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Flocculation and Formation of Open Structure of Kaolinite Suspension in the Presence of Polyvinylpyrrolidone

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Physicochemical and rheological properties of both concentrated and dilute suspensions of kaolinite were studied in the presence of polyvinylpyrrolidone (PVP). Bingham yield value, relative viscosity with respect to the plastic viscosity, volume fraction of the flow unit, and void fraction in the flow unit for the concentrated suspension were estimated from the flow curve obtained by means of a Couette-type rotary viscometer (Shimadzu UR-1). Mean diameter and volume fraction of the secondary particles in the dilute suspension were measured by a Coulter counter (TA-II). The optimum concentrations of PVP for the flocculation of kaolinite (1—50 g/100 ml), which were obtained by the two measuring methods mentioned above, were consistent with each other. The more the extent of flocculation increased by virtue of the interparticle bridging effect of PVP, the more the volume fraction of the secondary particles, which is viscometrically effective, increased although the weight concentration of kaolinite was kept constant. This result shows that the floc is of the open structure, and that the void fraction of the floc increases with the extent of the flocculation. The bulky floc, including much of the suspending medium, behaves as a flow unit in the suspension. The open structure was broken up when an excess amount of PVP as a dispersing agent was added.

Keywords——Coulter counter; yield value; flow curve; suspension; flocculation; mean diameter; kaolinite; polyvinylpyrrolidone; open structure

To understand the dispersion/flocculation properties and the flow behavior of suspensions is important in pharmaceutical preparations such as suspended syrups, parenteral suspensions, liniments, lotions, ointments and so on. From this viewpoints, many physicochemical studies on the suspension properties have been carried out up to the present. It is known that suspended particles aggregate to form a floc in the presence of intermediate concentrations of polymer, which forms bridges between particles through adsorption.[2-5] The mean diameter of the secondary particles in a dilute suspension and the Bingham yield value of a concentrated suspension increase with the degree of flocculation. At high concentrations of polymer, however, the suspension is again stabilized. Under these conditions the adsorbed polymer adopts a more extended configuration with loops and tails protruding out into the solution, thus enabling steric repulsive force to come into operation. The more the suspension is stabilized, the more both relative viscosity and elastic modulus of the suspension decrease owing to the disruption of the interparticle structure among the primary particles.[2,3,6] On the other hand, in the absence of adsorbed polymer, coagulation of colloidal particles occurs by virtue of either Brownian motion (Brownian coagulation process) or bulk fluid motion (shear coagulation process). When the latter process dominates, the coagulum appears as an elongated string of particles rather than a grape cluster, which appears through the former process.[7] However, the coagulum breaks up in a high shear field[8] in the same manner as the floc does.

In the previous papers,[9-14] flocculation of suspended particles was discussed on the basis of measurements of the mean diameter of secondary particles and/or Bingham yield value in the presence or absence of polyvinylpyrrolidone (PVP), sodium chondroitin-6-sulfate (Na_2Chs), or other polymers. The aim of this work is to relate flocculation/dispersion characteristics to the flow properties of both dilute and concentrated dispersions of kaolinite in the presence of PVP. The viscometrically effective volume of the secondary particles is much larger than the volume estimated from the density and weight of the primary particles, because the floc as the flow unit, which has an open structure, entraps much of the dispersing medium.[14] In the present paper, the effective volume fraction of the bulky flow unit will be discussed by considering the results obtained with a Coulter counter for the dilute suspensions and with a Couette-type rotary viscometer for the concentrated suspensions.

Experimental

Materials——Kaolinite was purchased from Wako Pure Chemical Industries Ltd., and was the same sample as that used before.[10-14] PVP (polyvinylpyrrolidone K-90) was purchased from Nakarai Chemicals Ltd., and its mean molecular weight was determined to be 7.0×10^5 by the measurement of intrinsic viscosity at 30 °C.[12,13]

Methods——A known weight of kaolinite was suspended in a given aqueous solution of PVP one night before the measurement. The volume fraction, ϕ_w, of kaolinite was calculated from the weight by taking the density of kaolinite of 2.6 g/cm^3 into consideration. The subscript "w" was added to show that this volume fraction was estimated from the weight and density of the kaolinite. Other volume fractions, ϕ_{cc} (Eq. 2) and ϕ_η (Eq. 4), will be discussed later.

