Experimental study of the rheology of water–kaolinite suspensions

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ABSTRACT

How the added electrolyte condition and size of primary sediment particles, as well as the particle concentration, affect the rheological behaviours of water–sediment suspension remains to be of interest in the sediment field. In this work, rheological experiments of water–kaolinite suspensions with different electrolyte conditions, two particle sizes and 39 solid concentrations were performed. The Bingham fluid model has been adopted to fit the experimental data, and the viscosity and Bingham shear stress values were calculated for each suspension. It has been found that an increase in electrolyte concentration and/or valence leads to a larger viscosity value of the suspension, whereas an increase in electrolyte valence yields a smaller Bingham shear stress value. A simple interpretation based on DLVO theory was presented in this study. It has also been observed that a fine-grained kaolinite suspension corresponds to larger suspension viscosity and Bingham shear stress values. Additionally, some experimental information on the viscosity–solid concentration and Bingham shear stress–solid concentration relationships were also presented in this study. For the viscosity–solid concentration data, the Krieger and Dougherty formula provided the best fit, and a simple exponential relation showed a good fit for the measured shear stress–solid concentration data.

Key words: electrolyte, experiment, kaolinite, rheology, suspension

HIGHLIGHT

This manuscript is valuable in terms of studying how the added electrolyte condition and size of primary sediment particles, as well as the particle concentration, affect the rheological behaviours of water–sediment suspension.

INTRODUCTION

There are large quantities of cohesive sediments in rivers, lakes, reservoirs and estuarine waters across the world (Winterwerp 1998; Son & Hsu 2008). In contrast to non-cohesive sediments such as sand and gravel, cohesive sediments possess complex electrochemical and biochemical characteristics (Son & Hsu 2008). These sediments can come into contact and adhere to each other due to Brownian motion, turbulent flow motion and differential settling, forming flocs in the suspension (Winterwerp 2002; Mietta et al. 2011). It is important to understand the cohesive sediment transport mechanism, since it can affect engineering constructions such as dredging operations of navigational channels, morphological changes of shorelines and water quality control in bodies of water (Bai et al. 2002; Huang & Aode 2009; Amarasinghe & Abelev 2015).

Transport of cohesive sediment can occur both in the water column and in the near-bottom layer (Van Kessel & Blom 1998). Sediment concentration is always larger in the latter. Hydrodynamic motion and transport of this near-bottom layer, which is often caused by water current and waves, always results in a high sediment transport rate (Van Kessel & Blom 1998; Bai et al. 2002). To predict the motion and transport characteristics of the near-bottom, highly concentrated layer, it is essential to understand rheological properties such as viscosity and shear stress when subjected to applied external forces (Granboulan et al. 1989; Faas & Wartel 2007). Furthermore, as some studies show, the viscosity of the near-bottom layer is important for the evaluation of the entrainment rate of sediment between the near-bottom layer and the overlying water layer (Kranenburg & Winterwerp 1997; Winterwerp & Kranenburg 1997). The hindering settling velocities of cohesive sediment flocs, which are important parameters in accurate predictive models for suspended sediment flux, are also related to the viscosity of the water–sediment mixture (Winterwerp 2002). In addition, investigating the viscous behaviour of cohesive sediment mixtures is of importance for many applications such as the penetration of heavy objects into cohesive seafloors.

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drag forces and acoustic properties of seafloor surfaces and subsurface vessels (Amarasinghe & Abelev 2015). Therefore, it can be concluded that studying the rheological properties of cohesive sediment suspensions would be helpful to improve the understanding of cohesive sediment transport in water.

