Effect of Polyvinylpyrrolidone and Sodium Lauroyl Isethionate on Kaolinite Suspension in an Aqueous Phase

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Suspension of concentrated kaolinite (20 g/30 ml-medium) in the presence of polyvinylpyrrolidone (PVP) and sodium lauroyl isethionate (SLI) was allowed to evaluate its degree of dispersion based on their rheological studies. Flow curves at low shear rate, measured by means of cone-plate method, showed a non-Newtonian flow. Plastic viscosity and Bingham yield value were derived from the flow curves. Relative viscosity, effective volume fraction and void fraction of secondary particle were also obtained. Results of dispersity and fluidity of the suspension were explained. PVP acted as a flocculant at a concentration lower than 0.1% but as a dispersant at a higher concentration. The presence of SLI could decrease both the Bingham yield value and suspension viscosity. Cooperative and competitive effects of PVP and SLI were found. Results indicated that SLI enhanced the degree of dispersion of kaolinite when PVP was less than 0.1%. The suspension, however, showed a maximum flocculation (*i.e.*, aggregation) at 4 mM SLI when the concentration of PVP was higher than 0.1%.

Key words   kaolinite; Newtonian flow; suspension; flocculant; viscosity; secondary particle

Kaolinite is a very useful raw material in industries, such as paints, paper, plastics, cosmetics, pharmaceuticals, and ceramics. Rheological properties and/or suspension stability of kaolinite are crucial factors in these products. The rheology and suspension of kaolinite has been studied intensively so far.[1—8] Nakagaki M., *et al.*[3—5] provided evidences that the divalent cations exert stronger effect than monovalent cations on a reduced viscosity and Bingham yield value of the suspension. In an aqueous suspension of kaolinite, the –NH group of urea, hydrazine and formamide, and the –OH group of alcohols form the hydrogen bonding with an –SiO group on kaolinite surface to alter fluidity of a suspension.[10,11] In this situation divalent cations manifest stronger effect than monovalent ones on the Bingham yield value.[3—6] The edge(+)/face(−) inter-particle interactions promote aggregation and increase the viscosity of a suspension. On the other hand, adsorption of multivalent anions decreases charge density on the edge, diminishing edge(+)/face(−) interparticle interaction, which results in reduction of the viscosity.[7] Johnson indicated that the kaolinite edge contains both silica- and alumina-like sites positively charged at low pH, but bears a negative charge at high pH. Kaolinite face contains by contrast only silica-like charge sites and remains negatively charged within a wide pH range.[12,13]

Heath and Todros[14] derived both a Bingham yield value and viscosity of kaolin suspension as a function of pH and electrolyte concentration. Their results showed a minimum viscosity around pH 7 and they assumed that the isoelectric point of particle's edges was around pH 7. Adsorption of polyacrylic acid (PAA) on kaolinite particles affected flocculation/dispersion of a suspension solution. PAA proved a higher suspension stability at low or high concentration than at a medium concentration.[1,2] The sodium salt of polyacrylic acid (Na-PAA) is adsorbed by alumina sites on the edge of kaolinite particles but not on the site of silica on basal plane of particles.[15] The acid form of carboxylic acid of PAA can be adsorbed via hydrogen bonding between the carbonyl group of carboxylic acid and the hydroxyl group on a surface

of the kaolinite basal plane.[16] Gebhardt and Fuerstenau[17] measured the adsorption amount of PAA by silica. Conceicao *et al.*[18] probed influence of carboxymethylcellulose on rheological behavior of kaolinite suspension in the presence of ammonium polycarbonate as a dispersant. The presence of carboxymethylcellulose in kaolinite suspension conferred a shear thinning behavior, especially in the low shear rate range, followed by a trend to Newtonian fluid behavior. Nakagaki M., *et al.*[3,4] pointed out that polyvinylpyrrolidone (PVP) acts on kaolinite suspension as a flocculating agent at concentration lower than 2×10^{-3}%, but as a dispersing agent above that point. Yalcin *et al.*[19] studied the influence of surfactants (sodium or ammonium dodecyl sulfate, SDS or ADS) on flow behavior of bentonite dispersion and concluded that surfactant showed different effects on viscosity and zeta potential of bentonite suspension, depending on their conditions.