The flow curve (*i.e.*, the relationship between shear rate (g) and shear stress (f)) of the kaolinite suspension was obtained by using a Couette-type rotary viscometer (Shimadzu UR-1) at 30 °C. In general, the flow curve was expressed as follows,

$$f - F_0 = g \cdot \eta_{PL} \qquad (1)$$

where F_0 and η_{PL} are the Bingham yield value and plastic viscosity of the suspension, respectively. When $F_0 = 0$, the flow curve becomes Newtonian and η_{PL} shows the Newtonian viscosity of the suspension in this case.

Particle size distribution (volume distribution) and the mean diameter (50% cumulative, d_m) of the secondary particles of the kaolinite were determined by means of a Coulter counter TA-II (Coulter Electronics Ltd.) with an aperture tube of 50 or 100 μm at room temperature (= *ca.* 22 °C). The measurement of d_w was done in 154 mM NaCl (=0.9%) under gentle stirring at frequent intervals immediately after the dilution of 1 g/100 ml (=1%) kaolinite suspension to 10^{-3} g/100 ml (=10^{-3}%). The d_m in 1% kaolinite suspension was estimated by extrapolation of the measured d_m to that at time zero. By this procedure the effects of particles sticking on the wall of the measuring vessel, which causes a count loss, and of the destruction of the secondary particles due to the dilution and stirring might be compensated. The data thus obtained were reproducible. Volume fraction (ϕ_{cc}) of the secondary particles in the 1% kaolinite suspension was estimated simultaneously with the determination of d_m through the extrapolation of ϕ_{cc} to that at time zero. The value of ϕ_{cc} was obtained through Eq. 2,

$$\phi_{cc} = \frac{10^3 \pi}{6} \sum_i (n_i \cdot d_i^3) \qquad (2)$$

where n_i and d_i are the particle number in unit volume (1 cm^3) and particle diameter, respectively, registered in each channel (the 16 volumetric size classes) of the Coulter counter ($i = 1 - 16$), and the numerical factor 10^3 is the dilution ratio of 1% to 10^{-3}%. The observed value of ϕ_{cc} was somewhat lower than ϕ_w (=3.83×10^{-3} for the 1% kaolinite suspension) probably because some of the kaolinite particles had been dispersed either to small flocs or primary particles undetectable by the Coulter counter. The kaolinite concentration in the present study was chosen as 1% in order to compare the results obtained here with those reported elsewhere,[12-14] although the concentration of 1% was too high to measure d_m directly without the dilution to $10^{-3}\%$.

Results and Discussion

Flow Curves

Flow curves were obtained while the shear rate, g, increased and decreased. However, those obtained while g decreased were more reproducible than those obtained while g increased.[11] Figure 1, therefore, shows the flow curves which were obtained while g decreased. The flow curve moved to the right-hand side with the addition of a small amount of PVP and came back to the left-hand side again on the addition of a further amount of PVP, while the kaolinite concentration was kept constant (15 g/30 ml; $\phi_w = 0.161$). The flow curve in the presence of a sufficient amount of PVP became Newtonian.

Bingham Yield Value

The Bingham yield value (F_0) was obtained from the intercept of the abscissa by extrapolating the flow curve to $g = 0$,[11] as shown in Fig. 1. The relationship between F_0, thus estimated, and the concentration (c_p) of added PVP is shown in Fig. 2. The value of F_0 decreased to zero after attaining a maximum. The concentration of PVP for the maximum F_0 and the minimum concentration of PVP for $F_0 = 0$ increased with the concentration of kaolinite (see Fig. 4).

