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ORIGINAL CONTRIBUTION

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A new concept for coal water mixture stabilization using a polyelectrolyte

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Abstract The stabilization mechanism of Sodium Polystyrene Sulphonate (PSSNa) on coal water mixture (CWM) has been examined using the following colloid chemical concept. It is realized that the stabilization of the CWM is due to an increase in electrostatic repulsion between the coal particles and the electrostatic repulsion is influenced strongly by the concentration of metal cations, especially Ca^{2+} eluted from the coal surface. The adsorption isotherm of PSSNa on the coal surface indicates a weak affinity type and the desorption amount of PSSNa is tremendously small in compared with the amount of adsorption. This indicates that a lot of PSSNa adsorbed weakly has been eliminated from the surface in the pre-washing process of desorption experiment. Furthermore, it appears that the ζ-potential determined by the Acoustosizer for concentrated coal suspension shows higher values than the values determined by the usual electrophoresis, and that the high values hold for a wide range of salt concentrations in the medium. All these results indicate that much PSSNa is adsorbed weakly on the coal surface and the component plays a role in the stability character of CWM, where a large contribution of depletion stabilization effect can be expected.

Key words Coal water mixture – sodium polystyrene sulphonate – depletion stabilization effect – concentrated dispersion – dynamic mobility

Introduction

Coal slurry fuels are expected in the near future to replace a part of world oil consumption. Stable coal slurry is necessary for transportation and long-term storage and, finally, for burning in a pseudo-liquid state. The use of chemicals as a dispersant or a stabilizer to achieve the desired properties of the dispersion has proven to be a very effective strategy [1], but there exists no scientific methodology for choosing a chemical to meet a specific system. This is because the stabilization mechanisms of each chemical are not completely understood.

It is generally thought that stabilization in a colloid system may be due to increases in the electrostatic repulsion and in the steric repulsion of the polymer layers between the particles [2]. Electrostatic repulsion is known to be an important factor controlling colloidal stabilization even in systems including polymer layers, because the conformation of adsorbed polymers is influenced by the charge density of particle surfaces. The surface of coal, as has been characterized by many others [3, 4], is very complex due to its heterogeneous nature and associated impurities. The electrical double layer results from the development of surface charge due to the adsorption/ionization of COH, COOH, and other functional groups, together with their counterions. It has been considered that the ζ-potential of coal particles can be varied by the addition of inorganic salts, surfactants, as well as charged polymers [4].

The effect of polymers on colloidal stabilization has been studied extensively [5]. It is believed that the chain length and the component structure of a polymer play a major role in the efficiency of dispersions, because the conformation of a polymer at the interface depends on the size and shape of the adsorption layer. Furthermore, it is known that the conformation of the polyelectrolyte will also be influenced by the presence of other dissolved chemicals such as inorganic ions and organic surface active ions in the system [6]. In this case, the existence of multiple stabilizing effects of the polyelectrolyte with these chemicals can be expected [7].

Recently, a depletion effect caused by the existence of free (or dissolved) polymers, which are not adsorbed on the suspending particles, has attracted considerable attention [8]. This effect is caused by the existence of free polymers in the bulk with a definite volume and, originally, this effect was interpreted by Asakura et al. [9] as a flocculation effect arising from the osmotic pressure of these polymers. However, if two particles are separated by free polymers, the system becomes stable and the depletion effect is exerted as a kind of stabilizing effect under these conditions. An interesting aspect of the depletion effect is that the resulting stabilization effect will continue for a long time, because the dissolved polymers between the particles prevent flocculation of the particles by their volumes [2, 5]. Therefore, if depletion stabilization is experimentally verified and if its application is proved to be useful in the CWM system, there would be a great impact on the CWM industrial field. Further, since stabilization due to the depletion effect is based on a new concept, it is expected that a new technology following this concept to stabilize the CWM will arise, and that new chemicals for stabilizing the CWM should be designed according to the new stabilizing concept.

