

Effect of Electrolyte on the Rheological Properties of Coal-Water Mixtures

Highly concentrated coal-water mixtures were prepared using two different types of dispersants, anionic and nonionic. Through experimental investigations of the effect of the electrolytes on their rheological properties, the mechanisms of the particle dispersion in both mixtures have been elucidated.

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Introduction

Concentrated coal-water mixtures (CWM's) have attracted great attention as an economical means of transportation of coal through pipelines, and their flow and stability properties are of great concern for the design of industrial flow and process equipment. In the production of CWM's, it is very important to establish criteria for controlling their rheological properties so as to obtain highly loaded mixtures with acceptable fluidity while maintaining sufficient stability against sedimentation of particles. CWM's usually contain about 60 to 75 wt. % coal, which is approximately equivalent to 65 to 75 vol. % (depending upon the apparent density and the water-holding capacity of the coal), far in excess of what are commonly described as concentrated suspensions. Although their rheological properties have been observed to be strongly influenced by a large number of variables, such as the size distribution of the particles, the physicochemical properties of the coals present, and type and amount of dispersants (Al Taweel et al., 1982), CWM's have not been studied systematically and are not as yet well understood due to their nature as poorly defined, complex suspensions from a colloid chemical point of view. However, in establishing the criteria for controlling CWM rheology, it is necessary to quantify the effects of the governing factors. It is also of considerable interest to investigate the relation between the macroscopic, or bulk properties of CWM's and their microscopic structure on the particle scale. In this paper, we present some results of experiments undertaken to add to the knowledge of factors governing the rheology of CWM's.

A typical CWM behaves as a non-Newtonian fluid at high solids concentrations, and some CWM's have significant time-dependent characteristics—e.g., shear-thinning, shear-thickening, thixotropy, rheopexy, and probably viscoelasticity—which result from the increasingly important role played by nonhydrodynamic, or colloid chemical interactions between suspended

particles, as average interparticle spacing decreases. At low solids concentrations, i.e., as the surface-surface separation increases, these interactions become less pronounced, and the CWM behaves as a Newtonian fluid.

A CWM is generally not monodisperse, but comprises a wide distribution of particle sizes, ranging from about 0.1 to 500 μm in diameter. This distribution encompasses particles of colloidal dimensions as well as those several orders of magnitude larger than usual colloidal particles. Particles in a suspension under shear experience many kinds of forces:

- Hydrodynamic forces, which include the viscous drag force of the suspending medium as well as particle-particle interaction through flow field disturbances induced by neighboring particles.
- Colloid chemical forces, including steric and electrostatic repulsive and London-van der Waals attractive forces.
- Forces due to gravitational, inertial, electroviscous, and thermal or molecular-collisional effects.

Electroviscous and thermal effects decrease with increasing diameter, and they may be of negligible order for particle sizes typical of CWM's (Thomas, 1963; Russel, 1980). It is expected that for large particles, the inertial force and viscous force from the suspending medium are significant, and that the colloid chemical forces become progressively more dominant with decreasing particle size (Gadala-Maria and Acrivos, 1980; Russel, 1980). Hence, CWM rheology will vary as the state of balance between hydrodynamic and nonhydrodynamic forces acting on the particles changes.

Since Einstein first derived a theoretical expression for the relative viscosity of an infinitely dilute suspension of rigid spheres, extensive theoretical and experimental studies have been conducted to determine a formula that is valid at higher concentrations, where both hydrodynamic and nonhydrodynamic interactions between particles should be important (Frisch and Simha, 1956; Rutgers, 1962; Herczyński and Pieńkowska, 1980). However, previous theoretical analysis typically has neglected inertial and colloid chemical forces, consid-

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ering only hydrodynamic interactions. Similarly, experimental investigations are usually conducted in well-characterized monodisperse systems where only hydrodynamic forces have appreciable influence on the motion and interaction of particles. However, at higher values of particle concentrations, the experimental data for relative viscosity exhibit a large degree of scatter, sometimes differing by an order of magnitude even for those well-defined systems (Jinescu, 1974; Jeffrey and Acrivos, 1976).

As the coal surface is hydrophobic by nature, CWM's comprise suspensions in which hydrophobic solid particles are forced to be dispersed in water by the action of electrostatic and/or steric repulsive forces created by the adsorption of the dispersing agents. Hence, the rheological properties of concentrated CWM's may be strongly dependent upon the colloid chemical interactions, and extremely sensitive to several factors affecting these interactions: the degree of flocculation has important contributions to the energy dissipation through formation and rupture of structural linkages (van Diemen and Stein, 1982).

