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Rheological properties of montmorillonite dispersions in dilute NaCl concentration investigated by ultrasonic spinning rheometry

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Abstract

Rheological changes of gelled montmorillonite dispersions with different NaCl concentrations and alkali conditions were evaluated by ultrasonic spinning rheometry. It uses velocity-profile information that is obtained in an open-cylindrical container under periodic oscillations. The measurement was conducted with a focus on the rheological behavior at a low shear rate $O(1 \text{ s}^{-1})$, which is difficult to measure because of shear banding. The rheometry represents the coexistence of gel and sol conditions in dispersions as profiles of the phase lag of oscillations that are propagated from the cylinder wall. The critical shear rate at a yielding point and the onset of shear-thinning behavior was quantified, which has been regarded as only an apparent or speculated value by many previous researchers. Viscoelasticity from particle networks in the dispersion was observed, and the networks deform like a spring, without breaking the structure under low-shear-rate conditions.

Keywords: Ultrasound, Rheometry, Montmorillonite, Shear banding, Shear-thinning viscosity

1. Introduction

1.1. Rheology of montmorillonite dispersions

Particles of montmorillonite (Mt), which is a type of smectite, are polygonal platelets with a $O(\text{nm})$ thickness and a 0.1- to 1- μm planiform size. When Mt powder swells in ionic solvents, the dispersions provide typical rheological characteristics arising from networks of Mt particles that are termed thixotropic characteristics (Vali and Bachmann, 1988; Velde, 2013), as summarized in the review by Barnes (1997). These characteristics have been utilized in field such as agriculture, civil engineering, and nuclear engineering, as drilling muds, adsorbents, and nanocomposites. In these applications, the networks must be understood, which are structuralized passively with a time-dependence and with physical bonding forces. An anomalous viscosity or viscoelasticity of the dispersion is given by structuring networks, which are affected by particle aggregation or flocculation as a result of particle attractive or forces. Three main factors influence the structuring: Van der Waals

attraction, electrostatic repulsion, and Coulomb attraction forces (Brandenburg and Lagaly, 1988; Tombácz and Szekeres, 2004).

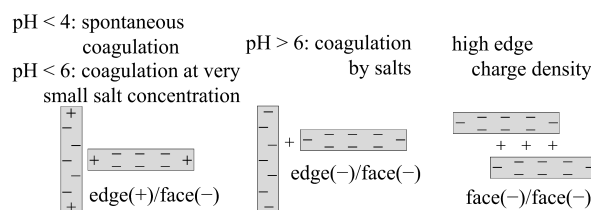


Figure 1: The different modes of coagulation of swelling Mt particles (Lagaly and Ziesmer, 2003)

According to Lagaly and Ziesmer (2003), the particle networks in Mt dispersions vary according to solvent pH and ionic strength as summarized in Fig. 1. The particle has electrocharacteristics of a large permanent negative face charge that arise from isomorphous substitution within the particle structure, and a pH-dependent edge charge at the end of the structure. The negative charge is compensated by exchangeable cations. The electrostatic interaction between the particles can change easily by pH and cation concentration in the solution. These electrical characteristics promote the structuring of stable networks at microscopic scales, and therefore, the dis-

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persions result in an anomalous viscosity or viscoelasticity in the macroscopic rheological properties (Abend and Lagaly, 2000).

Particle networks in the dispersion have various microscopic structures, which are classified into two types, namely, house-of-cards and band-type structure. The former is a stable structure with edge/face bonding, and is only formed in acidic media for edges that are positively charged, or in slightly alkaline media above the critical salt concentration (Lagaly and Ziesmer, 2003). If the concentration increases gradually beyond a critical value, the structure changes from the house-of-cards to the band-type structure (Abend and Lagaly, 2000). This occurs because the ionic strength shifts from an edge/face to a face/face network, which causes high densities of edge charges from an increase in salt concentration as shown in Fig. 1.

To understand the rheological properties of different structural networks, some factors have been investigated through experimental and theoretical research at microscopic scales (Rand et al., 1980; Bekkour et al., 2005; Goh et al., 2011). When structural transitions occur, the structure type and attractive force between each particle changes as expected from DLVO theory (Missana and Adell, 2000; Tombácz and Szekeres, 2004), which describes the forces between charged surfaces that interact through a liquid medium. Macroscopic responses result from these microstructures, the strength of interactions in each particle increases with respect to the salt concentration (Morvan et al., 1994). Brandenburg and Lagaly (1988) indicated that the viscosity changes significantly depending on the solvent, pH, fluid temperature, Mt powder density and sodium salt concentration, when they aimed to understand the electrical interactions between each particle.

At $\text{pH} < 6$ (isoelectric point), when particle networks are broken by a shear force, they can reconstruct instantly and spontaneously because of positive edge charges. This reconstruction is a key factor of thixotropy. In contrast, at $\text{pH} > 6$, the particles disperse homogeneously because of negative edge charges. However, salt addition allows each particle to structure networks because attractive forces exist through the cations. The thixotropy is also developed in this situation, and the thixotropic properties change with an increase in salt concentration unless the particles completely aggregate in fluid media.

A typical transition map at $\text{pH} > 6$ with changes in salt concentrations is deduced from some experimental investigations by using torque rheometry and microscopy (Brandenburg and Lagaly, 1988; Lagaly, 2006; Paineau et al., 2011; Cruz and Peng, 2016) as

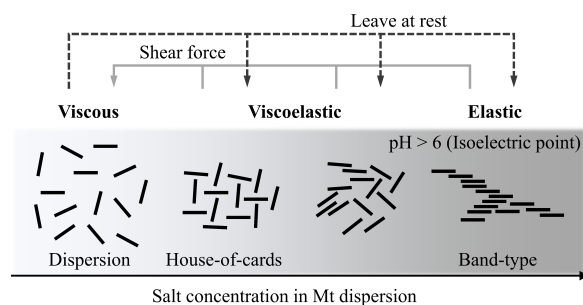


Figure 2: Regime map of particle networks in the Mt dispersion with changes in salt concentration, shear force and leave at rest, deduced from previous studies (Brandenburg and Lagaly, 1988; Lagaly, 2006; Paineau et al., 2011; Michot et al., 2013; Cruz and Peng, 2016)

summarized in Fig. 2. Each structure can be broken and the particles are dispersed by shear forces, and are reconstructed by leaving them at rest. The strength of particle networks indicates that this map is divided into three phases from the rheological observations, namely, a viscous, a viscoelastic, and an elastic phases. These represent totally dispersed, flocculated, and aggregated conditions, respectively.

Many investigations have been performed to reveal the quantitative mechanical response of dispersions and to control dynamic fluid behaviors. Experimental approaches are divided into two main types; an assumption of the microstructural network from a macrorheological response (Barnes and Carnali, 1990; Nakaishi, 1997; Zhuang et al., 2017), and an assumption of the macrorheological response from microscopy (Zhang et al., 2011; Mouzon et al., 2016). Because no measurement systems exist that enable us to obtain microscopic structural deformations directly, recent research is still focused mainly on only the macromechanical response under high-shear-rate conditions by using torque rheometers. Minimal research exists on the macrorheological response by using torque rheometry.

This has occurred because of limitations and problems from shear banding (Manneville, 2008; Olmsted, 2008; Divoux et al., 2016) and wall slip (Dogan et al., 2002) for applications to Bingham or Herschel–Bulkley fluids under low-shear-rate conditions, such as a co-existing gel and sol media. Few experimental investigations exist on thixotropic fluids with unsteady shearing, because torque rheometers can evaluate only macrorheological properties, including influences from the problems mentioned above. The properties are defined as an apparent viscosity or plastic viscosity, are the most significant sources of ambiguity for conventional torque rheometers, and are termed the “Couette inverse prob-

lem” (Nguyen et al., 1999; Ancey, 2005; Heirman et al., 2008).

1.2. Ultrasonic rheometry

To overcome these limitations and to reveal the rheological characteristics of dispersions with thixotropic behaviors, another rheometry approach was proposed recently in which ultrasonic waves are used (Ouriev and Windhab, 2003; Derakhshandeh et al., 2012; Gurung et al., 2016; Poelma, 2017). A rheometry using ultrasonic velocity profiling (UVP) (Takeda, 2012) was proposed; UVP can measure instantaneous velocity profiles along propagation lines of ultrasonic waves.

We proposed a rheometry using UVP for complex fluids in rotating cylindrical system without requiring an inner cylinder to measure the axial torque, termed ultrasonic spinning rheometry (USR) (Shiratori et al., 2013, 2015; Tasaka et al., 2015; Shiratori et al., 2016; Yoshida et al., 2017; Tasaka et al., 2018). This technique can be applied even for opaque liquids and for complex fluids.

With simple, open cylindrical containers, measurements of a wide range of target properties are possible. Different simple shear conditions are realized as spatial distributions by setting the oscillation frequency f and the amplitude Θ to different values. Shiratori et al. (2015) proposed a model-free USR for the quantitative evaluation of a shear-rate-dependent viscosity without using any rheological models. A supplemental axial torque measurement was used to satisfy the boundary conditions to solve the equations of motion.