The value of F_0 is one of the quantities which reflect the strength of the interparticle interaction in the concentrated suspension. PVP at intermediate concentration strengthened the gel structure by bridging among kaolinite particles, resulting in the increase in F_0, while PVP at high concentration loosened the gel structure by its dispersing action, resulting in the decrease in F_0.[12-14] The gel (*i.e.*, infinite floc) was split into the flocs of the flow unit (*i.e.*, secondary particles) when the shear stress became higher than F_0, which depends on the strength of the gel structure. The present result is in contrast with that obtained previously,[11] where F_0 decreased monotonously with the polymer concentration of Na_2Chs. In this case, Na_2Chs exhibited a protective dispersing effect on kaolinite over the whole concentration range studied.

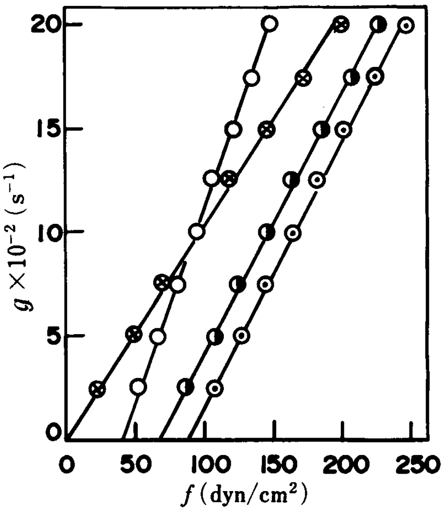

Fig. 1. Flow Curves of the Kaolinite Suspension

Kaolinite concentration = 15 g/30 ml ($\phi_w = 0.161$). PVP concentration (g/100 ml) = 0 (○), 0.03 (⊙), 0.10 (◑), and 1.00 (⊗).

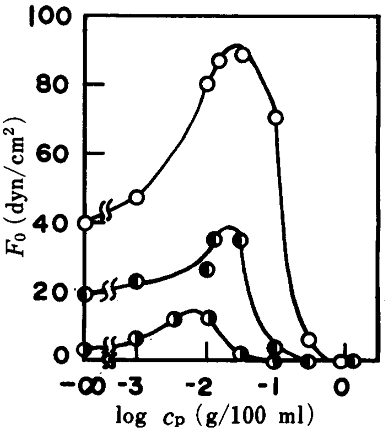

Fig. 2. Bingham Yield Value as a Function of the Concentration of PVP Added

Kaolinite concentration (g/30 ml) = 5 (◑, ϕ_w = 0.0602), 10 (◐, $\phi_w = 0.114$), and 15 (○, $\phi_w = 0.161$).

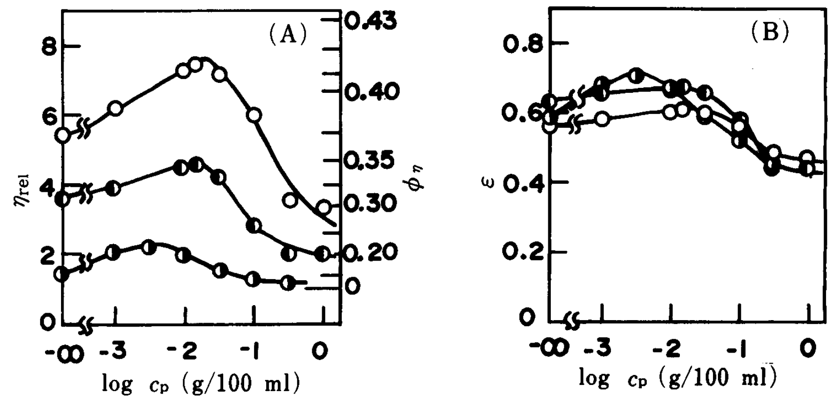

Fig. 3. Relative Viscosity, Vand's Volume Fraction, and Void Fraction in the Flow Unit as a Function of the Concentration of PVP Added

(A) η_{rel} and ϕ_η *vs.* c_p. (B) ε *vs.* c_p.
Kaolinite concentration (g/30 ml)=5 (◑, $\phi_w=0.0602$), 10 (◐, $\phi_w=0.114$), and 15 (○, $\phi_w=0.161$).

