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Changes of viscosity in stevensite aqueous dispersions with application of an electric field of the order of a few V/mm

Hiroshi Kimura [a,*], Aya Nakashima [a], Shinya Takahashi [a], Akira Tsuchida [a], Keiichi Kurosaka [b]

[a] *Department of Chemistry, Graduate School of Materials Science, Gifu University, Gifu 501-1193, Japan*
[b] *Chemical Division, Iwaki Laboratories, Kunimine Industries Co., Ltd., Fukushima 972-8312, Japan*

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ABSTRACT

A change in the viscosity of a deionized stevensite aqueous dispersion under an electric field of the order of a few V/mm was recently discovered. The dispersion shows a reversible change of viscosity with the application and removal of an AC electric field. Regarding the mechanism of the reversible viscosity change, it can be considered that the by applying an electric field, the stevensite forms some flocs and a weak network structure, which leads to the increased viscosity, while it returns to a well-dispersed state and its original viscosity by removing the electric field. The viscosity response of the stevensite dispersion for an AC electric field was faster than that of the hectorite dispersion in the same measuring condition. It is speculated that the quick viscosity change would be related to the unique charge distribution on the stevensite, which is known to form a finer network structure than hectorite, beyond a critical concentration of salt. This finding offers great potential for controlling the dispersion state and sedimentation/floatation velocity, by an electric field, of various colloidal particles dispersed in the clay mineral dispersions.

1. Introduction

It has been generally recognized that the plate-like hectorite in water forms a gel, i.e., a "house-of-cards" (Van Olphen, 1977), in the presence of salt beyond a certain concentration (Ishijima et al., 2000; Masuko et al., 2001). The hectorite normally has a positive charge on its face and a negative charge at its edge. The stevensite used in this study also forms a gel beyond a critical salt concentration, and the network structure composed of stevensite is finer and denser than that of hectorite, which was confirmed by Cryo-SEM by Masuko (2006). It can be speculated that the difference in fineness/roughness of the network structure is caused by the difference of the balance of an attractive force between the face-edge connection and a repulsive force between the faces of different particles. In general, a network composed of colloidal particles would have a rougher and looser structure in cases where the attractive force is dominant over the repulsive force. The attractive forces between the stevensite layers, therefore, would be relatively weaker than those of hectorite.

In water, an electrical double layer forms around the stevensite, and the net charge is negative. The electrical double layers are normally very thin; therefore, an electrostatic repulsive force between the stevensite layers is substantially small, and it leads to form a three-dimensional network structure. When the stevensite dispersion is deionized exhaustively, the network structure is collapsed by a strong electrostatic repulsive force between the layers of the stevensite mineral, and it is well dispersed as individual particles or flocs. This deionization process makes the dispersion from gel to sol, which has low viscosity, almost the same as that of water. It should be noted here that recent studies, e.g., by Tanaka et al. (2004) suggest that two types of isotropic disordered nonergodic states exist in colloidal dispersions: glass and gels. The difference between the two is that the nonergodicity, or elasticity, of gel stems from the existence of a percolated network, while that of glass stems from caging effects. The sample dispersion, used in this study, was in a very diluted state and the volume fraction of clay mineral, ϕ, was controlled to be 0.001. Therefore, it is highly plausible that the glassy state does not exist under this condition.

A control technique of dispersion state, fibration, and alignment, by an electric field, of a dispersed material has received increasing attention in recent years (Paineau et al., 2009; Dozov et al., 2011; Nakato et al., 2011, 2014; Shen et al., 2014). A change in the viscosity of a deionized aqueous dispersion of hectorite with the application and removal of an electric field of the order of several V/mm was recently discovered by Kimura et al. (2013). This suggests a mechanism by which, when an electric field is applied, hectorite in water forms a network-like structure. An AC electric field (0.001–0.004 Hz) was favorable to being able to reverse the viscosity when the electric field was removed (Kimura et al., 2014). In the case of a DC electric field, a gel-like film adhered to the positive electrode, which caused an incomplete recovery of the viscosity. The viscosity change of the hectorite dispersion caused by applying an electric field could be attributed to deformation of the electrical double layers, which effectively extinguished the

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* Corresponding author. Tel./fax: +81 58 293 2622.
E-mail address: kimurah@gifu-u.ac.jp (H. Kimura).

