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Flow Properties of Montmorillonite Suspended in Water with Surfactant

Tsugitoshi OGURA,* Masazumi TANOURA, Kiyoshi TATSUHARA, and Akio HIRAKI†
Advanced Technology Research Center, Mitsubishi Heavy Industries, Ltd.,
8-1, Sachiura, 1-Chome, Kanazawa-ku, Yokohama 236
† Nagasaki Research and Development Center, Mitsubishi Heavy Industries, Ltd.,
717-1, Fukahori-machi, 5-Chome, Nagasaki 850-91

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The flow properties of montmorillonite, one of the main clay components in coal, were studied in water suspensions to clarify the origins of the Bingham flow properties of coal water slurry (CWM) in the presence of a surfactant. The addition of anionic surfactants, such as sodium poly(isoprenesulfonate) and sodium polycarbonate, significantly decreased the apparent viscosity and Bingham yield value of the montmorillonite suspension, although the latter value never became zero, even when a large quantity of surfactant was added. The amount of water bound to montmorillonite particles, measured using ^{1}H NMR, was found to increase with the addition of a surfactant. The Bingham yield value and the relative viscosity of the montmorillonite suspension were described by Michaels' equation, $\tau_B = A(S\phi - S\phi_0)^3$ (Eq. 6), and by the modified Brinkman's equation, $\eta_r = (1 - S\phi)^{-k}$ (Eq. 8), respectively. In both equations, the sum volume of montmorillonite particles and its bound water ($S\phi$) is correlated to the flow properties through constants A and k. A reduction of both A and k suggests two different actions of the anionic surfactants in the montmorillonite suspension. A decrease in the A value indicates a reduction of the strength of the aggregate networks of montmorillonite at a low shear rate, while a decrease in the k value shows that the shape of the effective montmorillonite particle becomes more spherical due to an increase of bound water.

The coal water slurry (CWM) of a highly-loaded suspension must satisfy the requirements of low viscosity at high coal concentration (65%), high dispersion and storage stability. The present authors have found that the surfactant is adsorbed on the surface of coal particles and reduces the amount of the water bound to the coal particles. These lead to a high dispersion and a high concentration of coal particles in the slurry without a significant increase in viscosity.[1)] On the other hand, the stability depends on the yield value of the CWM suspension, which is due to the high dispersion of montmorillonite particles in CWM.[2)]

Coal particles alone without particular mineral[2)] do not exhibit any yield value, even in the presence of such a surfactant as the polymer-type anionic surfactant developed for CWM. The authors have also reported that although kaolinite, another coal mineral, provides yield value to its slurry, the surfactant reduces the yield value to zero.[2)] In contrast, the montmorillonite particles can provide yield value even when a surfactant is used, though the yield value changes in the presence of the surfactant. Based on such findings, they succeeded in stabilizing highly-loaded CWM of a particular coal of low mineral content by adding bentonite as well as a surfactant.

Mineral matter in coal has been studied in relation to deashing and controlling fly ash from CWM fuel. However, the role of mineral matter on the properties of CWM has been scarcely studied, although there are some papers which describe the effects of dissolved minerals on the properties of CWM and the adsorption of surfactants.[3,4)] The addition of attapalgite clay to stabilize CWM was also examined.[5,6)]

The authors have already reported that in highly-loaded aqueous suspensions of carbon black and heavy oil, the effective volume of the suspended particle, which defines the viscosity of the suspension, is the sum of its actual volume and the volume of water bound to them.[1,7)] However, the viscosity of a clay suspension has been supposed to be represented by the effective volume of the clay particles with the water bound to them,[8)] a quantitative determination of the bound water in a suspension, to determine the fluid properties of the suspension, has never been attempted.

In the present study, the flow properties of a water suspension of sodium montmorillonite in the presence of a surfactant were analyzed in order to elucidate the Bingham flow behavior of CWM. Focusing particularly on the bound water of the mineral particles, its molecular mobility was measured with ^{1}H NMR, based on relaxation in the magnetic field. Such an approach has proved to be very fruitful by the authors in describing the viscosity of a highly-loaded water suspension of heavy oil droplet with its effective volume including the bound water.[7)] The fluid properties of the montmorillonite suspension, particularly the Bingham yield value and the pseudo-viscosity, were analyzed using the effective volume.

