COAGULATION AND DISPERSION CHARACTERISTICS OF COAL WATER MIXTURES IN HIGHER TEMPERATURE RANGE

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The present investigation is aimed at finding the reason for the anomalous increase in viscosity of coal water mixtures (CWMs) in the higher temperature range ($>150^{\circ}\text{C}$). The ζ -potential of coal particles in the higher temperature range was measured with the addition of six kinds of surfactants. The experimental results showed that the ζ -potential of Wallarah coal with anionic surfactants still show negatively higher values in the higher temperature range; thus it was expected that no significant desorption of anionic surfactants occurs. Furthermore, from considerations based on the DLVO theory it was concluded that the temperature dependence of the dielectric constant of water affects the coagulation of coal particles.

Introduction

In processes that utilize CWM (coal water mixtures), many heat transfer operations are involved. For example, preheating of CWM in the coal gasification process¹⁰⁾ and thermal preconditioning of CWM both for feeding in a gas turbine system⁶⁾ and for the coal gasification process^{13, 14)} are effective in improving the efficiency of CWM utilization. Also, many heat exchangers are employed in the CWM production plant and the CWM boiler system. The temperature dependence of CWM viscosity should be well known in order to develop a precise design of CWM heat transfer operations. Tsutsumi *et al.*¹¹⁾ measured the viscosity of CWM at 20 to 120°C and concluded that the CWM viscosity was proportional to the solvent viscosity. The same tendency was reported by Cen *et al.* for CWM at 20 to 100°C ¹⁾. When the slurry temperature exceeds 150°C , an anomalous increase in CWM viscosity has been reported by Usui *et al.*¹²⁾ and Ninomiya *et al.*⁵⁾ As the solvent viscosity continues to decrease in this temperature range, it is expected that the agglomeration of coal particles is the reason for the anomalous increase in CWM viscosity. Various kinds of additives are employed to produce highly loaded CWM with low viscosity. Recently, polyanionic surfactants such as PSS (polystyrene sulfonic acid) and PMA (polymethacrylate) have been widely used⁴⁾. These anionic surfactants are adsorbed on the coal surface, and they increase the electrostatic repulsion force between the coal particles. Experimental evidence that the coagulation of coal particles occurs in the higher temperature range indicates that desorption or degradation of additives could occur. Also, the extraction of organic compounds and the swelling of coal particles were possible reasons for the viscosity increase of CWM in the higher temperature range. Usui *et al.*¹²⁾ discussed these phenomena and concluded that the combined

effect of swelling and of change of surface condition of coal was most responsible for the viscosity increase of CWM. Ninomiya *et al.*⁵⁾ observed almost the same viscosity-increasing phenomenon as are suggested by the data of Usui *et al.* They concluded that the viscosity increase of CWM is not significantly affected by the heat degradation of additives, the extraction of organic compounds or the swelling of coal particles. They suggested that the anomalous viscosity increase could be caused by the desorption of additives or the change of surface characteristics of coal particles. For further examination of the above-mentioned phenomenon, measurement of surface potential values of coal particles seems to be most effective to obtain a more profound insight for making clear the reason for CWM viscosity increase.

Thus, in this study we intended to carry out surface potential measurements in the higher temperature range. Discussion based on these experimental results may give us an index for selecting suitable additives for CWMs processed in that temperature range.

1. Experimental

1.1 Preparation of samples

A Wallarah coal was pulverized in a wet ball mill and the pulverized coal particles were dispersed into water. The solid content of samples was set at 10 ppm. It is necessary to prevent sedimentation of coal particles during ζ -potential measurement. Thus the sample was left at rest for 20 minutes' time and then the supernatant liquid was used as the sample. Six kinds of surfactants were used and the additive concentration was 0.3 wt%/solid. The surfactants used in this study are listed in Table 1.

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Table 1. Table 1 Surfactants used in this study

notation	composition	M.W.
<anionic>		
PMA	polymethacrylate	40,000~60,000
NSF	condensation product of formalin and naphthalene sulfonic acid	3,000
POS	polyolefin sulfonic acrylate	
PSS	polystyrene sulfonic acid	100,000
PSA	polysodium acrylic acid	28,000
<nonionic>		
Koal	(brand name)	
-500A	unknown in detail	

1.2 ζ -potential measurements

The ζ -potential of coal particles was determined by electrophoresis measurements. The experimental apparatus is schematically shown in Fig. 1.

