Behavior of Surfactants in a Highly Loaded Coal–Water Slurry. I. Effects of Surfactant Concentration on Its Properties

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)

Two types of anionic surfactants and one type of nonionic surfactant were investigated in order to clarify their roles and behaviors in a highly loaded coal–water slurry (CWM) of high coal concentration. Both saturated adsorption of the surfactant on coal particles and its presence in water were found to be necessary to prepare a practical CWM. The adsorption isotherms of the surfactants were described using the "Langmuir" equation. Each surfactant had a characteristic value of saturated adsorption. An estimation method of the required amount of the surfactant to prepare a practical CWM was proposed. The zeta potential of the CWM was found to vary with the coal concentration, and to be controlable using surfactants, thus failing to be a proper measure of the CWM at high coal concentrations.

Since CWM is recognized worldwide as being one of the most economical fluid fuels, several countries have been attempting to develop projects since the mid-1980's.[1,2] Currently, its development has continued primarily in Japan and China. In the development of commercially feasible CWM, surfactants have been recognized as playing the most important role. Although many manufacturers have reported fragmental data on the performance of their own surfactants[3—6] in limited regard to CWM, there have been very few reports concerning the behaviors and roles of surfactants from the viewpoint of interfacial science.[7—11] Unfortunately, there has been no work to suggest guidelines concerning what surfactant should be selected and how much should be applied.

A practical CWM as a liquid fuel must have such properties as an appropriate yield value to maintain its stability during a storage, a low apparent viscosity to accommodate CWM's spray for combustion and a high coal concentration for economical use.[12,13] In order to control these properties, an interfacial approach between the coal surface and surfactant should be required, significantly. Therefore, the behaviors and roles of surfactants as well as those of organic and inorganic constituents in coal should be clarified regarding CWM at high concentrations.

In this study, the properties and behaviors of surfactants which had been developed in a Japanese CWM project aimed at commercialization were investigated in relation to the rheological properties of CWM. The adsorption of surfactants on coal surfaces was analyzed in order to clarify the influence of their amount on the surface as well as the influence of their amount in water on the rheology of a CWM. The factors which may allow high concentrations of coal in a CWM were studied by measuring the zeta potential and viscosity. Based on such results, a reliable estimation method of the surfactant amount required to prepare a practical CWM can be proposed.

Experimental

Test Samples. An Australian bituminous coal often used for coal fluidization projects of Japan was selected as the coal for CWM preparation, its properties are listed in Table 1. This particular coal has been proven to exhibit satisfactory results concerning CWM production, storage and combustion in CWM development tests using a full-scaled boiler.[14]

Three types of surfactants, as additives required for CWM production, were selected by reviewing the results of full-scaled CWM development tests.[14] They are two types of polymer-type anionic surfactants, including naphthalenesulfonate–formaldehyde condensate (NSF) and poly(styrenesulfonate) (PSS), and one type of polymer-type nonionic surfactant, poly(oxyethylene) nonylphenyl ether (NPE).

The molecular weight distributions of the surfactants were observed by means of gelpermeation chromatography. The sulfonation rates of anionic surfactants were calculated

Table 1. Properties of Test Coal

Item analyzed		
Surface moisture	(%)	7.0
Proximate analysis		
Moisture	(%)	3.2
Fixed carbon	(%)	51.3
Volatile matter	(%)	31.7
Ash content	(%)	13.7
Ultimate analysis		
Carbon	(%)	84.2
Hydrogen	(%)	5.6
Sulfur	(%)	0.6
Oxygen	(%)	7.8
Nitrogen	(%)	1.8
Physical properties of crude coal		
Grindability	HGI	50
True specific gravity		1.427
Specific surface area	($m^2 g^{-1}$)	2.7
Pore volume	($ml g^{-1}$)	0.019

based on the amount of organic sulfate ion, which was determined as being the difference between the total amount of sulfate ion and the inorganic sulfate ion. The chain length of poly(oxyethylene) and the degree of ring condensation were measured on nonionic surfactants using NMR and FT-IR. Eight samples of NSF had mean molecular weights of 1700 to 6000; three samples of PSS had mean molecular weights of 6600 to 20000; and ten samples of NPE had degrees of ring condensation ranging from 1 to 5 and the chain length of ethylene oxide per benzene ring from 25 to 350.