Rheological properties of cohesive sediments have been investigated in many studies. Jiang & Mehta (1995) adopted mud samples obtained from the southwest coast of India, Lake Okeechobee in Florida and Mobile Bay in Alabama to carry out rheological experiments and, based on measured data, a small-strain rheological model has been developed to characterize the viscosity with improved accuracy. The rheological properties of both China clay, an artificial mud, and Caland channel mud, a natural mud, were investigated by Van Kessel & Blom (1998). In these experiments, rheological behaviour (viscosity, structural change and elastic effect) of a natural and an artificial mud have been compared. Bai et al. (2002) measured the rheological properties of cohesive sediment samples taken from the Haihe River and found that the cohesive sediment behaves like a Bingham fluid when the density is below 1,380–1,400 kg/m³, and may become a power-law fluid when the density increases beyond these values. Huang & Aode (2009) carried out a laboratory study of the steady and oscillatory (dynamic) rheology of mudflow in Hangzhou Bay, China. The Dual-Bingham plastic rheological model was found to provide a satisfactory simulation of the experimental data, and for the dynamic rheological properties, empirical formulae of the elastic modulus and dynamic viscosity were obtained in terms of exponential forms of sediment concentration with a high goodness of fit. Moreover, Goñi et al. (2015) evaluated the rheological properties of sediments flocculated in the presence of seawater salts and proposed a non-linear viscoelastic model to describe them. This model incorporates three parameters which are correlated to physical attributes of the material and was found to be a better fit for the experimental studies over the entire range of shear loads applied. Xu & Huhe (2016) measured the rheological properties of mudflows at Lianyungang. Furthermore, Spearman (2017) established a rheological framework of the sediment suspension for a range of sediment concentrations from the yield point to Newtonian flow by incorporating fractal theory and additional structural dynamics. This new model had the ability to match the equilibrium and time-dependent viscous rheology for a wide range of sediment suspensions of different concentrations and mineralogies. Yang et al. (2017) investigated the nature of the stratification and rheological properties of near-bed cohesive sediments in West Lake, Hangzhou, China. It has been found that bed sediments showed strong non-Newtonian and shear thinning behaviour, which could be described by the Carreau rheological model, and the yield stress was found to increase linearly with mud concentration. In these studies, both the natural and artificial cohesive sediments exhibited a non-Newtonian behaviour, and this behaviour could be described by some rheological models. The rheological properties of the sediment suspension were found to be closely related to sediment concentration. In particular, the apparent viscosity of the suspension increased exponentially with sediment concentration. Some recent works regarding non-Newtonian behaviour of the suspension can also be found in Di Federico et al. (2017) and Chiapponi et al. (2020).

However, there has been insufficient attention focused on the rheological properties of the cohesive sediment suspension when different electrolytes are added or when the primary particle size is changed. How electrolytes affect the flocculation characteristics of the suspension and hence the rheological behaviour, and what the impact of changing primary particle size on the rheological properties of the suspension remains unclear at the present. The purpose of this study was to investigate the rheological behaviour of water–sediment suspensions with different electrolyte conditions and primary particle sizes, as well as under different sediment concentrations, and explore the possible impacts of these factors on the rheological properties of the suspensions. This paper is structured as follows. Section 2 first introduces the experimental sediment material and the rheometer measuring system, and then provides a brief introduction for the procedure of experiment. Experimental results and further discussions regarding the rheological behaviour of the water–sediment suspensions with 59 solid concentrations, different electrolyte conditions and two primary particle sizes are presented in Section 3. Finally, Section 4 provides some concluding remarks. In fact, salinity-induced flocculation is very complicated, and covers particle chemistry, fluid mechanics, particle dynamics, etc. Although there is no very deep investigation regarding the physical mechanism of rheology, this study could have a merit in forwarding the study on the salinity-induced particle rheology.

**MATERIALS AND METHODS**

**Materials**

Similar to reported studies (Van Kessel & Blom 1998; Nasser & James 2009), this work used kaolinite as sediment material (analytically reagent) purchased from a manufacturer in Hebei province of China for rheological experiments.
The particle-size distribution in the kaolinite sample (referred to as ‘kaolinite sample #1’) was determined using a laser particle-size analyser (Horiba LA-920; Horiba Corporation, Tokyo, Japan). The measured size distribution in kaolinite sample #1 is plotted in Figure 1; Table 1 shows the median particle size $d_{50}$ (5.33 μm) and distribution statistics.

