1350 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 1350—1355(1993) [Vol. 66, No. 5

Behavior of Surfactants in a Highly Loaded Coal–Water Slurry. II. Effects of Coal Properties on the Behavior of a Surfactant

Tsugitoshi OGURA,* Masazumi TANOURA, 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

(Received November 4, 1992)

The roles and behaviors of two kinds of anionic surfactants were investigated in order to clarify their influence on the properties of a highly loaded coal water slurry (CWM) prepared from six kinds of coals. It was confirmed that the adsorbed surfactants on coal particles and their presence in water were both required for preparing practical CWMs of every type of coal. The ion concentrations of alkaline earth metals and protons derived from coal increased the adsorption of surfactants; the amounts of the adsorbed surfactants varied from coal to coal. A surfactant of molecular weight around 5000 was found to be preferentially adsorbed, and thus the most effective for controlling the properties of the CWM.

A highly loaded coal–water slurry (CWM) has been recognized as being one of most economically feasible types of fluid fuels. Its practical development is still being pursued in both Japan and China. Although there have been many reports on CWM, describing basically its performances;[1,2] studies concerning its interfacial science have been very limited.[3—7] Hence, the design of CWM preparation remains very empirical. Especially roles of the surfactants are far from being understood at a basic level. In a previous paper,[8] the authors clarified the adsorption behavior of a surfactant on coal in water. Its adsorption amount and its concentration in water influence very strongly the dispersion of coal particles and viscosity of the slurry, both of which are important properties of CWM.

In the present study influence of the properties of coal on the performance of highly loaded CWM was studied by examining six kinds of bituminous coals of variable ranks and mineral content. Two kinds of anionic surfactants were applied due to their excellent performance. The properties of coal in terms of its organic and inorganic portions were correlated with the achievable coal concentration, the apparent viscosity and the adsorbed amount of surfactant on coal particles. The adsorption of a surfactant on coal is expected to be very strongly governed by the surface properties of coal as well as the concentrations of cations in water derived from the coal, thus influencing the properties of a CWM.

Experimental

Test Samples Six kinds of bituminous coals were selected in the present study: four from Australia, one from the U. S. A., and the other from Japan. All of these coals had been proved to give satisfactory results in CWM development tests using a full-scaled boiler.[9]

Two types of surfactants, including naphthalenesulfonate–formaldehyde condensate (NSF) and poly(styrenesulfonate)(PSS), were selected according to a previous study.[8] NSF had a mean molecular weight of 3700 and a sulfonation rate of 98%; PSS had a mean molecular weight of 10000 and a sulfonation rate of 91%.

Analyses of Coal. Sample coals were characterized according to a maceral analysis of their reactives, a Fourier-transform infrared-spectrum analysis of the surface functional groups, the mercury porosimetry of specific surface areas and pore distributions, and a combination of Fourier-transform infrared-spectroscopy and X-ray diffraction for the analysis of mineral matter after low temperature ashing.[10]

Some analyses and properties of the coals are listed in Table 1. The soluble materials contained in coal were dissolved in water of CWM during the CWM preparation and storage periods. The concentrations of dissolved materials in water were analyzed according to the following procedure. One part of coarse-grained coal that was to pass through a 3 mm mesh sieve was mixed with two parts of water so as to prepare a CWM in which coal particles of less than 74 μm accounted for about 80% of the total weight of particles. This CWM was stored in a polyethylene bottle for 48 h while being stirred. The pH and concentrations of alkali metals and alkaline earth metals ions in the filtrate from the CWM were measured.

CWM Preparation. Coal was pulverized using a dry ball mill. Coarse particles greater than 150 μm were removed by a sieve. The mean particle diameters of six coals were set at 22—28 μm, with particles smaller than 1 μm accounting for 5 to 8% of the total amount. The procedures concerning CWM preparation and its viscosity measurement were described in a previous paper.[8]

Adsorption Tests of Surfactants. CWMs were prepared with coal concentrations of 62 to 63% and stored in sealed polymer bottles while being stirred. After storage for 24 h, the CWMs were passed through a milli-pore filter of 0.45 μm to obtain a filtrate for analysis of the surfactant concentration in the supernatant. The experimental details were described in a previous paper.[8]

Results

Relation between the Adsorption of Surfactants and Coal Particles. According to Rehácêk,[11] the relations between the amount of surfactant adsorbed on coal and the concentration of the surfactant