CWM Preparation and Viscosity Measurement. Coal was pulverized using a dry tube mill so that it could be passed through a screen of 150 μm. The mean particle diameter was 28 μm, particles of 1 μm or smaller accounted for about 7% of the total coal particles. About 300 g of CWM was prepared in a 800 ml-steel beaker. Pulverized coal was gradually added into water containing a surfactant while the mixing operation was continued by stirring with blades of the double-helical ribbon type running at 225 rpm. After all of the material was added, high-velocity mixing was applied using a TK-Homomixer at 4000 rpm. Slurry samples showing pseudo-plastic or Bingham-type flow were tested. The viscosity of CWM was measured at 25 °C at a shear rate of 0 to 150 s^{-1} using a Haake double-cylinder-type rotary viscometer (rotor MV-1P, measuring head MK-500). The viscosity at 100 s^{-1}, when the shear rate was decreasing, was defined as the apparent viscosity of the CWM measured. The coal concentration in CWM was calculated by deducting the amount of surfactant used from the solid amount obtained after drying the CWM at 110 °C. As an inherent characteristic of coal, the achievable coal concentration was defined as the concentration to show 1000 cp (1 Pa s) of the apparent viscosity, estimated from the relation between the apparent viscosity and the coal concentration of CWM.

Adsorption Tests of Surfactants. CWM's prepared to a coal concentration of 62.5% using the respective surfactants were stored in sealed polymer bottles under mixing for 24 h; they were then screened through a millipore filter of 0.45 μm to analyze the surfactant concentration in the filtrate. The surfactants, NSF, PSS, and NPE were analyzed using gelpermeation chromatography and ultraviolet spectroscopy, respectively. The respective analytical conditions are listed bellow:

① Gelpermeation chromatography

Apparatus	Gel permeation chromatograph HCL-803 (by Toyo Soda)
Column	TSK gel G4000SW+G3000SW (by Toyo Soda)
Detector	UV (Measured wavelength NSF 254 nm, PSS 225 nm)
Solvent	H_2O (70)/CH_3CN (30)+0.5 M-NaCl (1 M=1 $\mathrm{mol\,dm^{-3}}$)

② Ultraviolet absorption spectroscope

Apparatus	Ultraviolet spectrophotometer UV 160A (by Shimadzu)
Solvent	H_2O

Measured wavelength 225 nm

The difference between the amounts of the added and remaining surfactants in the filtrate was equivalent to the amount of adsorption on coal particles, according to the following equations:

$$X = 62.5 \times S_a/(100 - S_c), \tag{1}$$

$$Y = (X - S_w)/X, \tag{2}$$

and

$$Z = S_a \times Y \times 10 \tag{3}$$

where S_a is the amount of surfactant added to the coal (wt%), S_b the measured concentration of the surfactant in water (wt%), S_c the coal concentration (wt%), X the surfactant concentration in water (assuming that the total amount of surfactant is present in water (wt%)), Y the adsorption amount of surfactant (wt%), and Z the adsorption amount on coal ($\mathrm{mg\,g^{-1}}$).

Measurements of Zeta Potential. A Shimadzu-Micromeritics zeta potential analyzer was used to measure the zeta potential at a high coal concentration. The measuring conditions were determined according to the changes in the zeta potentials of the slurries which were prepared in the 5 to 60% range, being diluted by water.

Stirring and Mixing Tests. CWM prepared to coal concentrations of 64 to 65% with optimum amounts of each surfactant (0.8% for NSF, 0.6% for PSS, and 1.3% for NPE, respectively) was stirred and mixed using a TK-Homomixer running at 6000 rpm. The change in the CWM viscosity and surfactant concentration in water were measured during the mixing process.

Results

Selection of Surfactants. To perform optimize each type of surfactant, a CWM preparation test was conducted with a surfactant of 1.0% per coal, those surfactants showing the highest coal concentration at an apparent viscosity of 1000 cp were selected from each group. The relations between the coal concentration and the CWM viscosity with various NSF's provided by different manufacturers are shown in Fig. 1. Although the viscosity generally tended to increase rather sharply with a higher concentration of coal, the absolute value of the viscosity depended greatly on the kind of NSF, thus indicating the importance of the surfactant in CWM preparation. An inspection of the effects of the mean molecular weight showed that a NSF of larger molecular weight, up to 5000, except for one kind, appears to allow a higher concentration. A NSF larger than 5000 may reduce the concentration.