To investigate the effect of solid particle concentration on the rheological properties of water–kaolinite suspensions, we chose the mass concentration of kaolinite particles (i.e., the mass of the kaolinite particles divided by the total volume of the water–kaolinite suspension) in the suspension, $s$, to vary from 0 to 1,150 kg/m$^3$ in our experiments, ranging from a low to high concentration (Bai et al. 2002; Huang & Aode 2009). The upper limit value of the kaolinite concentration (i.e. 1,150 kg/m$^3$) was determined based on the experimental finding that the shear stress value of the suspension exceeds the upper measurement limit of the rheometer when particle concentrations are higher than 1,150 kg/m$^3$. Fixing the particle concentration of the suspension, $s$, at 500 kg/m$^3$ in this study we added 0.005–1.55 mol/L of monovalent electrolyte, sodium chloride (NaCl), into the water–kaolinite suspension to investigate the impact of electrolyte addition on the rheological properties of the suspension. This concentration range was similar to previously reported rheological experiments (Kelessidis et al. 2007; Goñi et al. 2015). For a comparison of monovalent, divalent and trivalent electrolytes, 0.005–1.55 mol/L of divalent electrolyte, calcium chloride (CaCl$_2$), and trivalent electrolyte, Al(NO$_3$)$_3$·9H$_2$O, were also added into the water–sediment suspension at a sediment concentration of 500 kg/m$^3$ respectively. Additionally, in this work we measured the rheological properties of another kaolinite sample (‘kaolinite sample #2’) at a fixed particle concentration of 500 kg/m$^3$ with varied concentrations of additional sodium chloride electrolyte at 0.005–1.55 mol/L. This was to investigate the possible influence of different particle sizes on the rheological properties of the water–sediment suspension. The size distribution of kaolinite sample #2 measured by a laser particle-size analyser is shown in Figure 1, with the median particle size, $d_{50}$, being

![Figure 1](image-url)
21.90 μm; the size-distribution statistics are presented in Table 1. The size of kaolinite sample #2 was much coarser than kaolinite sample #1, however the density of both samples is 2,650 kg/m³.

### Rheometer

Rheological properties of the water–kaolinite suspension were measured using a Brookfield RST-CCT40 rheometer (Brookfield Engineering Laboratories Incorporation, Middleboro, MA, USA). The rheometer system comprises a touch screen, an electronic unit and a measuring drive coupled with a coaxial cylinder system. The diagram of this rheometer system is shown in Figure 2(a).

Figure 2(b) shows a diagram of the coaxial cylinder system. This system consists of a shaft and a measuring bob, which are immersed in the sample cup (filled with the water–kaolinite sample; the total suspension volume is fixed at 68.5 mL). When the draft is driven at different angular speeds (measured in revolutions per minute, rpm) with the motor, the torque experienced by the measuring bob in the water–kaolinite suspension could be detected rapidly. The shear rate that was exerted on the water–kaolinite suspension could be obtained based on the angular speeds of the shaft using a shear rate factor, and the detected torque experienced by the measuring bob could be transformed to the shear stress in the suspension by using a shear stress factor. The dimensions of the coaxial cylinder system and all of the parameters for this standard measuring system are presented in Table 2. A comprehensive introduction to the rheometer configuration and measuring system can also be found on the official website: http://www.brookfieldengineering.com/products/rheometers.