Viscosity and Void Fraction

Plastic viscosity, η_{PL}, was obtained from the slope of the flow curve shown in Fig. 1 by means of Eq. 1. It increased with the concentration of PVP added while the concentration of kaolinite was kept constant. Heath and Tadros[2,3] have also shown that the plastic viscosity of a suspension of sodium montmorillonite (4%) or Aerosil (12%) increased rapidly with the concentration of polyvinylalcohol (PVA) added. However, they did not assume that η_{PL} reflected the gel structure at rest because η_{PL} was measured at relatively high shear rate where the gel structure at rest was already partially broken down.

In the present paper, however, the structure of the secondary particles as the flow units will be discussed by transforming the value of η_{PL} to the relative viscosity, η_{rel}, according to Eq. 3,

$$\eta_{rel}=\frac{\eta_{PL}}{\eta_0} \tag{3}$$

where η_0 is the medium viscosity. The value of η_{rel} decreased with the concentration of PVP after a maximum was attained (Fig. 3A), in a manner similar to F_0 shown in Fig. 2. The concentration of PVP at the maximum η_{rel} increased with the concentration of kaolinite (see Fig. 4).

Gillespie[15] suggested that the void fraction of an aggregate increased with the extent of aggregation. Therefore, the value of η_{rel}, obtained through Eq. 3, was analyzed by means of Vand's equation in order to characterize the flow unit of the kaolinite aggregate and to estimate the void fraction in it. Vand[16] derived the relationship between η_{rel} and effective volume fraction, ϕ_η, taking interparticle collision into consideration, as follows,

$$\ln \eta_{rel}=\frac{2.5\phi_\eta+2.70\phi_\eta^2+\cdots}{1-0.609\phi_\eta} \tag{4}$$

where ϕ_η is the viscometrically effective volume fraction and reflects, therefore, the volume fraction of the flow unit, the latter being the secondary particles containing the dispersing medium and primary particles. Vand showed that Eq. 4 was valid up to $\phi_\eta=0.5$. The value of ϕ_η is also graduated on the ordinate of the right-hand side in Fig. 3A. The increase in η_{rel}, therefore, means the formation of bulky secondary particles of the kaolinite. In other words, the floc of the flow unit becomes more open, entrapping more of the dispersing medium, when η_{rel} and ϕ_η increase.[17] The ratio, ϕ_η/ϕ_w, was 2.5—3.5 at the maximum point in Fig. 3A. The value of ϕ_η was significantly larger than that of ϕ_w.

The void fraction, ε, in the secondary particles may be calculated through Eq. 5,

$$\varepsilon=\frac{\phi_\eta-\phi_w}{\phi_\eta} \qquad (5)$$

The relationship between ε and the PVP concentration (c_p) is shown in Fig. 3B, where ε was in the range of *ca.* 0.4—0.7. These values are significantly higher than the value for the closest packing of unisize spheres (where $\varepsilon=0.26$). The value of ε decreased with the concentration of PVP after a maximum was attained. This behavior of ε is similar to that of F_0 in Fig. 2. Firth and Hunter[18)] evaluated ϕ_η/ϕ_w as 10.5 ± 0.4 for an aqueous dilute suspension of kaolinite ($\phi_w=0.022$), from which ε was estimated as around 0.9 by means of Eq. 5. This value, however, is considerably larger than that shown in Fig. 3B. This difference is probably owing to the difference in the sample and the concentration of the kaolinite.

The PVP concentration for the maximum η_{rel} and ε, as well as that for the maximum F_0, is shown in Fig. 4 (curve A) as a function of the kaolinite concentration. The optimum concentrations of PVP almost coincided with each other. These concentrations of PVP increased with the concentration of kaolinite because flocculation (curve A) and dispersion (curve B) are both caused through the adsorption of PVP on kaolinite.[12-14)] The distance between curve A and curve B is around 1.1—1.5 in $\log c_p$ unit, which corresponds to the fact that the minimum concentration for Newtonian flow is higher than the optimum concentration for the flocculation by a factor of 13—32.