Experimental

Test Sample. Kunipia-F (Kunimine Kogyo Co.), a highly purified sodium montmorillonite, was used. Its cation exchange capacity was reported by the maker to be 115 mequiv/100 g. Two types of polymer-type anionic surfactants, poly(sodium isoprenesulfonate) (POS: JSR Co.) and sodium polycarbonate (KM-7: Kao Corp.) were selected (described in previous papers[1,2)]). The latter was effective in decreasing the apparent viscosity of Taiheiyo CWM, which has a considerable amount of montmorillonite.[2)]

Suspension Preparation. It is well known that a suspension of montmorillonite is a thixotropic fluid, and that its fluidity strongly depends on the history of any shearing applied to the suspension (softening and recovery). It is, therefore, important to measure the viscosity of the suspension by strictly adjusting the history of the mechanical treatment.[10)] About 300 g of montmorillonite–water suspension was prepared in a plastic bottle. Montmorillonite powder was added to the water or to water containing a surfactant, then simply stirred and kept standing for over three days to allow the montmorillonite to swell sufficiently. The viscosity of the suspension was measured immediately after high-velocity mixing with a TK-Homomixer (Tokusyu-Kika Kogyo Co. model M) at 7000 rpm for 15 min. The apparent viscosity of the suspension at 100 s^{-1} of the decreasing shear rate stayed nearly constant over a period of 1 h after mixing. Immediately after the viscosity measurement, its magnetic relaxation was determined using ^{1}H NMR. The pH value of the suspension was in the range of 9.09 to 9.71.

Properties of the Suspension. The viscosity of the suspension was measured at 25 °C with a mode of $t_1=2$ min, $t_2=2.5$ min, and $t_3=2$ min with varying the shear rate from 0 to 150 s^{-1} using a Haake double-cylinder-type rotary viscometer (rotor MV-1P and MV-2P, measuring head MK-500). The ^{1}H NMR spin–spin relaxation time (T_2) was measured with a JEOL FT-NMR EX-90, using the Carr-Percell-Meiboom-Gill (CPMG) pulse sequence.

Results

Rheological Properties. A typical relationship between the shear stress and shear rate of the montmorillonite suspension is schematically shown in Fig. 1. A change in the shear stress with an increasing shear rate is represented by a dotted line, and that with a decreasing shear rate is represented by a solid line. Most of the suspensions in this study showed the Bingham fluid properties and, thus, the yield value and viscosity of each suspension were obtained according to the following definitions.

The Bingham yield value (τ_B;Pa) was obtained by extrapolating the linear portion of the solid line to the intercept. The apparent viscosity (η_{ap};cP) was obtained from Eq. 1 using the shear stress value (τ_{100}) at the shear rate of 100 s^{-1} of the solid line. The pseudo-viscosity (η_p;cP) was also obtained from the slope of the linear portion of the solid line.

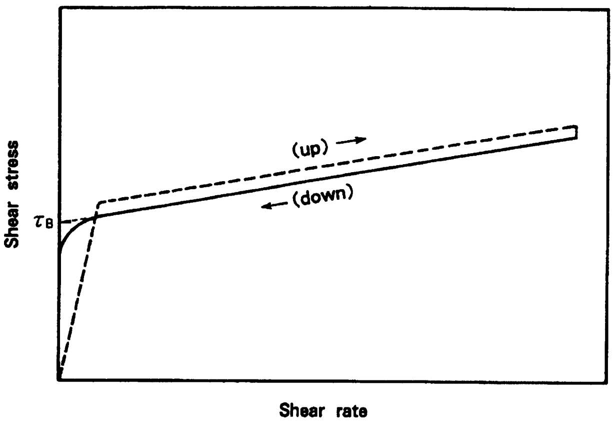

Fig. 1. Schematic rheogram of the montmorillonite suspension.

$$\eta_{ap} = \tau_{100} \times 10. \tag{1}$$

The viscosity of water was reported to be 0.890 cP (1 cP$=10^{-3}$ Pa s) at 25 °C. The viscosity of the surfactant solution (η_a;cP) was measured at 25 °C, while varying the surfactant concentration (C_a). The viscosity was correlated to the concentration of the surfactant by Eq. 2 for POS and Eq. 3 for KM-7, respectively:

$$\eta_a = 0.297 \times C_a + 0.890 \tag{2}$$

and

$$\eta_a = 0.191 \times C_a + 0.890. \tag{3}$$

The relative viscosity (η_r;-) was obtained from the following equation using η_p and η_a:

$$\eta_r = \eta_p/\eta_a. \tag{4}$$

The relationship between the apparent viscosity and the montmorillonite concentration and that between the yield value and the montmorillonite concentration are illustrated in Figs. 2 and 3, respectively. Both POS and KM-7 decreased the apparent viscosity and yield value of the suspension. The decreases in both values with KM-7 were always larger than those with POS, indicating the superiority of the former surfactant.