The Rheo3000 software (Rheo3000 1.2.1395.1, Brookfield Engineering Laboratories Incorporation, Middleboro, MA, USA) was coupled with the rheometer system. This software can be installed on a personal computer, and can be used to

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**Table 1** | Statistics of particle-size distributions in two kaolinite samples

| Sample          | Range (μm) | d_{10} (μm) | d_{20} (μm) | d_{30} (μm) | d_{50} (μm) | d_{90} (μm) | d_{10} (μm) |
|-----------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Kaolinite sample #1 | 1.00–101.46 | 2.50        | 3.91        | 5.33        | 7.10        | 15.16       |
| Kaolinite sample #2 | 1.15–220.10 | 3.10        | 10.05       | 21.90       | 39.10       | 70.52       |

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**Figure 2** | Schematic of the rheometer system (a) and measuring coaxial cylinder system (b).
remotely control the rheological measurement. In this experiment, the shear rate was set to range from 2.16 to 644.41 s\(^{-1}\), covering the low to high shear conditions (Van Kessel & Blom 1998; McMinn et al. 2004; Yang et al. 2017).

**Experimental procedure**

Each water–kaolinite sample was prepared using an electronically weighed quantity of kaolinite primary particles with the appropriate electrolyte condition and deionized water according to the set mass concentration value of the suspension and the required concentration of electrolyte. The rheological experiment was initiated upon careful injection of the sample into the cup. Dimensional configuration of the coaxial cylinder system ensured that the end effect in the sample cup could be negligible (Van Kessel & Blom 1998; Amarasinghe & Abelev 2015). The rotating angular speed of the shaft (corresponding to shear rate) was adjusted to increase gradually for 100 s, covering a shear rate range of 2.16–644.41 s\(^{-1}\). The torque experienced by the measuring bob (corresponding to shear stress) was measured rapidly. The measuring system could plot the relationship between shear stress and shear rate of the measured suspension in real time. All of the experimental data regarding the shear stress–shear rate relationship could be saved in the computer for further analysis. The experimental temperature was kept at 24 ± 0.2 °C.

There are several models that can be used to describe the shear stress–shear rate relationship of the solid–liquid suspension (a review can be found in Stickel & Powell (2005)), including the Newtonian, Bingham, Casson, Herschel–Bulkley, Ostwald and Steiger-Ory fluid models. All of these six models were tested to fit every group of experimental data regarding the shear stress–shear rate relationship. In this study, it was found that Newtonian and Bingham fluid models showed the best fit, with the highest coefficient of determination, \(R^2\), among all of the models. Furthermore, the Bingham model describes the rheological behaviour of the water–kaolinite suspension:

\[
\tau = \tau_B + \eta \gamma
\]

where \(\tau\) is the shear stress (Pa), \(\tau_B\) is the Bingham shear stress (Pa), \(\eta\) is the suspension viscosity (Pa\(\cdot\)s), and \(\gamma\) is the shear rate (s\(^{-1}\)). At \(\tau_B = 0\), Equation (1) becomes the Newtonian fluid model. Therefore, the Newtonian fluid model may be considered as a special case of the Bingham fluid model. In this study, the measured viscosity of all of the water–kaolinite suspension samples could be expressed in terms of a relative viscosity of the suspension, \(\eta_r\), as follows:

\[
\eta_r = \frac{\eta}{\eta_w}
\]

where \(\eta_w\) is the viscosity of deionized water at the experimental temperature, as previously used in several studies (Stickel & Powell 2005; Genovese 2012). Before every set of experiments, the viscosity of the deionized water was measured.

**RESULTS AND DISCUSSION**

**Effect of solid concentration**

Figure 3 shows the typical effect of solid concentration on the rheological curve of the water–kaolinite suspension. For a low concentration suspension (\(s = 0 \rightarrow 70 \rightarrow 220 \text{ kg/m}^3\)), the rheological curves were similar to each other; as the particle concentration of the suspension subsequently increases (\(s = 300 \rightarrow 380 \rightarrow 480 \text{ kg/m}^3\)), the rheological curve clearly rises, with an