SDS depressed flocculation in dilute kaolinite suspension at any concentrations.[20,21] Shimabayashi's prior study[20] on combination of SDS and PVP in kaolinite suspension concluded that flocculating effect and mean diameter of secondary particles of kaolinite declined with the increase in concentration of SDS. Complex formations between SDS and PVP and their adsorption onto kaolinite surface enhanced the dispersing effect.

Sodium lauroyl isethionate (SLI) is a mild, economical and environmentally responsible surfactant, and has become a new and useful ingredient for the formulation of consumer and pharmaceutical products. Very few research articles discuss the dispersion properties of SLI, especially the rheology of kaolinite suspension.

This paper discusses dispersing effects of SLI and PVP on kaolinite suspension from viewpoints of rheological properties. The effect of SDS on the stability of kaolinite suspension will be compared with the results obtained here.
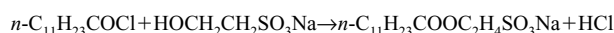
$$n\text{-}C_{11}H_{23}COCl + HOCH_2CH_2SO_3Na \rightarrow n\text{-}C_{11}H_{23}COOC_2H_4SO_3Na + HCl$$

Chart 1.   Chemical Structure and Synthesis of SLI

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Experimental

Materials Kaolinite (USP grade with 0.3 micron (dispersed) and 3.0 micron (un-dispersed) particle size) was purchased from Charles Co., U.S.A. SLI (Mw 330 g/mol) was synthesized and purified in our laboratory using the reaction of lauroyl chloride with sodium isethionate. Critical micellization concentration (cmc) of SLI was determined as 7 mM by means of surface tension measurement method. PVP was a gift from ISP Co. for this experiment; PVP K-30 had a mean molecular weight 2.8×10^4 g/mol, which was calculated from its intrinsic viscosity.[3]

Methods Various concentrations of SLI were added to the PVP solution (1—11 mM) and the surface tension was taken at adsorption equilibrium. Surface tension was measured by a Wilhelmy vertical plate method (Krüss Tensiometer K12) at 25 °C. The isothermal adsorption was plotted using surface tension *vs.* logarithm SLI concentration at different PVP concentrations (Fig. 1).

Kaolinite (60 g) were mixed well with 90 ml of PVP (0.001—1.0%) and/or SLI aqueous solutions and left to stand overnight. Flow curves of kaolinite suspension were obtained using a cone-and-plate rheometer (Brookfield DV-III) at low shear rate (1—15 s^{-1}). Viscosities of PVP and/or SLI solutions were determined by a Ubbelohde-type viscometer at 25 °C (Figs. 2a, b).

Fig. 1. Relation of Surface Tension with Logarithm of SLI Concentration in Different PVP Concentrations at 25 °C

Results and Discussion

Interaction of SLI with PVP in an Aqueous Solution It is well known that surfactant and water soluble polymer form complex in aqueous solution. Myers[21] proposed that the point where the surfactant begins to adsorb and form semi-micelle on polymer might be called a critical aggregation concentration, which was also defined as T_1 by Jones[22] and Breuer.[23] The concentration at which polymer was saturated with surfactant and micelle started forming in solution was defined as T_2. The surface tension *vs.* concentration curve of SLI mixed with different concentration of PVP was shown in Fig. 1 and was also revealed two transition points. The first transition point (T_1) was observed at 4 mM and the second transition point (T_2) was increased with increasing the concentration of PVP (8 mM for 0.1% PVP, 9 mM for 0.5% PVP and 10 mM for 1.0% PVP). The critical micelle concentration (cmc) of SLI in pure water was 7 mM at 25 °C. In contrast, Murata and Arai[24] had observed T_1 and T_2 values at 5 and 10 mM while SDS mixed with 0.1% of PVP. This result indicated the difference in the alkyl chain length between SDS and SLI, and perhaps also the possible hydrogen bonding in PVP amide groups, may play the important effect on the surface active behavior. Because of the higher hydrophobic chain length of SLI, therefore SLI exhibited a higher adsorption ability onto PVP than SDS.

