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The Role of Surfactants in Achieving Highly Loaded Aqueous Suspensions of Organic Particles

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 behaviors and roles of anionic surfactants in highly loaded aqueous suspensions of carbon black were investigated in order to clarify how they increase the achievable concentration while maintaining the apparent viscosity of a suspension. In a suspension, organic particles and the water bound to them define the effective volume of the solid particles, which determines the relative viscosity, as formulated by the Brinkman equation. The surfactant was found to be adsorbed on the organic particles, decreasing the amount of bound water, as measured by ^{1}H NMR. The result of the study was that a surfactant in a highly-loaded aqueous suspension plays the following three roles at the same time: (Role-1) The decrease in the bound water due to the surfactant allows an increase in the achievable solid concentration at a fixed viscosity by decreasing the effective volume fraction of solids in a suspension. (Role-2) The adsorption of the surfactant was also found to be necessary to inhibit the aggregation of dispersed particles; if, however, the amount of surfactant is insufficient, aggregation can occur even with mechanical stirring, owing to a hydrophobic interaction among the particles. (Role-3) The surfactant influences the viscosity of the suspension through the "k" factor of the Brinkman equation. Surfactants with larger molecules were found to give a larger k value, thus increasing the viscosity, probably because of their effects on the interactions between the dispersed particles.

Though a coal–water slurry (CWM) is one of the most economical fluid fuels, a basic understanding is still required for its better application. The present authors have reported the necessary properties of a CWM, such as the achievable coal concentration, the apparent viscosity, and the yield value.(1,2) Such properties were found to be subject to the nature of the organic and inorganic portions of coal in their respective interactions with the surfactant.(3) So far, the respective mechanisms by which such properties are developed have not been fully clarified. For example, the mechanism by which a surfactant can increase the achievable coal concentration at a fixed apparent viscosity is far from being established.

Dispersing agents, such as surface-active agents, have been used to disperse fine particles of hydrophobic materials in aqueous solution. In general, there are three principles for dispersing fine particles in water:(4) utilizing the repulsions between the particles with their zeta potentials or the steric hindrance of the adsorption layer, and the reduction of hydrophobic linkages among dispersed particles.

Although it has been explained why surfactants increase the dispersion of solid particles, it is not yet clear why they can increase the concentration of a suspension without an increase in the viscosity. The more hydrophilic groups of coal have been recognized by the present authors to lead to lower achievable coal concentrations of CWM.(2,5) Effective surfactants have been found to increase the achievable coal concentration, being adsorbed on the surface of the coal particles at their hydrophobic parts, and thus modifying them to be hydrophilic.(1) Hence, the relationship between the properties of coal and the achievable coal concentrations does not appear to be simple.

Several papers have been published concerning the dispersion of carbon black in aqueous solution, by oxidizing carbon black in the liquid phase,(6,7) with(8) or without the use of surfactants.(9) The adsorption behaviors of the anionic surfactants on the carbon-black particles were studied in relation to the surface properties of carbon black,(10—13) in order to explain the dispersion of carbon-black particles into water. However, the question about the achievable concentrations has not yet been answered.

In the present work, the influence of the concentrations of anionic surfactants on their adsorptions onto carbon-black particles in a highly loaded aqueous suspension was studied in order to clarify the behaviors and roles of surfactants in a CWM in increasing the achievable concentration. When the organic particles in a suspension are present with bound water, the effective volume of the dispersed particles is defined as the sum volume of the dispersed particles and bound water. The effective volume fraction of the solid particles (as described above), which influence the viscosity of the suspension is as formulated by Brinkman.(14) In other words, the amount of bound water, which should be strongly dependent on the surfactant, influences the viscosity even when the size of the particle is fixed.

Hence, in the present study, the amount of water bound to dispersed carbon-black particles was quantified in the presence of surfactants by measuring the relaxation of water with ^{1}H NMR and the dielectric responses, since the relaxation of water bound to dispersed particles is much slower than that of free water in

Table 1. List of the Surfactant

Surfactant	Molecular weight	Sulfonation ratio (mequiv/g)
Naphthalen sulfonate formaldehyde condensate (NSF)	4000	4.3
Poly(styrenesulfonate) (PSS)	10000	5.5
Poly(isoprenesulfonate) (POS)	25000	5.9

a dispersive medium.[15,16] The amount of bound water, thus quantified, may allow us to calculate an effective volume of the dispersed particles. The validity of the Brinkman equation was thus examined; the parameters in the equation can be discussed in terms of the properties of the surfactants.