Table 1. Analytical Data of Sample Coals

Item analyzed		Coal A	Coal B	Coal C	Coal D	Coal E	Coal F
(Proximate analysis)							
Moisture	(%)	3.2	3.2	3.3	5.1	5.8	3.0
Fixed carbon	(%)	51.4	52.8	50.8	44.7	35.1	56.1
Volatile matter	(%)	27.5	31.7	31.4	40.9	43.2	25.5
Ash content	(%)	17.0	13.0	14.5	9.3	15.9	14.7
(Ultimate analysis)							
Carbon	(%)	84.7	84.4	83.5	79.9	78.2	84.7
Hydrogen	(%)	5.6	5.9	5.6	6.2	6.3	5.4
Sulfur	(%)	7.5	7.3	8.6	11.6	14.0	7.5
Oxygen	(%)	7.5	7.3	8.6	11.6	14.0	7.5
Nitrogen	(%)	1.7	1.8	1.8	1.6	1.2	1.7
(Physical properties of raw coal)							
True density	(—)	1.457	1.424	1.431	1.390	1.439	1.471
Reactives in maceral analysis	(%)	62.1	72.7	75.6	91.3	73.1	63.5
OH group in functional group	(%)	3.7	3.9	4.6	8.3	9.8	4.5
Surface area	($m^2\,g^{-1}$)	1.9	3.5	1.8	1.7	1.5	2.3
Kaolinite in LTA	(%)	14	27	19	12	28	49
Clay in LTA	(%)	46	60	45	37	56	70
(Chemical analysis of water from CWM)							
pH	(—)	8.1	7.7	7.3	7.1	8.5	3.0
Na as Na_2O	(mg/kg)	60.3	115	190	64.3	163	28.4
K as K_2O	(mg/kg)	12.3	15.0	9.7	12.0	5.4	2.1
Ca as CaO	(mg/kg)	24.1	209	7.9	439	5.0	537
Mg as MgO	(mg/kg)	14.1	113	9.5	72.6	29.0	90.6

Table 2. Results of CWM Prepared with NSF and PSS

		Coal A	Coal B	Coal C	Coal D	Coal E	Coal F
Saturated adsorption value A_b ($mg\,g^{-1}$)	NSF	2.85	3.77	3.56	5.34	3.53	5.54
	PSS	2.33	2.87	2.47	3.38	2.29	4.20

in supernatant are as shown in Fig. 1. Plots of the amount of the adsorbed surfactant and the surfactant concentrations in water give straight lines after showing maximum amounts of adsorption with a very small concentration left in the supernatant. The amounts of adsorbed surfactants decreased linearly with increasing in-water surfactants after maximum adsorption. Saturated adsorption values were determined from the intersections of the respective straight lines with the ordinate. The saturated adsorption values (A_b) are listed in Table 2. Since the saturated adsorption values of NSF were always larger than those of PSS, the amount of PSS required to produce a practical CWM was smaller than that of NSF for every tested coal. The amount of surfactant adsorbed on the coal surface was very dependent upon the coal.

Required Amounts of Surfactants for Each Coal. In order to estimate the required amount of surfactant based on a previous report, both stirring and mixing tests were carried out for each coal. Based on the changes in the surfactant concentration in water and the apparent viscosity of CWMs according to the time of stirring, the lower-limit concentrations ($C_{\min}$) were obtained. The lower amounts of surfactants necessary to prepare CWMs of each coal were calculated using Eq. 1 based on the saturated adsorption values listed in Table 2 and the values of $C_{\min}$.

$$Co_{\min} = [A_b \times C_c \times 0.001 + C_{\min} \times (100 - C_c) \times 0.01]/(C_c \times 100), \quad (1)$$

where A_b is the saturated adsorption value ($mg\,g^{-1}$) and C_c is the coal concentration (wt%).

Standard amounts of the required surfactants for the respective coal species necessary to prepare 65% loaded CWM were estimated by the addition 0.15% to $Co_{\min}$ according to empirical knowledge from our CWM development tests. The lower-limit concentration of the surfactant in water ($C_{\min}$), the lower amounts of the required surfactant ($Co_{\min}$) and the standard amounts of required surfactants (C_s) are listed in Table 3.