The effects of the POS and KM-7 concentrations on the fluidity of the montmorillonite suspension are shown

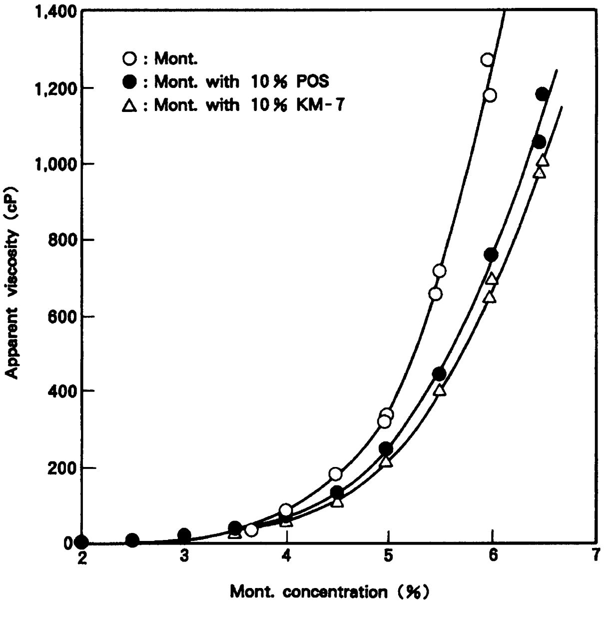

Fig. 2. Change of the apparent viscosity with the concentration of montmorillonite.

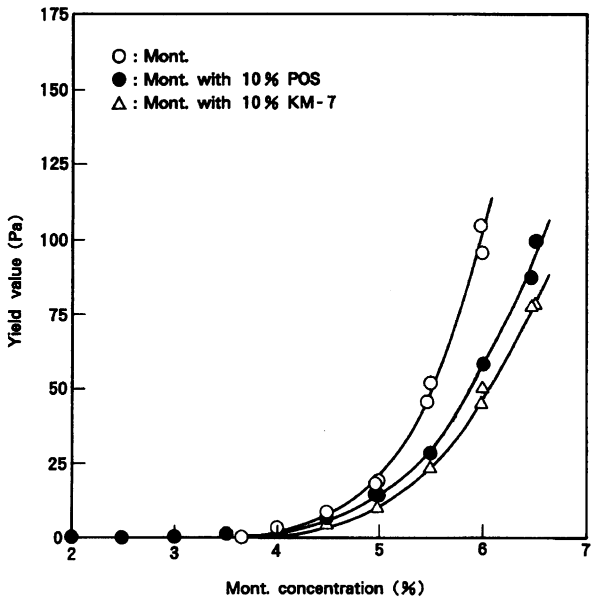

Fig. 3. Change of the yield value with the concentration of montmorillonite.