Tasaka et al. (2015) used USR to evaluate the effective viscosity of a liquid with tiny bubbles as a corresponding Newtonian viscosity in a UVP measurement volume under strong oscillatory shear flows. In an analysis of this approach, the phase lag of velocity fluctuations that propagated from the oscillating cylinder wall to the inner part of the fluid is related to the local effective viscosity. Here, the viscosity is determined from local information on the phase lag, and thus the method can provide spatial viscosity distributions. In an advanced USR analysis, Yoshida et al. (2017) developed the method for general complex fluids, such as strong viscoelastic fluids and fluids with dispersed O (10 mm) solid materials. Spatial effective viscosity profiles, yield stresses, and elastic moduli of Mt dispersions were evaluated by analyzing only the instantaneous velocity profiles.

Most recently, Tasaka et al. (2018) achieved a stable evaluation of the linear viscoelasticity in bubble suspensions as complex multiphase fluids using USR. From these branches of applicability in previous reports, USR system raises the possibility of evaluating rheological

properties in complex fluids in more robust methodology than conventional rheometry, such as rotational torque rheometry.

1.3. Objective

In this paper, unexamined rheological properties of Mt dispersions are evaluated by using USR. The rheological responses of the dispersion show great differences, especially under relatively low-shear-rate conditions in unsteady shear flows. USR is applicable to the existence of shear banding, which have been dealt with by using an empirical valuation because of the limitations mentioned above. USR can provide proof of critical shear rates to achieve particle-network breakdown as summarized in Fig. 2. The changes in critical shear rates with NaCl concentration for cases where sols and gels co-exist are explored to understand shear-rate-dependent viscosity and shear-banding effects.

2. Material & method

2.1. Conditions of test dispersions

Kunipia-F (Kunimine Industries Co., Ltd.) was used as the test material. According to Hrachová et al. (2009), its structural formula calculated from chemical analysis is $\text{Na}_{0.84}\text{Ca}_{0.05}\text{K}_{0.01}[\text{Si}_{7.82}\text{Al}_{0.18}][\text{Al}_{3.19}\text{Fe}_{0.21}\text{Mg}_{0.52}]\text{O}_{20}(\text{OH})_4$. Kunipia-F comprised 99 wt.% of Mt with other accessory minerals including quartz (chalcedony), feldspar, and calcite (Tachi et al., 2014). Exchangeable cations were composed of Na: 108, Ca: 9.18, K: 1.19, and Mg: 0.11 cmol(+)/kg (Tachi et al., 2014). The material included Na_2SO_4 : 4.17×10^5 mol/g and NaCl: 1.54×10^5 mol/g. To prepare fully swelled and homogeneous dispersions with 4.0 wt.% Mt, 40 g Kunipia-F was swelled in 0.5 L of pure water for two days (48 h). Then, the dispersion was stirred for 30 min and was kept for a day (24 h). After ensuring that the dispersion was fully swelled, c_x mol/L NaCl aqueous solution (0.5 L) was added. Before the experiments, the dispersion was kept for two additional days to ensure that it had reached equilibrium.

The speed of sound is an important property in ultrasonic measurements. The speed of sound in the dispersion is almost equal to that of water (1480 m/s). Here, the dispersion density is $\rho = 1040$ kg/m³. The pH in some prepared dispersions was measured by using a pH meter (TOA DKK Co., HM-30G) as shown in Table 1. The pH was almost constant under the alkali experimental conditions.

To achieve the shear-rate measurement range, 1 – 100 s⁻¹, the oscillation amplitude was set at different

Table 1: pH values in each c_x of Mt dispersion

c_x [mol/L]	0.01	0.02	0.04	0.08
pH	8.98	9.03	9.06	8.64

$\Theta = \pi/8, \pi/4, \pi/2, 3\pi/4$ rad with a fixed oscillation frequency, $f = 1.0$ Hz. To approach gel/sol transitions of the Mt dispersion as determined by NaCl concentration, especially under low-shear-rate conditions, concentrations were set to $c_x = 0.001 - 0.05$ mol/L according to Cruz and Peng (2016) and Barnes (1997). The experimental parameters are summarized in table 2. The test fluid temperature was kept constant at $T_0 = 20^\circ\text{C}$. After filling the cylinder with the dispersion, the dispersion was stirred vigorously to eliminate the influence of shear history (Barnes, 1997). For the velocity profile measurements, the UVP requires tracer particles to be dispersed uniformly in test fluids. Mt dispersions do not require any additional tracer particles for the measurements.

Table 2: Experimental NaCl concentration (c_x) and oscillating amplitude (Θ), where the oscillating frequency, f , was 1 Hz in these experimental parameters

#	c_x [mol/L]	Θ [rad]	#	c_x [mol/L]	Θ [rad]
1	0.001	$\pi/4$	8	0.02	$3\pi/4$
2	0.001	$\pi/2$	9	0.025	$\pi/2$
3	0.01	$\pi/8$	10	0.03	$\pi/2$
4	0.01	$\pi/2$	11	0.04	$\pi/2$
5	0.01	$3\pi/4$	12	0.04	$3\pi/4$
6	0.02	$\pi/4$	13	0.05	$3\pi/4$
7	0.02	$\pi/2$			

2.2. Experimental arrangement of ultrasonic spinning rheometry

An open vertical rotating cylinder made from acrylic resin with a 145-mm inner diameter ($2R$) and 65-mm-high, 2-mm-thick lateral wall, was used as the test container (Fig. 3a). The cylinder was mounted at the center of a 1000 mm $\times$ 1000 mm water bath to maintain a uniform temperature T_0 and to allow ultrasonic waves to propagate from outside the cylinder (Fig. 3b). Cylinder oscillations were controlled at a setting oscillation angle Θ and oscillation frequency f . Instantaneous velocity profiles of the fluids in regular oscillations were measured by using UVP. These parameters determine the maximum and minimum input shear strength for the test fluids, and should be selected carefully to achieve suitable conditions. For large fluctuations of the maximum shear flow, the flow condition could not maintain

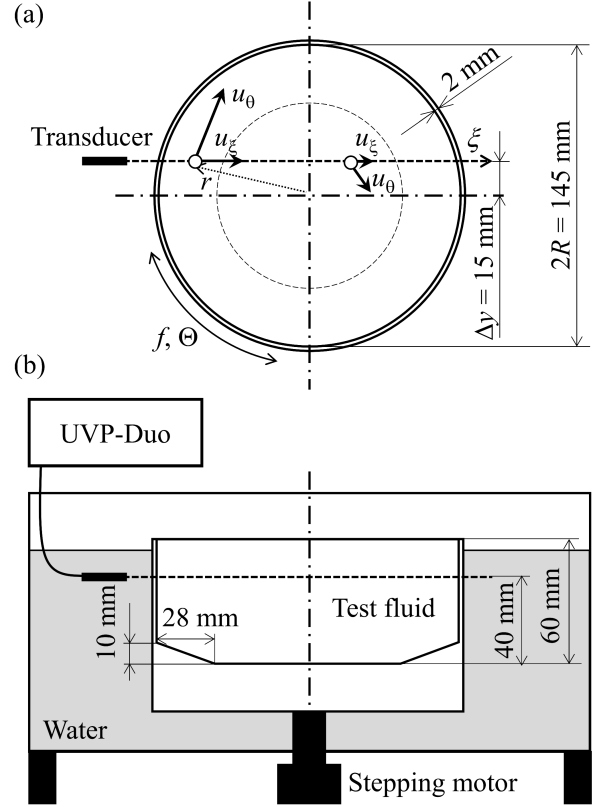


Figure 3: Schematic of the experimental apparatus for measuring velocity distributions of oscillating shear flows using UVP, (a) top view of rotating cylinder without the outside container, (b) side view

unidirectional shear flow because of the non-negligible meridional circulations.

To process captured echo signals and to calculate spatio-temporal velocity distributions, UVP-model Duo (Met-Flow S.A., Switzerland) was selected as the velocity measurement system. To obtain the azimuthal velocity component, an ultrasonic transducer of resonance frequency 4 MHz and 5 mm effective element diameter was mounted in the bath at a horizontal displacement, Δy , which is set in the off-axis from the cylinder center to obtain an azimuthal velocity component (see Fig. 3a). $\Delta y = 15$ mm was selected from empirical considerations based on the results of previous studies (Tasaka et al., 2015; Yoshida et al., 2017). Assuming that an axisymmetric flow field and the velocity component in the radial direction are negligible compared with the azimuthal component, the azimuthal velocity component u_θ is

$$u_\theta = \frac{u_\xi r}{\Delta y} \quad (1)$$

at a radial position r . Typical measurement resolutions

in time and space are 25 ms and 0.74 mm in the measurement direction ξ , respectively. The radial position in $r/R < \Delta y/R \approx 0.2$ cannot be measured due to the off-axis displacement of transducer (Fig. 3a). Further details of the configurations are given in previous papers (Tasaka et al., 2015; Yoshida et al., 2017).