Viscosity of an Aqueous Solution of PVP Mixed with SLI Relative viscosity (=viscosity of solution (SLI+ PVP+water)/viscosity of solvent (water), where concentration of PVP is fixed) of an aqueous solution of SLI mixed with PVP increased with an SLI concentration as well as a PVP concentration, as shown in Fig. 2a. SLI exerted some discernible effect on solution relative viscosity and T_2 at concentrations higher than 7 mM (cmc) in the absence of PVP. It means that the micelle formation of SLI in solution affecting the solution relative viscosity apparently. Breuer[23] listed a hydrophobicity index of some neutral polymers and concluded that there was partially polarized positive charge on PVP. The dip observed at 5 mM was indicated the electric charge of PVP was neutralized by adsorbing of SLI and bearing a negative charge while the concentration was higher than 5 mM. Due to anionic charge of SLI bound to PVP, the electrical repulsion accelerates an expansion of polymer coil,
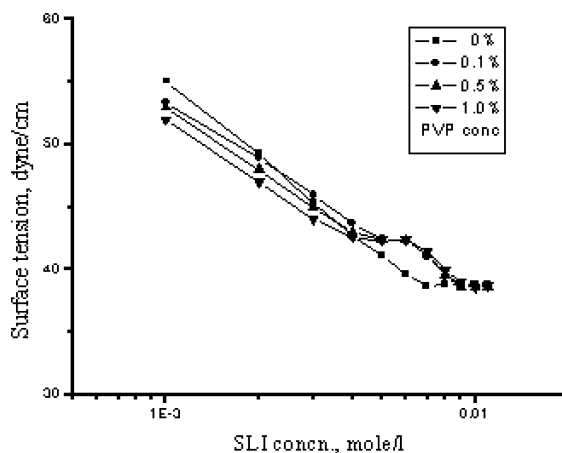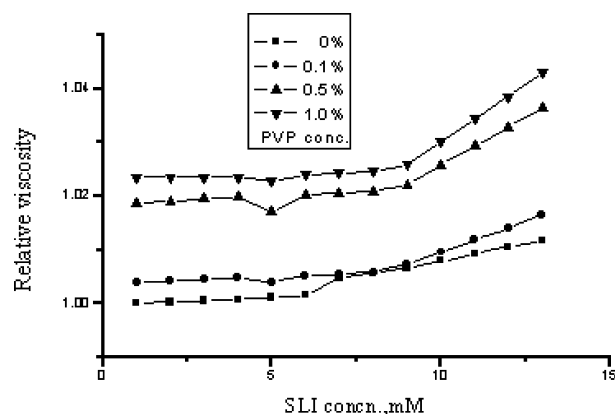

Fig. 2a. Relative Viscosity of PVP Solution at Various SLI at 25 °C
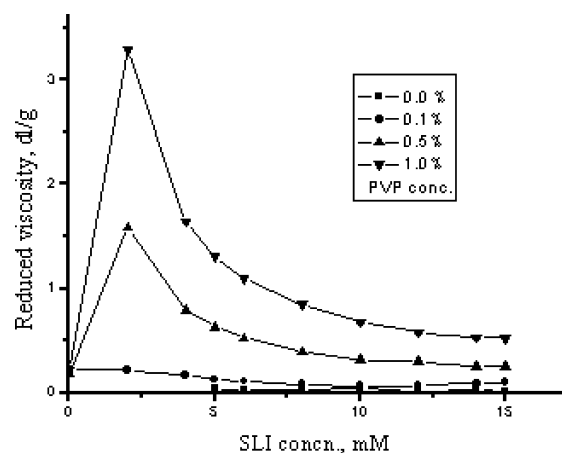[PVP] (g/dl=%(w/v))=0 (■), 0.1 (●), 0.5 (▲), and 1.0 (▼).

Fig. 2b. Reduced Viscosity of PVP Solution at Various SLI at 25 °C
[PVP] (g/dl=%(w/v))=0 (■), 0.1 (●), 0.5 (▲), and 1.0 (▼).

resulting in crisscrossing and tangling each other (Chart 2). The tangling of polymer backbone enhanced the solution viscosity, as shown in Fig. 2. Adsorption of surfactant onto PVP attain to saturation at T_2 (8 mM for 0.1% PVP, 9 mM for 0.5% PVP and 10 mM for 1.0% PVP, from Fig. 1) and intra-molecule electrical repulsion reaching maxima and micelle formation beginning.
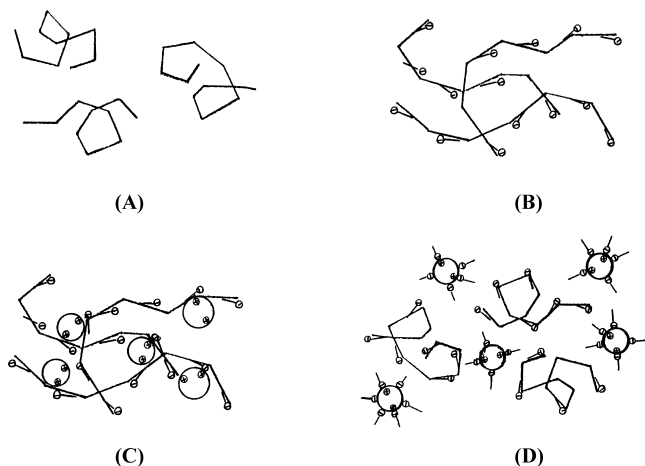
Chart 2.   (A) Neutral Polymer PVP in Aqueous Solution
(B) Increasing Viscosity