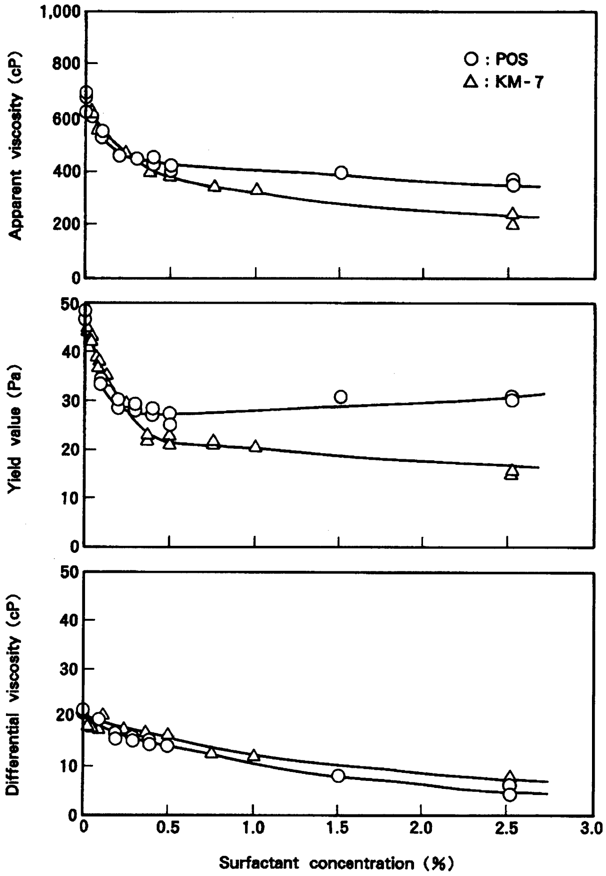

Fig. 4. Change of the rheological property with the concentration of surfactant (5.5% Montmorillonite suspension).

in Fig. 4. The apparent viscosity and yield value rapidly decreased with increasing POS concentration and became constant above 1.0% of POS. On the other hand, these values with KM-7 still decreased gradually above 1.0% of KM-7 after a rapid initial decrease. The pseudo-viscosities gradually decreased with increased concentration of both surfactants. The decrease with POS was larger than that with KM-7, since the decrease of the yield value with POS was less than that with KM-7. From these findings, it is inferred that such surfactants as POS and KM-7 mainly affect the yield value of the montmorillonite suspension, and that the effect with KM-7 is larger than that with POS.

Bound Water. Figure 5 shows the relationship between the ^{1}H spin–spin relaxation time (T_2) and the volume ratio of water/solid. This linear relationship indicates that the increase in the solid concentration decreased the water mobility, since the short T_2 indicates the immobility of water molecules.[11] The correlation coefficients in this figure are 0.96 for the suspension of montmorillonite alone and 0.99 for the suspensions prepared with surfactants. The relaxation time of the bound water molecules was estimated to be 2.6_8 ms with montmorillonite alone and 2.7_2 ms with the surfactant by extrapolating these linear lines to the intercept.

Discussion

When two types of water molecules with different mobilities (free and bound states) exist in the same suspension and the exchange reaction between them is fast, the mole fraction of the bound water (p_b) is represented by the following equation, as presented in a previous paper:[1]

$$p_b = (1/T_{ob} - 1/T_f)\,/\,(1/T_b - 1/T_f)\,, \qquad (5)$$

where T_{ob} is the measured relaxation time of the suspension; T_f and T_b are the relaxation times for the free

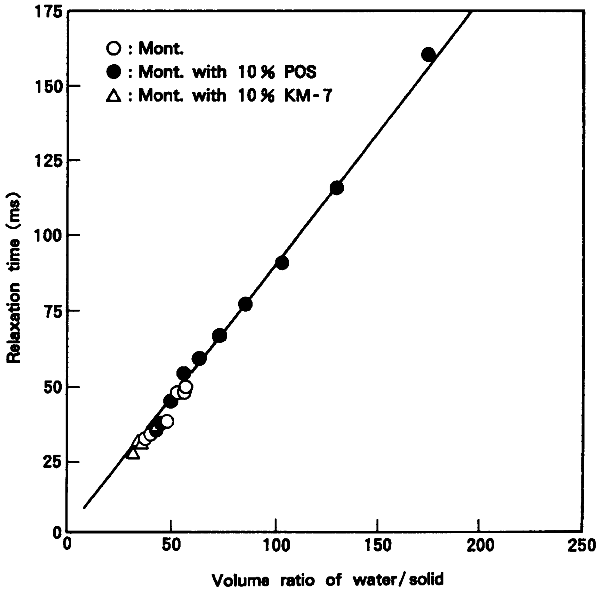

Fig. 5. Relation between the relaxation time and the volume ratio of water/solid.

and bound states, respectively. T_f was found to be 3.60 s from a measurement of the distilled water, and the values for T_b were obtained from Fig. 5.

Using Eq. 5, the amounts of bound water in suspension with or without surfactant were obtained and plotted against the montmorillonite concentration in Fig. 6. Regardless of the presence of a surfactant, the amount of bound water increased linearly with an increase in the montmorillonite concentration. The montmorillonite particle with a surfactant carried more bound water than those without a surfactant. The amount of bound water in a suspension of montmorillonite alone was found to be $1.2_8 \pm 0.04$ g/g-montmorillonite using the linear relationship shown in Fig. 6.