The cell temperature is controlled by an air bath with a thermostat. Temperature was varied from 25°C to 175°C. The high-pressure cell was made of stainless steel and was 15 × 15 × 100 mm in size. The inside wall of the cell was coated with insulating paint. When a 600-volt direct current is applied to the electrodes of the cell, the electrophoresis of coal particles begins, and the electrophoresis velocity is proportional to the surface potential of the particle. In this study, the electrophoresis velocity was measured by means of a LDV (laser Doppler velocimeter). In practical ζ -potential measurements by an electrophoresis method, the effect of electroendosmosis must be taken into account. However, the aspect ratio of the test cell used in this study was not large enough because of the difficulty of the high-pressure design. Also, it was found that the three-dimensional flow generated near the electrodes significantly affected the velocity profiles at the measuring point. To prevent these influences we fixed a honeycomb near the electrodes as shown in Fig. 1. It was expected that although a velocity distribution could occur in each honeycomb, the velocities at the outlet of the honeycomb might cancel each other. The distribution of electrophoresis velocity of each particle measured by a LDV is shown in Fig. 2. The measuring position is at the center of the cell, and y is the cross-sectional distance from the centerline of the cell. In this figure the abscissa represents y/b , where b is the half-width of the cell. Although some scatter of experimental data is observed, it may be concluded that the effects of electroendosmosis and the honeycomb are negligibly small. Thus we conclude that the velocity measured by LDV is the electrophoresis velocity of coal particles.

Fig. 1 Experimental apparatus **Fig. 2** Electrophoresis velocity distribution across the cell cross section (sample: Wallarah coal without additives, measured at 25°C)

1.3 Data processing to calculate the value of ζ -potential

Data processing to calculate the value of the ζ -potential is as follows. The voltage across the resistance R was measured with a data recorder (Yokogawa Electric Co. Ltd. LR-4220) as shown in Fig. 1. The resistance R was 200 Ω , so the electric current through the cell i was calculated using the relation $i = V/R$. The electric conductivity of the sample suspensions was measured by an electroconductivity meter (Simazu Seisakusyo 1220). But the sensor of this unit was made of glass, making it impossible to carry out measurements if the temperature of the sample liquid exceeded 100°C. Therefore, a high-pressure cell made of stainless steel as shown in Fig. 3 was prepared to replace the glass sensor. The cell was set in an air bath. Two electrodes were fixed in the cell and were connected to the electric conductivity meter. Electric conductivity λ was calculated by the following equation:

Fig. 3 High-pressure proof cell for measurement of electric conductivity

$$\lambda = K / (R') \quad (1)$$

where R' is the resistance measured by this equipment and K is the cell constant. K was measured by using 0.01N-KCl and the value of the cell constant was found to be 1.004 cm^{-1} .

In the electrophoresis experiment, the value of the applied voltage divided by the distance between the electrodes would not be equal to the voltage gradient because polarization and adsorption of particles on the cell would change the resistance of the cell. But if the constant current i can be measured, the effective voltage gradient E is calculable by

$$E = i / (\lambda A') \quad (2)$$

where A' is the cross-sectional area of the cell.

Finally, using the following Smoluchowski equation⁹⁾, we can calculate the value of the ζ -potential:

$$u = (\epsilon E \zeta) / (4\pi\eta) \quad (3)$$

where ϵ is a dielectric constant and η is the viscosity of the sample. In fact, the solids concentration of the sample is so low that the viscosity of the sample is nearly equal to that of water.

2. Results and Discussion

The experimental results for the electric conductivity of each sample are shown in **Fig. 4**, from which the linear relationship between the electric conductivity and $1/T$ was confirmed, even at temperatures higher than 100°C .

The experimental results of ζ -potential measurements are shown in **Fig. 5**. The ζ -potential of Wallarah coal without additives at 25°C was determined as -48.7 mV . Mori *et al.*³⁾ have proposed a correlation equation that can be used to determine the ζ -potential of the coal particles. Using the results of ultimate analysis for Wallarah coal, the ζ -potential of Wallarah coal without addi-

Fig. 4 Electric conductivity data for each sample

Fig. 5 Experimental results of ζ -potential measurements

tives at 25°C was calculated as -38.8 mV . Thus the value obtained in this study is around 25% negatively larger than the calculated value. As mentioned earlier in this paper, the flow in the cell is not completely two-dimensional due to the cell's high-pressure design. Although the experimental results in this study have a factor of around 25% error, we expect that the discussion of the effect of both temperature and additives on the ζ -potential of Wallarah coal is applicable in this study.

It is shown in **Fig. 5** that the ζ -potential tends to

Fig. 6 Total potential between Wallarah coal particles with 0.3 wt% of PSA

decrease for all the samples with increase in temperature. In particular, the ζ -potential of Wallarah coal without additives decreases greatly in the higher temperature range ($>150^\circ\text{C}$). Nevertheless, the ζ -potential of Wallarah coal with anionic surfactants still shows negatively higher values ($\zeta < -60\text{mV}$) in the higher temperature range. Thus we can conclude that no significant desorption of anionic surfactants occurs. In short, desorption of the additive is not the reason for the anomalous increase of CWM viscosity.