Achievable Coal Concentrations. The viscosities and coal concentrations of CWMs are illustrated in Figs. 2 and 3 with standard usages of NSF and PSS, respectively, indicating similar relations between

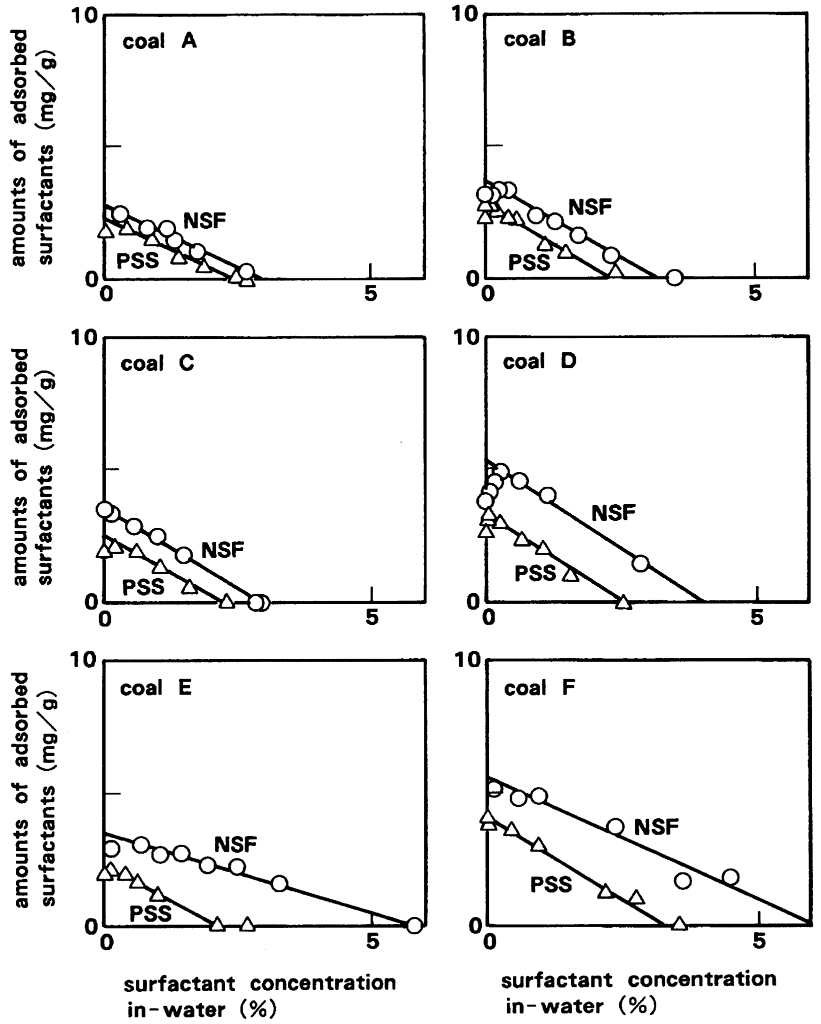

Fig. 1. Relations between the amount of adsorbed surfactant and the surfactant concentration in water.

Table 3. The Amounts of Surfactants for Preparation of CWM

	NSF			PSS		
	Lower limit in water C_{min} (%)	Required minimum amount Co_{min} (%)	Standard usage C_{s} (%)	Lower limit in water C_{min} (%)	Required minimum amount Co_{min} (%)	Standard usage C_{s} (%)
Coal A	0.25	0.42	0.6	0.20	0.34	0.5
Coal B	0.26	0.52	0.7	0.19	0.39	0.5
Coal C	0.27	0.50	0.7	0.20	0.35	0.5
Coal D	0.26	0.67	0.7	0.22	0.46	0.6
Coal E	0.24	0.48	0.6	0.19	0.33	0.5
Coal F	0.28	0.70	0.8	0.23	0.54	0.7

the coal concentrations and the apparent viscosities of CWMs. The achievable coal concentration of each coal with its apparent viscosity at 1000 cP ($1\,\mathrm{cP}=10^{-3}$ Pa s)(estimated from Figs. 2 and 3) are summarized in Table 4. The achievable coal concentration ranged from 63.7 (coal E) to 66.6% (coal F) with NSF and from 63.8 (coal E) to 67.8% (coal F) with PSS. It is noted that the order of coals in their achievable concentration was the same for both surfactants.

