simply obtained from the integration with initial condition. That is

$$\ln \left(\frac{h(t)}{h_0}\right) = \frac{\pi g D^4}{64 A L} \frac{\rho}{\eta} t$$

(6)

The viscosity of suspensions is obtained from the slope of the plot of $\ln(h(t)/h_0)$ vs. $t$.

2.3.1 Viscosity obtained by spiral viscometer

The relation between $\ln((h(t))/h_0)$ and $t$ is easily measured manually for each chemical condition. The results obtained for the case of coagulated suspension and electrostatically stable suspension are plotted in Figs. 7 and 8 respectively.

As demonstrated in both figures, viscosity changes remarkably against ionic strength. It should be noted that small flow rate is confirmed for the cases of extremely low ionic strength and high ionic strength and that for both cases, a considerable increase of viscosity was observed in the later period when pressure gradient is reduced.

3. Electroviscous effects of montmorillonite suspensions

3.1 Introduction

The development of EDL due to charging property of clay particles is reflected in the viscosity of suspensions. The formation of EDL around colloidal particles can cause the additional distortion energy of fluid, which is
called electroviscous effects. There are two types of electroviscous effects. The deformation of EDL due to fluid distortion of shear causes the primary electroviscous effect which increases the intrinsic viscosity that is also affected by the shape of particles. Many scientists investigated in detail the change of viscosity of suspensions due to this effect. The first systematic analysis was reported by Booth F. (1950). In the case of montmorillonite, another interest for electroviscous effect is the relation with spillover of counter ion of basal charge to that of edge charge (Chang F.R.C. and Sposito G., 1994, 1996; Chen J.S. et al., 1990; Secor R.B. and Radke C.J., 1985).

On the other hand, when two charged particles flowed to a close position by an external fluid motion, the EDL around colloidal particles overlap which generate the additional energy dissipation. It causes an increment of viscosity and this type of electroviscous effect the secondary electroviscous effect. It was treated theoretically by Russel W.B. (1976, 1978) for a suspension of charged spheres and has been regarded as one of the major factors of non-Newtonian behavior. Krieger I.M. and Eguiluz M. et al. (1976) pointed out that the secondary electroviscous effects have an influence on the relative viscosity of colloidal suspension where a given shear rate can vary by several orders of magnitude. Additionally, the effect was proved to relate to shear thinning behavior. Buscall R. (1991), Takamura K. and Van de Ven T.G.M. (2010) focused on the Dougherty-Krieger equation (D-K equation) to analyze the electroviscous effects. Especially, Takamura K et al. incorporated the particle interaction parameter into the D-K equation. They indicated that the secondary electroviscous effects became negligible at high shear rate when the parameter was given to the D-K equation as a function of Peclet number.

For montmorillonite suspensions, although experimental studies have been done, few studies focused on the electroviscous effects. Egashira K. (1979) found that the intrinsic viscosity of montmorillonite is 190, which is much larger than that of the theoretical value of spherical particles. However, he did not associate the high intrinsic viscosity of montmorillonite is 190, which is much larger than that of the theoretical value of spherical particles and has been regarded as one of the major factors of non-Newtonian behavior. Takamura K et al. (1991) to analyze the electroviscous effects, especially, Takamura K et al. incorporated the particle interaction parameter into the D-K equation. They indicated that the secondary electroviscous effects became negligible at high shear rate when the parameter was given to the D-K equation as a function of Peclet number. For montmorillonite suspensions, although experimental studies have been done, few studies focused on the electroviscous effects. Egashira K. (1979) found that the intrinsic viscosity of montmorillonite is 190, which is much larger than that of the theoretical value of spherical particles. However, he did not associate the high intrinsic viscosity with the electroviscous effects. Adachi Y. et al. (1998b) measured the viscosity of dilute montmorillonite suspension at high pH with the Ostwald viscometer. They found that the influence of the electroviscous effects was remarkable in the region of NaCl concentration less than 1.0 × 10^{-2} M. However, experimental data which show the dependence of the secondary electroviscous effect on the applied shear stress are not enough. An application of spiral viscometer can be regarded as the best method to confirm and evaluate effects which is theoretically predicted and confirmed for the suspension of charged particles.

3.2 Relationship between viscosity and electroviscous effects

3.2.1 Experimental detection of electroviscous effect

The increment of $K_1$ and $K_2$ can be related to as the primary and the secondary electroviscous effects, respectively. In the case of the dilute colloidal suspension composed of monodispersed sphere, the rheological behavior is characterized by the interaction between particles governed by electrostatic, viscous, and van der Waals forces etc. The balance among these factors is qualitatively determined by a characteristic length. It is called the effective collision radius (effective radius). Russel W.B. (1976, 1978) focused on this effective radius, $a_{eff}$ to theoretically solve the secondary electroviscous effect. Assuming the effective radius increase with developing EDL, he derived the following expression of relative viscosity as

$$\eta_r = 1 + \frac{5}{2} \alpha \phi + \frac{5}{2} (a \phi)^2 + \frac{3}{40} \left(\frac{a_{eff}}{a}\right)^5 \phi^2$$

(7)

$\alpha$ is a coefficient relating to the intrinsic viscosity. Also, this coefficient is affected by the primary electroviscous effect and can be calculated for sphere particles by Booth F. theory. However, because of the shape of montmorillonite particles, the theoretical value of the intrinsic viscosity does not strictly agree with that for sphere (Adachi Y. et al., 1998a).