Two important factors that strongly influence the colloid chemical interactions are the surface properties of coal and the ionic strength of the supernatant solution. Since coal is not a uniform substance but a mixture of carbonaceous materials and mineral matter, it has a variety of surface properties. The adsorption characteristics of dispersants may be affected by the coal surface properties, which in turn affect the nature of the solid-liquid interface and the interaction between the particles. Supernatant composition and ionic strength can vary since some of the mineral matter in the coal particles dissolves into water to form multivalent ions. It is well known that in a hydrophobic colloid system which is stabilized by electric charges on the particles, the ionic strength, i.e., the electrolyte concentration in the dispersing medium, has a significant effect on its stability against flocculation (Heimenz, 1977).

Experimental

Materials

The coal used in this study was an American bituminous coal from the Upper Freeport, Pennsylvania, seam; its analyses are given in Table 1. Ultimate and proximate analyses were performed using a Perkin-Elmer 240B Elemental Analyzer and Fisher Coal Analyzer model 490, respectively. The water-holding capacity of the coal was measured by a technique described elsewhere (Kaji et al., 1986). Two types of dispersants were employed, anionic and nonionic. The anionic dispersant was a sodium salt of sulfonated naphthalene-formaldehyde condensate (Nippon Oil and Fat Co., avg. mol wt., 1,900). The nonionic dispersant was provided by Dai-ichi Kogyo Seiyaku Co., Ltd. (avg. mol wt., 55,000). The dispersants were used as obtained. All the salts used in the experiment were reagent grade, and were used without further purification.

Table 1. Analyses of Coal

Dry, Ash-free, wt. %					Wet Basis, wt. %		
C	H	N	O by diff.	S	Ash	Volatile Matter	Moisture
83.1	5.4	1.5	7.6	2.4	11.5	30.6	1.9

CWM preparation and rheological measurements

Coal was first ground to under 3 mm dia. The ground coal was subsequently pulverized in the presence of water and a dispersing agent to form a homogeneous, fluid CWM. The resulting particle size distribution was measured by sieving with wire mesh screens (sieve openings between 297 and 20 μm) followed by analysis employing a centrifugal photosedimentometer that operates by means of a light-extinction method (Hitachi Horiba Capa 500). Samples with various top sizes were prepared to study the effect of particle size distribution on CWM rheology. The size distributions of the samples are shown in Figure 1. These samples were obtained by sieving the CWM with wire mesh screens of appropriately sized openings so that all samples had the same supernatant composition.

The amounts of anionic and nonionic dispersants were 0.7 and 1.0 wt. %, on a dry coal basis, respectively. During the preparation of the CWM using the anionic dispersant, an appropriate amount of sodium hydroxide was added to adjust pH. The pH of the resulting CWM was 8.1. No attempt was made to adjust the pH of the CWM with the nonionic dispersant, which had a pH value of 2.2. The solids concentrations of the CWM's were determined by measuring the weight loss on drying at 110°C for approximately 3 h. A correction was made for the amount of additives. The solid volume fraction, ϕ , was obtained by

$$\phi = \frac{V_s}{V_s + V_w - V_{ab}} = \frac{Cs/\rho_a}{Cs/\rho_a + 100 - Cs(1 + \gamma)} \quad (1)$$

where V_s is the volume of solid, V_w is the volume of total water in the CWM, V_{ab} is the volume of water absorbed by coal, Cs is wt. % of the coal, ρ_a is the apparent density of the coal (1.35 g/cm³), and γ is the water-holding capacity of the coal (0.027 g/g dry coal).

The volume fraction at maximum packing was obtained by concentrating the CWM by evaporating the water to the point where no fluidity was observed, followed by further concentration of the solids in a centrifuge, using a centrifugal acceleration of about $2.5 \times 10^6 \text{ cm/s}^2$. The volume fraction at maximum packing was then calculated from the solids concentration of the sediment by the formula given above.