The performance of NSF is roughly classified into two categories according to the sulfonation rate. The surfactants, which have different sulfonation rates below 83% and from 94 to 98%, exhibited very different performances. Based on these results, a NSF of its sulfonation rate exceeding 95%, and its mean molecular weight exceeding 3000, was selected.

A NSF of which the molecular weight and sulfonation rate were 3400 and 98%, respectively, was studied because of its superior performance and easy availability.

The optimization of PSS had already been studied within a range of its sulfonation rate (between 71 and 96%) by its manufacturer; the PSS of the rate at 90

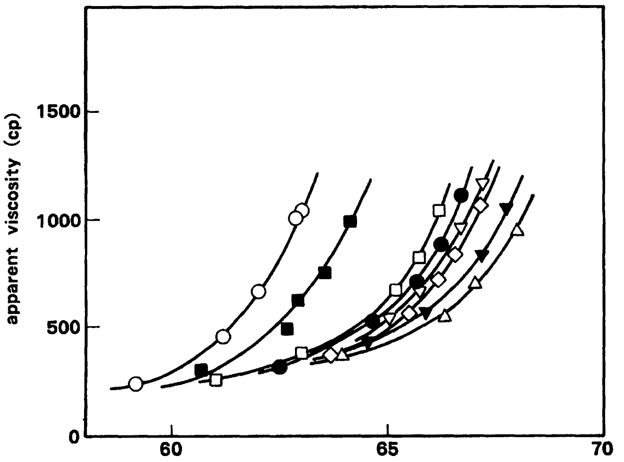

Fig. 1. Relations between the CWM's viscosity and concentration using each NFS. Mean Molecular weight; ○: 2940, ■: 1680, □: 2320, ●: 2430, ▽: 2900, ◇: 6630, ▼:3450, △:3990.

to 91% was selected as showing the highest coal concentration and storage performance. According to the effects of the molecular weight of PSS on the achievable coal concentration, as proposed by the manufacturer, a range of molecular weights of 6600 to 10000 was found to be adequate; thus, a particular one with a mean molecular weight of 10000 was selected due to its availability.

The effects of a cation in surfactants are illustrated in terms of the relationship between the coal concentration and the viscosity in Fig. 2. Ions also affected the achievable coal concentration, the sodium ion being found most favorable. The same trends concerning ion effects were found with NSF as well.

The relations between the achievable coal concentration estimated from the CWM preparation test using NPE and the molar ratio of ethylene oxide (EO) added per mole of nonylphenol are shown in Fig. 3. Although condensation degrees between 1 and 5 in NPE of nonionic surfactants indicated no relationship to the CWM productivity, a greater molar ratio of ethylene oxide sharply increased the concentration of coal until the ratio reached 100, at which point its effects reached the maximum to stay constant, even with a further increase in the amount of ethylene oxide per mole of nonylphenol. Thus, NPE carrying 100 moles of ethylene oxide per aromatic ring was typically selected for additional tests.

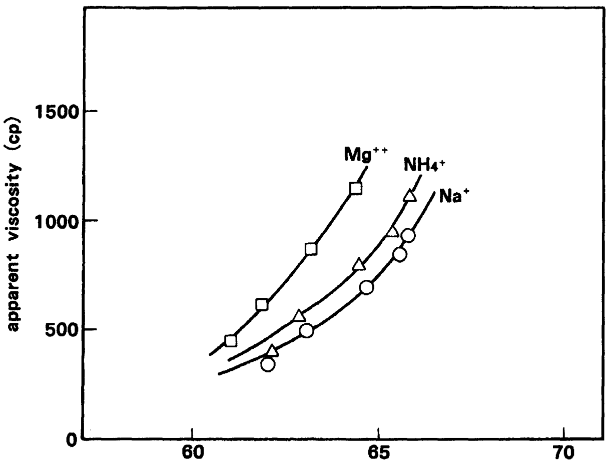

Fig. 2. Counter ion effects of PSS.