Next we discuss the coagulation and repulsion characteristics of coal particles, using the DLVO theory²⁾. Repulsion potential V_R and attractive potential V_A can be estimated by the following equations:

$$V_R = \frac{\epsilon d_1 d_2 (\psi_1 + \psi_2)^2}{8 (d_1 + d_2)} \times \left[\frac{2\psi_1\psi_2}{(\psi_1 + \psi_2)^2} \ln \left\{ \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right\} + \ln \{ 1 - \exp(-2\kappa h) \} \right] \quad (4)$$

$$V_A = -\frac{A d_1 d_2}{12 (d_1 + d_2) h} \quad (5)$$

where A , κ , ϵ , d_1 and d_2 are respectively the Hamaker constant, the Debye-Hückel constant, dielectric constant of water⁷⁾ and the sizes of the coal particles. It is very difficult to determine the Hamaker constant and the Debye-Hückel constant exactly. So, referring to previous papers^{5, 8)}, we selected the following values: $A = 10^{-20} \text{ J}$, $\kappa = 3 \times 10^8 \text{ m}^{-1}$. Also, d_1 and d_2 were set constant as $1 \mu\text{m}$, and ψ_1 and ψ_2 were set equal to the measured ζ -potential. Some examples of the total potential $V_R + V_A$ are shown in Fig. 6 for Wallarah coal with PSA. The ordinate represents $V_A + V_R$ divided by kT , where k is a Boltzmann constant and T is absolute temperature. It is well known that the critical value of $V_A + V_R$ between the coagulation and the dispersion of two particles is $15 kT$. Thus the data shown in Fig. 6 indicate that coal particles

Fig. 7 Temperature effect on maximum total potential of coal particles with various kinds of additives

with the addition of PSA are expected to be dispersed at 25°C , whereas in the higher temperature range they would coagulate. As expected from the above discussion, it is convenient to compare the maximum value of $V_A + V_R$ in various temperature ranges. Thus, in Fig. 7, the maximum values of total potential are plotted against the temperature. A dotted line indicates the value of $(V_A + V_R) = 15 kT$. This diagram indicates that all the samples are expected to lose their fluidity in the higher temperature range. As mentioned above, the values of ζ -potential were over -60 mV for the entire temperature range. The other significant parameter in the decrease of the total potential value with increase in temperature is the dielectric constant of water, which depends greatly on the temperature change⁷⁾. For example, the dielectric constant of water at 175°C is almost half that at 25°C . As the result of dielectric constant variation, the repulsion potential V_R is significantly affected by the temperature. In the above discussion, only one particle diameter, i.e. $d_1 = d_2 = 1 \mu\text{m}$, was employed. Moreover, the temperature dependence of the Hamaker constant is not precisely known at present. However, the above discussion may offer a qualitative explanation of the viscosity increase of CWM in the higher temperature range. Thus we can conclude that the temperature dependence of the dielectric constant of water is one of the reasons for the anomalous viscosity increase of CWMs in the higher temperature range.

Other conceivable reasons are as follows:

- 1) extraction of organic compounds from coal
- 2) swelling of coal particles
- 3) changes of surface condition of coal
- 4) extraction of electrolyte from coal

As noted previously, items 1) and 2) have been discussed by Usui *et al.*¹²⁾ and Ninomiya *et al.*⁵⁾ They concluded that these effects were not the main reason for the anomalous viscosity increase of CWM. However, further study is needed to clarify the effect of 3)

and 4) on the increase in CWM viscosity in the higher temperature range.

Conclusion

ζ -potentials of coal particles in the higher temperature range were measured by the electrophoresis method with a laser Doppler velocimeter. Experimental results showed that the ζ -potential of Wallarah coal with various kinds of anionic additives showed negatively higher values ($\zeta < -60\text{mV}$) over the entire temperature range (25 to 175°C). On the other hand, the dielectric constant of water decreased greatly with temperature increase. Therefore, prediction of the total potential by the DLVO theory indicated that the coal particles could be expected to coagulate in the higher temperature range. Although various kinds of additives were examined, none suitable for producing a CWM without coagulation in the higher temperature range was found. It may be necessary to study another additive, of which the repulsion mechanism is different from that of anionic surfactants.

Nomenclature

A	= Hamaker constant	[J]
A'	= cross-sectional area	[m ²]
b	= width of the cell	[mm]
d_1	= diameter of coal particle 1	[m]
d_2	= diameter of coal particle 2	[m]
E	= effective voltage gradient	[V/cm]
H	= distance between particle 1 and particle 2	[m]
i	= electric current	[A]
K	= cell constant	[cm ⁻¹]
k	= Boltzmann constant	[J/K]
R	= resistance	[Ω]
R'	= measured resistance	[Ω]
T	= absolute temperature	[K]

u	= electrophoresis velocity	[mm/s]
V	= voltage between the resistance	[V]
V_A	= attraction potential	[J]
V_R	= repulsion potential	[J]
y	= distance from center of cell	[mm]
ϵ	= dielectric constant	[J ⁻¹ C ² m ⁻¹]
ζ	= ζ -potential	[V]
η	= viscosity	[Pa·s]
κ	= Debye-Hückel constant	[m ⁻¹]
λ	= electric conductivity	[Ω ⁻¹ cm ⁻¹]
Ψ_1	= ζ -potential of coal particle 1	[V]
Ψ_2	= ζ -potential of coal particle 2	[V]

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