In this study, the stabilization mechanism of Sodium Polystyrene Sulfonate (PSSNa), which has been used widely [10] as a stabilizer for CWM, has been examined following the ordinal colloid chemical concept.

Experimental

Samples and preparation of CWM

The coal sample chosen for the present experiments was bituminous coal M and was analyzed in accordance with JISM 8812. The results of the analysis are reported elsewhere [4]. Various Sodium Polystyrene sulfonates (PSSNa) with different molecular masses prepared by Lion Co. Ltd. were used without further purification. The CWM was prepared by wet grinding using a ball mill and an original CWM with a 60 vol.% was used after diluting to 30 vol.% in 10^{-2} M KCl aqueous solution. The particle size and size distribution of the coal particles were determined to be $2a = 20\ \mu$m and $D_w/D_n = 7.5$ respectively, by the dynamic light-scattering method.

Measurements of apparent viscosity

The viscosity was measured by a Haake Model RV 12 Serial-type rotational viscometer with an MV II rotor and a profiled sensor. The shear rate was varied from 0 to 150 s^{-1} at 25 °C.

The apparent viscosity was calculated from the stress at 100 s^{-1} on the down curve.

Adsorption and desorption measurements of PSSNa

Determination of the amounts of PSSNa adsorbed was carried out by the usual depletion technique [4] at neutral pH. The polymer concentration that remained in the supernatant was measured by UV spectrometer using a calibration curve. The adsorption temperature was maintained at 20 °C within ± 0.05 °C.

The desorption process of PSSNa from the coal particle surface was measured as follows [11]. First, PSSNa coated coal suspensions were prepared under the same conditions as in the case of the adsorption experiments, and were then packed into the column by the slurry method. After connecting the column (a Teflon tube, $\phi = 0.8$ mm, $l = 20$ cm) to the elution system, eluents (various KCl solutions and distilled water) were pumped through the column. The concentration of the PSSNa desorbed from the coal surface was monitored by a UV detector, and recorded as a concentration vs. time curve. The resultant curve was integrated and the area was compared to a standard one.

Measurements of elution rate of metal cations

The elution concentration of each metal cation from the coal surface was measured as follows. Ten-ml portions of coal suspension were poured into a glass tube, after which the suspension was left standing for one night under gentle mixing at 25 °C. Only the coal particles were then separated from the medium, and the concentrations of the metal cations eluted from the coal surface were measured analytically by means of the Inductively Coupled Argon

Plasma (ICP) method (Jarrell–Ash 975). By observing the different concentrations in the solutions before and after the mixing process, the amounts of elution per unit coal weight were calculated using a calibration curve.

Measurements of the ζ-potential on coal suspensions

The ζ-potential of coal particles was determined by the usual electrophoretic apparatus and the Acoustosizer developed by Matec Applied science INC. The electrophoretic mobilities of all the coal particles were determined at various salt levels in an aqueous solution at 25 °C. The measurements of the mobility were performed with the Rank Brother Microelectrophoretic Apparatus (M-II) using a rectangular glass cell. The ζ-potential was derived using the Smoluchowski equation.

The dynamic mobility of coal particles was measured by using the Acoustosizer (system-800) at the concentrated state (30 vol.%). A detailed description of the construction and the procedure for the system-800 is in the literature [12].

The PSSNa adsorbed weakly on the coal surface was washed out by repeating several times the centrifugation-decantation-redispersion process. After each washing process, the ζ-potentials of coal particles at concentrated and diluted states were determined using the Acoustosizer and the usual electrophoresis.