Flow characteristics of the CWM's were measured using a Haake RV 12 rotational viscometer with MV-II sensor of coaxial cylinder geometry. The cup had a 21 mm ID; the bob was 18.4 mm OD, with an effective length of 60 mm. The tempera-

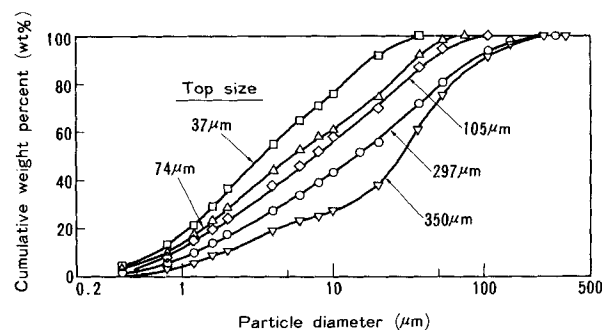


Figure 1. Size distribution of coal particles in sample CWM's.

ture of the sensor system and the sample within it was maintained at 20°C by circulating water through a jacket attached to the cup from a thermostated water bath.

Since CWM's may have time-dependent rheological properties, samples were subjected to shear in a persistent manner by means of a programmable control unit. Shear rate was increased at a constant rate from zero to 90 s⁻¹ over a period of 1 min, held constant for 1 min, then steadily decreased to zero in 1 min. The shear cycle was repeated three times. The flow curve of the third cycle was taken to be representative of the flow properties of the sample CWM. The apparent viscosity was calculated using the shear stress at 18 s⁻¹ on the downward curve of the third cycle. Although the apparent viscosity at 90 s⁻¹ changed slightly with the shear cycle, the value at 18 s⁻¹ was confirmed as remaining fairly constant on further repetition of the cycle if the electrolyte concentration was not too high. Thus, the system was considered to have reached a dynamic equilibrium at 18 s⁻¹ through the shear history.

The electrolyte concentrations in the supernatant solution were adjusted by adding a fixed amount of aqueous electrolyte solutions of various known concentrations. Care was taken to maintain the pH value at as close to the original value as possible, with the stipulation that the metal ions did not precipitate as hydroxides.

Results and Discussion

CWM with anionic dispersant

Effect of Size Distribution and Characterization of the System. The flow curves of the samples are shown in Figure 2. All CWM's tested have a shear-thickening property at shear rates greater than about 10 s⁻¹. This rheological behavior generally is observed for well-dispersed colloids (Umeyama et al., 1975) and is attributed to structural dilatancy. At shear rates of less than 10 s⁻¹, the CWM's with small top sizes display an apparent shear-thinning behavior, with quasi-yield stress increasing as top size decreases. This point is discussed further in a later section.

Apparent viscosities of the samples are plotted as a function of solids concentration, Figure 3. It can be seen that an increase in top size, i.e., a broadening of the particle size distribution, results in a reduction of viscosity at a given solids concentration. Since all the samples have the same supernatant composition, the difference in viscosity is expected to be due solely to the difference in the particle size distribution. Numerous studies have been performed to obtain viscosity-concentration relationships for concentrated suspensions. Dougherty and Krieger developed

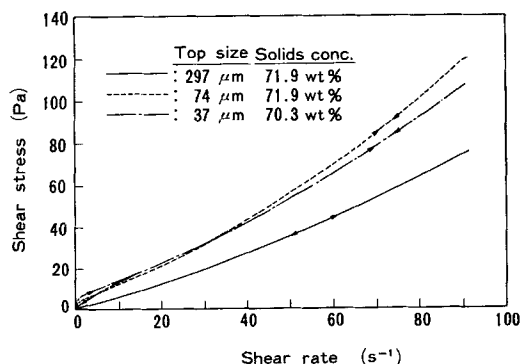


Figure 2. Flow curves of CWM's with various top sizes.

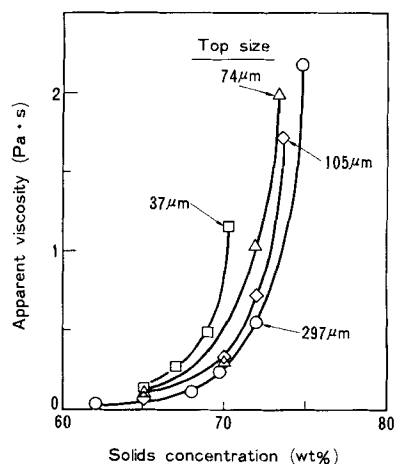


Figure 3. Effect of particle size distribution on the apparent viscosity.

an equation for noninteracting rigid spheres that agrees well with experimental data for well-dispersed systems over a wide range of concentrations (Krieger, 1972):