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**Table 2 | Parameters for the standard measuring system**

| Parameters                  | Values        | Parameters                  | Values        |
|-----------------------------|---------------|-----------------------------|---------------|
| Shear rate range (s\(^{-1}\)) | 0.0215–2,790  | Shaft radius \(R_1\) (mm)   | 3.5           |
| Shear stress range (Pa)     | 0.89–594      | Sample cup radius \(R_2\) (mm) | 21.0          |
| Viscosity range (Pa\(\cdot\)s) | 0.003–27,600  | Measuring bob radius \(R_3\) (mm) | 20.0          |
| Sample quantity (mL)       | 68.5          | Length of shaft immersed \(L_1\) (mm) | 20            |
| Shear rate factor (s\(^{-1}\)/rpm) | 2.1480      | Length of measuring bob \(L_2\) (mm) | 60           |
| Shear stress factor (Pa)    | 0.2969        | Distance from lower edge of measuring bob to sample cup bottom \(L_3\) (mm) | 20.5          |

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increasing slope and intercept at the vertical axis (i.e., shear stress axis). For the highly concentrated suspension ($s = 620 \rightarrow 780 \text{ kg/m}^3$), the rheological curve rises significantly. For a fixed shear rate, the shear stress experienced by the suspension increases with increasing concentration of solid. Additionally, it is obvious that the shear rate at which the measured shear stress becomes non-zero decreases with increasing particle concentration of the suspension. These findings indicate that as the particle concentration increases, particle crowding prevents shear motion within the suspension, yielding a larger shear stress of the suspension.

Table 3 presents a complete data set of Bingham model parameters for all of the tested water–kaolinite samples at different solid concentrations. Measured relative viscosity values of all of the water–kaolinite suspensions are shown in Figure 4 as a function of increasing solid concentration. In this figure, the horizontal axis represents the volumetric concentration of the primary kaolinite particles in the suspension (or concentration by volume), $\phi$ (equal to mass concentration divided by the density of the kaolinite primary particles), as used in several previous studies (Stickel & Powell 2005; Genovese 2012). It is obvious that as solid concentration increases, the suspension viscosity shows a slow increase for $0 < \phi < 0.21$, and then exhibits a rapidly increasing trend for $0.21 < \phi < 0.43$. For a dilute suspension, the increase in solid concentration results in particle crowding in the suspension, yielding an increasing suspension viscosity. As the solid concentration increases, especially in the highly concentrated suspension, there may be no free space for shear motion to occur within the suspension, therefore the suspension viscosity rapidly rises.

Many semi-empirical or empirical models have been proposed to describe the suspension viscosity as a function of solid concentration, i.e., the $\eta_r$–$\phi$ relationship. Zhu et al. (2017) summarized these into seven representative models: Einstein equation (19)(06), Batchelor formula (1977), Roscoe formula (1952), Krieger and Dougherty formula (1959), Chong formula (1971), Dabak formula (1986) and Boyer formula (2011). Table 4 presents specific parameterizations of these models, which have been tested to fit the experimental data, as also shown in Figure 3. The correlation coefficients, $R^2$, vary from 0.28 to 0.95. Across the entire concentration range, the Roscoe formula consistently overestimates the measured viscosity values.
With increasing values of $\phi$, all of the formulae except the Roscoe formula predict the viscosity accurately for $0 < \phi < 0.13$. For $\phi > 0.13$, the Chong, Boyer and Dabak formulae begin to slightly overestimate the viscosity values, whereas for $\phi > 0.15$, the Batchelor formula and Einstein equation begin to underestimate the viscosity. For $0.13 < \phi < 0.22$, the Krieger and Dougherty formula provides a better fit, but for $\phi > 0.24$ it begins to underestimate the viscosity. For $\phi > 0.26$, the Dabak formula begins to underestimate the measured viscosity values, whereas the Chong and Boyer formulae underestimate the viscosity for $\phi > 0.28$ on. At $\phi = 0.43$, the Chong, Boyer and Dabak formulae deviate significantly from the measured viscosity values. Across the entire range of solid concentrations, the Chong formula is close to the Boyer formula except for a narrow range of $0.37 < \phi < 0.43$, during which the viscosity values predicted by the Chong formula are larger than those predicted by the Boyer formula. In total, the Krieger and Dougherty formula provides the best fit to the measured viscosity–solid concentration values with the highest correlation coefficient $R^2$ of 0.95. This is followed by the Boyer formula with a high correlation coefficient of 0.88, and then the Chong and Dabak formulae with an identical coefficient of 0.86.