Results and discussion

Effect of polyelectrolyte and metal cations on the viscosity of coal slurry

Coal surface is very complex due to the heterogeneous nature of coal and associated impurities. The electrostatic double layer results from the development of surface charge due to adsorption (or ionization) of ionic compounds (or functional groups), together with their counter ions [2]. It is known that the ζ-potential of coal slurry can be changed by the addition of mono-, and di-valent cations, as well as charged polymers. Figure 1 shows the influence of polyelectrolyte (PSSNa) on the viscosity of coal slurry. Viscosity is considered to be a reliable measure of the stability of coal slurry [2] and a low viscosity value is desirable. As seen from the figure, the addition of PSSNa brings about a good result for a long-term stabilization and keeps a low viscosity of the slurry for a longer period (ca. 50 h longer) than the system without PSSNa.

Furthermore, it is recognized that the long-term stability of coal slurry is also influenced by the existence of metal ions eluted from the coal surface. Figure 2 shows the elution concentration vs. elapsed time curves for some typical metal cations under the zero PSSNa conditions. It is known that the elution rate of di-valent cations is higher than the value of monovalent ions and, especially, the concentration of Ca^{2+} increases vigorously with elapsed time.

Furthermore, very interesting behavior can be detected in Fig. 3, where the elution rate of Ca^{2+} has been determined under the different KCl concentrations. It is realized that the elution rate of Ca^{2+} is greatly accelerated by the existence of K^+ in the medium, especially in K^+ concentrations higher than 10^{-4} M. This may be due to the hydration effect of K^+ for the coal surface, i.e., adsorption of hydrated K^+ will raise the hydrophilicity of coal surface and will result in an acceleration of elution rate of Ca^{2+}

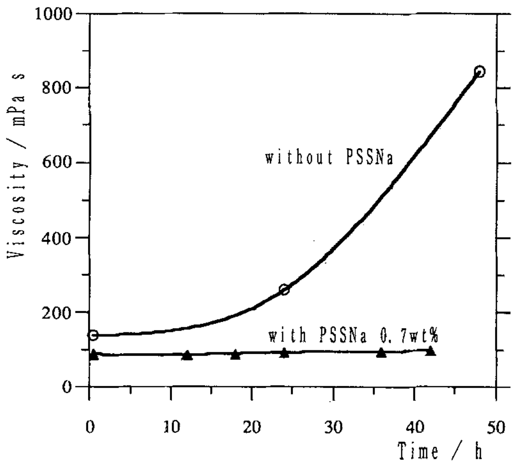


Fig. 1 Time dependence of viscosity of coal slurry without and with PSSNa (0.7 wt%)

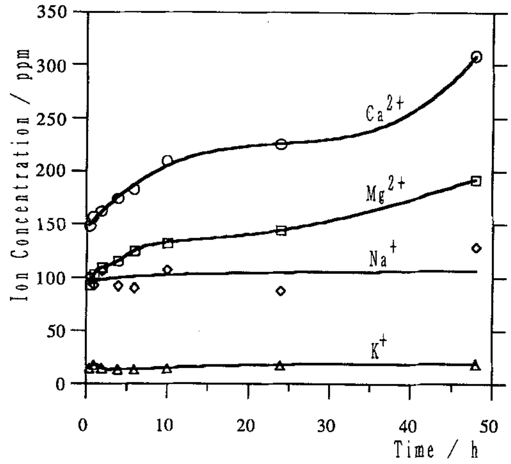


Fig. 2 Elution concentration of typical metal cations vs. elapsed time curves for zero PSSNa system