Correlation Analyses between the Saturated Adsorption Value and the Coal Properties. The coal properties given in Table 1 were correlated to the saturated adsorption values (A_{b}) for each coal sample listed in Table 2. CWMs with NSF and PSS exhibited fine correlations to three properties: the calcium content (correlation coefficient γ; 0.94, 0.95) and the alkaline earth metals content in water (γ; 0.92, 0.93) showed positive correlations (Fig. 4), while the pH of

Table 4. Achievable Coal Concentration

Surfactant	Coal A	Coal B	Coal C	Coal D	Coal E	Coal F
NSF	64.9	65.8	66.3	65.5	63.7	66.6
PSS	66.6	67.2	67.3	66.6	63.8	67.8

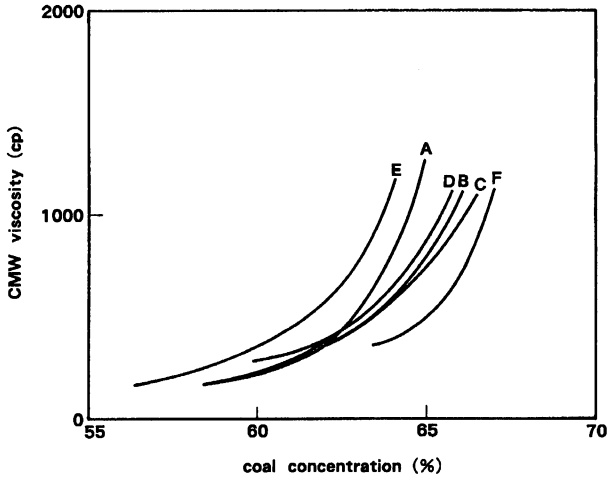

Fig. 2. Relations between the CWM viscosity and the coal concentration using NSF.

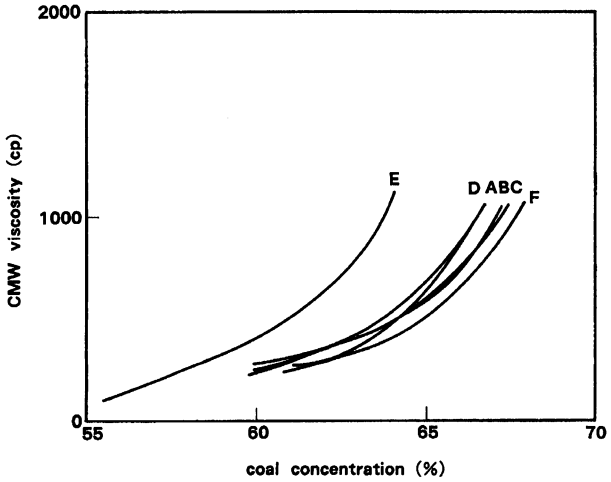

Fig. 3. Relations between the CWM viscosity and the coal concentration using PSS.

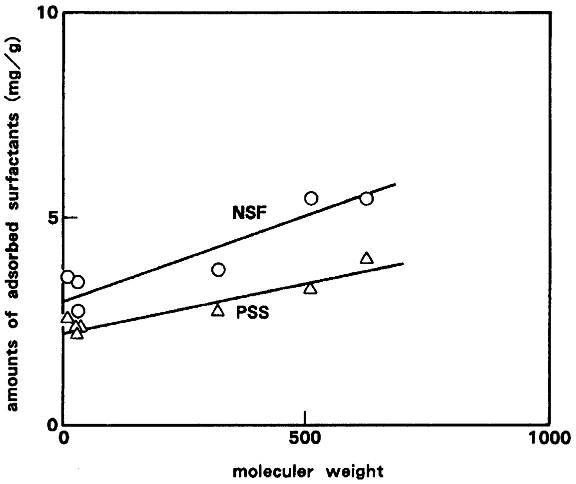

Fig. 4. Effects of the soluble alkaline earth metal ions on the adsorbed amounts of the surfactant.