Surfactant Adsorption to Coal Particles. The adsorption isotherms are illustrated in Fig. 4 based on selecting the concentrations of surfactants in water as well as the amounts of adsorption on coal particles. All of the surfactants increased their amount of adsorption on coal particles along with an increase in their concentrations in water up to 0.06% in NSF, 0.04% in PSS, and 0.06% in NPE respectively; where the adsorbed amount reached 3.3, 2.7, and 9.0 mg g^{-1}, respectively, and remained constant with higher concentrations of surfactants in water up to 0.67% in NSF, 0.40% in PSS, and 1.75% in NPE, respectively. An inspection of Fig. 4 shows that all of the adsorption isotherms are of the general "Langmuir" form with a plateau where the constant amount of surfactant was adsorbed, regardless of its concentration in water. It should be noted that the amount of adsorbed surfactant decreased as the surfactant concentration further increased, with no surfactant remaining on the coal particles after the surfactant concentration in water reached 3.84% with NSF, 3.28% with PSS, and 7.14% with NPE, respectively.

Zeta Potential. The relationship between the zeta potential and the coal concentration is shown in Fig. 5. The potential was found to decrease sharply upon an increase of the concentration until 25%; the

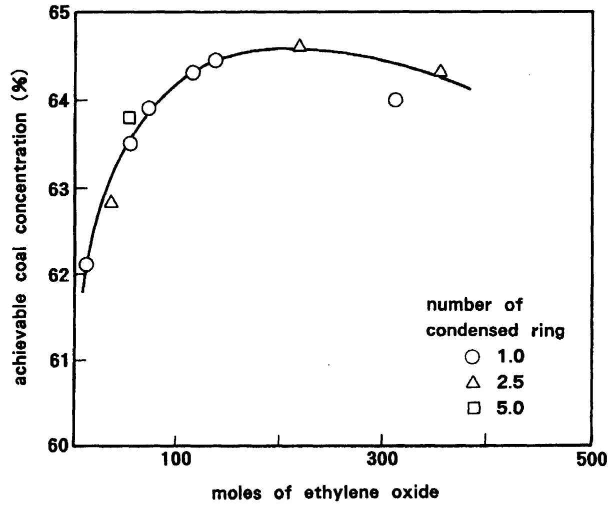

Fig. 3. Relation between the achievable coal concentration and the added molar ratio of ethylene oxide of NPE.

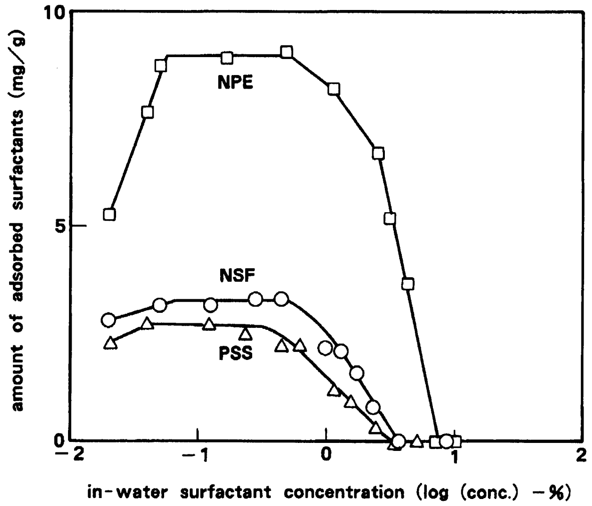

Fig. 4. Relations between the amounts of adsorbed the surfactant and surfactant concentration in water.

value remained rather stable until 35%. The potential increased sharply above this concentration. Thus, 30% loaded slurry was selected in order to measure the reproducible zeta potential values with experimental errors of less than 5%.

The relations between the zeta potential and the surfactant concentration in water are shown in Fig. 6. When any surfactant was applied above 0.25% per coal, a characteristic zeta potential for each surfactant was observed. The zeta potential changed from the values of the original coal particles to those characteristic of the respective surfactants. A nonionic surfactant, NPE of very small amount (0.2%), increased very sharply the zeta potential value along with an increase of the surfactant; NSF and PSS, however, significantly decreased the zeta potential values, first to give minimums, and then gradually increased the potential with their increase. The surfactant concentrations in water which allowed a re-increase of the zeta potential were 3.0% in NSF and 2.5% in PSS, respectively. Among the three tested surfactants, NSF appears to be more effective in reducing the potential.