The effect of the surfactant on the amount of bound water in shown in Fig. 7, where 5.5% montmorillonite suspensions were prepared with various concentrations of surfactants. The amount of bound water increased linearly with the increase in the concentration of both POS and KM-7, although both T_b values of the suspensions with surfactants and without a surfactant are almost the same as that obtained from Fig. 5. The ratio of bound water to the surfactant by weight is found to be $1.2_3 \pm 0.08$ g/g-surfactant with both surfactants.

The sodium montmorillonite particle in the suspension was reported not to adsorb the high molecular weight lignosulfonate[12)] and polymer-type anionic surfactants used in a series of our studies.[2)] Nevertheless, the surfactant increased the effective volume of montmorillonite by increasing the amount of bound water; the surfactant decreased the apparent viscosity and yield value. Because the amount of adsorbed surfactant on the montmorillonite particle was obtained by the difference between the added and remaining surfactant in the filtrate of the suspension[12,13)] and the montmorillonite was dispersed as very fine particles in the dilute suspension,[15)] it is necessary to measure the surfactant in situ in order to clarify the action of the surfactant in the montmorillonite suspension.

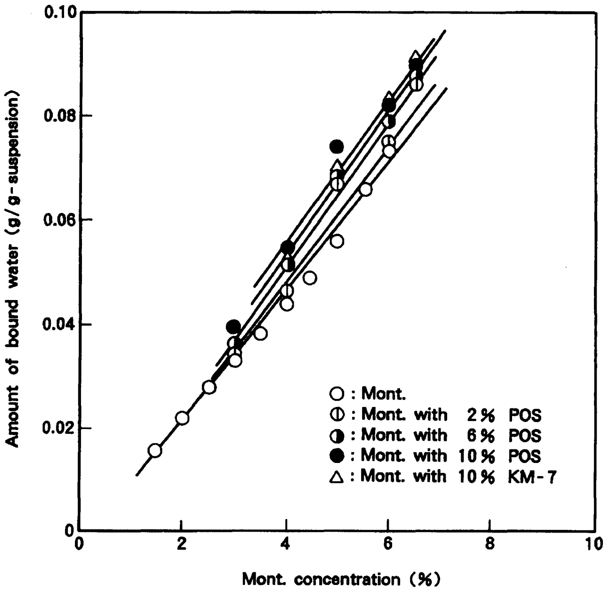

Fig. 6. Relation between the amount of bound water and the concentration of montmorillonite.

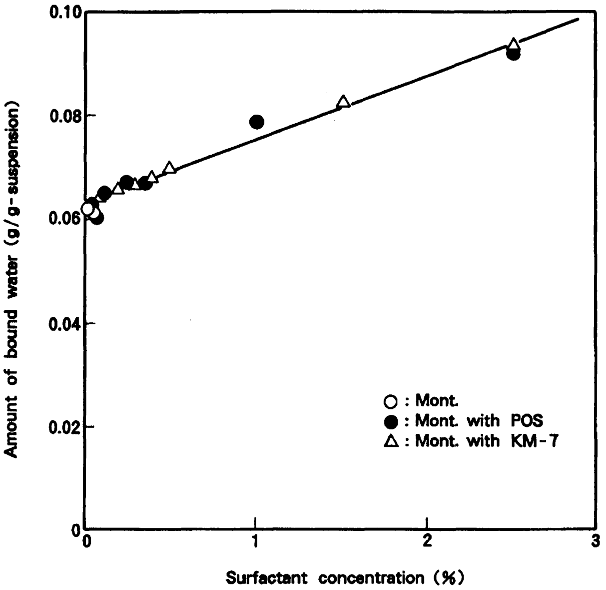

Fig. 7. Effect of the surfactant concentration on the amount of bound water.