Electrical repulsion due to anionic SLI bound to neutral PVP accelerates an expansion of polymer coil, resulting in crisscrossing and tangling each other.

(C) Aggregation of Kaolinite

PVP, which is negatively charged after the binding with SLI, was adsorbed to the positively charged sites on the kaolinite edges, resulting in aggregation of kaolinite particles, where the concentration of SLI is low.

(D) Dispersion of Kaolinite

Due to electric repulsion between negative charges associated with PVP and those on the surface of kaolinite, the particles are dispersed, where the particles were negatively charged through the charge inversion at a high concentration of SLI after the adsorption of excess amount of SLI on the surface.
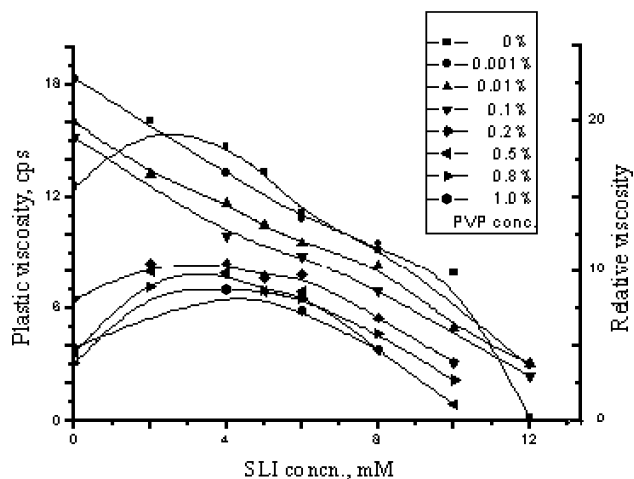

Fig. 3a.   Plastic and Relative Viscosities of Kaolinite Suspension as a Function of a Concentration of SLI

[PVP] (g/dl) = 0 (■), 0.001 (●), 0.01 (▲), 0.1 (▼), 0.2 (◆), 0.5 (◀), 0.8 (▶) and 1.0 (⬤).
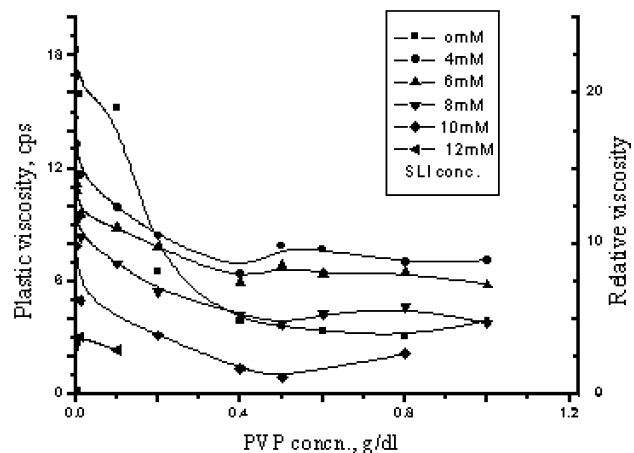

Fig. 3b.   Plastic and Relative Viscosities of Kaolinite Suspension as a Function of a Concentration of PVP

[SLI] (mM) = 0 (■), 4 (●), 6 (▲), 8 (▼), 10 (◆) and 12 (◀).

On the other hand, reduced viscosity (= (relative viscosity − 1)/PVP concentration, dl/g), declined dramatically with a concentration of SLI when PVP concentration was kept constant (Fig. 2b). This phenomenon was apparent in particular at high concentrations of PVP.