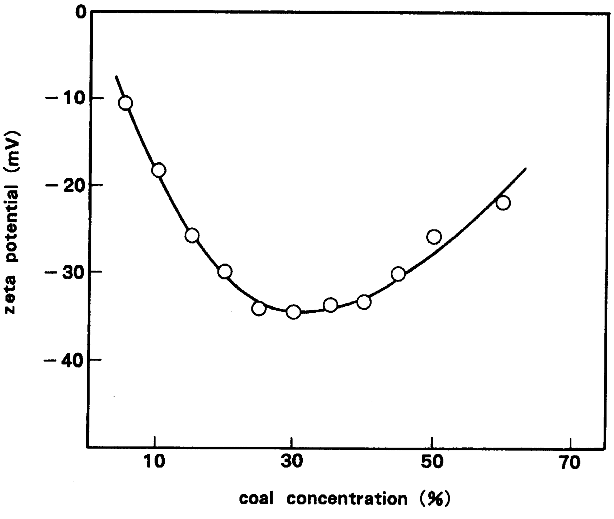

Fig. 5. Effect of the coal concentration on the observed zeta potential.

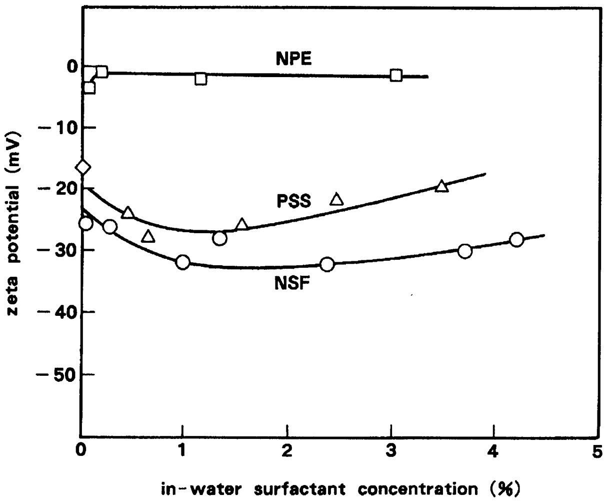

Fig. 6. Effects of the surfactant concentration in water on the zeta potential of CWM.

Rheology of CWM. The relationships between the concentration of a surfactant in water and the CWM viscosity are illustrated in Fig. 7. The CWM viscosity remained constant when the surfactant concentration in water exceeded 0.16% with NSF, 0.14% with PSS, and 0.18% with NPE. The CWM viscosity re-increased when the surfactant concentration in water exceeded 2.53% with NSF, 2.41% with PSS, and 4.27% with NPE.

The changes in the viscosity and the concentrations of the surfactants in water were measured during the stirring and mixing test. The relations between the stirring time versus the CWM viscosity and surfactant concentration in water are illustrated in Fig. 8. The viscosities of CWMs using the three surfactants initially sharply

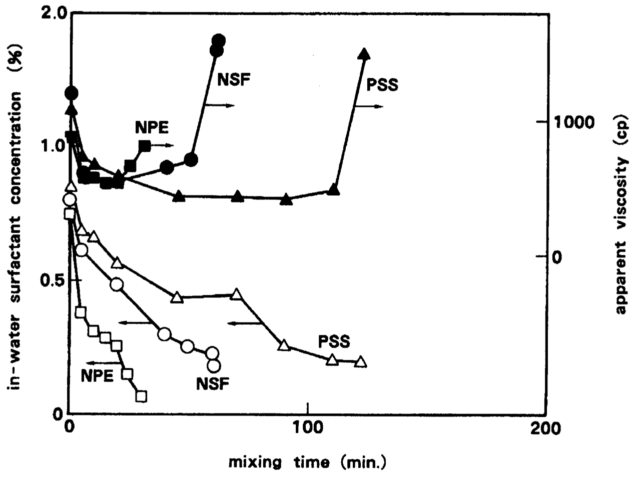

Fig. 7. Effects of the surfactant concentration in water on the viscosity of CWM.

decreased upon mixing, became almost constant, and then sharply rose, being independent of the concentrations of these surfactants. The concentration of surfactants in water decreased monotonously upon mixing. Such changes upon mixing were most rapid with NPE, slower with NSF, and then PSS, in that order. Hence, the decrease in the viscosity during the initial period of mixing is apparently due to the adsorption of surfactants to coal particles due to stirring, as indicated by decreased amounts of surfactants in the water. The sharp increases in the viscosities during the latter half of mixing is probably due to excessive decreases in the surfactant concentrations in water, which became less than 0.26% with NSF, 0.21% with PSS, and 0.26% with NPE.