Experimental

Test Sample. Carbon-black MA-100 and #5 (Mitsubishi Chemical Co.) were selected for the present investigation. According to the manufacturer's analyses, the diameter measured by SEM and the surface area measured by the BET method were 22 nm and 134 $m^2 g^{-1}$ for MA-100 and 85 nm and 25 $m^2 g^{-1}$ for #5. The particle size of the carbon black in a suspension was measured using a CILAS HR850 Granulometer. The mean and 90% pass-through diameters was 0.26 and 0.74 μm for MA-100 and 0.54 and 5.55 μm for # 5, respectively, in the presence of a surfactant (NSF). The specific gravity of MA-100 was 1.841.

Three kinds of polymer-type anionic surfactants (naphthalenesulfonate–formaldehyde condensate (NSF), poly(styrenesulfonate) (PSS) and poly(isoprenesulfonate) (POS)) were adopted, as reported previously.[3] The properties of these surfactants are summarized in Table 1. Special-grade reagents were used to control the pH and electrolyte concentration in the suspension.

Suspension Preparation. About 300 g of the carbon-black water suspension was prepared in a 800 ml steel beaker. First, carbon-black powder (90 g for MA-100 or 150 for # 5) was gradually added to an aqueous solution of a surfactant in the beaker. All of the powder was added within 20 min with continuous stirring using double helical blades running at 225 rpm; then, high-velocity mixing was carried out with a TK-Homomixer at 4000 rpm. On the basis of the pH of a practical CWM, every suspension was adjusted to a pH range of 7.0 to 8.0.

Properties of the Suspension. The viscosity of the suspension was measured at 25.0 °C with modes of $t_1=2$ min, $t_2=2.5$ min, and $t_3=2$ min within a shear rate of 0 to 150 s^{-1} using a Haake double cylinder-type rotary viscometer (rotor MV-1P, measuring head MK-500). Based on the apparent viscosity of a practical CWM,[1—3] the viscosity at 100 s^{-1} in the decreasing process of the shear rate was used as the apparent viscosity of the suspension. The solid concentration in each suspension was calculated by subtracting the amount of surfactant used from the amount of solid obtained after drying the suspension at 110 °C. A measurement of the particle-size distribution was carried out using a CILAS HR850 Granulometer.

The prepared suspension was stored for 24 h in sealed plastic bottles under mixing; the filtrate was then obtained by filtering through a 0.45 μm millipore filter after ultracentrifugation. The concentration of the surfactant in the filtrate was measured by gelpermeation chromatography; the amount of the surfactant adsorbed on the solid particles was determined from the difference between the amounts of added and in-water surfactant.

The mobility of the water molecules in the suspension was qualitatively measured by the dielectric relaxation method. Dielectric relaxation measurements were performed over a frequency range from 10^5 to 10^{10} Hz using a time-domain refractometry (TDR) method.[17] An incident pulse of 200 mV pulse height with a rise time of less than 35 ps was applied to the sample, passing through a flexible coaxial line and the sample cell. The reflected pulse, along with the dielectric information about the samples, was digitized using a digitizing oscilloscope; a numerical Fourier transformation and a least-squares fitting were then performed with a microcomputer. The relaxation time of the water in the suspensions was also measured by the Carr–Purcell and Meiboom-Gill (CPMG) method using an FT-NMR (JEOL. EX-90).

Results

Adsorption Behaviors of Surfactants. The amount of adsorbed POS are plotted against the concentration in water in Fig. 1, in comparison with the data of NSF and PSS reported in a previous paper.[3] The adsorption behavior of POS is in the "Langmuir" type, and is similar to the behaviors of NSF and PSS. The adsorption value of POS reached equilibrium at a concentration of 0.08 mmol dm^{-3} or above, which was attained by adding 10% or more POS to carbon-black; the equilibrium value was about half of NSF or PSS.