Flow Curve   The flow curve of the Bingham model:

$$F - F_o = g \cdot \eta_{pl} \tag{1}$$

where F_o, η_{pl}, g, and F represent Bingham yield value, plastic viscosity, shear rate, and applied shear strain, respectively. The flow curve, data not shown here, is a plot of shear strain as a function of shear rate. Slope of the curve is a plastic viscosity, and the intercept extrapolating the flow curve to zero shear rate is a Bingham yield value. Flow curves of a concentrated kaolinite suspension were obtained at low shear rate $(1—15\,\mathrm{s}^{-1})$ in this study. The flow curves exhibited a Bingham plastic flow at a low concentration of PVP but a Newtonian flow at higher concentration of PVP and SLI. This is rationalized in terms of adsorption of PVP, as follows. That is, PVP is operating as an interparticle bridging reagent at low concentrations, resulting in flocculation. This bridging effect disappears at a higher concentration of PVP[9] and appears as a dispersing effect instead. Thus, PVP acted as a flocculant at a low concentrations (less than 0.1%) but as a dispersant at a high concentrations. Similar results were observed elsewhere.[3,4]

SDS acted as a dispersant for a kaolinite suspension.[3,4] The results obtained here also demonstrate that SLI is exhibits dispersing and thinning effects on a kaolinite suspension. Yalcin T., et al.[19] also pointed out that SDS adsorbed on the surface of clay platelets affecting an electrical double layer interaction, therefore altering rheological behavior of clay-water suspensions and the degree of dispersion/aggregation of the systems.

The intermolecular complex of nonionic PVP with anionic SDS could be adsorbed to the surface of kaolinite to make the secondary particles of the suspension smaller at high shear rates.[3] Our results show that anionic surfactant SLI causes a thinning effect at low PVP concentrations (less than 0.1%) but a thickening effect at higher concentrations, as shown in Fig. 3a.

Plastic Viscosity and Relative Viscosity   The plastic viscosity of kaolinite suspension is shown as a function of a concentration of SLI in Fig. 3a and of PVP in Fig. 3b. These results are quite similar to those observed by Nakagaki et al.[3] These results can be explained by considering the chain segments of PVP being adsorbed onto kaolinite particles which led to the flocculating interaction between kaolinite particles, resulting in an increase in plastic viscosity. Luckham and Rossi[9] showed that strong flocculation results from effective bridging, which requires expansion of the polymer to a point large enough to bridge the particles and still have sufficient free surface for the polymer adsorption. Healy and

La Mer,[25)] and Welzen *et al.*[26)] established the concept of "half-surface coverage" for optimum flocculation. If more than the optimum concentration of polymer is added to the system, the extent of flocculation would be reduced and the suspension might be stabilized. The kaolinite edge contains both silica- and alumina-like sites bearing positive charges in distilled water (pH <7). Addition of anionic surfactant (less than 4 mM of SLI) to kaolinite suspensions can neutralize positive charges on the edge of kaolinite and increase the bridging effect (Chart 2). Thinning of the plastic viscosity was attributed to gradual adsorption of surfactants, which causes charge reversion as well as repulsion between kaolinite particles.

Adding SLI to a kaolinite suspension with less than 0.1% PVP lowered the plastic viscosity linearly with increasing SLI, as shown in Fig. 3a. Anionic surfactant was absorbed onto the surface of kaolinite to displace adsorbed PVP, reducing the bridging effect on concentrated kaolinite particles. In a mixture of SLI and PVP (more than 0.1%) in the kaolinite suspension, the dispersion reaches its highest plastic viscosity around 4 mM (T_1), after which an increase in the concentration of SLI caused the suspension to have smaller secondary particles with a thinner plastic viscosity. Surfactant absorbed onto the kaolinite surface enhances the hydrophobic quality of kaolinite particles when SLI is below 4 mM (T_1). Furthermore, hydrophobic interaction between PVP and kaolinite particles increased the bridging effect and also plastic viscosity of the solution. Progressing addition of SLI accelerates the binding of SLI-kaolinite to PVP up to 4 mM. This fact induces electrical repulsion between the PVP-SLI complex and kaolinite-SLI (greater than 4 mM), leading to decreases in plastic viscosity.