Discussion

CWM as a fluid fuel is required in order to provide a stable and adequate viscosity throughout its handling, such as its transport, storage, and combustion. CWM should thus show a pseudo-plastic or Bingham-type flow in its rheological properties.[13] CWM of high coal concentration in water can obtain such properties through the aid of surfactants.

Since the surfactant is adsorbed on the coal particles, it must also be present in water so as to provide a low viscosity of the CWM fluid, since coal particles should be dispersed according to the densest packing. However, excess surfactant in water increases the viscosity of water due to its polymeric nature. Thus, the most adequate form and amount of the adsorbed surfactants were clarified in the present study.

The above discussion suggests the importance of adsorption concerning the performance of surfactants. The amount and state of their adsorption are of the greatest concern. A higher content of hydrophilic groups is favorable for both NSF and PSS. A proper molecular-weight distribution is also necessary. The molar ratio of ethylene oxide per mole of nonyl phenol appears to be a key quantity regarding NPE. The number defines both the extent of the hydrophilic properties as well as the molecular size.

The adsorption of the surfactant is sensitively influenced by the amount added and its structure. The polymer-type surfactants presently investigated exhibited adsorption behavior more or less similar to those of alkyd resin on TiO_2 analyzed by Rehácêk.[15] Because of the common features, the adsorption of the present surfactants was analyzed according to his procedure. Assuming that an adsorption layer surrounds a coal particle, the adsorption amount expressed as the surfactant concentration in water C (%) after reaching equilibrium was formulated based on Eq. 4, were M_a ($\mathrm{g\,g^{-1}}$), C_a (%),and A_b ($\mathrm{mg\,g^{-1}}$) are amount of solution in the adsorption layer per gram of coal, surfactant concentration in the adsorption layer and the amount of surfactant adsorbed on coal, respectively:

$$A_\mathrm{b} = M_\mathrm{a} \times (C_\mathrm{a} - C). \tag{4}$$

The relationships between the surfactant concentration in water and the adsorption amount according to Eq. 4 are shown in Fig. 9, where the polymeric behaviors of NSF, PSS, and NPE are clearly indicated in their adsorptions. The respective intrinsic values, (A_b, C_a, and M_a) of NSF, PSS, and NPE, as obtained from Fig. 9, are 3.69 $\mathrm{mg\,g^{-1}}$, 2.98% and 0.012 $\mathrm{mg\,g^{-1}}$, 2.73 $\mathrm{mg\,g^{-1}}$, 2.53%, and 0.011 $\mathrm{g\,g^{-1}}$, and 9.62 $\mathrm{mg\,g^{-1}}$, 7.02%, and 0.014 $\mathrm{g\,g^{-1}}$, respectively. The thicknesses of the adsorption layers of NSF, PSS, and NPE, calculated by assuming a specific surface area of 2.7 $\mathrm{m^2\,g^{-1}}$ of pulverized coal and surfactant densities of 1.011, 1.012, and 1.011 at a concentration C_a of the respective surfac-

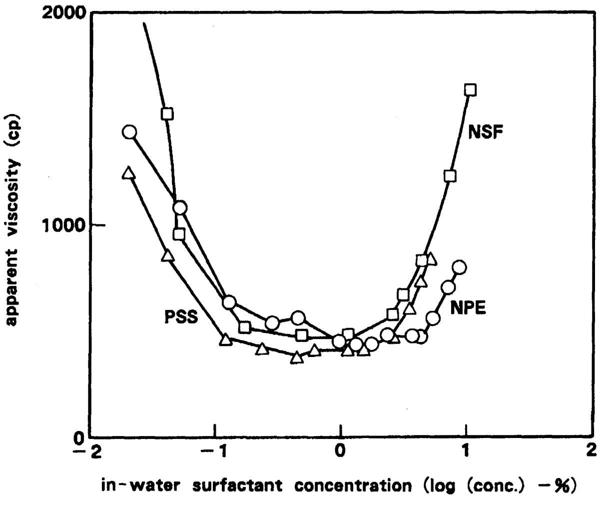

Fig. 8. Changes of the CWM viscosity and surfactant concentration in water during stirring and mixing tests.