Since the electroviscous effects are affected by the flow field, it is considered as limitation due to the Peclet number is imposed. In fact, Eqn. (7) can be applied at only lower Peclet number. Peclet number is the dimensionless function described by the timescale for diffusive motion relative to that for convection of flow and defined as follows

$$Pe = \frac{6 \pi a^3 \tau}{kT}$$

(8)

Where $\tau$ indicates the shear stress, and $a$ indicates the hydrodynamic diameter (Adachi Y., 1995). Regardless of Peclet number, it is useful that D-K equation, by which Van de Ven T.G.M. and Mason S.G., (1977) and Buscall R. (1991) to analyze the electroviscous effects.

$$\eta_r = \left(1 - \frac{\phi_{eff}}{\phi_{max}}\right)^{-2.5 \phi_{max}}$$

(9)

Where,

$$\phi_{eff} = \phi \left(\frac{a_{eff}}{a}\right)^3$$

(10)

$\phi_{max}$ indicates packing volume fraction. Eqn. (9) and Eqn. (10) were used to estimate the experimental values of $a_{eff}$ by fitting that to our experimental data assuming
$\phi_{\text{max}} = 0.74$ regardless of shear rate argued by Van de Ven T.M. (1989).

3.2.2 Theoretical background of effective radius

The effective radius $a_{\text{eff}}$ is regarded as the distance inducing the distortion of the particle trajectory as shown in Fig. 9. This value may be estimated from the balance between the electrostatic repulsive factor and factors inducing collision (Russel W.B., 1978).

The Brownian motion is dominant where Peclet number is small, the theoretical effective radius is determined by the balance between electrical repulsive energy, $V_e(r)$, and the diffusive energy, $kT$, as follows;

$$\frac{V_e(r)}{kT} \approx 1 \quad \text{at} \quad r = a_{\text{eff}} \quad (11)$$

where,

$$V_e(r) = \frac{4\pi\varepsilon_0\varepsilon_r a_r^2 \zeta^2 \kappa}{kT} \exp(2\kappa r) \frac{\exp(-kr)}{kr} \quad (12)$$

$r$ indicates the distance from a center of the particle. The effective radius is

$$a_{\text{eff}} = k^{-1} \ln \left[ \frac{\beta}{\ln(\beta / \ln \beta)} \right] \quad (13)$$

On the contrary, when the Peclet number is larger than one, the shear stress contributes to the interaction. The mean effective radius can be estimated from the balance between the hydrodynamic force and electrostatic repulsive force (Goodwin J.W. and Hughes R.W., 2000). The hydrodynamic force is calculated from the Stokes drag as follows;

$$F_{sh} = 3\pi \eta a_{\text{eff}}$$

The electrostatic repulsive force is;

$$F_e = 4\pi\varepsilon_0\varepsilon_r a_r^2 \zeta^2 \exp(2\kappa r) \frac{1 + \kappa a_{\text{eff}}}{a_{\text{eff}}} \exp(-\kappa a_{\text{eff}})$$

Balancing these two forces we get;

$$\frac{1 + \kappa a_{\text{eff}}}{a_{\text{eff}}} \exp(-\kappa a_{\text{eff}}) = \frac{3\pi}{4\pi\varepsilon_0\varepsilon_r a_r^2 \zeta^2 \exp(2\kappa r)} \quad (16)$$

Therefore, we can calculate the effective radius based on the Eqn. (13) and Eqn. (16) according to Peclet number.

3.3 Relationship effective radius and long-distance interaction

The obtained data of the relative viscosity of montmorillonite suspensions are shown against volume fraction in Fig. 10. Although the viscosity measured by two different types of viscometers, the relative viscosity increases with a decrease of ionic strength regardless of viscometers.

The tendency which the relative viscosity increased rapidly rather than linear against volume fraction is remarkable especially for the data obtained by spiral viscometer. Therefore, the secondary electroviscous effect clearly influences the viscosity under low shear stress. The
obtained relative viscosities are represented against the applied shear stress in Fig. 11.

Below ionic strength of $10^{-5}$ M, it is significant that the increment of the relative viscosity with decreasing shear stress. Such rheological behavior of so-called shear thinning phenomena was confirmed in the investigations for colloidal suspensions (Krieger I.M. and Eguiluz M., 1976; Buscall R., 1991; Takamura K. and Van de Ven T.G.M., 2010). Based on the experimental data, we calculated and plotted the effective radius as a function of ionic strength against Peclet number in Fig. 12.