Figure 5 shows the measured Bingham shear stresses of the water–kaolinite suspensions as a function of solid concentration. Bingham shear stress ($\tau_B$) appears only when the mass concentration of the primary particles ($s$) exceeds 580 kg/m$^3$ in this study (as presented in Table 3), as similarly reported by Kranenburg (1994). As this figure shows, $\tau_B$ significantly increases with increasing $\phi$. A simple and empirically exponential relation, $\tau_B = 0.0006e^{(27.929+\phi)}$, was found to fit the experimental data very well with a high correlation coefficient of 0.98, where 0.0006 and 27.929 are two empirically fitted constants. Bingham shear stress $\tau_B$ is the shear stress experienced by the suspension at zero shear rate based on the Bingham fluid model. Bingham shear stress is considered to be an important parameter (e.g., Buscall & White 1987; Nguyen & Boger 1992; Møller et al. 2006), and furthermore, it could be regarded as indicative of the inherent strength of the suspension under static conditions (Barnes 1999). In the suspension, with increasing solid concentration, cohesive primary particles will collide and adhere to each other due to Brownian motion. Some flocs comprising primary particles and confined water (within the floc) are formed. When the solid concentration of the suspension is low, these flocs are almost independent. In this case,
**Figure 4** | Measured relative viscosity values of the water–kaolinite suspensions as a function of solid volumetric concentration and their comparison with different models (here $\phi_m$ is taken as 0.44 based on the measured experimental data in this study).

**Table 4** | Specific parameterizations of proposed semi-empirical or empirical models presented in previous studies (adapted from Zhu et al. 2017)

| Model name                        | Parameterization                                                                 |
|-----------------------------------|----------------------------------------------------------------------------------|
| Einstein equation (1906)          | $\eta = 1 + B\phi$                                                              |
| Batchelor formula (1977)          | $\eta = 1 + B\phi + k\phi^2 + O(\phi^3)$                                       |
| Roscoe formula (1952)             | $\eta = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5}$                          |
| Krieger and Dougherty formula (1959) | $\eta = \left(1 - \frac{\phi}{\phi_m}\right)^{-B_m}$                       |
| Chong formula (1971)              | $\eta = \left(1 + 0.75\frac{\phi}{\phi_m}\right)^2$                           |
| Dabak formula (1986)              | $\eta = \left[1 + \frac{2.5\phi\phi_m}{2(\phi_m - \phi)}\right]^2$            |
| Boyer formula (2011)              | $\eta = 1 + \frac{5}{2}\phi\left(1 - \frac{\phi}{\phi_m}\right)^{-1} + m^c\left(\frac{\phi}{\phi_m - \phi}\right)^2$, with $m^c = \mu_1 + \frac{(\mu_2 - \mu_1)}{1 + I_0\phi^2(\phi_m - \phi)^2}$ |

Caption: $B$ is the Einstein coefficient with a theoretical value of 2.5 for hard spheres; $k$ is equal to 6.2 for Brownian suspensions in any flow, and for non-Brownian suspensions in a staining flow, $k = 7.6$; $\phi_m$ is the maximum packing concentration of particles in the suspension, at which there is no longer sufficient fluid to lubricate relative particle motion, and thereby the viscosity reaches the infinity; $\mu_1 = 0.32$, $\mu_2 = 0.7$ and $I_0 = 0.005$ were suggested in the study of Boyer et al. (2011).
the suspension cannot resist any shear motion, which indicates that the suspension could flow once an external shear rate is applied on it. However, as the solid concentration of the suspension increases, many flocs are formed in the suspension. These flocs can adhere to each other in the highly concentrated suspension, and consequently a network structure (or a gel), which is composed of flocs and free water between flocs, may be formed (Kranenburg 1994; Winterwerp 2002). This network structure has an inherent strength. When an external shear motion is exerted on the suspension, it may deform and rotate, and as a result the suspension does not flow. Until the applied shear stress exceeds the inherent strength, the network structure may be disrupted and, in this case, the suspension begins to flow and exhibits a shear thinning behaviour. A high solid concentration of the suspension corresponds to a stronger inherent strength of the network structure, leading to a larger Bingham shear stress value.