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electrostatic repulsive force between hectorites. This idea can be applicable to other smectite clay minerals. We focused on stevensite in this study. The viscosity change of stevensite dispersions by the application and removal of an electric field was investigated.

2. Materials and methods

2.1. Stevensite samples

The synthesized stevensite used in this work was plate-like, ca. 40 nm in diameter, 1 nm in thickness, and 2.5 g/cm^3 in specific gravity. The chemical formula of stevensite is $(Ca_{0.5},Na)_{0.33}(Mg,Fe)_3Si_4O_{10}(OH)_2 \cdot nH_2O$. The clay mineral was gently dispersed into purified water using a magnetic stirrer, with the coexistence of ion-exchange resins (AG501-X8 (D), 20–50 mesh, Bio-Rad Laboratories, Inc.) to collapse the network structure and disperse stevensite individually or in the form of some flocs. The dispersion was stored for at least 12 months. The water used for sample preparation was purified with a Milli-Q reagent grade system (Milli-Q Advantage, Millipore Co.). The volume fraction of stevensite mineral, ϕ, was 0.001 (weight fraction, $w = 2.5$ g/L), at which a large viscosity increase of hectorite dispersion had been observed in our previous study. The ζ-potential of stevensite was measured to be ca. −45 mV. The net charge of the stevensite was negative.

2.2. Rheological measurements under an electric field

A modified coaxial-type rheometer (Rheosol-G2000W-GF, UBM Co., Ltd.) capable of applying an electric field was used. The torque was detected from the twist angle of the torsion wire connected to the inner cylinder. In this study, the diameter of the wire was 0.3 mm, which made sensitive ER measurements possible. An outer cup and an inner cylinder were made of stainless steel. The outer cup and inner cylinder played the role of electrodes in applying a homogeneous DC or AC electric field to the dispersions using a synthesized function generator (FG110, Yokogawa Meters & Instruments Corp.) The gap between the inner cylinder and the outer cup was 0.5 mm. The shear rate, $\dot{\gamma}$, was controlled by the rotational speed of the outer cup. In our stress–strain $\alpha - \gamma$ measurements, the $\dot{\gamma}$-values increased slowly and linearly, and the values of the acceleration of the shear rates, $d\dot{\gamma}/dt$, were 1.8×10^{-6} s^{-2}, 1.8×10^{-5} s^{-2}, and 1.8×10^{-4} s^{-2}. Flow curves and stress–strain measurements were completed within 2 h, after the dispersion was set. Under this situation, almost no time-dependent change of the rheological properties was observed. Regarding an AC electric field, the effective electric field, V_{eff}, was given by $V_{eff} = V_p / \sqrt{2}$. Here, V_p is the peak electric field of sinusoidal voltage. The effective electric field strength, E_{eff}, was 8.0 V/mm at a maximum. All of the measurements were made at 25 °C.

3. Results and discussion

First, the shear stress change by applying and removing an electric field was examined for the stevensite aqueous dispersions at E and $E_{eff} = 8.0$ V/mm. (See Fig. 1). Without an electric field, the shear stress did not show any change during the measurement. When a DC electric field was applied, the shear stress gradually increased and reached a steady value through a maximum value. Then, as the electric field was removed, the shear stress showed a maximum again and gradually decreased, although it did not recover to the original value before the electric was field applied. Under an AC field at $f_E = 0.001$ Hz and 0.005 Hz, the shear stress oscillated sinusoidally at twice the speed of the electric field strength. When the electric field was switched off, the shear stress quickly returned to the original stress value. The magnitude of electrically-induced shear stress decreased as the f_E raised, and the shear stress did not show any change with the application of an electric field at $f_E = 0.001$ Hz.