Also, we draw lines that showed theoretical effective radius. This value can vary depending on the zeta potential (Tsujimoto Y. et al., 2014). In addition, the values of salt-free suspension were calculated as ionic strength of $5 \times 10^{-6}$ M. At higher ionic strength, both experimental and theoretical effective radius did not change much against Peclet number.

As ionic strength become lower, it was remarkable that effective radius change depending on the Peclet number. This tendency qualitatively agreed with the theoretical prediction. Also, these experimental values are larger than the reciprocal Debye length. Further, the effective radius of the salt-free suspensions reached to about 1000 nm. This value corresponded to the interparticle distance calculated for yield stress (Adachi Y., 1999; Sakairi N. et al., 2005). Therefore, long-distance interaction that depended on the balance of various forces has worked among montmorillonite particles.

4. Yield stress

4.1 Simplified view

As noted in the analysis of electroviscous effects, the behavior of zero shear limit is critically important when effects of electrostatic repulsive force are dominant. Another clear relation between colloidal interaction and macroscopic data can be referred in the analysis of yield stress. By applying Hershe-Bulkley equation to the flow curve measured using cone-plate viscometer for the suspension of Na-montmorillonite, Fuji K. et al. (1996) obtained the yield stress as a function of solid volume fraction as follows.

$$\tau_0 = 3.6 \times 10^{13} \phi^{7.24} (0.008 < \phi < 0.026) \quad (17)$$

Significant point of this result is that $\tau_0$ increases rapidly by the five orders of magnitude in the very narrow range of $\phi$. The power 7.24 is an important index to characterize this change. It should be noted that such rapid increase of $\tau_0$ can be found in the literature of land consolidation (Sudo S. and Yasutomi R., 1961; Yasutomi R. and Sudo S., 1962) with much smaller proportional constant.

In order to explain this relation, Adachi Y. (1999) and Sakairi N. et al. (2005) assumed the parallel array of montmorillonite sheets which are electrostatically dispersed in the water as illustrated in Fig. 13. That is, microscopically, suspended montmorillonite sheets array in parallel due to volumetric restriction to minimize the free
energy of the dispersed system. The suspension is considered to be composed of certain domains in which parallel arrays of layers are formed.

At the point of yielding, it is assumed that the stress due to exerted force equals microscopic electric repulsion. With the picture of a parallel array, the volume fraction of montmorillonite sheet can be expressed as,

$$\phi = \frac{\delta}{d + \delta} \quad (18)$$

When the dominant force acting between clay layers is the electrostatic repulsive force between two plates, Gouy–Chapman theory to predict an osmotic pressure can be used to estimate the repulsion between two plates (Hiemenz P.C., 1986). That is, the force per unit area is estimated as,

$$Fr = \frac{64n_0kT}{\delta} \tanh \left( \frac{ze\psi_0}{4kT} \right) \exp \left( -k\delta \right) \quad (19)$$

If we can assume that this force is equal to the yield stress, and if we use the relation of Eqn. (19) based on the assumption of parallel array of montmorillonite sheets, \( \tau_0 \) can be written as a function of \( \phi \) as,

$$\tau_0 = \frac{64n_0kT}{\delta} \tanh \left( \frac{ze\psi_0}{4kT} \right) \exp \left( -k\delta \right) \left( \frac{1}{\alpha_e \phi} - 1 \right) \quad (20)$$

\( \alpha_e \) is the correction factor tentatively introduced to count the purity of material.

Calculated values of \( \tau_0 \) on the basis of Eqn. (20) assuming the NaCl concentration of 0.001 M are plotted in Fig. 14 together with the previously reported data (Fujii K. et al., 1996; Sudo S. and Yasutomi R., 1961; Yasutomi R. and Sudo S., 1962). Supprizingly, relatively good agreements are obtained if we apply \( \alpha_e = 1 \): broken line \( \alpha_e = 0.5 \): dotted line \( \alpha_e = 0.1 \). Reprinted with permission from Ref. (Adachi Y., 1999). Copyright: (1999) The Japanese Society of Irrigation, Drainage and Rural Engineering.

4.2 Vane method

The proposed model explained in the previous section was experimentally confirmed by the measurement as a function of the volume fraction and ionic strength. Application of vane is one of the most simple and direct method to determine the yield stress for a wider range of the volume fraction of clays without changing the geometry of the sensor. The advantage is the prevention of slip flow which might be induced by other conventional methods, such as concentric rotary viscometer. Our used vane consists of four blades welded perpendicular to each other to the central shaft (Fig. 15). Approximately 300 ml
suspension was used. The slip flow which might be induced beneath as well as along the cylindrical plane overlapping the rotational zone of the blade can be considerably prevented. Due to the small volume of exclusion during the insertion of the vane, the gel structure of the suspension can be maintained. The shear stress was obtained by the measurement of Torque, \( T \), using the following equation,

\[
T = \left( \frac{\pi D^3}{2} \right) \left( \frac{H}{D} + \frac{1}{3} \right) r
\]

(21)

Within the small displacement, the shear stress linearly increases (Dzuy N.Q. and Boger D., 1983, 1985). However, the proportional relation will collapse at a certain limit, indicating the maximum value of shear stress. This maximum value was taken as the yield stress of the sample. In order to prepare uniformly mixed suspensions, we mixed suspension from time to time, waiting a long period, during which probable swelling may take place to let whole samples be more or less uniform.