The relative viscosity is defined as:

$$\eta_r = \eta_{pl} / \eta_m \qquad (2)$$

where η_{pl} and η_m are plastic and medium viscosities, which may reflect a change of flow unit. At low concentration of PVP (<0.1%), relative and plastic viscosity diminishes linearly with a concentration of SLI, as shown in Fig. 3a. With PVP concentration above 0.1%, relative viscosity maximizes when increasing the concentration of SLI having the same trend as plastic viscosity. Similar change with a maximum is observed at various PVP concentrations with fixed SLI concentration and below 12 mM in Fig. 3b. Heath and Tadros[14)] claimed that the behavior of plastic viscosity is not correlated with gel structure of montmorillonite suspensions, since the structure of montmorillonite was partially broken under a relatively high shear rate. In this research most kaolinite solution gel structures were intact under low shear rates; hence the PVP polymer plays a key role in reducing plastic viscosity and relative viscosity.

Bingham Yield Value Figure 4a shows the Bingham yield values of kaolinite suspension at various concentrations of SLI and PVP. A maximum Bingham yield value was observed in solutions containing about 4 mM SLI. Bingham yield value and bridging effects were enhanced when the anionic surfactant SLI (below 4 mM) was adsorbed onto kaolinite particles prior to the polymer PVP (*i.e.*, increasing PVP-particles interaction), and then the thinning effect appears (above 4 mM SLI) due to electrical charges of adsorption of an aionic complex of SLI and PVP on the kaolinite surface,
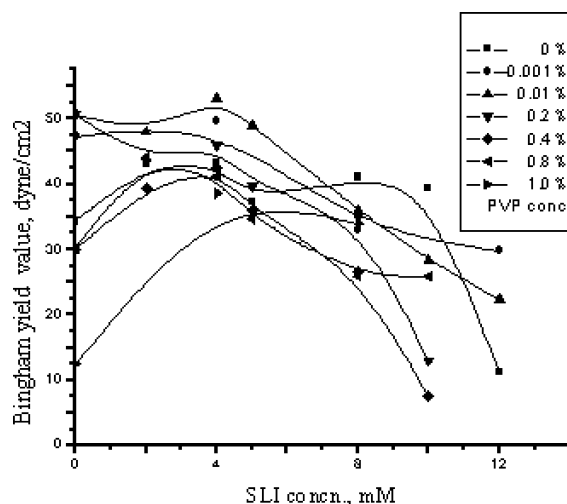

Fig. 4a. Bingham Yield Value of Kaolinite Suspension as a Function of a Concentration of SLI

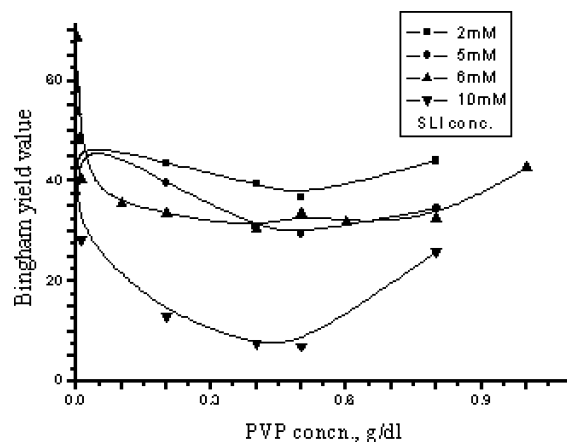[PVP] (g/dl=%(w/v))=0 (■), 0.001 (●), 0.01 (▲), 0.2 (▼), 0.4 (◆), 0.8 (◄) and 1.0 (►).

Fig. 4b. Bingham Yield Value of Kaolinite Suspension as a Function of a Concentration of PVP

[SLI] (mM)=2 (■), 5 (●), 6 (▲), 10 (▼).

resulting in repulsive and dispersive effect between particles.

Figure 4b shows a minimum in Bingham yield value for the suspension containing around 0.5 g/dl PVP. This fact suggests that the gel structure of kaolinite particles was destroyed under the shear rate into small size particles. Heath and Tadros[14)] showed similar results from their study of an aqueous suspension containing 4% sodium montmorillonite. The absorption amount at the maximum onto particles corresponded with one quarter coverage by polyvinylalcohol (PVA). The bridging effect at a low concentration of PVA caused flocculation. The polymer behaves as dispersant when the concentration increased, resulting in diminishing the Bingham yield value as well as plastic viscosity. In contrast to SDS[20)] and cetyltrimethyl ammonium bromide[13)] at high shear rate, Bingham yield values declined linearly with an increase in the surfactant concentration at a constant concentration of polymer. They decreased to near zero at high concentrations of surfactant, resulting in Newtonian flow.