2.3. Analysis of effective Newtonian viscosity

To evaluate rheological properties, phase-lag analysis was used, and details of the procedure are summarized in Appendix. If the parameter, Θ or f , changes, the measurable range of the shear rate profiles also changes. In terms of parameter settings, it is very important to satisfy unidirectional flow in the cylindrical container. To expand the measurable range of shear rate, the oscillation amplitude, Θ , was changed. Here, silicone oil (KF-96 300 cSt, Shin-Etsu silicone, Shin-Etsu Chemical Co. Ltd., Japan) of which its kinematic viscosity precisely is given as 300 mm²/s under low shear rates, $\dot{\gamma} < O(10^3 \text{ s}^{-1})$, is used to validate the precision of rheological evaluation. The oil temperature was kept constant at $T_0 = 25^\circ\text{C}$ by using a thermostatic bath.

Four oscillation amplitudes, $\Theta = \pi/8, \pi/4, \pi/2, 3\pi/4$ rad, were examined and the results of the rheological evaluation are shown in Fig. 4. The vertical and horizontal axes indicate the effective Newtonian kinematic viscosity ν and shear rate $\dot{\gamma}_{\text{eff}}$ that were obtained from measured velocity profiles (see Appendix). Here, the dashed line shows $\nu = 300 \text{ mm}^2/\text{s}$, which is an ideal kinematic viscosity in silicon oil (300 cSt) at 25°C .

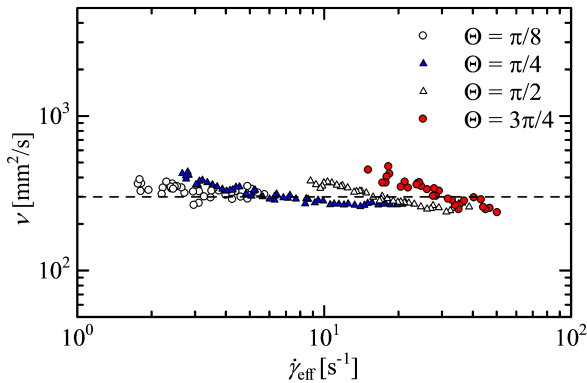


Figure 4: Measurement results in limited radial range ($0.6 < r/R$) of shear rate and kinematic viscosity in silicon oil (300 mm²/s), where each symbol indicates a different oscillating amplitude, $\Theta = \pi/8, \pi/4, \pi/2, 3\pi/4$ rad

Results at $\Theta = \pi/8, \pi/4$ rad are almost equal to the index value in each shear rate profile. Irrespective of the oscillating amplitudes, Θ , the viscosity results are close

to a true value (300 mm²/s). This provides supporting evidence of the measurement precision, especially in the range of $10^0 < \dot{\gamma}_{\text{eff}} < 10^2 \text{ s}^{-1}$. However, deviations from the value in low $\dot{\gamma}_{\text{eff}}$ regions, such as near the center of the cylinder, become larger than any other region. This occurs because, when the velocity fluctuations are small near the center of the cylinder, quantifications of phase-lag profiles can be influenced strongly by measurement noises. In addition, relative differences in ultrasonic measurement volume at each radial position influence the results. From these reasons, the regions to evaluate the viscosity are limited to $r/R < 0.6$ in this report, although it is possible to widen the regions by enhance the noise filtering methods.

3. Results of rheological evaluation for Mt dispersion

3.1. Velocity and phase-lag profiles

The azimuthal velocity, u_θ , were obtained instantaneously by substituting velocity obtained using UVP, u_ξ , to Eq. 1, where the schematic of positional relations between spatial displacement of the ultrasonic beam emitted from transducer and radial position in the oscillating cylindrical container (Fig. 5a). The oscillation was controlled by sine functional angular velocity, $u_{\text{wall}}(t) = 2\pi^2 f R \Theta / 180 \sin 2\pi f t$ ($= U_{\text{wall}} \sin 2\pi f t$) (Fig. 5b). Thus, velocity in the test fluid is propagated as unsteady shear flows (Fig. 5c), where the measured velocity is at case of $c_x = 0.001$ (Table 2: # = 2). From these velocity profiles, the shear wave propagates inside from the cylinder wall, where the highest shear rate is applied near the cylinder wall. UVP with high temporal resolutions $O(10 \text{ ms})$ can measure the test fluid motions as spatio-temporal velocity profiles. Moreover, noises in instantaneous velocity profiles are eliminated by averaging in 100 periods of oscillation (100 s).

With the assumption of axisymmetric and unidirectional flow in the azimuthal direction, the spatio-temporal velocity map obtained by the UVP can be converted into a radial-temporal distribution of the azimuthal velocity component. The phase-averaged velocity profiles $u_\theta(r, t)$ in 100 periods of oscillation (100 s) is shown in Fig. 6, measured at $f = 1.0 \text{ Hz}$, $\Theta = \pi/2$ rad, and $c_x = 0.001, 0.01, 0.02, 0.03, 0.04$ (Table 2: # = 2, 4, 7, 10, 11). The vertical and horizontal axes indicate the radial positions normalized by the radius of the cylindrical container, R , and the spin-cycle time. The gray-scale contours represent the azimuthal velocity normalized by the maximum azimuthal velocity at the cylinder wall, U_{wall} . Here, disposing the

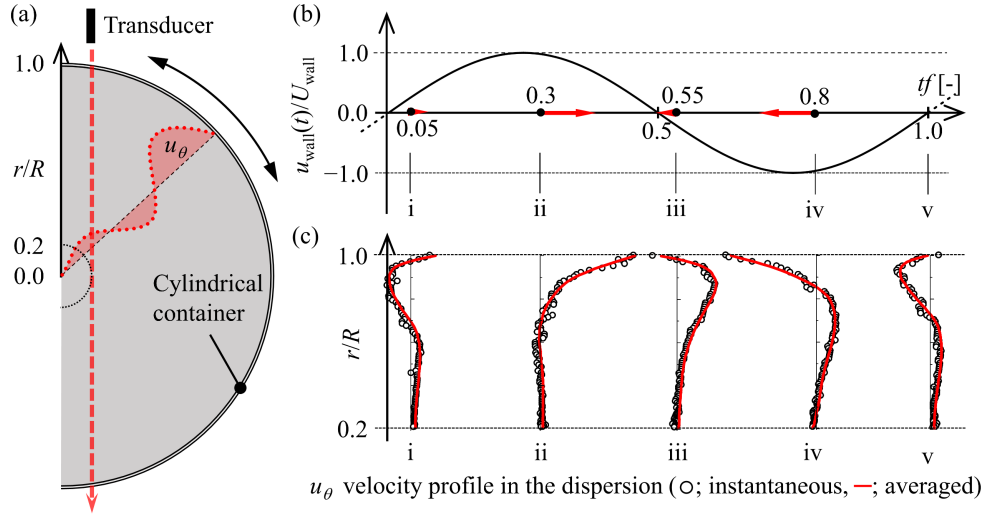


Figure 5: (a) Schematic of oscillating cylindrical container and transducer displacement, (b) oscillation angular velocity fluctuation of cylinder wall $u_{\text{wall}}(t)/U_{\text{wall}}$, (c) instantaneous and averaged azimuthal velocity profiles u_θ at each spin-cycle tf (i–v) at case of $c_x = 0.001$ (Table 2: # = 2)