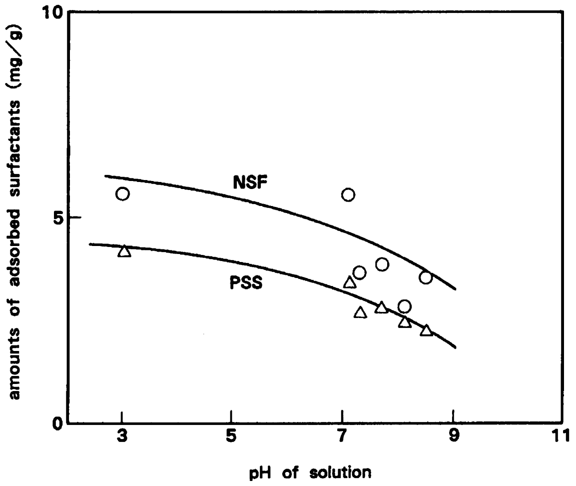

Fig. 5. Effects of the pH on the adsorbed amounts of the surfactant.

an aqueous solution (γ; 0.73, 0.92) showed a negative correlation (Fig. 5). The ash content in coal showed a negative correlation (γ; 0.73) only with NSF, whereas the alkali metals content in water showed a negative correlation (γ; 0.71) only with PSS. The other properties of coal did not show any significant correlation. Thus, surfactant adsorption to coal particles was found to be strongly influenced by the substances dissolved from coal.

Molecular Weight Distribution of Adsorbed Surfactants. The molecular weight distributions of surfactants present in water were measured by changing the dose of the surfactant per coal D for CWM production within a range of 0.3 to 1.0%/coal. As shown in Fig. 6, a portion of the lower molecular weight surfactants remained in water when the amount of NSF (500—20000 molecular weight) added was less than 0.8%. As the amount was increased, the higher molecular weight portion appeared in water. The portion of higher molecular weight of NSF around 3000 tends to be preferentially adsorbed on the coal particles. In contrast, PSS, of which molecular weight distributed in the range 2500 to 80000, left higher molecular weight compounds in water, even when the amount of PSS was less than 0.6%. Hence, the portion of lower molecular weight of PSS around 10000 tend to be adsorbed preferentially on the coal particles.

In order to study the effects of coal species on the

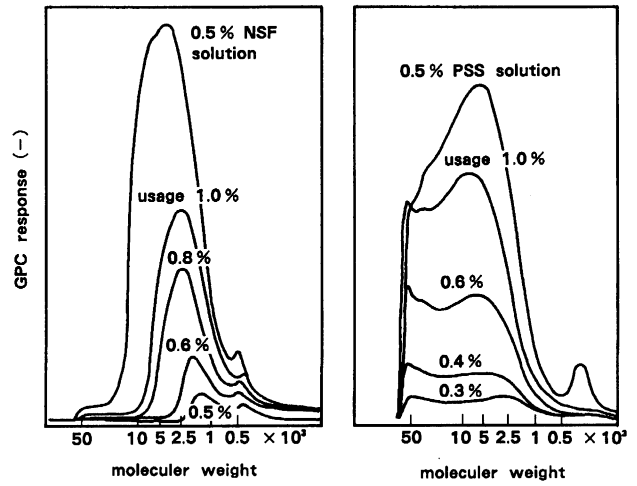

Fig. 6. Gel permeation chromatograph analysis of the surfactants in each CWM's supernatant, prepared with varying the usage of surfactants.

adsorption of a surfactant, the distributions of NSF in water of CWMs prepared by use of 0.8% NSF and stored for 24 h were measured. The molecular weight distributions of adsorbed NSF were estimated from the differences between the molecular weight distributions of NSF and those of NSF in water after storage; they are summarized in Fig. 7. Because the portion of higher molecular weight of NSF was found to be adsorbed as shown in Fig. 7 when a coal had a smaller saturated adsorption value (coal E and coal D), preferential adsorption of the higher molecular weight components of NSF was confirmed. However, NSF was adsorbed regardless of its molecular weight when coal had a larger saturated adsorption value (coal F). According to the results illustrated in Figs. 6 and 7, it should be noted that the components distributed in the 3000 to 10000 range of molecular weight are effective in both NSF and PSS.