Volume Fraction Vand derived an equation to describe the relationship between solution relative viscosity (η_r) and dispersed phase volume fraction (ϕ), or actually effective
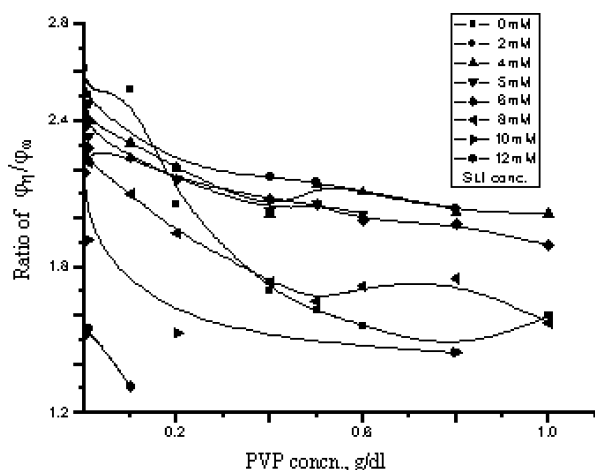
Fig. 5.   Ratio of Effective Volume Fraction to Real Volume Fraction of Kaolinite Suspension as a Function of a Concentration of PVP

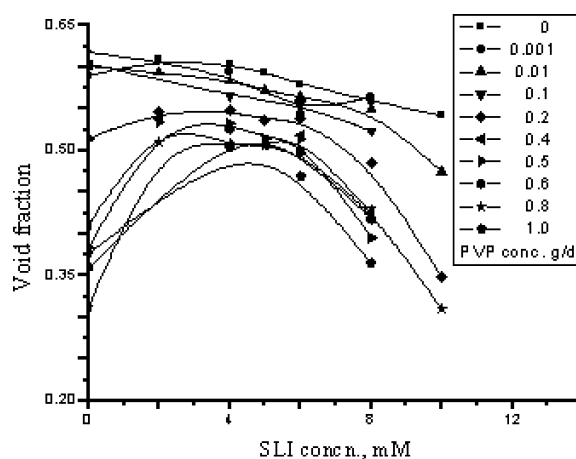[SLI] (mM)=0 (■), 2 (●), 4 (▲), 5 (▼), 6 (◆), 8 (◄), 10 (►) and 12 (◆).

Fig. 6.   Void Fraction of Kaolinite Suspension as a Function of a Concentration of SLI

[PVP] (g/dl)=0 (■), 0.001 (●), 0.01 (▲), 0.1 (▼), 0.2 (◆), 0.4 (◄), 0.5 (►), 0.6 (●), 0.8 (★) and 1.0 (◆).

volume fraction (ϕ_η), as follows:

$$\ln \eta_r = (2.5\phi_\eta + 2.7\phi_\eta^2 + \ldots)/(1-0.609\phi_\eta) \qquad (3)$$

The ϕ_η can be obtained by measuring η_{pl} from Eq. 3. The effective volume fraction of an aggregated suspension (*i.e.*, secondary particles) contains not only the volume fraction of primary solid particles (real volume fraction, $\phi_\omega=0.204$) but also the dispersing medium entrapped in an aggregate responding to flow properties and suspension flow unit. Formation of bulky secondary particles of kaolinite boosts relative viscosity of suspension liquid. The ratio of effective volume fraction to real volume fraction, ϕ_η/ϕ_ω, can be used to judge the flocculation extent of solid particles. The values of ϕ_η/ϕ_ω range from 1.4 to 2.6 in our results (Fig. 5). Firth *et al.*[27,28] obtained the value of ϕ_η/ϕ_ω as 10.5 for aqueous suspension of kaolinite from plastic viscosity, attributing this large value to the anisometric nature of the kaolinite particles. In this work, the largest value (2.6) emanates from bridging effect at low concentration of PVP (0.001%), the smallest (1.4) from the dispersing property at concentrations of PVP (0.1—0.8 g/dl) and SLI (10—12 mM).