Measurement with the Coulter Counter

The solid line in Fig. 5 shows the size distribution of the secondary particles of the kaolinite 3 min after dilution (see Experimental). The mean diameter, d_m, and the volume fraction, ϕ_{cc}, with respect to the 1% kaolinite suspension obtained by means of Eq. 2, were 5.63 μm and 3.73×10^{-3}, respectively. The dotted line shows that of the same suspension just after vigorous stirring for a short period (= *ca.* 10 s). The values of d_m and ϕ_{cc} decreased to 5.16 μm and 3.66×10^{-3}, respectively, owing to the destruction of the secondary particles (*i.e.*, flocs) by agitation. These decreases in d_m and ϕ_{cc} in a dilute suspension correspond to the

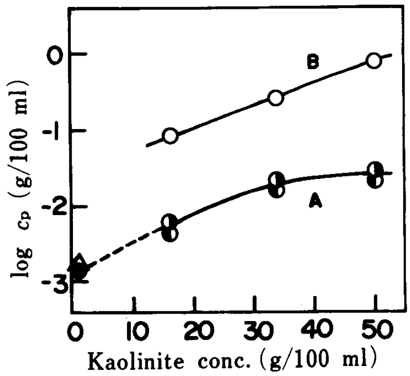

Fig. 4. Optimum Concentration of PVP for Kaolinite Flocculation (A) and Minimum Concentration of PVP Required for Newtonian Flow of the Kaolinite Suspension (B)

◑, concentration of PVP for the maximum of F_0; ◐, concentration of PVP for the maximum of η_{rel} and ε; ●, concentration of PVP for the maximum of d_m; △, concentration of PVP for the maximum of ϕ_{cc}; ○, minimum concentration of PVP for $F_0=0$.

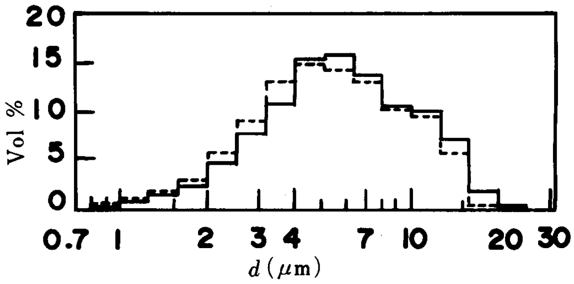

Fig. 5. Size Distribution of Kaolinite Particles in the Suspension

The solid line shows the size distribution obtained 3 min after the dilution of the kaolinite suspension from 1% to 10^{-3}% under gentle stirring ($d_m=5.63$ μm and $\phi_{cc}=3.73\times10^{-3}$). The dotted line shows that obtained after the same procedure as mentioned above and vigorous stirring for 10 s ($d_m=5.16$ μm and $\phi_{cc}=3.66\times10^{-3}$). $c_p=10^{-3}$ g/100 ml.

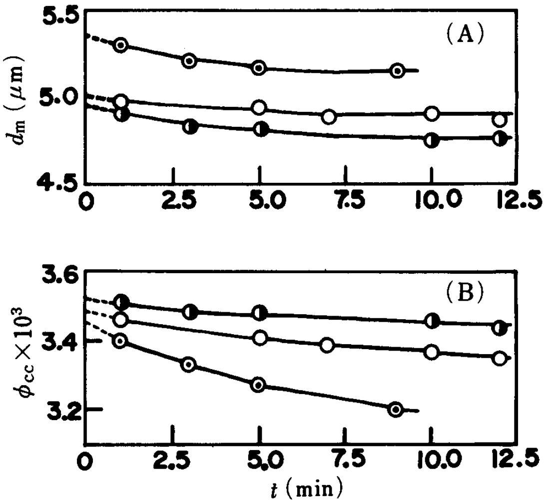

Fig. 6. Time Courses of d_m and ϕ_{cc} after Dilution

Concentration of kaolinite before the dilution = 1 g/100 ml.

Concentration of PVP before the dilution (g/100 ml) = 0 (○), 10^{-5} (◑), and 10^{-2} (⊙).

Figs. A and B show the time course of d_m and that of ϕ_{cc}, respectively.