The samples were stirred strongly for 1 min with a reagent spoon in the beaker and placed under static conditions for another 1 min to avoid thixotropic effects. Then the vane was inserted gently into the suspension. The insertion took 30 s and the rotation was started, waiting for another 30 s after the end of insertion. All measurements were performed with the rotational speed set at 0.02 rpm. The measurement of yield stress for a fixed ionic strength was carried out by diluting the suspension with an electrolyte solution of ionic strength and pH equivalent to those of the bulk solution. The control of pH was done with solutions of NaOH and HCl.

4.3 Yield stress as a function of volume fraction and ionic strength

In Fig. 16, the obtained values of yield stress are plotted as a function of volume fraction of montmorillonite together with the theoretical calculations. As indicated in the figure, experimentally obtained data qualitatively reproduced the theoretical tendency.

However, in quantitative sense, significantly large differences were turned out. That is, when the ionic strength is over \( 10^{-3} \) M, the calculated value on the basis of Eqn. (20) with \( \alpha_c = 1 \) overestimates the yield stress, while under \( 10^{-3} \) M the prediction underestimates the experimental values. We infer this discrepancy to the effective thickness of sheet and introduced the correction factor, \( \alpha_t \), for the layer thickness. Then the equation to predict the yield stress can be written as,

\[
\tau_0 = 64n_k kT \tanh\left( \frac{z e \phi \eta}{4kT} \right) \exp\left( -\kappa \alpha_t \left( \frac{1}{\phi} - 1 \right) \right)
\]

(22)

It should be noted that \( \phi \ll 1 \).

In Fig. 17, the calculated value of \( \alpha_t \) is plotted against \( \phi \). The very interesting result is that the value of \( \alpha_t \) is almost constant against \( \phi \). The mean value of \( \alpha_t \) for each ionic strength.
strength is plotted in Fig. 18. As demonstrated in this figure, the clear relationship between $\alpha_t$ and $n_0$ is obtained as,

$$\alpha_t = 3.4 \times 10^{-9} n_0^{-0.256}$$  \hspace{1cm} (23)

It is very interesting to note that square of $\alpha_t$ is proportional to $\kappa^{-1}$. In Fig. 19, additional measurement of yield stress for different pH value is plotted.

As demonstrated in this figure, significant dependency of pH is confirmed for the system with the concentration of NaCl larger than $10 \times 10^{-3}$ M. The increment of the yield stress appeared with the decrease of pH value is considered be ascribed to the effect of attraction between negatively charged face of plane sheet and positively charged edge as depicted in Fig. 20. It will be very interesting to examine same effect for the system lower ionic strength where spillover effect of basal counter positive Na ions shield the effect of positively charged edge. More experiments are necessary in this domain.

5. Strength of flocs

5.1 Simple formalism

In the previous two sections, we have focused on the system of electrostatically dispersed system. On the contrary, gel transition is also induced in the region of attractive gel which is referred as coagulation. In this regime, the unit of motion is a floc. Therefore, the physical properties of a floc have been regarded as the most important subject and numerous papers are reported on this subject so far. Among them the structure and the strength of flocs are the most fundamental and important (Adachi Y. and Ooi S., 1990). That is, geometrical structure of the formed flocs can be approximated as fractal objects and the size of flocs are determined by the balance of cohesive force between composing particles and mechanically exerted forces on flocs. Rate of sedimentation and rheological properties are largely affected by these natures. Break up of a droplet like aggregate were firstly visualized in shear flow (Kao S.V. and Mason S.G., 1975). More systematic studies on the strength of flocs were reported by Sonntag and Russel for a floc made of polystyrene latex particles (Sonntag R.C and Russel W.B., 1987a, 1987b, 1988). Later, on this subject, Kobayashi et al. (1999) proposed a simple theory, that is,

$$F_c = N_c \times f$$  \hspace{1cm} (24)

It should be noted that $N_c$ reflects the information of restructuring of clusters in the floc and $f$ represents the physicochemical information such as interaction between particles composing the floc. The size of floc is determined when the hydrodynamic shear force, $F_h$, scaled as

$$F_h \approx \mu G D_t^2$$  \hspace{1cm} (25)

overcomes $F_c$. When $f$ is constant irrespective of the size
of the floc, the following scaling relation can be derived assuming \( N_c \) is constant,

\[
D_f \approx G^{-0.5}
\]  

(26)

Such scaling relation has been numerically obtained by several researchers (Doi M. and Chen D., 1989; Higashitani K. et al., 2001). Many experimental data are also reported (Bubakova P. et al., 2013; Ehrl L. et al., 2008; Frappier G. et al., 2010; Jarvis P. et al., 2005; Kobayashi M., 2005; Léa G. et al., 2019; Soos M. et al., 2008). However, no data was available as for montmorillonite floc until recently. This situation has motivated our recent research on montmorillonite floc (Adachi Y. et al., 2019).