Void Fraction   Void fraction (ε) in secondary particles may be calculated through the equation

$$\varepsilon = (\phi_\eta - \phi_\omega)/\phi_\eta \qquad (4)$$

where ε signifies a ratio of the volume of dispersing medium contained in the flow unit to the whole volume of the flow unit. Smaller ε value means higher dispersing of the suspension. The ε values of 0.62 and 0.31 in Fig. 6 correspond to 2.6 and 1.4 of ϕ_η/ϕ_ω in Fig. 6. Shimabayashi *et al.* obtained a minimum value ($\varepsilon=0.29$) at 2.0 g/dl PVP and 10 mM SDS from a rheology study of kaolinite in PVP and SDS solution (20 g in 30 ml) at high shear rate (250—2000 s^{-1}). Performance of both anionic surfactants SLI and SDS is quite similar in kaolinite dispersing system, though functional groups are a little different, that is, sulfonate group in SLI and sulfate group in SDS.

Although SDS, SLI and PVP show dispersing abilities, flow properties of high kaolinite suspensions vary to some extent between low and high shear rate. According to the results of Shimabayashi *et al.*,[20] gradual increasing of the con-

centration of SDS with constant concentration of PVP in kaolinite suspension gets better dispersing effects; and gradual increasing in the concentration of PVP with constant concentration of SDS obtains the maximum values of relative viscosity, effective volume fraction, Bingham yield value and void fraction at high shear rates. That was owing to the fact that PVP acts as an aggregating agent at a low concentration (<0.1%), but a dispersing agent at a high concentration. Contrary to high shear rate, our results (Figs. 3—6) indicate that under constant concentration of SLI, the dispersing effect can be improved by increasing concentration of PVP; increasing the concentration of SLI at constant concentrations of PVP shows a maximum bridging effect around 4 mM at low shear rate. Low concentration (<0.1%) of PVP already shows flocculent effect; addition of surfactant acts only as a dispersant to decrease the viscosity linearly. Adsorption of anionic surfactant (SLI) onto a neutral water-soluble polymer (PVP) will build up charges on the polymer chain, leading to polymer coil expansion and cross-linking between solid particles in solution to cause larger secondary particles and thicker suspension viscosity (Figs. 3—6). When adsorption concentration of SLI onto the PVP surface is greater than 4 mM, formation of hemi-micelles on the polymer chain causes greater viscosity and other suspension parameters. Since a gel structure is less disturbed at low shear rates than high shear rates, we observe effects of SLI on the conformation change of PVP in solution through the variation of reduced viscosity and void fraction.

From the results of flow curves with low shear rate, we observed that PVP acts as a flocculant at concentrations less than 0.1%, and as a good dispersant at a higher concentration in high solid content of kaolinite suspension. The surfactant SLI shows dispersing effects when PVP is less than 0.1%, otherwise PVP will work as a flocculant unless SLI concentration exceeds critical micelle concentration (T_2, 8 mM for 0.1% PVP, 9 mM for 0.5% PVP and 10 mM for 1.0% PVP, from Fig. 1) and flocculation effect peaks at 4 mM (T_1). Adsorption of surfactant onto the polymer chain from solution should be considered as a performance of dispersing property. Jones[22] proposed that the polymer is able to absorb surfactant at a concentration of surfactant T_1 and reach satura-

tion at T_2. Cockbain[29] found T_1 weakly dependent on the amount of polymer and T_2 representing saturation of polymer site proportional to polymer concentration in solution. When the charged surfactant is mixed with a neutral polymer, the adsorption process will change the electrical neutrality of polymer and the conformation of polymer chain in solution.

Adsorption of PVP with SDS at TiO_2/solution interface was studied by Ma,[30] the amount of SDS adsorbed by TiO_2 decreased with an increase in a concentration of PVP, but the amount of PVP adsorbed onto TiO_2 was increased with an increase in a concentration of SDS with a maximum at 4 mM (T_1). This implies PVP-SDS complex formed in solution is not adsorbed at TiO_2/solution interface, leading to little effect on dispersion but boosting the solution viscosity. Adsorption of surfactant or PVP on solid particles raises dispersibility, which depends on concentrations of a surfactant monomer and/or of free PVP. Hence flow parameters of kaolinite suspension mixed with SLI show a maximum at 4 mM (T_1) and better dispersion at concentrations higher than T_2.

In summary, the kaolinite could be well-dispersed in the presence of SLI alone or the SLI mixing with PVP in concentrations less than 0.1%. Flocculation was observed when adding SLI together with PVP in concentrations over 0.1% up to the reach of saturation adsorption point that SLI onto PVP (T_2) with a maximum at 4 mM (T_1).

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