**Effect of electrolyte**

Figures 6 and 7 show the measured relative viscosity and Bingham shear stress values of the suspensions when 34 NaCl, CaCl₂ and Al(NO₃)₃·9H₂O concentrations \( n \) from 0.005 to 1.55 mol/L have been added. It can be seen from Figure 6 that, despite some data scattering, there exists a upward trend that an increase in electrolyte concentration leads to a larger suspension viscosity, especially for the case of Al(NO₃)₃·9H₂O floculant for which an linearly fitting relation: \( y = 0.6631x + 1.8468 \), has a correlation coefficient with experimental data above 0.69. However, there seems no obvious trend between the Bingham shear stress and electrolyte concentration in Figure 7.

Furthermore, Figures 8 and 9 compare the viscosity and Bingham shear stress values of the water–kaolinite suspensions at different electrolyte valences in the box plot form. It can be found that in terms of average value of each box, an improvement in electrolyte valence leads to an increasing suspension viscosity and a decreasing Bingham shear stress. There seems less previous studies on the particle suspension rheology with electrolyte of a large concentration range (from lowly to highly-concentrated condition) added into it.
A possible interpretation for this result could be made using DLVO theory. Cohesive kaolinite primary particles can collide and adhere to each other due to Brownian motion in the suspension. The collision and adhesion efficiencies greatly depend on the binding effects of the short-range forces between the pairs of colliding particles/flocs, including the van der Waals attractive force and the double-layer electrostatic repulsive force (Thomas et al. 1999). According to the classical DLVO theory (see details in Thomas et al. (1999)), if an increase in electrolyte concentration and/or valence occurs, the van der Waals attractive force does not change but the thickness of the double layer will reduce. This will lead to a decreased double-layer repulsive force and a corresponding reduced height of the repulsion barrier. Once the height of the repulsion barrier reduces, an increasing abundance of primary particles can overcome the barrier, and a greater number of adhesions can occur, meaning that there are more flocs formed in the suspension. With more flocs adhering with each other, the suspension will become denser. This means that there are less space and large resistance for the suspension to flow when an external shear stress is applied into the suspension. Therefore, a suspension with a large electrolyte concentration and/or a high electrolyte valence added into it has a large viscosity value. However, these flocs in the suspension are always fragile and porous, and the contacting conditions among flocs may be unstable, which could lead to a weak gel-like network structure in the suspension. As a result, the shear stress value even shows a decaying trend with an increasing electrolyte valence. More experimental observations and theoretical analysis regarding the electrolyte-induced rheology mechanism should be performed in the future.

Effect of primary particle size
Fixing the particle concentration ($s = 500 \text{ kg/m}^3$) and electrolyte type (NaCl electrolyte), this study compared rheological properties of water–kaolinite samples with different grain size distributions. Figures 10 and 11 show the measured
Figure 7 | Measured Bingham shear stress values of the water–kaolinite suspensions with different NaCl, CaCl₂, and Al(NO₃)₃·9H₂O electrolyte concentrations (s = 500 kg/m³).

Figure 8 | Relative viscosity values of the water–kaolinite suspensions with different electrolyte valences.
**Figure 9** | Bingham shear stress values of the water–kaolinite suspensions with different electrolyte valences.