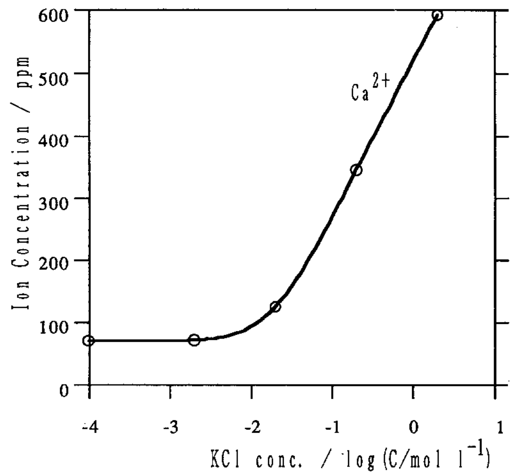


Fig. 3 Influence of KCl concentration on the elution rate of Ca^{2+} ions

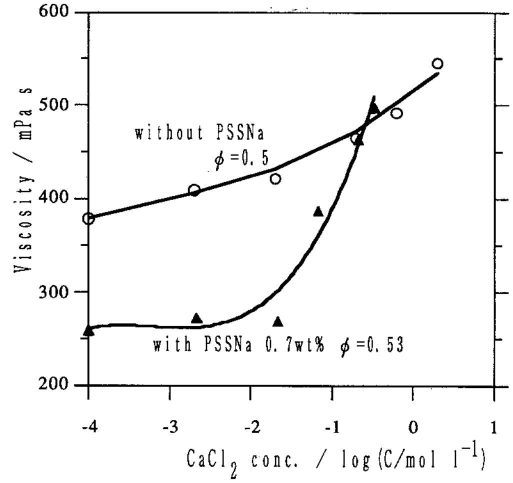


Fig. 4 Viscosity vs. $CaCl_2$ conc. curves for the systems with and without PSSNa

It is usually considered that the Ca^{2+} ion has a high binding character on solid surfaces and its existence will influence dissociation or the adsorption degree of polar molecules at the surface. So, it is assumed that the variation of the Ca^{2+} concentration in the medium will strongly influence the stability of coal slurry. Figure 4 shows the viscosity of the CWM vs. $CaCl_2$ concentration curves for the systems with and without PSSNa (0.7 wt.%). It is apparent that the viscosity increased vigorously with increasing Ca^{2+} ion concentrations in the system including PSSNa. This result indicates that Ca^{2+} ion also affects the dissociation and conformation of adsorbing PSSNa, because the electrostatic repulsion between the coal particles treated by PSSNa, plays an important role in the stability of CWM.

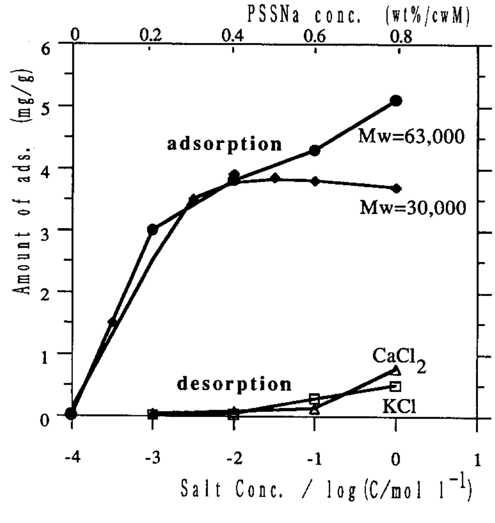
Adsorption/desorption behavior of PSSNa and the ζ-potential of coal slurry

In this study, a new method for studying the polymer desorption process, "the Continuous Elution Method," has been employed [11]. It is thought that this new technique will provide new information on the conformation of adsorbed PSSNa on the coal surface.

Figure 5 shows some typical adsorption isotherms of PSSNa with different molecular masses on the coal surfaces, where the volume fraction of coal particles was fixed at 30%, and the amounts of adsorption were determined by the usual depletion technique. The isotherm indicates a weak affinity type and indefinite amounts of saturation can be detected. This type of isotherm will be based on the electrostatic repulsive force between the negative charge of coal surface and sulfonic group in PSSNa molecule [13].