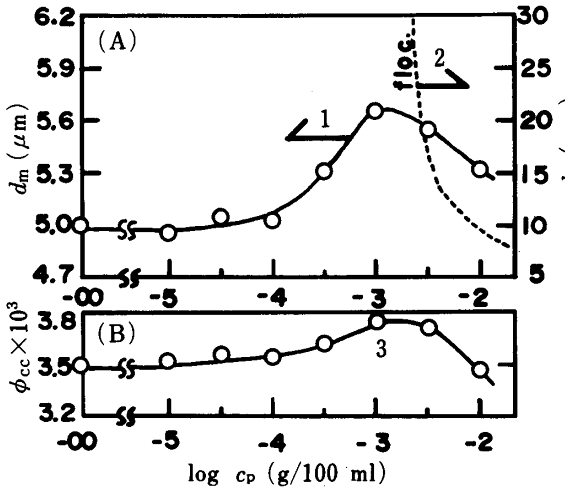

Fig. 7. Effect of PVP Concentration on d_m and ϕ_{cc}

The curves 1 and 3 show the results obtained by means of a Coulter counter in the present paper. The curve 2 shows the mean diameter of the same kaolinite particles measured through a sedimentation balance in 1% kaolinite suspension, quoted from the previous paper.[12] The PVP concentration on the abscissa is that in the 1% kaolinite suspension.

collapse of the gel structure (*i.e.*, the infinite floc) in a concentrated suspension through shear stress higher than F_0.

Time courses for d_m and ϕ_{cc}, measured by a Coulter counter, are shown in Fig. 6, from which d_m and ϕ_{cc} for the 1% kaolinite suspension were determined by extrapolation to zero time as shown by the dotted line (see Experimental).

The relationship between c_p and d_m or ϕ_{cc} was obtained, as shown in Figs. 7A and B with open circles and solid lines. The increase in ϕ_{cc} synchronizes with the increase in d_m even though the weight concentration of kaolinite is kept constant. This fact shows that the more the size of the secondary particle increases, the more the extent of the open structure including the dispersing medium increases. This is the same trend as that mentioned in the previous section for the concentrated suspension.

The dotted line in Fig. 7A shows the relationship between c_p and d_m which had been obtained previously by means of a sedimentation balance in the 1% kaolinite suspension.[12] This value is considerably higher than that shown by the solid line. The former increases steeply with formation of large flocs visible with the naked eye at around $c_p = 2\times10^{-3}$ g/100 ml, while the latter just attains the maximum ($d_m = 5.7\,\mu$m) at almost the same concentration of PVP. Therefore, the data obtained with a Coulter counter through the procedure shown in Fig. 6 seem to reflect properly the effect of the concentration of PVP at least qualitatively, although they do not agree exactly with those obtained by the sedimentation balance method.

When the PVP concentrations at the maxima of d_m and ϕ_{cc} are plotted in Fig. 4 at the kaolinite concentration = 1 g/100 ml, they fall on the extrapolated portion (shown with the dotted line) of curve A, which shows the optimum concentration of PVP for the flocculation of the concentrated kaolinite suspension. This result means that the curve of the optimum concentration of PVP estimated from the maximum points of F_0 and η_{rel} is consistent with that estimated from the maximum points of d_m and ϕ_{cc}. Thus, the extended curve A shows the optimum concentration of PVP for the flocculation of kaolinite suspension over a wide concentration range (1—50 g/100 ml).

In summary, methods for estimating the volume fraction of the floc and/or flow unit have been presented. The flow properties of the kaolinite suspension and the structure of the flow unit were discussed by taking into consideration the volume fraction of the secondary particles. The more the degree of flocculation increases through the interparticle bridging effect of the added PVP, the more the floc becomes open and entraps the dispersing medium, resulting in increases of the size and the viscometrically effective volume fraction of the flow unit. Floc and/or gel were destroyed or reduced in size by shear stress, stirring, dilution, and addition of an excess amount of PVP, resulting in an increase in the fluidity of the suspension. The optimum concentration of PVP for the flocculation of kaolinite was determined as the concentration where ϕ_η and F_0 become maximum or where d_m and ϕ_{cc} attain their maximum. The results obtained with these two measuring methods were consistent with each other.

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