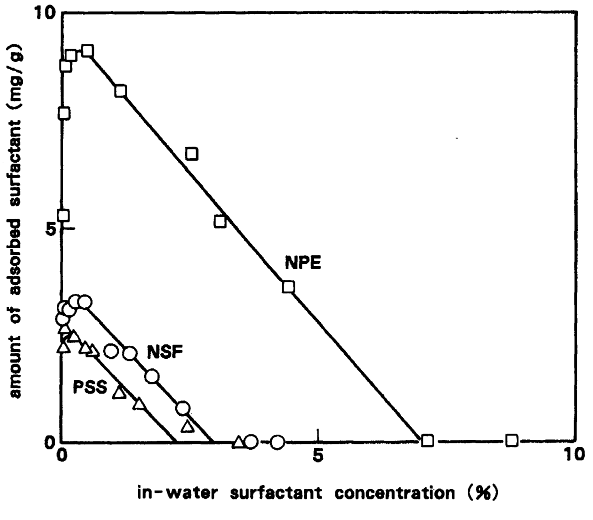

Fig. 9. Relations between the amounts of adsorbed surfactants and the surfactant concentrations in water.

Table 2. Properties of Surfactants

Surfactant	Amount of adsorption A_b (mg g^{-1})	Required surfactant concentration: Adsorption layer C_a(%)	Lower limit in water C_{min}(%)	Upper limit in water C_{max}(%)	Weight of adsorpsion layer M_a (g g^{-1})
NSF	3.69	2.98	0.26	2.94	0.012
PSS	2.73	2.58	0.21	2.41	0.011
NPE	9.62	7.02	0.26	4.27	0.014

tants, are 4.4, 4.0, and 5.1 nm, respectively.

It is, therefore, expected that these surfactants, though different in type, can function similarly in CWM production and form an adsorption layer on coal particles, thus allowing the high coal concentration at low viscosity. The dosing amount of surfactant required for CWM production increases in the order PSS, NSF, and NPE according to the thickness of the adsorption layer. This order agreed with that of the achieved coal concentration of CWM using each surfactant.[16)]

As evidenced in Fig. 7, the required amounts of the surfactant in water which could keep the viscosity constant (0.16% in NSF, 0.14% in PSS, and 0.18% in NPE) were greater than those of the saturated adsorption derived from Fig. 4 (0.06% in NSF, 0.04% in PSS, and 0.06% in NPE). This indicates that a surfactant must be present in water in a certain amount in order to disperse coal particles saturated with the adsorbed surfactant in order to produce a low-viscosity fluid of CWM. However, an excess amount of surfactant in water increases the viscosity of CWM due to their behavior as polymers, as shown in Fig. 7 (2.53% in NSF, 2.41% in PSS, and 4.27 in NPE).

Based on the concentration characteristic of each surfactant where the viscosity increases sharply, as shown in Fig. 8 (0.26% in NSF, 0.21% in PSS, and 0.26% in NPE), the required amounts of surfactants were estimated. These obtained values were found to be in a good agreement to those obtained from adsorption tests given in Fig. 7, indicating that surfactants work similarly under handling conditions as well as under the production of CWM.

As mentioned above, NSF, PSS and NPE have saturated adsorption values, respectively; these values are related to the achievable coal concentrations. The dosing amount of surfactant required for CWM production increases in the order PSS, NSF, and NPE according to the saturated adsorption value. The adsorption layer of a surfactant on solid particles can affect the degree of coal concentration and dispersing power of solid particles.