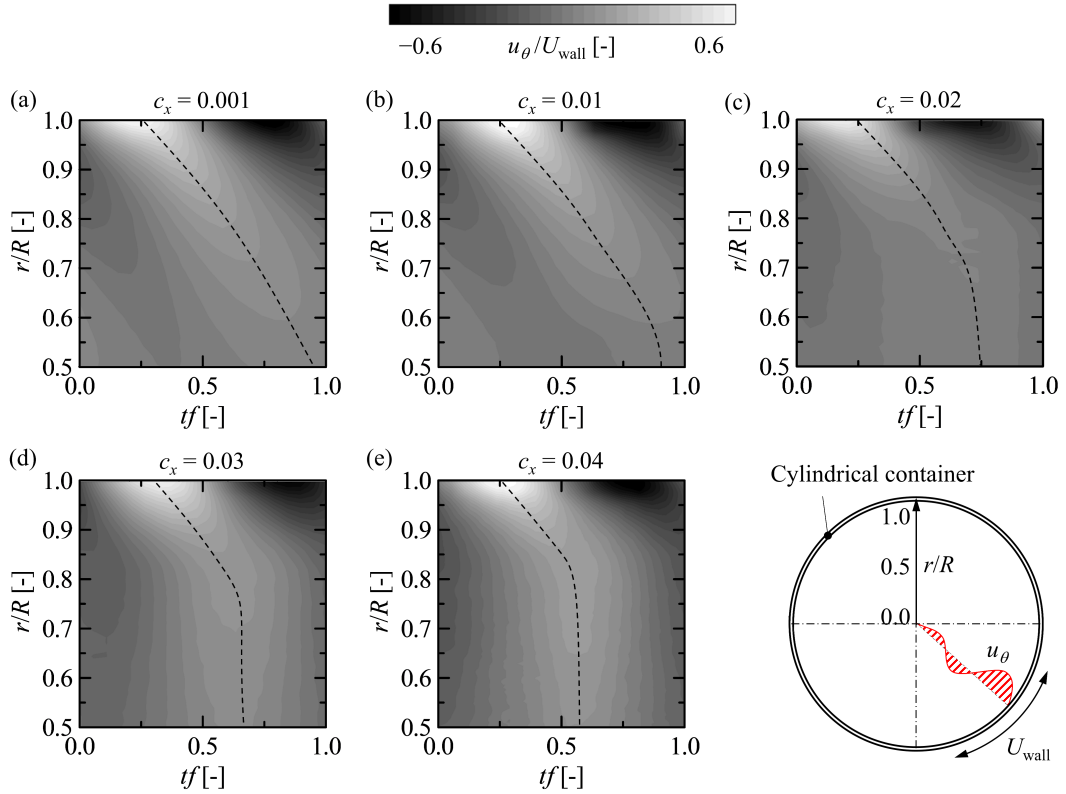


Figure 6: Radial-temporal distributions of azimuthal velocity of the Mt dispersion in 4.0 wt.% powder in different NaCl aqueous solutions, $c_x =$ (a) 0.001, (b) 0.01, (c) 0.02, (d) 0.03, (e) 0.04 mol/L, where the oscillation frequency, amplitude, maximum angular velocity, temperature, and recovery time are $f = 1.0$ Hz, $\Theta = \pi/2$ rad, $U_{\text{wall}} = 715.5$ mm/s, $T_0 = 20^\circ\text{C}$, and 100 min, respectively

instantaneous velocity profiles shown in Fig. 5c in parallel, the gray-scale contour of Fig. 6a was obtained.

Phase lags in the velocity fluctuations result from the oscillating cylinder wall, and these behaviors change with increases in NaCl concentration. In Fig. 6a, for the lowest case of c_x , the phase lags propagate from the wall to inside the fluid media, and keep the wave speeds approximately constant. A comparison between Fig. 6a and b shows little difference between the velocity distribution near the central region in $r/R < 0.6$. This difference shows a change in momentum propagation because of the transition in rheological properties. Moreover, this region with a constant phase lag developed gradually for $r/R < 0.8 - 0.9$ with an increase in NaCl concentration. As shown for $c_x = 0.04$ mol/L, the region reaches $r/R = 0.85$.

To quantify these phase lags in the velocity fluctuation, a discrete Fourier transform (DFT) was applied. The oscillation in this system was kept at a constant frequency ($f = 1.0$ Hz), so the response of fluid motion appears at this dominant frequency. Radial profiles of the phase lags calculated from the velocity distributions shown in Fig. 6 are summarized in Fig. 7a. The vertical and horizontal axes show the radial position normalized by the radius of the cylindrical container and the phase lag that is propagated from the wall, and each symbol represents different NaCl concentrations.

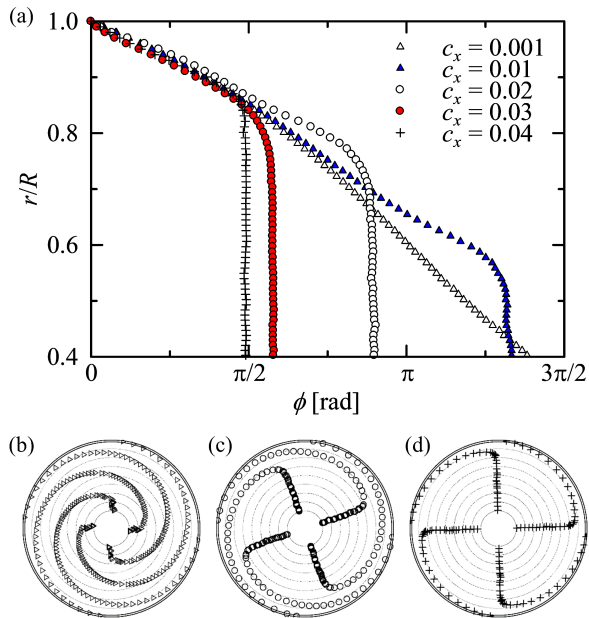


Figure 7: (a) Radial profiles of phase lag of local velocity fluctuations from the cylinder wall at each NaCl concentration in Fig. 6, and reconstructed schematics of phase-lag profiles at (b) $c_x = 0.001$, (c) 0.02, and (d) 0.04 mol/L

For an easy and intuitive understanding of the entire outline of the plots, illustrations drawn from the relationships between the ϕ and r/R in Fig. 7b–d were reconstructed. At $c_x = 0.001$ mol/L, the phase-lag profile maintains an almost constant gradient in each radial position. The gradient reflects the momentum propagation that is observed in the velocity fluctuation as mentioned in Fig. 6. For $c_x (= 0.01$ mol/L) that is ten-times larger, a bending point in the profile appears near $r/R = 0.6$. The point shifts gradually to the wall with an increase in c_x .

At the inner side of the point, the profile plateaus with no significant change in phase lag. The plateau indicates that a rigid-body medium exists and thus the dispersion is in a gel condition. In contrast, the region with a slope implies that the test material flows with phase-lag profiles, and thus it is regarded as existing in the viscous or viscoelastic state, such as a sol or a quasi-sol. The phase lag at $c_x = 0.01$ mol/L plateaus for $r/R \leq 0.6$. For $c_x = 0.02$ mol/L, the plateau expands to $r/R = 0.75$. At $c_x = 0.03$ mol/L, the region reaches $r/R = 0.8$. At $c_x = 0.04$ mol/L, an interface exists between the phase-lag profiles with gradients and that with plateaus becomes sharper than other conditions. From previous research, the gel strength and salt concentration of Mt dispersions are correlated positively in $c_x \leq 0.1$ (Abend and Lagaly, 2000). The interface can be seen clearly because of the increase in gel strength.

Restorative forces exist at the interface between the gel and the sol, and thus the profiles with bending include viscoelasticity. If gels do not possess any viscoelastic characteristics around the interface, the gel regions could not be oscillated followed by an unsteady shear force from the viscous regions. For stably structured dispersions of strong particle networks, strong repulsive or attractive forces exist because of the high response to deformations. Hence, at the gel/sol interface, a curvature of the phase-lag profiles may relate to a viscoelasticity in the Mt dispersions.

3.2. Particle network recovery in the dispersion

Ionic strength enhances not only the gel strength but also recovery time scale of the particle network in thixotropic fluids. But actually, measurements using a torque rheometer to obtain the recovery time scale have to take many repeated trials of high and low amplitude shearing. USR system can reveal instantaneous response placed important information in thixotropy, such as a time dependence. By utilizing real time monitoring in the advantage of USR, behaviors of the time dependence in Mt dispersion can be captured quantitatively.

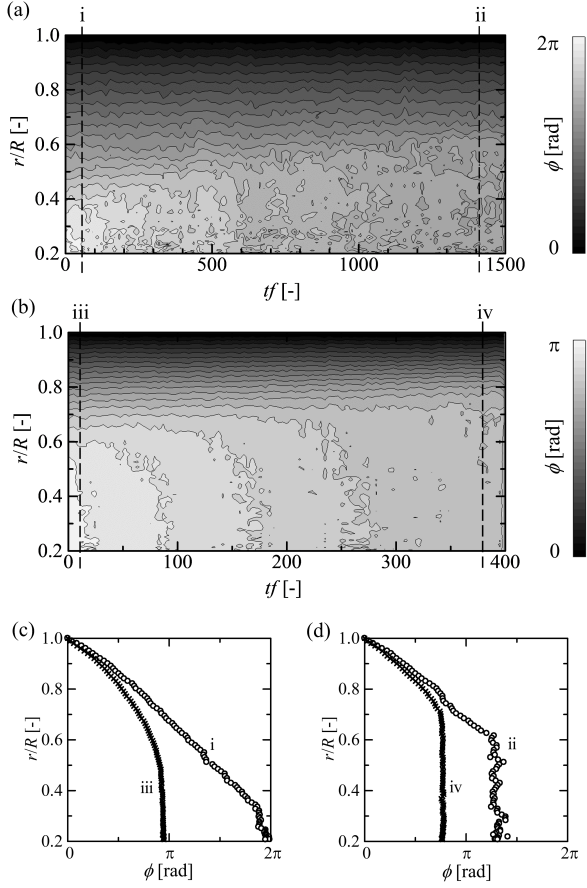


Figure 8: Radial-time distribution of phase lag in local velocity fluctuations from a cylinder wall for Mt dispersion at (a) $c_x = 0.02$ mol/L and (b) $c_x = 0.04$ mol/L immediately after stirring, where the oscillation frequency, amplitude, and temperature are $f = 1.0$ Hz, $\Theta = 3\pi/4$ rad, and $T_0 = 20^\circ\text{C}$, respectively, and (c) and (d) are the extracted phase-lag profiles from (a) and (b) at i: $tf = 50$, ii: $tf = 1400$, iii: $tf = 10$, iv: $tf = 380$

The ionic strength enhances the gel strength and the recovery time scale of the particle network in thixotropic fluids. However, measurements to obtain the recovery time scales require many repeated trials of high- and low-amplitude shearing. A USR system can reveal an instantaneous response, which indicates the importance of thixotropy, such as time dependence. An advantage of USR is the use of real-time monitoring, in which the time-dependent behavior of the Mt dispersion can be captured quantitatively.