In Figure 5, the results obtained by the Continuous Elution Method are also shown and indicate the dependency of the desorption amount of PSSNa from coal surfaces on the salt concentration of the medium in the pre-adsorption process. Ordinarily, the desorption amount is extremely small compared with the value detected in the adsorption experiment, especially in the low salt concentration range. This result indicates that a lot of weakly adsorbed PSSNa has been eliminated from the surface in the pre-washing process in the desorption experiments using the same salt solution. i.e., indicating that a lot of PSSNa is accumulated near the coal surface and

Fig. 5 Adsorption isotherms and desorption amounts of PSSNa at the different salt conditions



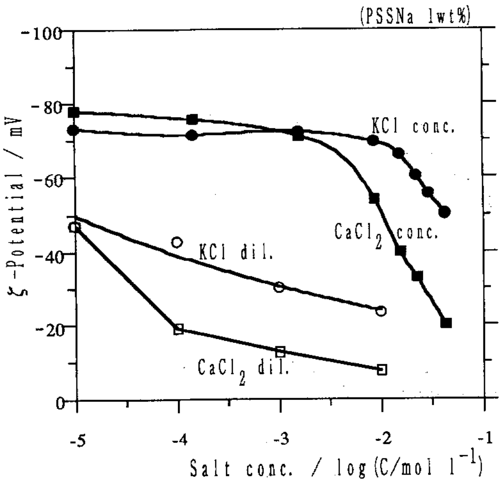
that these molecules will be desorbed easily from the surface by flowing the medium liquid.

Such a speculation can be realized by measurement of the ζ-potential for (coal + PSSNa) systems. In Fig. 6, the results of ζ-potential measurements which were conducted with the usual electrophoretic technique for dilute suspensions and those obtained by the Acoustosizer for the concentrated coal slurry, are compared. The characteristic feature is that the results obtained by the Acoustosizer show higher ζ-potentials than the values determined by the usual electrophoresis and these high values hold for a wide range of salt concentrations.

It is generally considered that the ζ-potential, especially determined by the usual electrophoretic technique is very dependent on the dilution conditions, because the environment on the coal surface will be affected considerably by the way of dilution. Therefore, weakly adsorbed PSSNa on the coal surface will be desorbed from the surface in the dilution process and the ζ-potential determined at the diluted state shows a lower value than the potential determined at the concentrated state.

Furthermore, the existence of polyelectrolytes adsorbed weakly on the coal surface has been confirmed by washing experiments with concentrated coal slurry. In Fig. 7, the ζ-potentials of CWM after washing with 10^{-2} M KCl solution are compared with the initial value of the ζ-potential as a function of the number of washings, where the measurement was performed in two different ways, i.e., with the first way, the ζ-potential at each washing time was determined by the Acoustosizer in the concentrated state and with the second, the ζ-potential at each washing was determined by using electrophoresis after diluting the sample to 0.01 vol.% with distilled water. As may be seen, washing two or three times has a significant effect on the ζ-potential of the coal surface and suggests that the part of PSSNa adsorbed weakly has been eliminated from the coal surface at this level. Further, Fig. 7 indicates that the efficiency of washing out depends on the composition of the washing medium, and low ζ-potentials in the second way (using distilled water) have been detected. All these results indicate that the part of PSSNa adsorbed weakly influences the value of the ζ-potential and plays a role in their electrostatic character in the coal slurry system.

Fig. 6 Results of ζ-potential measurements at the different salt conditions ●, ■) in concentrate systems. ○, □) in dilute systems