5.2 Shear experiment with Couette chamber

Uniform laminar shear flow was generated in a concentric cylindrical vessel called the Couette chamber. The configuration of the set-up is shown in Fig. 21. The rotation of outer cylinder generates stable laminar shear flow. The gap distance was designed sufficiently large to adjust the big size of montmorillonite floc. As indicated in the figure, the chamber was installed so that the direction of the \( \alpha \) of rotation will become horizontal. This is important to avoid the effect of sedimentation by gravity when flocs are developed during experiment. The flowing flocs can be simply observed by an illumination of slit LED light source through a high-speed camera. The snapshot is demonstrated in Fig. 22.

From such image of flowing flocs, we obtain the size distribution of flowing flocs for each rate of shear and ionic strength as demonstrated in Fig. 23. Generation of such size distribution of fractal floc in the flow field is not completely solved (Maggi F. et al., 2007; Spicer P.T. and Pratsinis S.E., 1996). Using such size distribution, we can obtain effective volume fraction of solid which can be used for the estimation of viscosity (Mori Y. and Ototake N., 1956). Then the viscosity will be estimated as a function of shear rate.

By this method Kobayashi M. et al. (2000) successfully expressed the shear thinning behavior of coagulated suspension. Such trial is worth to be done for different chemical condition which will yield different cohesive strength of neighboring particles.

Since the formalism of Eqn. (26) is based on the maximum size, we tentatively plotted the \( D_{90} \) against shear rate in Fig. 24. Absolute values of obtained slopes were found to be slightly larger than 0.5. Our interpretation of this result is that the enforcement of internal floc is induced by the increase of the number between clusters, \( N_c \), in the structure of a floc. Large flocs are considered to have more chances to be rearranged into more closely packed structure.

Assuming \( N_c \) is equal to three, Miyahara estimated the cohesive strength of coagulated montmorillonite (Miyahara K. et al., 2002). The order of magnitude obtained from the

---

**Fig. 21** Experimental setup for shearing experiment. Reprinted with permission from Ref. (Adachi Y. et al., 2019). Copyright: (2019) Springer-Verlag GmbH.

**Fig. 22** Snapshots of flowing flocs at 2.0 M. Reprinted with permission from Ref. (Adachi Y. et al., 2019). Copyright: (2019) Springer-Verlag GmbH.

**Fig. 23** Cumulative frequency of \( D_{max} \) at 3.0 M. Reprinted with permission from Ref. (Adachi Y. et al., 2019). Copyright: (2019) Springer-Verlag GmbH.
The value of viscosity of capillary viscometer corresponds to the value obtained from break up of flocs. On the other hand, it is noteworthy that there is monotonously upward shift of the size of floc against ionic strength. This means monotonous increment of cohesive strength between montmorillonite sheets with an increase of ionic strength. Our interpretation of this result is demonstrated in Fig. 25.

That is the approach of montmorillonite sheets by van der Waals attractive force is disturbed by the presence of short-range repulsion due to the adsorbed ions with hydration water present at the gap between two surfaces. The increase of ionic strength results in the decrease of effective size of adsorbed ions (Boström M. et al., 2001; Higashitani K. et al., 2017; Pashley R.M., 1981).