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c} \quad (2)$$

where η_r and η are the relative and apparent viscosities of CWM, respectively, η_0 is the viscosity of the supporting medium, ϕ is the volume fraction, ϕ_c is the volume fraction at maximum packing, and $[\eta]$ is the intrinsic viscosity. This relationship predicts lower values of η_r for broader size distributions of particles, since a broad distribution would normally lead to higher values of ϕ_c . The present viscosity data are plotted in a manner suggested by the previous equation, Figure 4. The values of ϕ_c for each size distribution are listed in the figure. The viscosity of water (1 mPa·s at 20 °C) was taken to be η_0 . All data points fall on a single straight line with $[\eta] = 3.8$. This is slightly

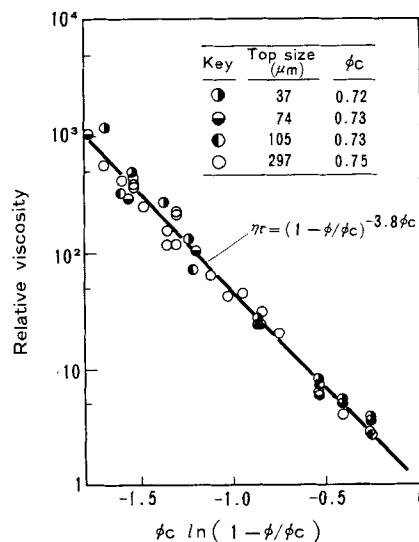


Figure 4. Dependence of relative viscosity on solid volume fraction.

larger than the Einstein value of 2.5. This difference may be attributed to the deviation of the coal particles from sphericity. There is good agreement between the model and data up to a solids concentration of approximately 90% of ϕ_c . This suggests that the coal particles in the samples may be well-dispersed by the action of the dispersing agent, that no significant sign of flocculation is apparent, and that the particle size distribution influences the apparent viscosity only through the values of ϕ_c .

Effect of Cations. The effect of hydrogen ion concentration (pH) on the apparent viscosity of CWM's of various solids concentrations is presented in Figure 5. The pH values were adjusted by adding hydrochloric acid to the CWM. It can be seen that the viscosity of CWM's increased with decreasing pH, i.e., with increasing hydrogen ion concentration in the supernatant solution. It appears that denser CWM's are more sensitive to changes in pH. This may arise from the fact that at high solids concentrations, the particles are close together and the effect of the particle-particle interaction forces is expected to be large.

The effects of other cations were examined by adding solutions of various electrolytes of known concentrations. The results are shown in Figure 6. The apparent viscosity of one CWM (71 wt. % solids) is plotted against the logarithm of the molar concentration ($\log C$) of the added species in the supernatant solution. At low concentrations, the effect of added cations is barely detectable. But as concentrations increase beyond critical values, the apparent viscosity of the CWM increases sharply with electrolyte concentrations.

The coal particles in a CWM with anionic dispersant are expected to be negatively charged due to the adsorption of the dissociated dispersant molecules. The effects of pH and cations on the apparent viscosity of a CWM can be interpreted as resulting from the partial neutralization of the electrical charge of the particles by the compression of the electrical double layer around them, thus decreasing the repulsive interaction forces caused by the overlap of the double layers (Verwey, 1947).

The data of Figure 6 also show clearly that the cation concentration at which the sharp increase in apparent viscosity of a CWM occurs depends on the valency of the cation, i.e., the higher the valency, the lower the critical concentration. This behavior is in accord with the empirical rule for the critical flocculation concentration for coagulation of hydrophobic colloids,

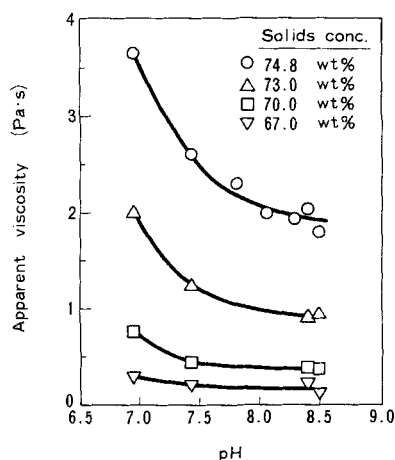


Figure 5. Effect of pH on apparent viscosity of CWM.
Top size, 297 μm

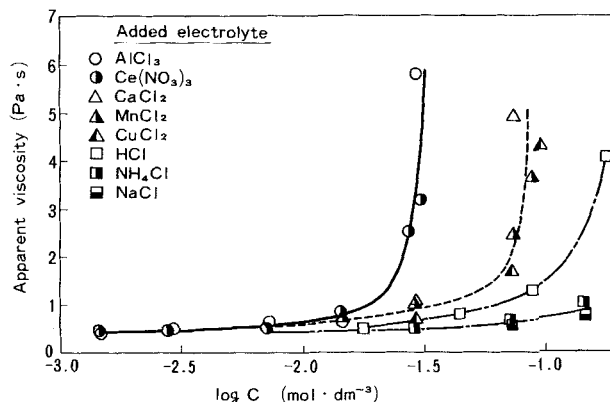


Figure 6. Effect of cations on the apparent viscosity of CWM.