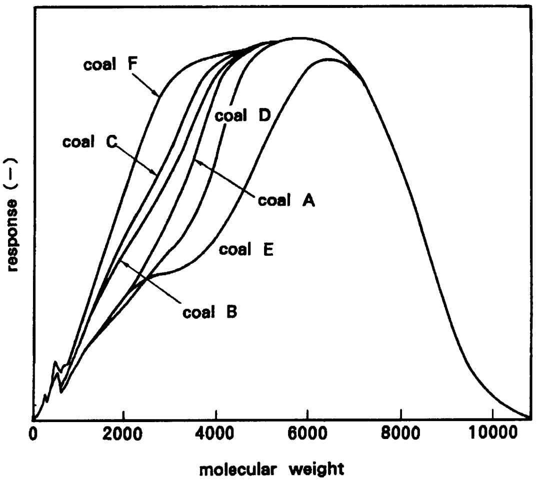

Fig. 7. Changes of NSF's molecular weight distribution adsorbed on coal particles.

Coal Properties and Achieved Coal Concentration. As shown in Table 4, the achievable coal concentration for each coal was different according to the surfactant type, PSS giving higher concentrations than NSF. The correlation coefficients between the achievable coal concentrations and the coal properties were analyzed for each surfactant. The majority of coal properties gave a correlation coefficient of 0.7 or larger.

The properties which gave negative correlations were the inherent moisture content (correlation coeffieient, γ; 0.74, 0.85), the volatile matter content (γ; 0.65, 0.77), the hydrogen content (γ; 0.71, 0.76), the oxygen content (γ; 0.72, 0.86), the amount of surface hydroxyl groups (γ; 0.66, 0.80), the H/C number of the atomic ratio (γ; 0.73, 0.86), the O/C number of the atomic ratio (γ; 0.73, 0.86), and the specific surface area (γ; 0.86, 0.70); those exhibiting positive correlations were the fixed carbon content (γ; 0.86, 0.95) and the carbon content (γ; 0.69, 0.83). Of these coal properties, the inherent moisture content, oxygen content, amount of surface hydroxyl group, and O/C number of the atomic ratio, all giving negative correlations, appear to be commonly associated with the hydrophilic property of the coal surfaces.

As described above, the correlation coefficients with PSS were larger than those with NSF in all cases. Because PSS had smaller adsorption values and the volumetric concentration of apparent coal particles was much closer to that of the actual coal particles in CWM in the presence of PSS, the CWM produced with this surfactant may exhibit more distinct relationships between the properties of the coal and the achievable coal concentration.

Discussion

The present study revealed that both the amount of the surfactant adsorbed on coal particles and that dissolved in water are required to prepare practical CWMs.

Because of the agreement between the adsorption behavior shown in Fig. 1 and that given in a previous report,[8] it is concluded that NSF and PSS are adsorbed on coal particles in a monolayer, which is described by the "Langmuir" from under the practical CWM conditions given in Table 3. The saturated adsorption values are subject to the contents of alkali metals, alkaline earth metals and protons in the water of the CWM, all of which result from the dissolution of mineral matter in coal. The effects of the cation concentrations observed with CWM are similar to those of the adsorption on carbon black in an aqueous solution of sodium alkylsulfate (AS), sodium α-alkenesulfonate (AOS), and bis(2-ethylhexyl)sodium sulfosuccinate (Aerosol OT) which were studied by Arai[12] and by Saleeb,[13] respectively. Because of the common hydrophilic groups of NSF, PSS, AS, AOS, and Aerosol OT, it is estimated that NSF and PSS are adsorbed on coal particles at their hydrophobic part to form a monolayer of the surfactant with polar groups directed outward, as observed in the adsorption of Aerosol OT on carbon black. Since the dissolved cations interact with the hydrophilic part of the surfactant adsorbed on the coal particle to decrease the electrostatic energy among the adsorbed molecules, the amount of adsorbed surfactant increases with increased concentration of the dissolved cations. Such an enhanced adsorption may increase the amount of surfactants required for the proper CWM properties.

The present study found that the apparent viscosity and achievalbe coal concentration of a CWM are strongly influenced by the properties of the coal as well as the surfactant. Especially, the inherent moisture, the oxygen content, the amount of surface hydroxyl group, and the O/C number of the atomic ratio, which are associated with the hydrophilic property of a coal surface tend to lower the achievable coal concentration. These results agree very well with a report describing the relations between the achievable coal concentration and the water-holding capacity.[14,15] It was therefore confirmed that when the hydrophilic property of coal is large, preparing a highly loaded CWM is very difficult, because the thicker hydrated layers surround the coal particles.