Particle Size Distribution and Rheological Behavior of the Suspension. Histograms of the particle-size distribution and rheograms for suspensions using POS in the 2 to 10% range are shown in Fig. 2.

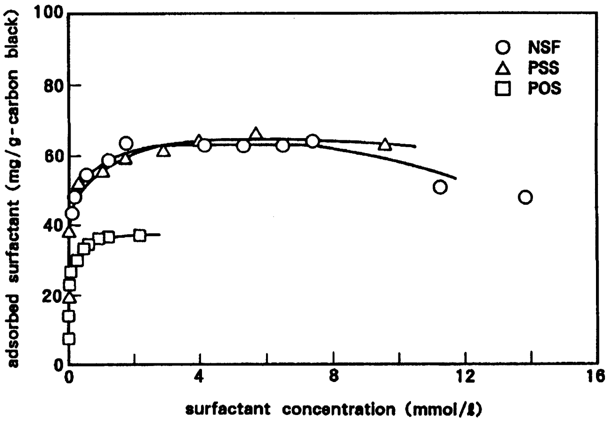

Fig. 1. Adsorption behavior of surfactant on the carbon-black.

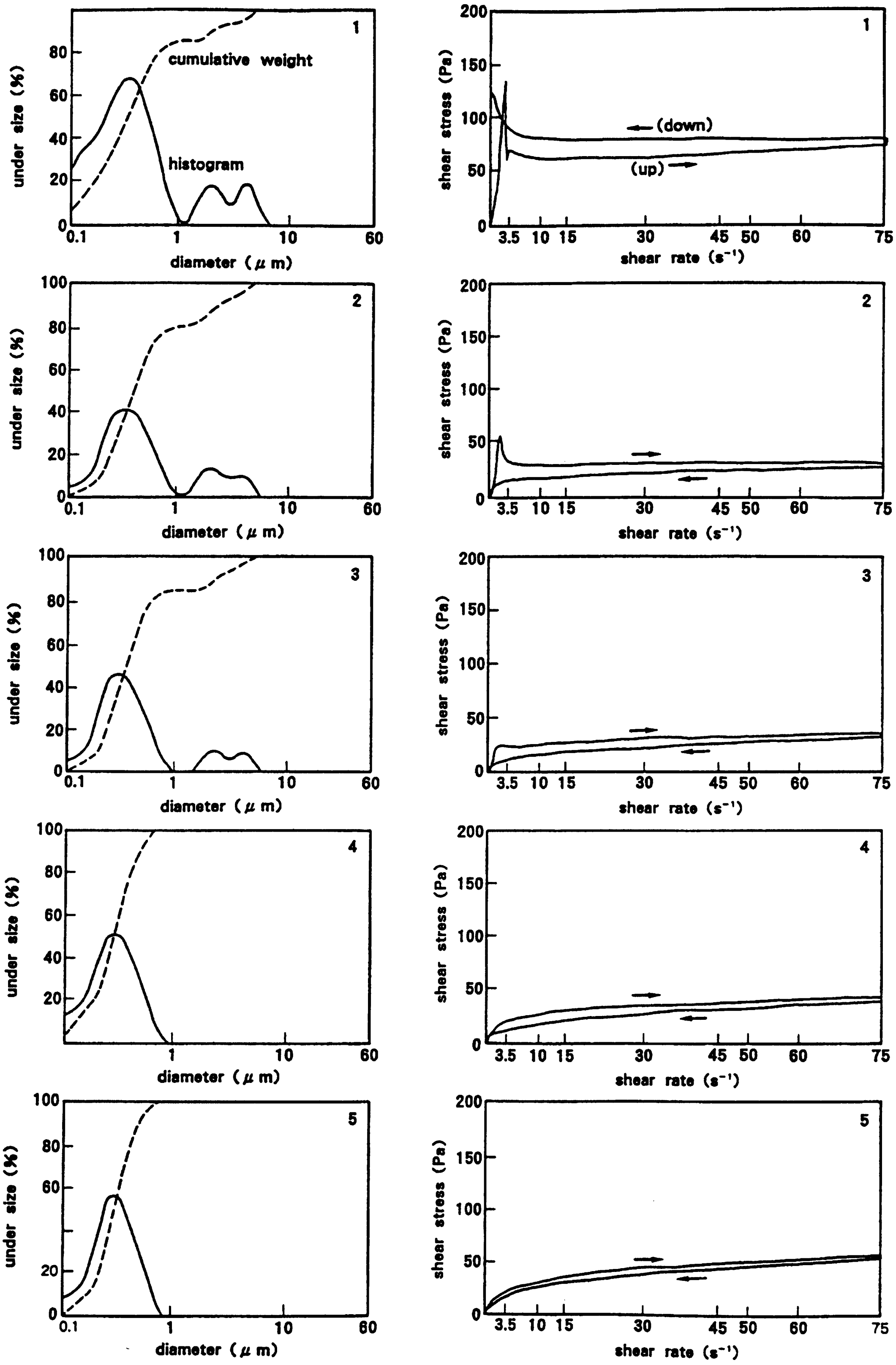

Fig. 2. Histograms of the distributed particles and rheograms of the suspension.

When POS was less than 6% (① to ③ in Fig. 2), particles larger than 1 μm were found. When more than 8% POS (④, ⑤) was applied, no particles larger than 1 μm were observed. This suggests that particles larger than 1 μm are actually aggregated particles that form because of an insufficient amount of surfactant, and that the amount of POS required to disperse MA-100 is 8%/carbon-black or above.

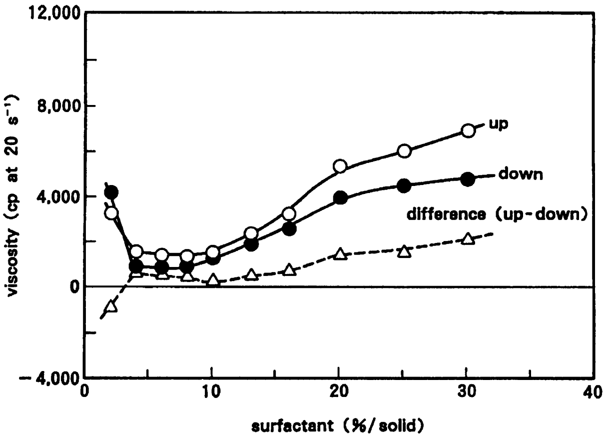

Fig. 3. Relations between the amount of surfactant and the viscosities.

In rheograms of the suspensions prepared with less than 6% POS, a characteristic change in the shear stress was observed at low shear rates when the shear rate was increasing. The viscosity, calculated from the shear stress value at 20 s^{-1} in the rheograms from Fig. 2, is plotted in Fig. 3 against the usage of POS. In Fig. 3, the change in the viscosity that occurs with increasing the shear rate is denoted as "up", and that with decreasing the shear rate is denoted as "down". The difference between the viscosities of up and down is also shown in Fig. 3. The viscosity decreased sharply when a POS of less than 5% was used, and stayed constant until the POS level reached 10%. However, the viscosity of the suspension increased when the POS level topped 12%, which allowed the POS concentration in water to be more than 1.9%. The difference in the apparent viscosity was negative when use of the surfactant was less than 5%, but became positive with increased use. A negative value in the difference of the viscosities was observed with a suspension prepared with 2% POS, indicating that the dispersed particles in the suspension aggregated with each other because of this insufficient amount of surfactant used while the suspension was being mixed mechanically.

Relaxation Time of Water Molecules in Suspension. The dielectric relaxation curve of a water suspension of 15% carbon-black without a surfactant is illustrated in Fig. 4. The observed dielectric relaxation curve ($\log \varepsilon''$) is indicated by the dotted line, and is decomposed into four relaxation processes. A higher frequency of the dielectric relaxation reflects a higher mobility. The two peaks on the left, assigned to the surface polarization on the electrode and ion-pair movement in the suspension, respectively, are independent of the water mobilities. The two right-hand peaks reflect the presence of two kinds of water with different mobilities, i.e., bound water (peak B in Fig. 4) and free water (peak A).[17]