6. Sedimentation

Flocculated montmorillonite and other clay minerals are abundantly available in coastal sediment area. They play a very significant role as a unit of transportation and can influence a wide array of environmental phenomena. Sedimentation behavior of a coastal sediment can be categorized into three distinctive regimes in accordance with suspension concentration, which are dilute, semi-dilute, and concentrated (Imai G., 1980, 1981). In the dilute regime, the formed flocs settle independently with no distinct interface between flocculated sediment and supernatant. By contrast, in the semi-dilute regime, there is a clear interface boundary between sediment and supernatant. This means that in the semi-dilute regime, flocs in the sediment appear to interact to form a network of sedimentation that has a clear interface boundary with the transparent supernatant zone. In this regime, there appears idle time prior to settling phase due to the mutual interactions among the flocs which hindered the settling process. Lastly, in the concentrated regime, an initially formed network structure of flocculated sediment settles very slowly under its own weight. Semi-dilute regime can be further classified into three different stages: 1) Flocculation (Waiting time), 2) Sedimentation (Gel collapse) (Bartlett P. et al., 2012) and 3) Consolidation (Fig. 26). At the onset of the flocculation stage, uniform dispersion is formed and gradually grow to form small colloidal flocs (Fig. 26a-b). At this stage, we can identify the clear interface boundary between the flocculated Na-montmorillonite and the transparent supernatant. The flocculation and sedimentation process are ongoing even though the rate of sedimentation is very small reflecting the small size of flocs. The intersection point for tangents of linear parts between the flocculation stage and sedimentation stage with maximum sedimentation rate is denoted as the flocculation time, \( t_f \). The waiting time prior to gel collapse continues as the flocs grow bigger to form a space-filling structure of sediment (Fig. 26c). The stress is concentrated at some contacting points (marked as black circles) in the network due to self-weight of the sediment (Fig. 26d). The apparent sedimentation rate is essentially low as the point will resist against the compression by self-weight of the network. However, once the network could no longer stand for the stress, it starts to break down and mark the onset of gel collapse. Prediction of such gel collapse has attracted many attentions by many physicists (Manley S. et al., 2005; Poon W.C.K. et al., 1999; Poon W.C.K., 2002; Cipelletti L. et al., 2000; Allain C. et al., 1995; Chang W.Z. and Leong Y.K., 2014). Coarsening effect due to heterogeneity is presumably related to this scenario (Buscall R. et al., 2009). Abrupt gel collapse initiates the set in of rapid sedimentation stage. Development of crack void while flocs fall
down during gel collapse created the water channeling in the network. Downward motion of flocculated sediment will induce the generation of upward plume of water which flutters slightly (Fig. 26e). Lastly, during consolidation stage, the flocs settle down slowly due to its self-weight to fill the space underneath that was left to develop early consolidation at the bottom of the cylinder (Winterwerp J.C. and Kestern W.G.M.V., 2004; Imai G., 1981) (Fig. 26f).

Owing to the specific characteristics of Na-montmorillonite to form enormously big flocs irrespective of pH value (Miyahara K. et al., 1998) under the condition of high concentration of NaCl, we carefully observed the sedimentation behavior of strongly flocculated Na-montmorillonite in semi-dilute regime. In our recent studies, we measured the changes of interface between sediment and supernatant in varied initial height of suspension as a function of elapsed time for different levels of salt concentration (Wu M. and Adachi Y., 2017; Ghazali M.E.B. et al., 2019). Na-montmorillonite slurry coagulated under different ionic strengths, ranging from 0.25 M to 1.5 M of NaCl, was placed in a settling cylinder and was left to settle after manual mixing by end-over-end method.

The result of the position of the boundary as function of elapsed time is depicted in Fig. 27. However, the main experimental focus of the later study is to investigate the dependency of cylinder height on sedimentation behavior, which was not reflected in the previous study.

6.1 Waiting time for gel collapse

We also developed an interest in the early stage of sedimentation to elucidate the relation between microscopic
heterogeneous interaction of clay particles and macroscopic behavior of Na-montmorillonite sedimentation. Our previous study by Wu M. and Adachi Y. (2017) highlighted the duration of initial flocculation stage prior to the gravitational collapse of Na-montmorillonite suspension as a function of ionic strength. We have confirmed that ionic strength is inversely proportional to the duration time of initial flocculation stage denoted as $\tau$ (**Fig. 28**).

That is, the duration time for the system undergoing rapid coagulation under sufficiently high ionic strength is shorter (but not to be zero). The progress of small crack in the weakly touched sediment network escalated after the onset of gel collapsed as depicted in **Fig. 29**. This point was considered to be a certain degree of flocculation where the formed gel network of floccs collapsed due to its self-weight, hence the result, $\tau$, can be interpreted as the time required to reach the point of flocculation (Wu M. and Adachi Y. 2017).

It is basically determined by the inverse rate of flocculation. This interpretation was consistent with the colloidal stability analysis of Tombacz E. et al. (1988), who pointed out the dominancy of Edge-Face interaction detected as the difference in critical coagulation concentration which appeared in the lower pH under lower ionic strength. Our result of the difference in $\tau$ also correlates with this trend.

### 6.2 Sedimentation turbulence

Maximum settling velocity was plotted against cylinder height as shown in **Fig. 30**. It appears that the maximum settling velocity was varied depending on the height of initial slurry and the value was increased steadily with an increase of initial slurry height (Ghazali M.E.B. et al., 2019).

The results also demonstrate that the maximum velocity increases with NaCl concentration. Increasing salt concentration decreases the repulsive electrostatic effect, breaking weak Edge-Face bonds and residual strong Edge-Face bonds, and results in bigger flocs (Wu M. and Adachi Y., 2016). In this stage, the bigger flocs (i.e. formed in high salt concentration) will settle down faster than the smaller one. By the velocity difference, collision of settling flocs will take place which leads to the development of the flocs. In the higher cylinder, the traveling distance of falling flocs becomes longer. The development of larger flocs will settle down faster than the smaller flocs, resulting in a faster settling velocity.