The hydrophilic and hydrophobic properties of coal give reverse coefficients in their correlations to the achievable concentrations. This is explained as follows. As described above, anionic surfactants, such as NSF and PSS, are adsorbed on the hydrophobic parts of coal particles and increase the coal concentration of CWM. This is because the surfactant converts the hydrophobic parts of coal particles to be hydrophilic, and the repulsion force of the adsorbed surfactant molecules inhibits the aggregation of the dispersed particles. On the other hand, the increase in the hydrophilic property of coal leads to an increase in the bound water surrounding the coal particles, and lowers the coal concentration, because of the increased apparent volume of the dispersed particles. This reverse relation indicates that the amount of the hydrated water surrounding the surfactant is less than that of the hydrophilic part of coal particles. The reasons for this phenomenon will be clarified in a subsequent paper.

The mean molecular weight of NSF was found to be 3700, its main components are distributed over the 500 to 20000 range, while those of PSS were 10000 and distributed over the range of 2500 to 80000. As shown in Figs. 6 and 7, a portion of higher molecular weight NSF is preferentially adsorbed on coal, while a portion of lower molecular weight PSS is adsorbed, indicating a preferential adsorption of the same range of molecular-weight distribution centered at 5000. It is inferred that the molecular-weight distribution of the anionic surfactants should be properly designed for the highest adsorption behavior, although reasons for preferential adsorption of a particular molecular weight range still remains unclarified at the present stage.

On the basis of the above discussion, the effects of the coal properties on the behaviors of surfactants in CWM were obtained as follows: (1) Each coal had a characteristic value of the saturated adsorption. (2) The ion concentrations of alkaline earth metals and the proton in water increased the amount of the adsorbed surfactant. (3) The components of their molecular weight around 5000 in surfactants were preferentially adsorbed to be most effective for controlling the properties of CWM. (4) Both the adsorbed and free surfactants present in water were required to prepare the practical CWM of each type of coal.

The work described here was carried out through the courtesy of Mitsubishi Heavy Industries, Ltd.; this paper is published by permission of the same company. The authors would like to thank Professor Isao Mochida at Kyushu University for his many valuable comments and advice during the course of this work. We also thank to several companies for kind gifts of surface-active agents.

References

1) "Proceedings of International Symposium on Coal Slurry Combustion and Technology," U.S.A., 1983—1986.

2) "Proceedings of the 12th International Conference on Slurry Technology," Louisiana, U.S.A., 1987.

3) C. H. Chang and R. L. Rowell, "6th International Symposium on Coal Slurry Combustion and Technology," Florida, U.S.A., 1984, Abstr., p. 219.

4) E. Z. Casassa, G. D. Parfitt, A. S. Rao, and E. W. Toor, Ref. 3, 1984 Abstr., p. 251.

5) K. Esumi, A. Yokouchi, S. Watanabe, K. Meguro, and E. Honda, *Nenryo Kyokai Shi*, **64**, 345 (1985).

6) C. Tanaka, Y. Yamagata, S. Suzuki, and H. Yotsumoto, *Kogai-Shigen Kenkyusho Ihou*, **14**, No. 2, 127 (1984).

7) H. Yotsumoto, T. Kokubo, T. Moro, S. Suzuki, Y. Yamagata, and C. Tanaka, *Kogai-Shigen Kenkyusho Ihou*, **14**, No. 3, 37 (1985).

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

9) R. Shirato, H. Konishi, K. Abe, T. Takahashi, S. Kaneko, H. Hunatsu, K. Shoji, K. Kawano, and I. Shimpo, "8th International Symposium on Coal Slurry Combustion and Technology," Florida, U.S.A., 1986.

10) C. Karr, Jr., "Analytical Methods for Coal and Coal Products," Academic Press, New York, Vol. 2.

11) H. Kitahara, *Shikizai Kyokai Shi*, **50**, 681(1977), (K. Rehácêk: *Farbe+Lack*, **76**, 656 (1970)).

12) H. Arai and K. Yoshizaki, *J. Colloid Interface Sci.*, **35**, 149 (1971).

13) F. J. Saleeb, *Kolloid-Z. Z. Polym.*, **239**, 602 (1965).

14) R. Kaji, Y. Muranaka, K. Otsuka, and Y. Hishinuma, *Fuel*, **65**, 288 (1986).

15) W. P. Liang and L. Jiang, "8th International Symposium on Coal Slurry Combustion and Technology," Florida, U.S.A., 1986, Abstr., p. 19.