71 wt. %; top size, 297 μm

known as the Schulze-Hardy rule (Jirgensons and Straumanis, 1962), and supports the previous interpretation that the coal particles in a CWM with anionic dispersant are dispersed mainly by electrical repulsive forces arising from negative surface charges. In such a system, the electrolytes in the solution strongly influence the degree of particle dispersion, and thus govern the CWM rheology (Russel, 1978).

From Figure 6, we observe that variations in the concentration of the hydrogen ion affect the CWM viscosity much more strongly than other monovalent ions. Similar effects have been noted in other colloid systems (Jirgensons and Straumanis, 1962). This may be indicative of an enhanced adsorption of the hydrogen ion onto the surface of the coal particle due to its small ionic radius.

The previous results also are in qualitative agreement with the Derjagin-Landau-Verwey-Overbeek (DLVO) theory of hydrophobic colloid stability (Verwey and Overbeek, 1948). The theory predicts the critical flocculation concentrations to be proportional to $1/z^n$, with $n = 6$ for a surface at a very high potential (Verwey, 1947) and $n = 2$ for more realistic low potentials (Lyklema, 1981). Here, z is the valency of the counterion. If critical flocculation concentrations are assumed to be those at which the CWM has an apparent viscosity of 1 Pa·s, about 2.4 times the original value before adding the electrolytes, then the present data yield values of 0.17, 0.032, and 0.016 mol·dm⁻³ for mono-, di-, and trivalent cations, respectively. Substituting these values into the above relationship, we obtain $n \approx 2.3$. Concentrations of the ionic species in the supernatant solution of the original CWM (equivalent to 71 wt. % solids) are listed in Table 2. These ionic species result from the dissolution of mineral matter

Table 2. Concentrations of Ionic Species in Supernatant Solution

Species	Conc. mmol · dm ⁻³	Species	Conc. mmol · dm ⁻³
Na ⁺	316	Al ³⁺	0.007
K ⁺	5.1	Si	0.3
NH ₄ ⁺	2.6	Cl ⁻	25.6
Ca ²⁺	3.9	F ⁻	1.0
Mg ²⁺	0.5	S	28.3

Fe²⁺, Fe³⁺, Cr, V³⁺, Cu²⁺, Mn: trace

present in the coal particles. The high concentration of sodium ion is due to its presence in the dispersant and the addition of NaOH for pH adjustment during CWM preparation. Sodium ion concentration is assumed to be balanced by the unadsorbed dispersant anions in the supernatant. Taking into account these ions present in the original CWM, and assuming that the effect of the ions of the same valency is additive and independent of the effect of the ions of different valency, the ratio of the critical flocculation concentrations for mono-, di-, trivalent ions would be 100 : 7.3 : 3.2, which, on the basis of the previous relationship, yields $n \approx 3.6$.

These calculated values of n are closer to the value of 2 predicted for the low potential limit. The agreement between the present experimental results and the theory is considered to be unexpectedly good, considering the complexity of the test system and the fact that the flow field may induce deviations in the ion distribution in the diffuse double layer from the distribution corresponding to a state of thermodynamic equilibrium for the case of suspension under shear.

Electrolytes also have a pronounced effect on the flow characteristics of CWM's. An example of changes in the flow curve of a CWM resulting from the addition of calcium chloride is shown in Figure 7. When the electrolyte concentration is low and the particles are well dispersed, the CWM displays a shear-thickening behavior over the range of shear rates examined. As the electrolyte concentration increases, the shear stress at low shear rates increases sharply, the CWM begins to have a quasi-yield stress, and the flow characteristics shifts to shear-thinning. The property of rheopexy becomes significant at high electrolyte concentrations. The emergence of the quasi-yield stress can be explained qualitatively by considering the formation of a network structure, principally incorporating small particles, due to increased attractive forces. Particles are expected to flocculate upon collision when the attractive force between them is greater than the viscous and/or inertial force. The shear-thinning behavior may result from the breakdown of the network structure by the greater viscous force at high shear rates (Russel, 1978). The property of rheopexy may result from the difference in the rates of formation and rupture of the structural linkages at a given shear rate. The rate of flocculation may be a function of the relative magnitudes of the forces acting on the particles and the collision frequency between them, both of which are influenced by the rate of shear, particle size, and solids concentration. The rate of deflocculation may be a function of the

amount of linkages, or flocs, already present, which may vary according to the shear history of the CWM (Umeya and Kanno, 1979). Hence, the rheological properties of a CWM are determined subtly by the relative magnitudes of the particle-particle interaction forces and the force induced by the external shear, and by the rates of flocculation and deflocculation of the particles.