**Fig. 28** Flocculation time as a function of ionic strength for the different pH values (pH = 4.0 and pH = 9.5). Due to the un-coagulated suspension under the condition of pH 9.5 and ionic strength 0.05 M NaCl, the relative movement of boundary between supernatant and coagulated suspension could not be recorded in **Fig. 2**. Therefore, the duration time at the condition (pH 9.5 and NaCl 0.05 M) cannot be calculated. Reprinted with permission from Ref. (Wu M. and Adachi Y., 2017). Copyright: (2017) Springer-Verlag GmbH Germany.

**Fig. 29** Generation of small cracks in the weakly connected sediment structure during gel collapse.

**Fig. 30** Maximum velocity as function of cylinder height at different levels of ionic strength (Ghazali M.E.B. et al., 2019).
of flocs along the long traveling distance is coupled with the turbulence. This sequence creates a feed-forward mechanism which will further enhance the sedimentation process.

In the case of taller cylinder, the traveling distance of falling flocs becomes longer, the falling flocs will then have more chances to collide with the other small flocs and becomes still bigger in size and mass to accelerate the settling speed. As the result, the rapid sedimentation commenced at a different period of time (Imai G., 1981; Dobias B. et al., 1993). Each floc settled differently in term of velocity, due to different size and density. The void formed simultaneously is connected to create channeling of counter flow. The observed pattern of fluctuation was similar to a turbulent flow (Pope S.B, 2000). We term this phenomenon as the “sedimentation turbulence” (Ghazali M.E.B. et al., 2019). This phenomenon is not well described in the previous study (Michaels A.S. and Bolger J.C., 1962; Wu M. and Adachi Y., 2017; Miyahara K. et al., 2001, 2004) in which direct application of the result of fluidized led for non-flocculated materials was done (Richardson J.F. and Zaki W.N., 1954).

The floc motion induces a turbulent flow, which will induce further development of flocs. That is, floc formation is due to turbulent flow passing through, which increases the settling velocity. Consequently, the flocs will collide with the neighboring flocs to grow into bigger flocs.

7. Conclusion and remarks for the future

In the present article, we focus on the behavior of aqueous dispersion of Na-montmorillonite in the dilute condition to elucidate the relation between the level of colloidal and interface chemistry such as microscopic interaction of colloidal particles and the level of macroscopic properties which will control the hydrological transport phenomena and the massive motion of the materials. The review was started to examine the simple viscosity as a function of ionic strength which is in accordance with the DLVO scheme.

In the limit of low ionic strength, viscosity increases dramatically demonstrating the electro-viscous effect especially due to the interaction of EDLs formed around the suspended particles. The data obtained using our homemade spiral viscometer confirms the long-range interaction between the flowing montmorillonite sheets which will contribute to enhance the viscosity significantly in the limit of zero shear rate. The value of yield stress obtained by vane was found to be clearly reduced to that of electrostatic repulsion due to the interaction of EDLs. Unfortunately, we are not able to convert the repulsion to attraction which stands for the deformation. However, the estimated distance obtained from the analysis of actual force between two sheets was estimated to be longer than the Debye reciprocal length implying the significance of long-range interaction. More systematic data against pH will elucidate the role of spillover effects of EDL of basal part and Edge-Face interaction.

On the contrary, the data obtained for the region of higher ionic strength, viscosity increases monotonously with an increase of ionic strength. This tendency was confirmed by the measurement on the size of flowing flocs. Our interpretation was the presence of additional repulsion due to the adsorption of hydrated sodium ions whose diameter decreases with an increase of ionic concentration in the region of ionic concentration higher than CCC. The observation of sediment volume also confirms the tendency. One important finding for the sedimentation behavior is to find out the clear evidence for the feed-forward enhancement of the rate of sediment. That is, the sedimentation induces flocculation and flocculation will enhance the rate of sedimentation and so on. We term this behavior as sedimentation turbulence. Another important result was obtained for the difference of waiting prior to gel collapse against pH and ionic strength. That is, pH dependency exists for the concentration below 0.5 M but will disappear for the concentration higher than 1.0 M.

Although, our applied methods in the previous studies are done with very primitive instruments; viscosity measurement with Ostowald capillary viscometer, Spiral capillary viscometer, observation of floc in a simple shear flow, sedimentation behavior in the mess cylinder, we can conclude that there are five different regimes. They are, EDL dominative repulsive phase, pH-dependent repulsive phase, dispersed phase, pH-dependent attractive, pH-independent attractive phase. Continuous study for precise pH dependency will clarify this picture. In addition, further investigation for different chemical conditions (Penner D. and Lagaly G., 2001; Montoro M.A. and Francisca F.M., 2019), such as effect of divalent ions (Kobayashi S. and Adachi Y., 2008) and effect of organic substances (Wilkinson N. et al., 2017; Tombacz E. et al., 1998) will provide us very useful result for the consideration of natural colloid.