The surfactant concentration obtained by the stirring and mixing test is at its lower limit concentration (C_{min}) in water, that in the adsorption test is at its upper limit concentration (C_{max}) in water. These values as well as the intrinsic values for each surfactant (A_b, C_a, and M_a) are summarized in Table 2. The range of surfactant amounts required to prepare the coal concentration of C_c (%) can be obtained from Eq. 5 using the values given in Table 2. The first term of the right-hand side in Eq. 5 refers to the adsorption of the surfactant to the surfaces of coal particles; the second term refers to its dissolution into water from coal particle surfaces; the third term refers to how much of it is present in water.

$$\begin{aligned} Co_{min} &= [A_b \times C_c \times 0.001 + M_a \times C_a \times C_c \times 0.01 \\ &\quad + C_{min} \times (100 - C_c) \times 0.01]/(C_c \times 100) \\ Co_{max} &= [A_b \times C_c \times 0.001 + M_a \times C_a \times C_c \times 0.01 \\ &\quad + C_{max} \times (100 - C_c) \times 0.01]/(C_c \times 100) \end{aligned} \tag{5}$$

Calculations of the amount of surfactant required to prepare CWM at 65% coal concentration yield the required minimum amount per coal (Co_{min}) and the usage upper limit (Co_{max}) of 0.54 and 1.99% for NSF; 0.41 and 1.60% for PSS; and 1.20 and 3.36% for NPE, respectively. By using the upper limit of the surfactant concentration where monolayer adsorption occurs (Fig. 4) instead of the C_{max} value, the favorable amount of surfactant per coal is deduced to be in the range 0.54 to 0.77% with NSF, 0.41 to 0.52% with PSS, and 1.20 to 2.00% with NPE. Since the required minimum amounts are almost the same regarding the concentrations of the three surfactants in water, the required amounts of surfactants are concluded to be dominantly governed by their saturated adsorption to coal particles.

The zeta potential was determined as a measure of CWM preparation. However, the values were found to be very strongly dependent on the coal concentration, as far as highly loaded CWM is concerned. The potential value thus has only a small significance on the behavior of CWM. The relation between the potential and the surfactant concentration in water shown in Fig. 6 may confirm the above conclusion. The change in the zeta potential is principally due to the dispersion of coal particles in a slurry and adsorption of the surfactant. Coal particles appear to easily precipitate at a low concentration range, but hard to migrate in a high coal concentration range, thus influencing the value of the zeta-potential.

On the basis of the above discussion, the roles and behaviors of surfactants under CWM conditions of high coal concentration were clarified as follows: (1) Both saturated adsorption of the surfactant on coal particles and its presence in water were required to prepare favorable properties of CWM, such as low viscosity and high coal concentration. (2) The adsorption isotherms of the surfactants were described by "Langmuir" form, giving a definite saturated adsorption. (3) An empirical equation which can be used to calculate the required amount of surfactant was proposed for the preparation of a practical CWM. (4) The zeta potential was found to change greatly with the coal concentration. Its charge was controlled by the surfactants.

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 several companies (Kao, Lion, and Neos) 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) "Proceeding of the 12th International Conference on Slurry Technology," Louisiana, U.S.A., 1987.

3) L. L. Stigsson, C. A. Johansson, and R. G. Carlson, "6th International Symposium on Coal Slurry Combustion and Technology," Florida, U.S.A., 1984, Abstr., p. 403.

4) Y. Kiyonaga and M. Narita, "6th International Symposium on Coal Slurry Combustion," Florida, U.S.A., June, 1984, Abstr., p. 403.

5) S. Watanabe and K. Katabe, "6th International Symposium on Coal Slurry Combustion," Florida, U.S.A., June, 1984, Abstr., p. 467.

6) Y. Ogura, N. Uejima, Y. Mizuno, and A. Naka, "8th International Symposium on Coal Slurry Fuels Preparation and Utilization," Florida, U.S.A., May, 1986, Abstr., p. 129.

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

8) E. Z. Casassa, G. D. Parfitt, A. S. Rao, and E. W. Toor, Ref. 7, 1984, Abstr., p. 251.

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

10) C. Tanaka, Y. Yamagata, S. Suzuki, and H. Yotsumoto, *Kogai-Shigen Kenkyusho Ihou*, **14**, No. 2, 27 (1984).

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

12) H. Yamamoto, T. Matsuo, K. Arase, H. Hunatsu, Y. Nakashima, and S. Kaneko, *Mitsubishi Zyuko Giho*, **22**, 444 (1985).

13) D. Ercolani, E. Carniani, and G. Gabrielli, "12th International Conference on Slurry Technology," New Orleans, U.S.A., 1987, Abstr., p. 277.

14) 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, Abstr., p. 738.

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

16) G. D. Botsaris and Y. Glazman, " 5th International Symposium on Coal Slurry Combustion and Technology," Florida, U.S.A., 1983, Abstr., p. 1181.