To evaluate the recovery speed at different c_x , Mt dispersions at two NaCl concentrations (Table 2: # = 8, 12) were prepared. After filling the cylindrical container with dispersion and stirring it sufficiently to break down the particle networks, velocity measure-

ments were conducted for 1500 s. To quantify the change in phase lag with time, DFT analysis was conducted every four cycles ($tf = 4$). Time variations of the phase lag are shown in Fig. 8, where the vertical and horizontal axes indicate the radial position that is normalized by the cylinder radius and the periodic cycles. The gray scale indicates phase lags from the cylindrical container wall, where different scales are provided for each distribution for better visibility.

In Fig. 8a, the phase lag for $c_x = 0.02$ shows an almost linear slope in the entire radial position immediately after the measurement started and is shown in Fig. 8c-i as an instantaneous profile. According to the relationship between the profile shape and the rheological properties mentioned above, the dispersion is a quasi-Newtonian sol state in the entire cylinder. As the oscillation periods increase, tf , the profiles converge gradually to a certain shape at $tf \sim 1400$. This result means that the profiles reach the terminal equilibrium state under the set oscillation conditions. The profiles at $tf = 1400$ as shown in Fig. 8d-ii are different from that at $tf = 50$ (Fig. 8c-i). The profile bends at around $r/R = 0.6$, which means that the dispersion layer restores the network structures as the gel region ($r/R \leq 0.6$) inside the quasi-Newtonian sol region ($r/R \geq 0.6$).

The profiles for $c_x = 0.04$ in Fig. 8b change significantly more than those for $c_x = 0.02$ with the convergence time being approximately $tf = 380$. Immediately after the measurement starts (Fig. 8b), the profiles as extracted in Fig. 8c-iii show a more gradual variation than those of Fig. 8c-i. The profile of Fig. 8c-i has an almost linear shape, whereas that of Fig. 8c-iii has a round and a plateau region. In previous research (Yoshida et al., 2017), the shape of Fig. 8c-iii is similar to that of polymer solutions with viscoelastic characteristics, thus the dispersion in $c_x = 0.04$ immediately after stirring behaves like a viscoelastic body. Here, the viscoelastic characteristics result from microscopic structures that are maintained by the particle networks even after strong stirring. After reaching terminal equilibrium states, although the profiles of Fig. 8d-ii and iv have similar shapes, considerable differences exist. The profile of Fig. 8d-iv has a wider plateau region, which indicates a wider gel region than that in Fig. 8d-ii. The profile of Fig. 8d-ii shows a sharper bending than that of Fig. 8d-iv. Both differences may be explained by a dependence of the robustness of the particle networks on the NaCl concentration. At lower concentrations, weaker particle networks cannot sustain the microscopic structures. The viscoelasticity and stronger gelling do not manifest under an applied periodic shear

stress, whereas the solution with a larger concentration achieves such properties. These results mean that the recovery speed of particle networks and the viscoelastic response of the networks are influenced strongly by changes in NaCl concentration.

3.3. Evaluations of shear-rate-dependent viscosity

In § 3.1 and 3.2, the phase-lag profiles that are obtained from velocity distributions provide key information to approach the rheological properties under conditions with the co-existence of a gel and sol response. To evaluate the shear-rate-dependent viscosity of the Mt dispersions, we have explained the basic concepts and validations in § 2.3, and some data processing will be described in Appendix. Experiments were conducted with parameters as summarized in Table 2.

The results of kinematic viscosity measurements with different oscillation amplitudes to widen the range of exerted shear rates are summarized in Fig. 9a. The measurement conditions are specified in Table 2 ($\# = 1, 2, 3, 5, 6, 8, 9, 10, 13$). The vertical and horizontal axes show a kinematic viscosity and effective shear rate, respectively. Here, in previous reports (Tasaka et al., 2015; Yoshida et al., 2017), the obtained viscosity was calculated by assuming that all non-Newtonian effects, such as the viscoelasticity and shear-thinning viscosity, can be reflected into an effective Newtonian viscosity.

For $c_x = 0.001$, as indicated by open circle symbols, plateau regions exist with deviations in $1.0 < \dot{\gamma}_{\text{eff}} < 3.0 \text{ s}^{-1}$. The tendency changes gradually to a monotonic decrease for $\dot{\gamma}_{\text{eff}} > 3.0 \text{ s}^{-1}$, where Mt dispersion has a sol condition. It may exhibit homogeneous dispersed behaviors, which is regarded as viscous fluids. Thus, the velocity fluctuations propagated constantly with viscous damping from the cylinder wall to the center. At the turning point of the tendency between the plateau and the monotonic decrease, a critical shear rate exists, which is able to achieve a shear-thinning behavior. One of the reasons why this occurs is that plate-like particles could be aligned in the circumferential direction.

The result for $c_x = 0.01$ exhibits a large difference from that for $c_x = 0.001$, especially for $\dot{\gamma}_{\text{eff}} < 2.0 \text{ s}^{-1}$, where the kinematic viscosity decreases significantly as the shear rate increases. This occurs because a certain critical shear amplitude exists at $\dot{\gamma}_{\text{eff}} \approx 2.0 \text{ s}^{-1}$ between a gel and a sol states. The constant-viscosity state appears in $2.0 < \dot{\gamma}_{\text{eff}} < 5.0 \text{ s}^{-1}$. From the state at a higher shear rate than 5.0 s^{-1} , the viscosity decreases with an almost constant gradient at $c_x = 0.01$.

For larger concentration cases at $c_x = 0.02$ and 0.025 , the tendency in variation is almost the same as the case for $c_x = 0.01$, but the critical shear rate increases. For

$c_x = 0.03$, the kinematic viscosity decreases monotonically and the range for the constant viscosity disappears (Fig. 9a). The profile for $c_x = 0.05$ appears as a parallel shift of the profiles for $c_x = 0.03$ to the larger $\dot{\gamma}_{\text{eff}}$ side. According to previous research (Rand et al., 1980; Barnes et al., 1989; Goh et al., 2011), a dispersion gel strength increases as the cation concentration increases because of aggregation or flocculation, which is a consequence of enhancements in electrical attractive effects.

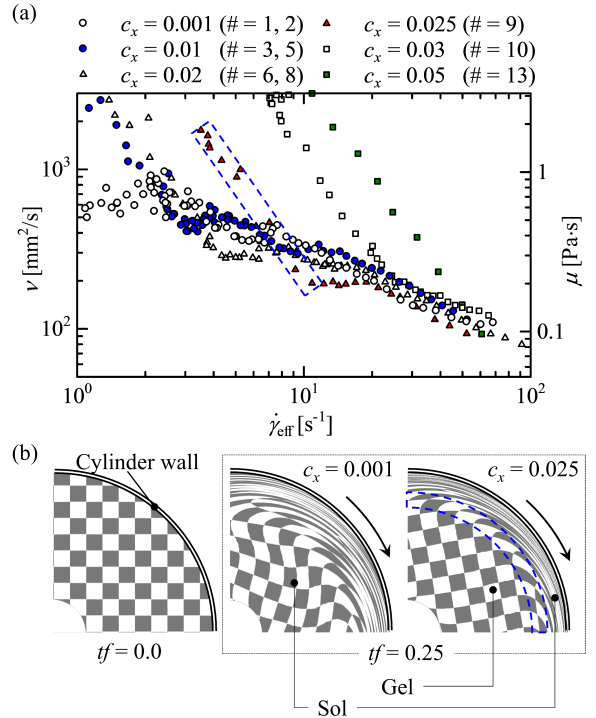


Figure 9: (a) Measurements of shear rate and kinematic viscosity in Mt dispersion, where each symbol indicates oscillation amplitude Θ and NaCl concentration c_x , (b) visualized images of deformation obtained from velocity profiles in $tf = 0.25$ at cases of $c_x = 0.001$, and 0.025

Here, actual deformations of Mt dispersions ($\# = 2, 9$) in unsteady oscillations were visualized using measured u_θ to be compared with the viscosity measurement results. From visualized images (Fig. 9b), the square grids were deformed at all radial positions when $c_x = 0.001$ and $tf = 0.25$. On the other hand, when $c_x = 0.025$ and $tf = 0.25$, the grids kept its shape inside of the cylinder wall from dash-enclosed region. In comparison of the anomalous viscosity regions (dash-enclosed line as shown in Fig. 9) and deformation visualized by azimuthal velocity profiles, the regions placed in intermediate between gel and sol.