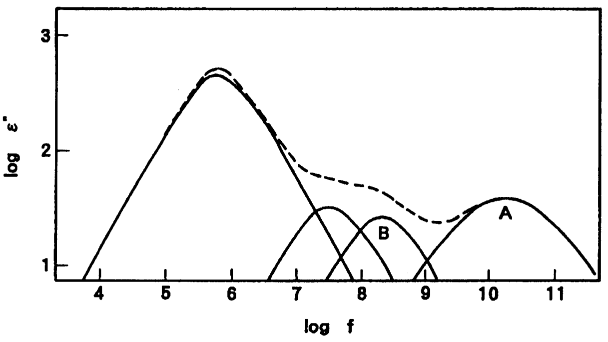

Fig. 4. Spectrum of carbon-black water suspension (Dielectric relaxation method).

Typical decays of the residual magnetization of the carbon-black water suspensions, prepared under different conditions, are illustrated in Fig. 5, where the residual magnetization of the protons in suspension was also measured by ^{1}H NMR spectroscopy using the CPMG method. Although Miyamoto et al.[18] reported that CWM with a definitely insufficient amount of surfactant showed two exponential decays, single exponential decays were always observed for the present suspensions with a sufficient amount of surfactant, as shown in Fig. 5. Two exponential decays were observed only when the suspension was unstable. Such a single-exponential decay indicates that a rapid exchange between bound and free water may be achieved for sufficiently dispersed solids; the exchange is faster than the relaxation time of the water molecules.

Hence, the average relaxation time was calculated from the slope of the exponential decays of the residual magnetization. The relationships between the average relaxation time (T_2) and water concentration of MA-100 carbon-black water suspensions, with or without surfactants, are illustrated in Fig. 6. Since the relaxation times in the suspensions without surfactants were always shorter, compared with those of the same solid concentrations of suspensions with surfactants as

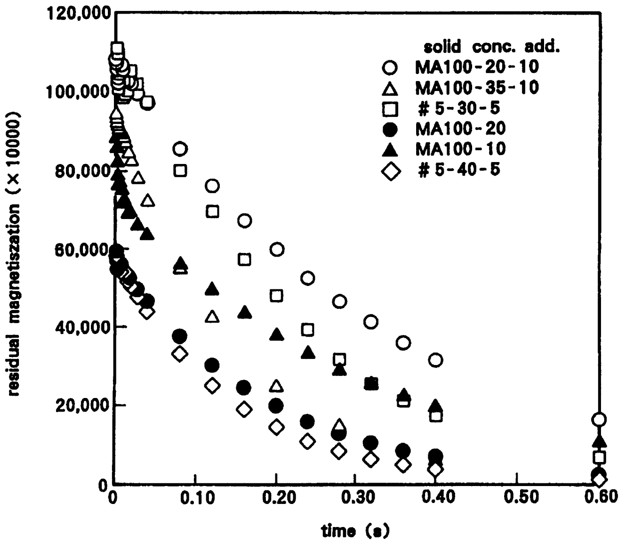

Fig. 5. Changes of the residual magnetization.

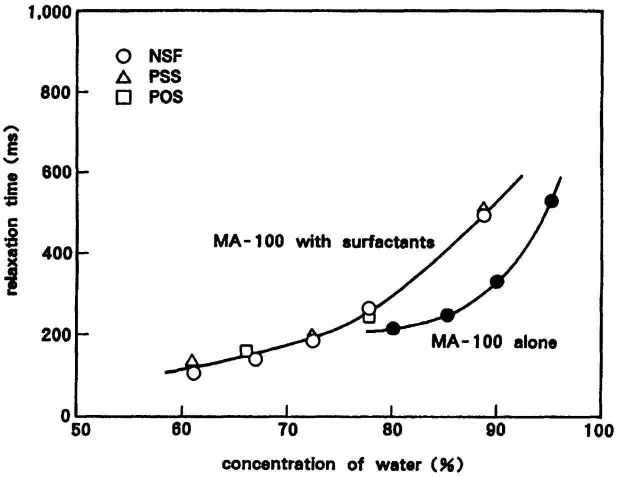

Fig. 6. Relationship between the relaxation time and the amount of water.