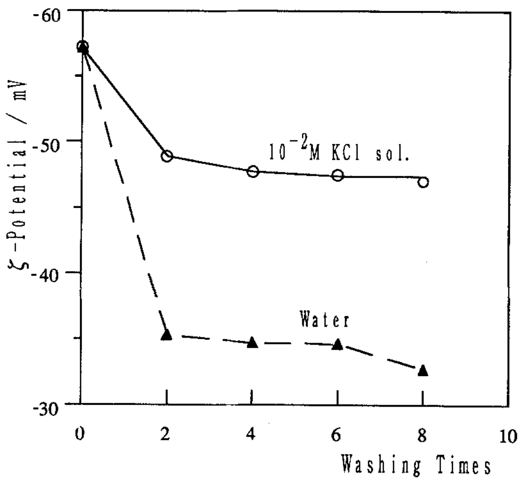
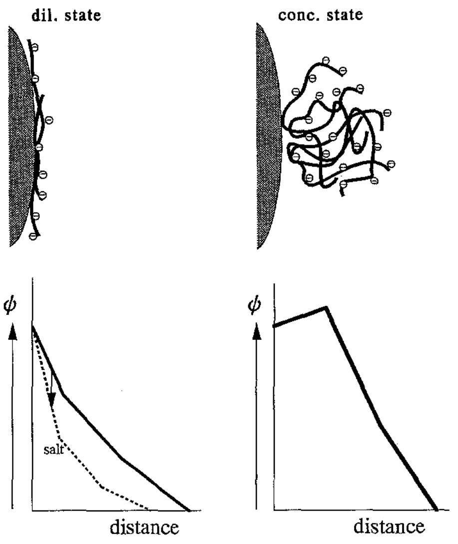


Fig. 7 Relation between number of washings and ζ-potential at each washing ○) determined by the Acoustosizer using 10^{-2} mol KCl. ▲) determined by the usual electrophoresis using pure water

Stabilization mechanism of PSSNa on coal slurry

It is generally understood that the stabilization in a concentrated suspension is mainly due to the electrostatic repulsion between the particles and the steric repulsion of polymer layers on the surfaces. Especially in an aqueous suspension such as CWM, a large contribution from electrostatic repulsion can be expected.

Recently, however, the depletion effect, especially the repletion stabilizing effect has attracted much attention [2] as a new stabilizing effect for colloid stability. If the situation where polymer molecules dissolved in a solution separate the two particles is encountered, the system becomes stable. Further, approach of the two particles will create a layer of pure solvent between the particles. This is essentially a result of demixing polymer and solvent, clearly a thermodynamically unfavorable process. Therefore, the particles cannot come closer than a distance roughly equal to the size of the polymer molecule, and the system may thus be aggregatively stable. Hence, the important factor for depletion stabilization is the molecular volume of the free polymer in the solution. According to this concept, this effect may be expected to act quite vigorously when the polymer is a polyelectrolyte such as PSSNa, since polyelectrolytes have a more expanded conformation because of their charges in the molecule and are strongly solvated in an aqueous electrolyte solution. Figure 8 shows a hypothetical picture showing the conformation of PSSNa adsorbed weakly on the coal surface estimated from the experimental results on the adsorption behavior of PSSNa and on the ζ-potential measurements for coal slurry covered by PSSNa. The low affinity isotherm of PSSNa indicates that PSSNa molecules will be adsorbed weakly on the coal surface and it is estimated that the conformation of adsorbing PSSNa will not be so different from the one in the bulk solution where PSSNa molecules have an expanded conformation from their charges. This conformation of PSSNa will be convenient for operating a strong volume restriction (or depletion stabilization) effect and also for exerting an effective electrostatic repulsion between the particles. These charges in PSSNa will contribute to the enhancement of the ζ-potential of the coal particles after treatment with PSSNa and will shift their slipping plane to the outer side of their surface. Figure 8 shows the differences in the surface potential profile between the coal surfaces adsorbed weakly by PSSNa and without PSSNa. The surface layer of the (coal + PSSNa) system becomes thicker and the position of the highest potential is located at a more outer layer than the real surface on coal particles. All these effects of PSSNa contribute to hold a high ζ-potential for a wide range of salt concentrations and effectively result in the long-term stabilization of coal water mixture.



(a) (b)

Fig. 8 Hypothetical picture showing the conformation of PSSNa adsorbed weakly on the coal surface with appropriate potential profile

From all the results obtained, it is suggested that polyelectrolytes, especially PSSNa are good stabilizers for CWM, and affect its stability by some combination of the electrostatic, steric, and depletion stabilization effects.

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