When Mt dispersion in stable gel state deforms, responses from the deformation appear as restorative and repulsive forces. Typical responses in viscoelastic media are similar to the mechanical characteristics of a spring. So, the viscoelastic effects appear as an effective Newtonian viscosity in the negative slope, shown in Fig. 9a (dash-enclosed line). Furthermore, the viscoelastic response changes at a critical shear rate because of the breakdown of stable particle networks.

The relations of the effective Newtonian viscosity, the NaCl concentration, and inferable particle networks are schematically considered in Fig. 10. These schematics of the inferable particle networks are based on previous researches (Lagaly and Ziesmer, 2003; Lagaly, 2006). If the particle networks change from the house-of-cards to the band-type structure with increases in salt concentration, the rheological response in different types of particle networks shows a clear difference in viscoelasticity. The experimental results indicate anomalous viscosity conditions that are caused by the house-of-cards structures at low salt concentrations occur at a lower shear rate compared with the band-type structures at high salt concentrations. This means that the viscoelasticity changes with structural transitions that are caused by salt concentrations. The rheological response of the band-type structure, therefore, shows a relatively stronger viscoelasticity than that of the house-of-cards.

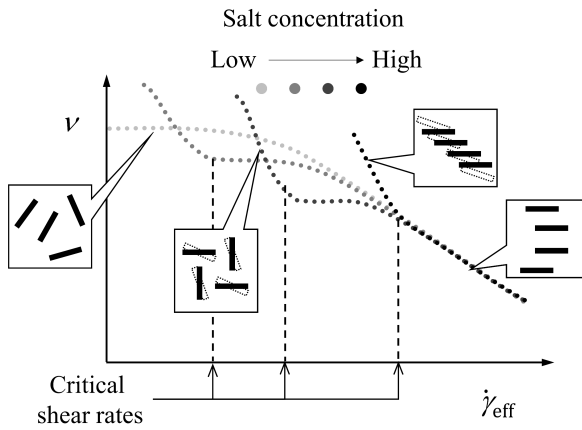


Figure 10: Schematic of relationship between different NaCl concentrations, shear rate, and kinematic viscosity, considering experimental results of Mt dispersion shown in Fig. 9; e.g., the left region of the critical shear rate shows a viscoelastic response, and the right is a Newtonian (plateau region) and shear-thinning (inclination region) viscous response

3.4. Flow curve under shear banding

To produce flow curves from the experimental results, the shear stress, $\tau(r)$, can be calculated from $\nu(r)$ and

$\dot{\gamma}_{\text{eff}}(r)$ by Newton's law of viscosity as:

$$\tau(r) = \mu(r)\dot{\gamma}_{\text{eff}}(r) = \rho\nu(r)\dot{\gamma}_{\text{eff}}(r) \quad (2)$$

where τ and ρ denote the shear stress and density of the test fluid, respectively. From this equation, it is assumed that $\nu(r)$ accommodates with $\dot{\gamma}_{\text{eff}}(r)$ at each "local" radial position, where the shear stress profiles are obtained without torque measurement. The flow curve is a rheological expression, which can represent the fluid characteristics from relations between the shear rate and the shear stress, and especially the shear-rate-dependent viscosity.

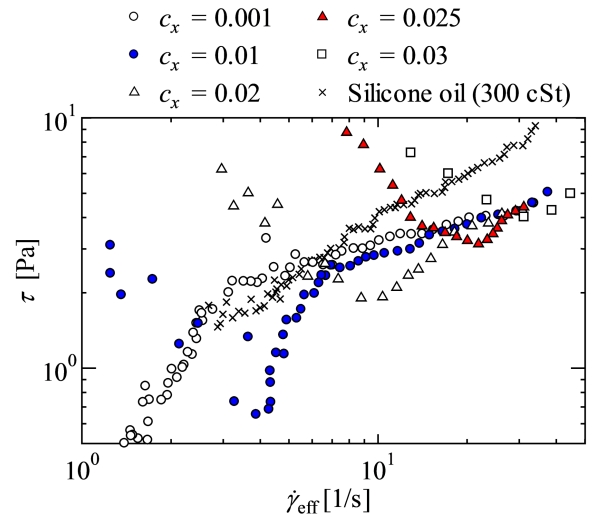


Figure 11: Flow curves of Mt dispersion with different NaCl concentrations (Table 2: # = 2, 4, 7, 9, 10) and silicon oil (300 mm²/s, $T_0 = 25^\circ\text{C}$, $\Theta = \pi/2$ rad)

Flow curves from these experiments are provided in Table 2 (# = 2, 4, 7, 9, 10) and are shown in Fig. 11. The vertical and horizontal axes indicate the shear stress τ and effective shear rate $\dot{\gamma}_{\text{eff}}$, respectively. To compare the difference between Newtonian and non-Newtonian fluids, experimental results of the silicone oil (300 mm²/s) mentioned in § 2.3 were also plotted on the same graph. The silicone oil flow curve has an almost constant gradient for each effective shear rate, $\dot{\gamma}_{\text{eff}}$. Thus, the flow curve that is obtained in this study is identical to that obtained by empirical knowledge.

For $c_x = 0.001$, the shear stress increases monotonically with respect to the effective shear rate, but its slope changes at $\dot{\gamma}_{\text{eff}} \approx 3 \text{ s}^{-1}$. For $c_x = 0.01$, for $\dot{\gamma}_{\text{eff}}$ close to 1 s^{-1} , the shear stress is larger than that at $c_x = 0.001$. It decreases significantly with an increase in $\dot{\gamma}_{\text{eff}}$, and reaches a minimum at $\dot{\gamma}_{\text{eff}} \approx 4 \text{ s}^{-1}$. Beyond this shear rate, the shear stress increases linearly and its slope

changes at $\dot{\gamma}_{\text{eff}} \approx 7 \text{ s}^{-1}$, which is similar to the behavior for $c_x = 0.001$. For larger c_x , the flow curves shift to a higher shear rate and maintain their shape, and thus the shear stresses increase at each turning point, where the slope of the curves changes.

According to previous research using a rotational torque rheometer (Tombácz and Szekeres, 2004), flow curves under similar conditions to the Mt dispersions was estimated. The flow curves, however, are unclear in evaluations of rheological characteristics especially under the condition of $\dot{\gamma} < O(1 \text{ s}^{-1})$ due to limitations on the rotational torque rheometry. Thus, plastic or apparent viscosity has been used to express the rheological properties. The flow curves of Mt dispersion in this report have a negative slope below the critical shear rate. Møller et al. (2008) have already proofed by two different types of measurement that flow curves of yield stress fluid have a negative slope below the critical shear rate, which was used gel formed from an aqueous suspension of charged colloidal particles. The fact of this previous report offers evidence that the flow curves revealed rheological properties of Mt dispersions in lower shear rate. It cannot be evaluated directly using rotational torque rheometry due to influences of shear banding.

In the rotational torque measurements, shear banding phenomena is an unavoidable problem especially when low shear rates are applied to yield stress fluids. According to Møller et al. (2006), flow curves at a lower shear rate than at critical shear rates are difficult to obtain because of instabilities in flow behaviors. In that case, shear banding is somewhat trivially observed when the yield stress of the fluid under scrutiny lies between the maximum and minimum local stresses (Divoux et al., 2016). Then, the shear stresses obtained from torque measurements were outputted as broad stress plateaus in the flow curves. Since the shear banding has variety of expressions and definitions and changes depending on rheological approaches what is focusing on, we consider that shear banding is what the flow curve behaves as typical multiple functions (e.g. Fig. 4 in Divoux et al. (2016)).