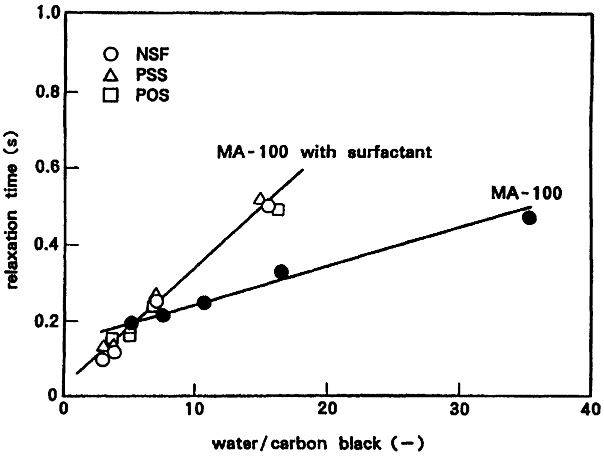

Fig. 7. Relationship between the relaxation time and the volume ratio of water to carbon-black.

shown in Fig. 6, the average mobility of water molecules in the suspension without a surfactant was estimated to be smaller than that with a surfactant. The influences of the three surfactants on the mobility of water were basically the same, as shown in Fig. 6.

Discussion The adsorption behavior of polymer-type anionic surfactants on the carbon-black particles, shown in Fig. 1, confirms that such surfactants act on the carbon black in the same way as they do on coal particles.[3] When the use of a surfactant is insufficient, aggregation of the dispersed particles occur even at a shear rate of 20 s^{-1}, as shown in Figs. 2 and 3. From the mean diameter of the dispersed particles in the 0.24 to 0.32 μm range, which was obtained in a suspension prepared with a 10% use of the surfactant, we could see that the average particle consisted of several hundred primary particles. However, the mean diameter of 6.2 μm, obtained in a suspension without a surfactant, indicates that the average particle consisted of ten-thousand or more primary particles.

This confirms that a surfactant adsorbed on the surface of a carbon-black particle prevents the aggregation of suspended particles. When the amount of the surfactant is insufficient, aggregation of the suspended particles is demonstrated by a characteristic change in the shear stress, as shown in the rheogram. Thus, it is definite that one of the functions of a surfactant in a highly loaded suspension is to depress the aggregation of dispersed organic particles.

The presence of bound and free water in the suspension was confirmed by the dielectric relaxation, as shown in Fig. 4. The presence of these types of water in such suspensions agreed with the classification of bound and free water in their respective frequency regions, as reported in a study of collagen.[17] It was thus assumed that these two types of water molecules with different mobilities were present in the carbon-black water suspension.

The relationships between T_2 and the ratio of water to carbon black (MA-100) in the suspension are illustrated in Fig. 7. If the T_2 value of the water bound to the nearest surface of a carbon-black particle is defined as T_b, these values, with and without a surfactant, can be estimated as the intercept of the straight line to the vertical axis.

The T_b values for the bound water were estimated to be 0.15_7 s without a surfactant and 0.037 s with a surfactant. It should be considered that the surfactant adsorbed to the surfaces of suspended particles is to bind strongly the water molecules surrounded to them.

When two types of water molecules with different states of mobility are present in a suspension, and the exchange between their different states is fast, the observed relaxation time, (T_{ob}), is give by the following Eq. 1:[15]

$$1/T_{ob} = p_f/T_f + p_b/T_b, \tag{1}$$

where p and T are the mole fractions and relaxation times, respectively. Suffixes f and b designate the free and bound states, respectively. The relaxation time of free water was obtained to be 3.60 s from a measurement of distilled water.

When the amounts of bound water and the total water in a 1 g suspension are defined as A (g/g-solid) and W (g), respectively, the mole fractions of the free and bound water are described by

$$p_f = [W - A \times (1 - W)]/W$$

and

$$p_b = [A \times (1 - W)]/W \tag{2}$$

From Eqs. 1 and 2, we can see that the mole fraction of the bound water in the suspension is described by

$$p_b = (1/T_{ob} - 1/T_f)/(1/T_b - 1/T_f). \tag{3}$$

By substituting the T_{ob} found in Fig. 6 into Eqs. 2 and 3, A was calculated to be 4.5 for a suspension without a surfactant and 0.52, 0.48 and 0.51 for suspensions with NSF, PSS, and POS, respectively.