If the rheology of CWM's is controlled by the relative strengths of various forces acting on individual coal particles in a sheared CWM, then, as particle size exerts an influence on some of these forces, particle size distribution may affect CWM rheology. Variations in the flow curves of CWM's of differing size distributions at low shear rates (less than about 10 s^{-1}), Figure 2, may be explained accordingly by considering the relative magnitudes of viscous and colloid chemical forces.

DLVO theory for an electrically stabilized colloid yields a potential energy function between two particles having a secondary minimum at a large separation, a deep primary minimum at the contact point, and a positive maximum in the intermediate region (Overbeek, 1984). High surface electric charges and low ionic strength result in a high potential maximum and a long range of repulsive force. The opposite situation results in a lowering of the potential maximum, leading finally to its disappearance. In the extreme case where ionic strength is very high, the potential curve becomes negative, i.e., an attractive force exists between the particles over the whole range of surface-surface separation. The behavior indicated in Figure 2 may arise from the existence of a secondary minimum in the interparticle potential function that is deep enough to hold the small particles together under imposed shears of less than about 10 s^{-1} , but not strong enough to balance the viscous forces experienced by the larger particles.

In a CWM with larger top sizes, the formation of structural linkages by small particles may be retarded by the presence of the large particles. Moreover, these structural linkages may be ruptured easily by the motion of the large particles induced by the external shear. Viscous forces may be of sufficient magnitude to break up the structure even at very low shear rates, resulting in diminished quasi-yield stress. As top size decreases, there is a corresponding decrease in average particle size, resulting in a decrease in the mean particle separation at constant solids concentration (Buscall et al., 1982). Here, the structural linkages between particles are expected to be denser and firmer, and to form faster, due to the higher collision frequencies of small particles, than in the case of the CWM with larger top sizes.

The effect of particle size distribution may be detected in the data obtained to determine the effect of CaCl_2 addition on CWM flow curves, Figures 8 and 9. At high electrolyte concentration, the CWM with a top size of $37 \mu\text{m}$ has a large quasi-yield stress and a shear stress maximum which appears on the upward curve at a shear rate of approximately 5 s^{-1} . This indicates formation of stronger particle linkages in the low shear rate region. Conversely, the flow curve of the CWM with a top size of $350 \mu\text{m}$ does not change appreciably with the addition of CaCl_2 , owing to the lower content of small particles, as can be seen in Figure 1. The data indicate that the CWM shows a weak shear-thinning behavior with the increase in the calcium ion concentration in the supernatant.

The effect of CaCl_2 on the apparent viscosities of CWM's with different particle size distributions is presented in Figure

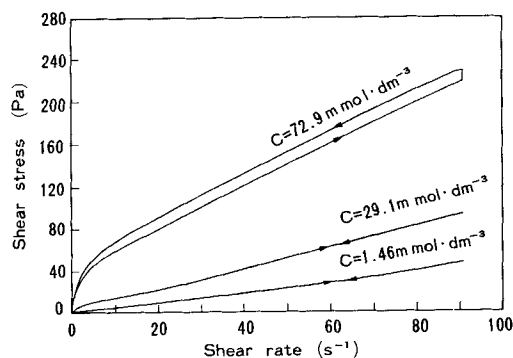


Figure 7. Changes in flow curve of CWM on addition of CaCl_2 .