**Figure 10** | Measured relative viscosity values of the water–kaolinite suspensions of different kaolinite samples (kaolinite sample #1: A, and kaolinite sample #2: B).
relative viscosity values and Bingham shear stress values of suspensions containing kaolinite samples #1 and #2 in the box-plot form, respectively. It is obvious that a fine-grained suspension has larger viscosity and Bingham shear stress values.

A simple explanation for this phenomenon was presented as follows. For a fine-grained suspension, the specific surface area of each kaolinite primary particle (equal to the surface area divided by the volume, and equal to six divided by the volume for a spherical particle) is large, and as a result it is prone to flocculation, since the flocculation capacity of cohesive particles is proportional to their specific surface area as revealed by several studies (Zhang et al. 1989; Kretzschmar et al. 1997; Sakhawoth et al. 2017). With an increasing rate of flocculation occurring between primary particles the network structure in the suspension becomes increasingly compact. At a fixed particle concentration, the concentration of primary particles becomes large for a fine-grained suspension. This will lead to the fact that more and more primary particles can fill the gel-like network structure. As a result, the network structure has larger resistance and yield shear stress to resist the shear motion when an external shear stress is exerted on the fine-grained suspension compared with the coarse-grained suspension.

CONCLUDING REMARKS

This study reports rheological experiments of water–kaolinite suspensions at 39 solid concentrations, different electrolyte conditions and two types of primary particle sizes. Rheological properties of the suspensions were measured using a Brookfield RST-CCT40 rheometer and an attached measuring system. The Bingham fluid model has been adopted to fit the rheological data with the highest coefficient of determination compared with other models and, furthermore, the viscosity and Bingham shear stress values were calculated for each water–kaolinite suspension. Some concluding remarks are summarized here:

Figure 11 | Measured Bingham shear stress values of the water–kaolinite suspensions of different kaolinite samples (kaolinite sample #1: A, and kaolinite sample #2: B).
1. With increasing solid concentration, the suspension viscosity shows an initial slow increase, and then exhibits a rapid increase. Among all of the proposed semi-empirical or empirical models that describe the viscosity–solid concentration relationship, the Krieger and Dougherty formula provides the best fitting result to the measured data. Only as the solid concentration exceeds a critical value, a gel-like network structure is formed in the suspension and the Bingham shear stress of the suspension appears. The Bingham shear stress rises significantly with increasing solid concentration, for which a simple exponential relation shows a better fit with a correlation coefficient of 0.98.

2. When electrolyte is added to the water-kaolinite suspension, an increase in electrolyte concentration and/or valence of electrolyte leads to a larger viscosity value of the suspension; however, an increasing electrolyte valence yields a smaller Bingham shear stress. A simple interpretation based on DLVO theory is presented as follows. An increase in the electrolyte concentration and/or valence of electrolyte causes a decrease in the double-layer repulsive force between two colliding kaolinite particles/flocs, and the height of the repulsive barrier reduces. More primary particles can overcome the barrier, and consequently more flocs are formed in the suspension. As a result, the gel-like network structure in the suspension will become more compact, which means that there are less space and large resistance for the suspension to flow when an external shear stress is applied into it. However, these flocs in the suspension are always fragile and porous, and the contacting conditions among flocs may be unstable, which could lead to a weak gel-like network structure in the suspension. Thus, the shear stress value even shows a decaying trend with an increasing electrolyte valence.

3. It has been found that a fine-grained kaolinite suspension corresponds to larger suspension viscosity and Bingham shear stress values. This is because the specific surface area of each kaolinite primary particle is large for a fine-grained suspension, and consequently the suspension is prone to flocculation. With an increasing amount of flocculation occurring between primary particles, the network structure in the suspension becomes more compact. At a fixed particle concentration, the concentration of primary particles becomes large for the fine-grained suspension, which may cause more and more particles to fill the structure. After the suspension begins to flow, the fine-grained suspension can resist the shear motion more strongly than the coarse-grained suspension.

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Data Availability Statement

All relevant data are included in the paper or its Supplementary Information.

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