The authors have already reported that the fluidity of a highly loaded oil-in-water emulsion can be sufficiently expressed by Eq. 4, using the effective volume of the dispersed particles, which includes the amount of bound water determined by ^{1}H NMR,[16]

$$\eta_{\mathrm{re}} = (1 - S\phi)^{-k}, \tag{4}$$

where η_{re} is the relative viscosity, $S\phi$ the effective volume fraction, and k the shape factor of the dispersed particles. According to a previous report which considered the fluidity of a highly loaded emulsion, it should be considered that the volume of bound water, obtained by using ^{1}H NMR, acts as a unit with the carbon-black particles. The effective volume of carbon-black in a suspension is estimated to be nine-times larger than that of a solid alone for a suspension without a surfactant, and two-times larger for a suspension with a surfactant.

A surfactant decreases the amount of water bound to the dispersed particles, thus increasing the amount of free water, but strengthening the binding of water to the solid. This smaller amount of bound water on an organic particle due to a surfactant allows higher concentrations of the dispersed solid in the suspension, because its effective volume becomes smaller.

The effective volumes of the dispersed particles in the suspension prepared with 10% NSF, 10% PSS, and 10% POS were calculated using the amounts of bound water obtained, as above described. The relationships between the relative viscosities and the effective volume fractions are summarized in Fig. 8.

Each solid line in Fig. 8 is the relationship calculated by a least-squares method according to Eq. 4. The shape-factor values were found to be 6.1 for NSF, 7.9 for PSS, and 10.5 for POS, respectively, showing that these values are useful for evaluating the function of the surfactant in the suspension. It is particularly interesting that the order of the k values of NSF, PSS, and POS is the reverse of that of the mean molecular weights of the surfactants. Because the presence of a surfactant in the water of a suspension is required to maintain good fluidity, it is assumed that this k value indicates the effect of the interactions between the dispersed particles, or between the dispersed particles and the free surfactant in the water. Detailed knowledge concerning the behavior of a surfactant is required to discuss the functions of a surfactant in more detail.

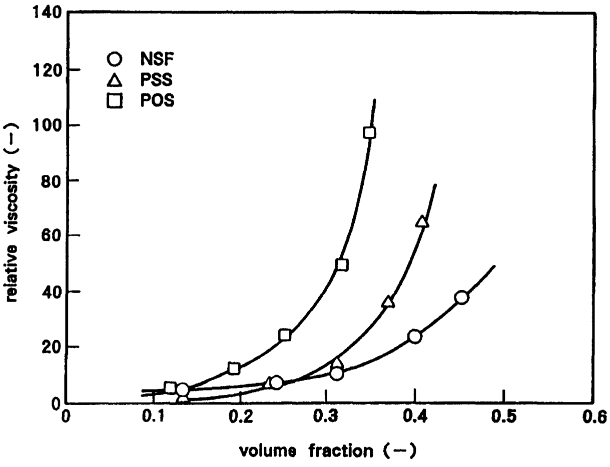

Fig. 8. Effect of the surfactants on the relative viscosity.

On the basis of the above discussion, the following conclusions were reached regarding the behaviors and roles of surfactants in the preparation of highly loaded aqueous suspensions of carbon-black: (1) The tested surfactants adsorbed on the dispersed carbon-black particles decrease the amount of bound water and intensify the bonding of water to the surface, as revealed by ^{1}H NMR measurement, thus decreasing the effective volume of the particles in the suspension. This effect is one of the reasons why a surfactant can increase the concentration of solids in a suspension without increasing the viscosity. (2) Adsorbed surfactants decrease the aggregation of particles. Their aggregation takes place even during mechanical stirring, when the amount of surfactant is less than the saturated adsorption value of the particles. (3) The k value of Brinkman's equation, which is obtained as the effective volume including the amount of bound water, reflects the effect of the surfactant on the fluidity of the suspension.

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