71 wt. %; top size, $297 \mu\text{m}$

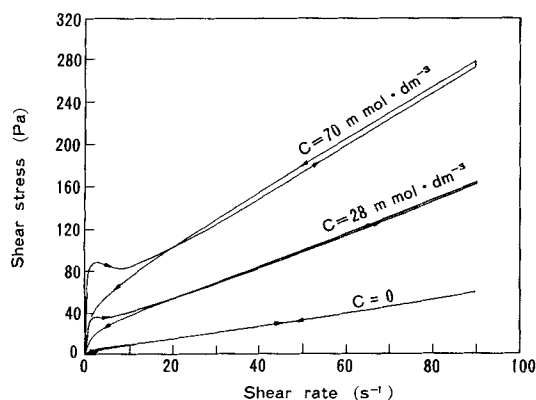


Figure 8. Changes in flow curve of CWM on addition of CaCl_2 .
69 wt. %; top size, 37 μm

10. Here, the ratio of the apparent viscosity to the viscosity of the original CWM (η^0 , before addition of CaCl_2) is plotted against the logarithm of the concentrations of the added electrolyte in the supernatant. No dependence on top size is observed. Note that the apparent viscosity was calculated using the shear stress at the shear rate of 18 s^{-1} on the downward curve. At this point, the CWM has experienced higher shear and the network structure formed at lower shear rates may be destroyed; a dynamic equilibrium is considered to have been established. The data suggest that if well-dispersed CWM's with different size distributions are prepared so as to have the same apparent viscosity at a given shear rate, i.e., the energy dissipation due to hydrodynamic effects are equivalent at the shear rate, then they will display identical apparent viscosity increases upon addition of electrolytes, provided that they have the same supernatant composition. This might indicate that energy dissipations due to the hydrodynamic interactions and the colloid chemical interactions are linearly additive in the present system.

Effect of Anions. The effect of adding sodium salts of various anions on the apparent viscosity of CWM is presented in Figure 11. The data indicate that the presence of anions does not alter the CWM flow properties. Ions around a charged particle at thermodynamic equilibrium are distributed in proportion to $\exp(-ze\psi/kT)$, according to the Boltzmann principle (Overbeek, 1984). Thus, the concentration of the coions (positive $z\psi$)

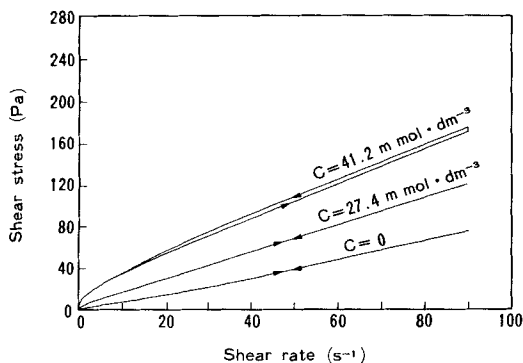


Figure 9. Changes in flow curve of CWM on addition of CaCl_2 .
69 wt. %; top size, 350 μm

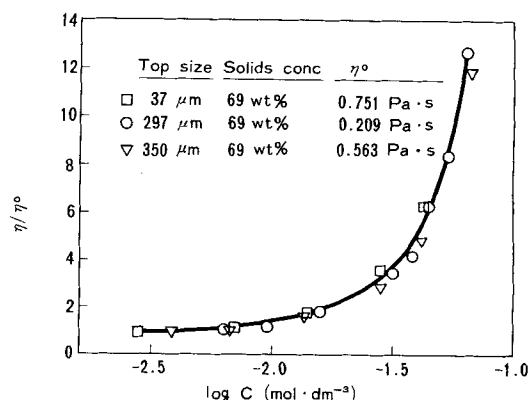


Figure 10. Effect of CaCl_2 addition on apparent viscosity of CWM's.

is negligibly small compared to the counterions (negative $z\psi$). The coal particles in the present CWM were determined to be negatively charged, based upon the experimental results on the effect of cations. Hence, anions are expected to have little effect on the rheological characteristics of the present CWM's. A slight increase in the apparent viscosity at concentrations higher than about $0.1 \text{ mol} \cdot \text{dm}^{-3}$ is attributed to the presence of positively charged sodium ions, mentioned previously.

CWM with nonionic dispersant

The flow curve of the CWM with 72 wt. % solids, employing a nonionic dispersant, is shown in Figure 12. This CWM exhibits shear-thickening behavior identical to that of the CWM employing an anionic dispersant with no additional electrolyte, in which particles are well dispersed. However, addition of electrolytes results in markedly different behavior. The effect of CaCl_2 addition on the apparent viscosity is shown in Figure 13. Coal particles suspended in water are known to be negatively charged even in the absence of anionic dispersants (Coca et al., 1982). This is probably due to the dissociation of the surface functional groups. However, as seen from the figure, electrolyte addition does not change the apparent viscosity of the CWM with nonionic dispersant. The flow curve also is not affected. It appears