Table 3: Estimated results of critical values in shear stress and shear rate

$c_x [\text{mol/L}]$	0.001	0.01	0.02	0.025	0.03	0.04
$\dot{\gamma}_y [1/\text{s}]$	—	3.88	8.78	22.83	31.20	42.15
$\tau_y [\text{Pa}]$	—	0.65	1.91	2.80	4.01	5.04
$\dot{\gamma}_s [1/\text{s}]$	2.55	7.47	18.13	27.41	—	—
$\tau_s [\text{Pa}]$	1.65	2.51	3.50	4.10	—	—

Based on the results, the flow curves are explained as shown in Fig. 12; critical shear rates and stresses lead to

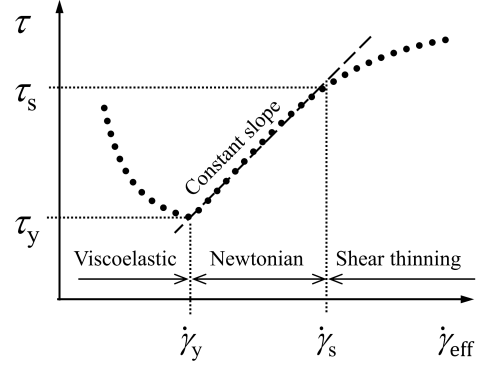


Figure 12: Schematic of flow curve in gelled Mt dispersion divided into three regions, where τ_y , τ_s , $\dot{\gamma}_y$, and $\dot{\gamma}_s$ indicate the yield stress, critical shear stress at the onset of shear thinning, the critical shear rate at the yield stress, and the critical shear rate at the start of shear thinning, respectively

changes in rheological properties. Here, τ_y , τ_s , $\dot{\gamma}_y$, and $\dot{\gamma}_s$ indicate the yield stress, critical shear stress at the onset of shear thinning, critical shear rate at the yield stress, and critical shear rate at the onset of shear thinning, respectively. Assuming that the flow curves follow this tendency, the critical values are estimated as summarized in Table 3.

Viscoelastic effects appear in the results for $\dot{\gamma}_{\text{eff}} < \dot{\gamma}_y$ as shown in Fig. 12; the shear stress profiles decrease significantly with an increasing $\dot{\gamma}_{\text{eff}}$ because of sharp changes in kinematic viscosity shown at the left of the critical shear rate in Fig. 10. In these rheometry measurements, the kinematic viscosity is obtained as a local effective viscosity, which reflects all viscoelastic effects and represents a Newtonian viscosity. Thus, these significant changes on the flow curves at a lower effective shear rate than $\dot{\gamma}_y$ reflect viscoelastic responses.

Important findings in this section are summarized as follows; (1) the rheological properties of the Mt dispersion with a dilute NaCl concentration are a Newtonian and shear-thinning viscosity; (2) the yield stress, τ_y , appears for NaCl concentrations larger than the critical value ($c_x > 0.01 \text{ mol/L}$ in this paper), where τ_y and $\dot{\gamma}_y$ increase with an increase in c_x ; (3) shear-thinning behaviors occur at the critical shear stress and shear rate, τ_s and $\dot{\gamma}_s$, respectively, which increase with an increasing c_x . Considering changes in the flow curves with an increase in NaCl concentration, three important findings are caused by attractive forces of particle networks, which can affect the rheological responses under low-shear-rate conditions; (4) states of Newtonian viscosity are not observed for $c_x > 0.03$ in the studied range of $\dot{\gamma}_{\text{eff}}$.

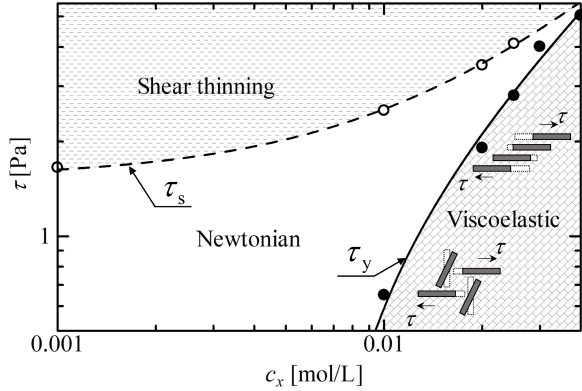


Figure 13: Critical values (τ_s , τ_y) and NaCl concentration

Critical values that were estimated at different c_x are arranged in Fig. 13, which indicates that the Newtonian viscosity state shrinks with an increasing c_x . Viscoelasticity magnifications result because particle networks are considered to deform flexibly like springs above critical salt concentrations without breaking. If this viscoelastic effect is dominant in connections between the particles, states of Newtonian viscosity may disappear. Then, $\dot{\gamma}_s$ becomes unclear for $c_x > 0.03$.

Fluids in which particles are dispersed homogeneously can indicate a Newtonian viscosity. Attractive forces in the particle network increase with an increase in c_x , so homogeneous particle dispersions may be difficult to maintain. Instead, particles maintain networks under unsteady shearing and responses against the shear force emerge as a viscoelasticity. The Newtonian viscosity region shrinks with an increase in c_x as shown in Fig. 13. Hence, a sudden yielding and shear-thinning response against shear forces is observed at $c_x \approx 0.04$. The particle networks can be shifted from the house-of-cards to the band-type structure with an increase in c_x . This occurs because, at $c_x \approx 0.04$, the particle networks of the band-type structure can deform more easily than the house-of-cards structure because of sliding in the shearing direction. A higher critical shear stress results than for the house-of-cards because of increases in the bonding force between particles.

4. Conclusion

Ultrasonic spinning rheometry (USR) was adopted to study the rheological properties of gelled Mt dispersions under low shear rates, which has been difficult to be measured by conventional torque rheometries because of the instability of thixotropic fluid flows and the ap-

pearance of shear banding. Significant findings in these experimental results for Mt dispersions at different NaCl concentration are as follows:

1. Mt dispersion with a dilute NaCl concentration exhibit a Newtonian and shear-thinning response, depending on shear rate.
2. Recovery speed of the particle networks changes with respect to the ionic strength of the dispersion.
3. Critical shear rate and stress at the yielding and shear-thinning point increases with an increase in NaCl concentration.
4. Viscoelastic effects are dominant above a critical NaCl concentration because of the high attractive force in each particle.

The viscoelastic effects are enhanced with an increase in NaCl concentration. At a low shear rate ($O(1 \sim 10 \text{ s}^{-1})$), the Mt particle networks, which have different structures based on the NaCl concentration, can maintain their structure and exhibit stretching behaviors such as that of a spring. For NaCl concentrations that exceed a certain critical value, the state of Newtonian viscosity may disappear because of the viscoelastic effects in connections of each particle. Thus, we speculate that changes in viscoelasticity with changes in NaCl concentrations imply structural transitions from the house-of-cards to the band-type networks.

Because the rheological responses dramatically shift with a change in the microscopic-particle networks, an alternative approach is strongly desired instead of the conventional torque rheometry. USR has a large potential in resolving unexamined issues and completely understanding in the rheological characteristics of Mt dispersions.

Appendix A. Data processing to quantify rheological properties

The flow diagram of the phase-lag analysis for simultaneous evaluations of the shear-rate-dependent viscosity and shear rate profile at each radial position is provided in Fig. A.14. The procedure of this method is explained step by step in this below.

For silicon oil, with the assumption of axisymmetric and unidirectional flows in the azimuthal direction, the spatio-temporal velocity map obtained by the UVP can be converted into a radial-temporal distribution of the azimuthal velocity component from Eq. 1.

The azimuthal velocity distributions obtained at oscillation after 100 s with an oscillation frequency $f = 1.0 \text{ Hz}$ and an amplitude $\Theta = \pi/2 \text{ rad}$ (Fig. A.15a). The

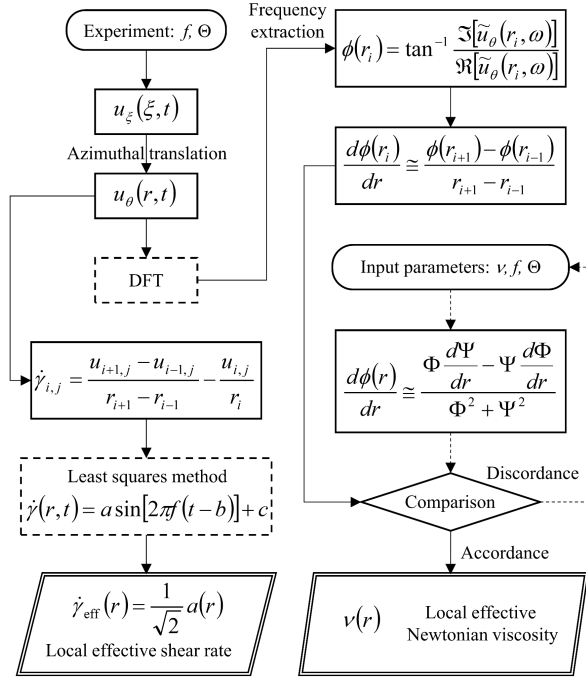


Figure A.14: Schematic outline of the analytical process of USR to evaluate “local” Newtonian viscosity and effective shear-rate profiles

vertical and horizontal axes indicate the radial positions that are normalized by the radius of the cylindrical container, R , and the spin-cycle time. The gray scale contours represent the azimuthal velocity that is normalized by the maximum azimuthal velocity at the cylinder wall. From these distributions, the oscillation of the azimuthal velocity propagates as a damped wave from the wall to the center of the cylinder. From Fig. A.15a, the phase lag in velocity fluctuations from the cylinder wall to the inner parts of the fluid develops into the inner region of the fluid layer with time.

Here, the phase lag $\phi(r)$ from the cylinder wall was calculated by using discrete Fourier transform (DFT) analysis on the spatio-temporal velocity distribution of unsteady shear flows measured by UVP. The phase-lag profiles were subjected to Fourier-transform and frequency extraction at a dominant component (oscillation frequency; $f = 1.0$ Hz) as shown in Fig. A.15b.