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### Nomenclature

| Symbol | Description |
|--------|-------------|
| $\alpha$ | Corrective Factor |
| $\beta$ | Representative of long formulae |
| $\varepsilon$ | Dielectric constant ($C^2/J \cdot m$) |
| $\varepsilon_0$ | Dielectric constant of vacuum ($C^2/J \cdot m$) |
| $\varepsilon_r$ | Relative dielectric constant of water ($C^2/J \cdot m$) |
| $\kappa$ | Debye reciprocal length |
| $\eta$ | Viscosity (mPa-s) |
| $\eta_0$ | Viscosity of solvent (mPa-s) |
| $\eta_t$ | Relative Viscosity (mPa-s) |
| $\eta_s$ | Viscosity of suspension (mPa-s) |
| $\delta$ | Layer thickness (nm) |
| $\rho$ | Density of fluid (kg/m$^3$) |
| $\tau$ | Time of initial flocculation stage (min) |
| $\tau_0$ | Yield stress |
| $\tau_e$ | Shear stress at end of torque (Pa) |
| $\tau_s$ | Shear stress at side of torque (Pa) |
| $\tau_y$ | Yield stress (Pa) |
| $\phi$ | Volume fraction [-] |
| $\phi_{\text{max}}$ | Packing volume fraction [-] |
| $\phi_{\text{eff}}$ | Effective volume fraction [-] |
| $\psi_0$ | Surface potential (mV) |
| $\xi$ | Zeta potential (mV) |
| $a_{\text{eff}}$ | Effective radius (nm) |
| CCC | Critical Coagulation Concentration |
| $D$ | Diameter of the vane (mm), Inner diameter of capillary tube (mm) |
| $D_{99}$ | Floc diameter (mm) |
| $D_f$ | Diameter of floc |
| $D_{\text{max}}$ | Maximum floc size (mm) |
| $d$ | Mean distance of clay layers (nm) |
| EDL | Electric Double Layer |
| $e$ | Elementary charge (C) |
| $F_e$ | Electrostatic repulsive force |
| $F_r$ | Force per unit area (Pascals) |
| $F_{\text{sh}}$ | Hydrodynamic force |
| $G$ | Shear Rate (s$^{-1}$) |
| $g$ | Gravitational acceleration (m/s$^2$) |
| $H$ | Height of the blade (mm) |
| $h$ | Difference of the levels (mm) |
| $h'$ | Distance (mm) |
| $h_0$ | Distance (mm) |
| $h_k$ | Distance (mm) |
| $K_1$ | Intrinsic viscosity (ml/g) |
| $K_2$ | Huggins’ coefficient [-] |
| $k$ | Boltzmann constant (J/K) |
| $kT$ | Diffusive energy (J) |
| $L$ | Length of capillary tube (m) |
| $n_0$ | Number concentration of the ions (M) |
| $n_i$ | Ionic concentration (M) |
| $P_e$ | Peclet number [-] |
| $Q$ | Flow rate in the tube |
| $r$ | Distance from a center of the particle (nm) |
| rpm | revolution per minute |
| $T$ | Absolute temperature (K) |
| $T_e$ | End of torque (Nm) |
| $T_s$ | Side of torque (Nm) |
| $t$ | Time (sec, min) |
| $V_e(r)$ | Electrical repulsive energy (J) |
| $z$ | Valence of electrolyte solution [-] |

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Yasuhisa Adachi is Professor of Life and Environmental Science in Tsukuba University. He has diploma and PhD from the University of Tokyo (Agricultural Eng.). His research has focused on flocculation for more than 30 years. Currently he is the leader of research unit, Bio-resources Colloid Engineering in University of Tsukuba. Main subjects are kinetics of coagulation and flocculation, structure of resulted floc, sedimentation and rheology of flocculated material. He was awarded an academic award from Japanese Society of Irrigation, Drainage and Rural Engineering in 2015.

**Yoko (Tsujimoto) Kawashima**

Yoko (Tsujimoto) Kawashima received her PhD from University of Tsukuba back in 2014. Her doctoral thesis is entitled “Electrokinetics and rheological behavior of clay suspensions in electrostatically dispersed state”. Currently, she works in the material section in Public Works Research Institute for the proper evaluation of asphalt.

**Muhamad Ezral Bin Ghazali**

Muhamad Ezral Bin Ghazali is a young researcher currently pursuing his doctoral degree at University of Tsukuba, Japan. He graduated with Master of Philosophy from Malaysia-Japan International Institute of Technology, University of Technology, Malaysia (UTM), and was awarded with Japanese Government (Monbukagakusho) Scholarship to further his studies in Japan. His area of studies include natural coagulant and flocculation in water treatment. Currently, his research focused on sedimentation behaviour of montmorillonite.