In this study, the prepared montmorillonite suspension was kept for over three days to allow for its sufficient swelling; the viscosity of the suspension was then measured immediately after high-velocity mixing, which was applied to break up the aggregates of montmorillonite. Therefore, the montmorillonite may disperses in fine particles with bound water which was obtained when using ^{1}H NMR. The yield value of such a continuous network of the fine particles at a low shear rate can be expressed according to Michaels:[16)]

$$\tau = A\,(S\phi - S\phi_0)^3\,, \tag{6}$$

where ϕ and ϕ_0 are the volume fraction of montmorillonite, the minimum volume fraction required to form a continuous aggregate network, respectively; A is a constant. S is a coefficient expressed as the sum of the volume of montmorillonite and bound water; $S\phi$ is thus an effective volume fraction of montmorillonite. Equation 6 can be modified to

$$\tau^{1/3} = A^{1/3}\,(S\phi - S\phi_0)\,. \tag{7}$$

According to Eq. 7, $\tau^{1/3}$ is plotted against the effective volume of the solid particle in Fig. 8. Linear relationships between $\tau^{1/3}$ and the effective volume were obtained in accordance with Eq. 7. The correlation coefficients obtained by a least-squares method were 0.99 with montmorillonite alone, 0.98 with 10% POS, and 0.99 with 10% KM-7. The respective minimum volume fraction and constant A calculated from these rela-

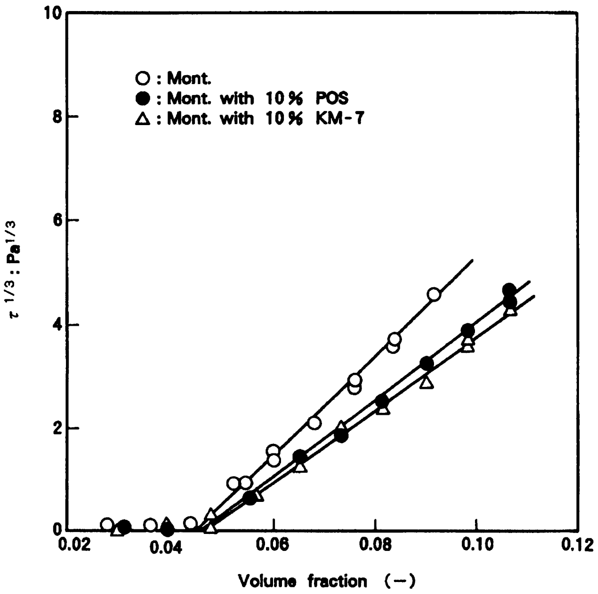

Fig. 8. Relation between $\tau^{1/3}$ and the volume fraction of solid particle.

tionships are 0.04_5, 0.83×10^6 for montmorillonite alone, 0.04_6, 0.33×10^6 for 10% KM-7, and 004_7, 0.42×10^6 for 10% POS, respectively. The surfactant effected very little the minimum volume fraction required to form a continuous aggregate network at a low shear rate.

The relative viscosity can be expressed by the volume fraction of the solid particle including the volume of water bound to them, as follows:

$$\eta_r = (1 - S\phi)^{-k}, \qquad (8)$$

where k is a shape factor. The values of k calculated by the least-squares method are found to be 62 for montmorillonite alone, 50 for 10% POS, and 50 for 10% KM-7, respectively.

The effect of the surfactant on fluidity can be discussed based on constants A and k. According to Michaels,[16] constant A in Eq. 6 is proportional to the bonding force among the suspended particles and inversely proportional to the average diameter of the suspended particles. When the bonding force of the network structure of montmorillonite in its suspension is assumed to be 100, by assuming that the average diameter of montmorillonite particle of each suspension is same, that would be 40 with 10% KM-7 and 50 for 10% POS, respectively. It is inferred that the anionic surfactant decreases the bonding force of the edge-to-face bond of the plate-like montmorillonite particles in the network structure due to its presence in the neighborhood of the edge of montmorillonite.

10% usage of the surfactant decreased the constant k in Eq. 8 from 62 to 50, and increased the ratio of the effective volume to montmorillonite volume from 4.41 to 4.75. The bound water of such an amount may alter the shape of the suspended particles to be more spherical, thus decreasing the value of k, the shape factor.

The montmorillonite, a major component of mineral matter in coal, gives the yield value which is required to endow a storage stability to CWM, even in the presence of the surfactant. It was clarified that one of the causes of the CWM yield value was a continuous network formation of the suspended montmorillonite. It is inferred that very fine particle of the montmorillonite are separated from coal in the grinding step of the CWM-producing system, and that these particles form a continuous network at the low-shear region. The surfactant decrease the bonding force in the network structure of the suspended montmorillonite, thus reducing the yield value of the CWM. On the other hand, the surfactant increases the effective volume fraction of suspended solids, which increases the pseudo-viscosity of the suspension. However, the former effect of the surfactant is larger than the latter effect. This situation results in a lower apparent viscosity of the CWM. The difference in the effect of the surfactant on the yield value is mainly observed in the bonding force of the network.