Fig. 2(a) depicts the dependence of the DC electric field strength on the flow curves for stevensite aqueous dispersion in a deionized state. In the absence of the electric field, the dispersion was a Newtonian-like fluid, and the stress was very close to that of water. When the electric field of 2.0 V/mmDC was applied, the shear stress increased slightly while maintaining the Newtonian-like property. At $E = 4.0$ V/mmDC, the shear stress greatly increased, and the dispersion showed a solid-like property. At a shear rate larger than ca. 50 s^{-1}, the dispersion showed a Newtonian-like behavior, and the shear stress was very close to the water's value. It should be noted here that the stress values at high shear rates were lower than those at a lower electric field strength, $E = 2.0$ V/mmDC. In this measuring condition, an adhesion of stevensite on the positive electrode would be dominant. In this case, a slipping layer of water-rich region would form in the vicinity of the outer cup of rheometer. At higher field strengths, $E = 4.0$ and 6.0 V/mmDC, the shear stress further increased, and the dispersion showed a solid-like behavior, even at high shear rates.

Next, the flow curves for various salt concentrations, in the absence of an electric field, were obtained (Fig. 2(b)). At salt concentrations [NaCl] higher than 0.01 M, the shear stress clearly increased as the salt concentration increased and saturated at [NaCl] = 0.1 M. The increase of shear stress would be due to the formation of a house-of-cards structure in the presence of salt, because of weakening of electrostatic repulsive force between the stevensite mineral (Kimura et al., 2011).

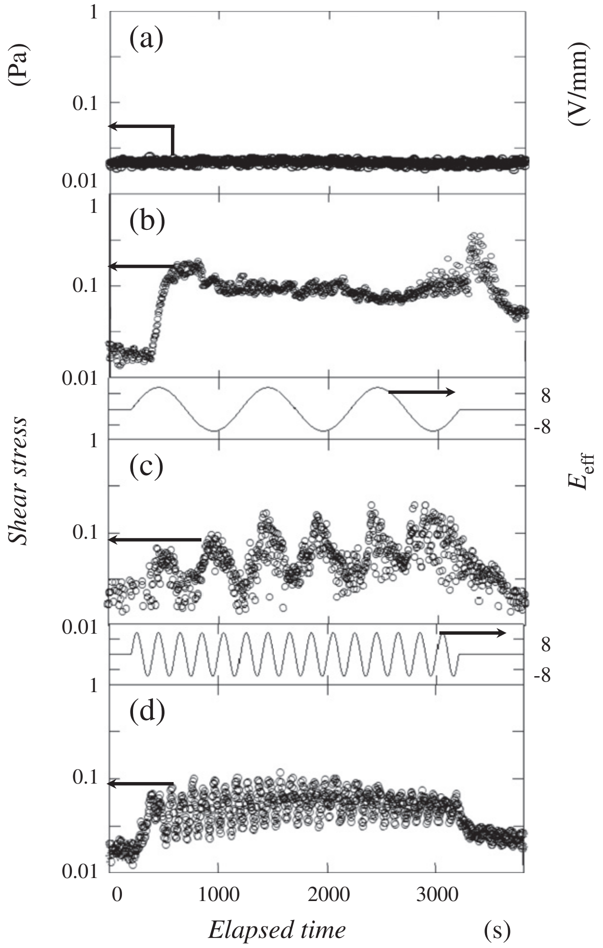

Fig. 1. Change in shear stress of stevensite aqueous dispersion with the application and removal of an electric field. $\dot{\gamma} = 19$ s^{-1}. (a) In the absence of an electric field, (b) a DC electric field, $E = 8.0$ V/mm, (c) an AC electric field, $E_{eff} = 8.0$ V/mm, $f_E = 0.001$ Hz, (d) $f_E = 0.005$ Hz.