To achieve an inverse analysis of the effective Newtonian viscosity, by comparing the experimental and analytical phase lag of the gradient profiles, Tasaka et al. (2015) derived an analytical solution for the spatio-temporal velocity distribution of Newtonian fluids. When an axisymmetric flow field and unidirectional flow in the azimuthal direction are assumed, the Navier-

Stokes equation for incompressible fluids reduces to:

$$\frac{\partial u_\theta}{\partial t} = \nu \left(\frac{\partial^2 u_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r^2} \right), \quad (\text{A.1})$$

where ν is the fluid kinematic viscosity. Given the initial condition, $u_\theta(r, t = 0) = 0$, and boundary conditions, $u_\theta(r = R, t) = U_{\text{wall}} \sin \omega t$ and $u_\theta(r = 0, t) = 0$, an analytical solution is found, where $\omega = 2\pi f$. Eq. A.1 can be reduced to the cylindrical Bessel differential equation by separating variables according to t and r . By inserting the infinite series, the equation can be solved as:

$$u_\theta(r, t) = \frac{U_{\text{wall}}}{\Phi^2 + \Psi^2} \left[(\Phi \Phi_R + \Psi \Psi_R) \sin \omega t + (\Phi_R \Psi - \Phi \Psi_R) \cos \omega t \right], \quad (\text{A.2})$$

where Φ , Φ_R , Ψ , and Ψ_R indicate the infinite series. Details of the derivation are given in Tasaka et al. (2015). The sum identity in Eq. A.2 can be simplified to:

$$u_\theta(r, t) = U_{\text{wall}} \alpha(r) \sin(\omega t + \phi(r)). \quad (\text{A.3})$$

The phase lag, $\phi(r)$, of the synthetic wave is derived as:

$$\phi(r) = \tan^{-1} \frac{\Phi_R \Psi - \Phi \Psi_R}{\Phi \Phi_R + \Psi \Psi_R}. \quad (\text{A.4})$$

And, $\alpha(r)$ is given as:

$$\alpha(r) = \frac{\sqrt{(\Phi \Phi_R + \Psi \Psi_R)^2 + (\Phi \Psi_R - \Phi_R \Psi)^2}}{\Phi^2 + \Psi^2}. \quad (\text{A.5})$$

By differentiating Eq. A.4 in r , the phase-lag gradients are written as:

$$\frac{d\phi(r)}{dr} = \frac{1}{\Phi^2 + \Psi^2} \left(\Phi \frac{d\Psi}{dr} - \frac{d\Phi}{dr} \Psi \right). \quad (\text{A.6})$$

The gradient of the phase lag that is obtained from experiments is calculated from:

$$\frac{d\phi(r_i)}{dr} = \frac{\phi(r_{i+1}) - \phi(r_{i-1}))}{r_{i+1} - r_{i-1}}, \quad i = 1, 2, 3, \dots, \quad (\text{A.7})$$

where the suffixes i and j indicate the position and time, respectively.

The local effective Newtonian viscosity is evaluated quantitatively by comparing the phase-lag gradients between the analytical solutions and the experimental results. Plots of the gradient in the phase lag of the spatio-temporal velocity distribution are shown in Fig. A.15c, where the gray contour represents the gradient profiles calculated from the analytical solutions using the Newtonian viscosity for various kinematic viscosities. The dashed line indicates the given viscosity of the silicon oil ($\nu = 300 \text{ mm}^2/\text{s}$). The effective Newtonian viscosity

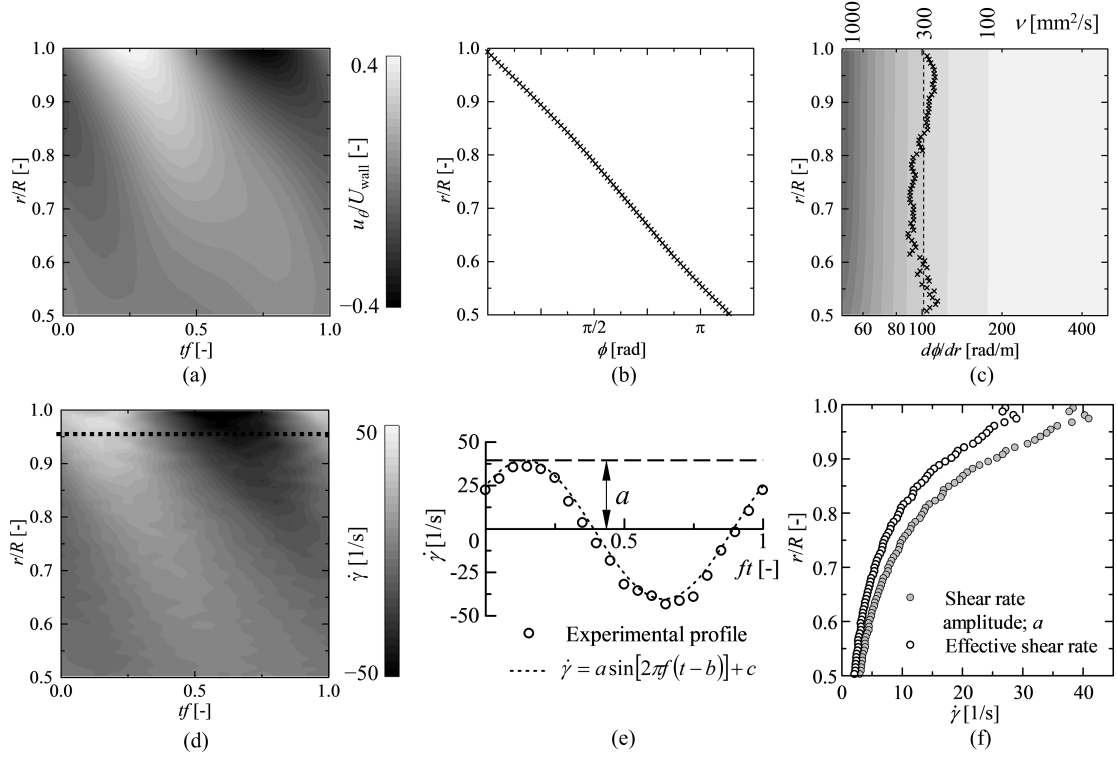


Figure A.15: Example of data processing for velocity distribution of silicon oil ($\nu = 300 \text{ mm}^2/\text{s}$), where the oscillation frequency, amplitude, maximum angular velocity, and temperature are $f = 1.0 \text{ Hz}$, $\Theta = \pi/2 \text{ rad}$, $U_{\text{wall}} = 715.5 \text{ mm/s}$, and $T_0 = 25^\circ\text{C}$, respectively; (a) azimuthal velocity distributions; (b) phase-lag profiles from cylinder wall; (c) gradient of phase-lag profiles, where the contour indicates a kinematic viscosity that is calculated from an analytical solution using Eq. A.6; (d) shear-rate distribution differential calculated from azimuthal velocity distribution (a); (e) shear-rate profiles in local radial position located on a dotted line in (d), where dotted curve indicates results fitted by using the least-squares method; (f) shear rate amplitude, a , and effective shear rate profiles in each radial position

is determined from the local intersections of the gradient profiles with the contour of the corresponding viscosities (Yoshida et al., 2017). If non-Newtonian fluids are selected as test materials, it is possible to determine the local effective viscosities that reflect all viscoelastic effects as the Newtonian viscosity.

In contrast with the conventional torque rheometer, USR can provide shear-rate profiles over a wide range by analyzing the velocity distribution directly in a single measurement. In cylindrical coordinates, the shear rate is given by the azimuthal velocity component as:

$$\dot{\gamma}(r, t) = \frac{\partial u_\theta(r, t)}{\partial r} - \frac{u_\theta(r, t)}{r}. \quad (\text{A.8})$$

The shear rate distribution is derived as:

$$\dot{\gamma}_{i,j} = \frac{u_{i+1,j} - u_{i-1,j}}{r_{i+1} - r_{i-1}} - \frac{u_{i,j}}{r_i} \quad (\text{A.9})$$

with a discretized form of Eq. A.8. The shear-rate distribution in Fig. A.15d is given as:

$$\dot{\gamma}(r, t) = a \sin[2\pi f(t - b)] + c \quad (\text{A.10})$$

at each radial position, where a indicates the amplitude of fluctuation at each radial position. The effective shear rates are given as

$$\dot{\gamma}_{\text{eff}}(r) = \frac{1}{\sqrt{2}} a(r). \quad (\text{A.11})$$

Here, $a(r)$ can be calculated from the least-squares method for sine functions. Effective-shear-rate profiles that are obtained from the fitting result of the least-squares method are shown in Fig. A.15e. These plots coincide reasonably well with the fitting results, and in Fig. A.15f, there is no significant influence of noises that are amplified by the differential calculation.

Acknowledgment

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