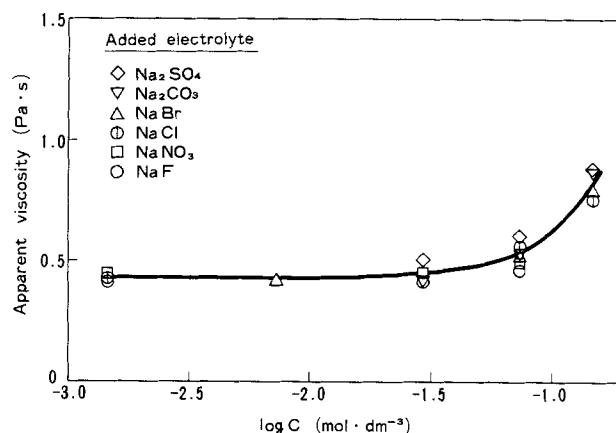


Figure 11. Effect of anions on apparent viscosity of CWM.
71 wt. %; top size, 297 μm

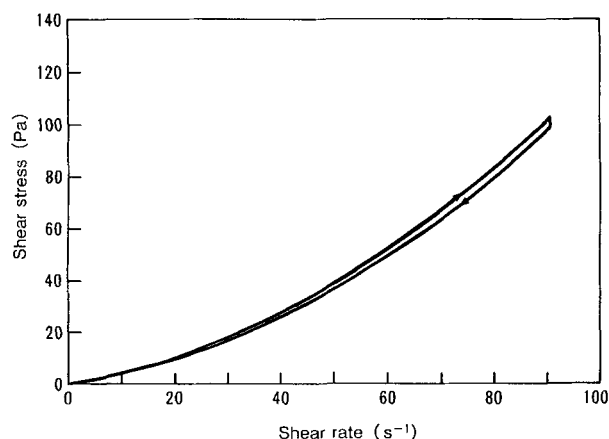


Figure 12. Flow curve of CWM with nonionic dispersant.
72 wt. %

that the electrostatic repulsive force may not influence significantly the dispersion of particles in the CWM. These results imply that particle coagulation is prevented, and dispersion effected, solely by a steric stabilization effect.

Conclusions

Highly concentrated coal-water mixtures containing more than 70 wt. % coal were prepared using anionic and nonionic dispersants, and their rheological characteristics were investigated. It was found that nonhydrodynamic interactions between the coal particles were of considerable importance in determining CWM rheological properties at high solids concentrations. The rheological behavior of the CWM employing an anionic dispersant was influenced significantly by the addition of electrolytes and the apparent viscosity increased drastically. The ratio of concentrations of the mono-, di-, and trivalent cations at which this increase was detected agreed qualitatively with predictions of the DLVO theory. Hence, it was concluded that the coal particles in the CWM were dispersed mainly by electrostatic repulsive force. In the case of the CWM using a nonionic dispersant, it was determined that particle coagulation was prevented by a steric stabilization effect, since no electrolyte effect was observed.

The present experimental results represent a systematic study which demonstrates the effect of nonhydrodynamic interparticle interactions on suspension rheology. These data are expected to

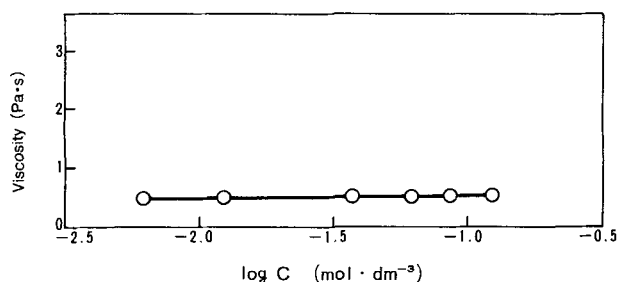


Figure 13. Effect of CaCl_2 addition on apparent viscosity of CWM with nonionic dispersant.
71 wt. %

be particularly helpful in the preparation of CWM's with desirable flow characteristics.

Notation

- C = ionic concentration
- C_s = wt. % of coal
- e = elementary charge
- k = Boltzmann constant
- T = absolute temperature
- V_{ab} = volume of water absorbed by coal
- V_s = volume of coal
- V_w = volume of total water
- z = valency of ion

Greek letters

- γ = water-holding capacity of coal
- η = apparent viscosity
- η^0 = apparent viscosity of original CWM
- η_0 = viscosity of supporting medium
- η_r = relative viscosity
- $[\eta]$ = intrinsic viscosity
- ρ_a = apparent density of coal
- ϕ = solid volume fraction
- ϕ_c = volume fraction at maximum packing
- ψ = electric potential

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Manuscript received Feb. 25, 1986.