It is well known that the fluidity of thixotropic fluids, such as a montmorillonite suspension, is depend on the characteristic properties of the suspension and the measuring method. Is this study the viscosity of the montmorillonite suspension was measured on the basis of the measuring method for a practical CWM in order to correlate to a practical CWM. However, the differences between the effects of POS and KM-7 shown in Figs. 2 and 3 were not fully explained by the changes in effective volume, bonding force, and shape factor. In order to obtain a detailed knowledge concerning the montmorillonite suspension, it is necessary to monitor how the strain of the suspension behaves as a function of time, because a difference between KM-7 and POS was clearly observed in the change of the rheograms at a low shear rate when the shear rate was increasing.

On the basis of the above discussion, the behavior of montmorillonite suspensions with two types of anionic surfactants, sodium poly(isoprenesulfonate) and sodium polycarbonate, which had been developed for CWM, were clarified as follows:

(1) The amount of bound water in a suspension of montmorillonite alone was found to be $1.2_8\pm0.04$ g/g-montmorillonite by ^{1}H NMR.

(2) The amount of bound water increased with an increase in the use of both POS and KM-7. The ratio of bound water to surfactant by weight is found to be $1.2_3\pm0.08$ g/g-surfactant.

(3) Surfactants reduce the bonding force among the particles at low shear rates, decreasing the yield value of the suspension. When the bonding force of the net work structure of montmorillonite in its suspension is defined to be 100, that would be 50 and 40 with 10% of POS and KM-7, respectively.

(4) The usage of 10% surfactant decreased the shape

factor (k) from 62 to 50, thus reducing the differential viscosity of suspension.

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References

1) T. Ogura, M. Tanoura, and A. Hiraki, in submission.

2) T. Ogura, M. Tanoura, and A. Hiraki, *Bull. Chem. Soc. Jpn.*, **66**, 1633 (1993).

3) R. Kaji, Y. Muranaka, H. Miyadera, and T. Hishinuma, *Nenryo-Kyokai-Shi*, **66**, 842 (1987).

4) L. Y. Sadler and K. G. Sim, "12th International Conference on Slurry Technology," New Orleans, U.S.A., 1971, Abstr., p. 271.

5) R. J. Purcell, Jr., and E. W. Sawyer, Jr., "6th International Symposium on Coal Slurry Combustion and Technology," Orlando, U.S.A., 1984, Abstr., p. 423.

6) N. Nakabayashi, N. Sato, H. Ito, S. Tatsumi, Y. Kajibata, and S. Takao, "8th International Symposium on Coal Slurry Fuels Preparation and Utilization," Orlando, U.S.A., 1986, Abstr., p. 55.

7) M. Tanoura, K. Tatsuhara, A. Hiraki, and T. Ogura, "Proceedings of First World Congress on Emulsion," France (1993), in submission.

8) K. Wada, Y. Nitawaki, and K. Egashira, *Clay Sci.*, **5**, 313 (1981).

9) K. Egashira, *Clay Sci.*, **5**, 137 (1978).

10) S. Ito, T. Iwasaki, and K. Torii, *Nendo-Kagaku*, **28**, 175 (1988).

11) H. Uedaira, M. Ikura, and H. Uedaira, *Bull. Chem. Soc. Jpn.*, **62**, 1 (1989).

12) M. Koyama, *Nihon Kagaku Kaishi*, **1974**, 847.

13) T. Ogura, M. Tanoura, and A. Hiraki, *Bull. Chem. Soc. Jpn.*, **66**, 1343 (1993).

14) T. Ogura, M. Tanoura, and A. Hiraki, *Bull. Chem. Soc. Jpn.*, **66**, 1350 (1993).

15) Xiaofu Zhao, Kohei Urano, and Sadao Ogasawara, *J. Chem. Soc. Jpn.*, **1989**, 209.

16) A. Michaels and J. Bolger, *Ind. Eng. Chem. Fundam.*, **1**, 153 (1962).