ORDERED STRUCTURE OF MONODISPERSED PARTICLES FILTERED AT CONSTANT PRESSURE

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The formation of ordered and disordered cakes of monodispersed PSL particles by constant-pressure filtration is investigated. It is found that ordering occurs under the condition where the transition of a dispersed phase of particles to an ordered one, like the Alder transition, takes place above the cake surface, and that common cakes are composed of both disordered and ordered domains with specific cake resistances of 0.9×10^{13} and 1.5×10^{13} m/kg respectively. An equation for a constant-pressure filtration in which the dependence of the cake structure on the flow rate is taken into account is proposed and is found to be successfully applicable to cakes composed of ordered and disordered domains.

Introduction

Monodispersed spherical particles suspended in water form an ordered structure when the suspensions are deionized and the repulsive force of the electric double layer acts strongly between particles^{7,8)}. The mechanism of this ordering has been explained by the Alder transition as predicted using the molecular dynamic method, which says that particles can be crystallized by the repulsive force between them¹⁾. The ordered structure of this kind is soft and easily destroyed because particles do not contact each other directly. Hence this ordered structure is not adequate when ordered solid materials are required.

A few methods to obtain a solid material of ordered structure have been proposed. A simple method is sedimentation by gravitation, but it requires a very long time to get cakes of ordered structure²⁾. Centrifugation accelerates the sedimentation rate and en-

ables us to obtain the solid state ordered structure³⁾. Filtration is another promising method. Bridger *et al.* found that cakes of close-packed structure were obtainable by constant-pressure filtration although there was a transition point at which the cake structure deformed from porous to close-packed structure.⁴⁾ However, their experiment was carried out under limited experimental conditions and so the conditions for ordering and the mechanism of ordering are not yet clear.

In this study, the mechanism and experimental conditions for the formation of ordered and disordered cakes in the constant-pressure filtration of monodispersed latex particles, as shown in **Fig. 1**, are investigated. And a filtration equation in which the dependence of cake structure on the flow rate of filtrate is taken into account is proposed to analyze the data of the flow rate versus the cake weight.

1. Experimental

Monodispersed polystyrene latex (PSL) particles were prepared by the method of soap-free polymeri-

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Fig. 1. Structures of filled cakes at $P=98$ kPa and $\phi_p=0.025$. (a) $C_e=1 \times 10^{-2}$ mol/l (b) $C_e=1 \times 10^{-5}$ mol/l

zation. The particles were purified by centrifugal separation and electrodialysis. They were confirmed to be monodispersed and of $0.5 \mu\text{m}$ diameter by a scanning electron microscope (SEM). A 10 vol% suspension of particles in water was prepared and used as the stock suspension for the present experiment. Desired suspensions were prepared by diluting the stock suspension to a given concentration and mixing it with NaCl solution of a given concentration just before the experiment.

Figure 2 shows a schematic drawing of the batch-type filtration employed in the present study. The filtration vessel was a stainless-steel cylinder of 1.0 cm inner diameter and 5.0 cm height, and was kept in a temperature-controlled water bath of $25 \pm 0.1^\circ\text{C}$. The filtration medium was a membrane filter of pore size $0.1 \mu\text{m}$. Pressure was applied by compressed nitrogen gas at 49 to 980 kPa. The variation in weight of filtrate with time was measured on an electric balance, and the weight of cake per unit area, W_c , and the flow rate of filtrate, q , were calculated from the data stored in a computer connected to the balance. Here W_c and q were given by $W_c = \rho s v / (1 - s/s_c)$ and $q = dv/dt$ respectively, where v is the volume of filtrate per unit area, ρ the filtrate density, s and s_c the mass fraction of the solid in the suspension and that in the cake respectively, and t the time. Filtration was terminated approximately at $W_c = 1.0 \text{ kg/m}^2$. The cross-section

Fig. 2. (a) Schematic drawing of batch system of filtration. (b) Details of filtration apparatus.

of dried cakes was observed with the SEM to examine the ordering of the cake structure. The packing density of dried cakes was measured on a mercury porosity meter.

2. Result and Discussion

According to Ruth's theory of constant-pressure filtration, the filtration equation is expressed as follows⁴⁾.

$$P/\mu q = \alpha W_c + R_m \quad (1)$$

where P is the constant applied pressure, μ the viscosity of filtrate, α the specific cake resistance, and R_m the resistance of the medium. It is clear that the value of α is given as the slope of the plot of $P/\mu q$ vs. W_c . In this equation the value of α is assumed to be constant; that is, the local structure of cake does not vary during the filtration. However, the present experiment indicates that the specific cake resistance is not necessarily constant. Examples of the relations of $P/\mu q$ vs. W_c are illustrated in Fig. 3. Line (a) for a suspension of the electrolyte concentration $C_e=0.01$ mol/l, the particle volume fraction $\phi_p=0.025$ at $P=98$ kPa, is straight so that α is constant. The cake structure observed with the SEM was found to be disordered everywhere as shown in Fig. 1(a), and the packing density of the cake, ϕ_c , was about 0.62. It is known that ϕ_c is 0.63 when equal spheres are packed at random¹⁰⁾. These results imply that particles in this

Fig. 3. Typical relations of $P/q\mu$ vs. W_c at $\phi_p=0.025$. (a) $P=98$ kPa and $C_e=1 \times 10^{-2}$ mol/l; (b) $P=98$ kPa and $C_e=1 \times 10^{-5}$ mol/l; (c) $P=780$ kPa and $C_e=1 \times 10^{-5}$ mol/l. The solid lines are fitted lines. The broken lines correspond to fitted line (a)

cake are randomly but closely packed.

Line (b) for a suspension of $C_e=1 \times 10^{-5}$ mol/l and $\phi_p=0.025$ at $P=98$ kPa is also found to be nearly straight, except at the beginning of filtration; that is, $W_c < 0.1$ kg/m². However, the value of α is 1.5 times larger than that for line (a) and the cake structure is ordered as illustrated in Fig. 1(b). The value of ϕ_c for this cake is found to be 0.67. This value is greater than that for a randomly close-packed structure but smaller than that (0.74) for a regularly close-packed structure of equal spheres. These results imply that the cake is composed of both ordered domains of high packing density and domain boundaries of low density.

Lines (a) and (b) are extreme cases, and most relations of $P/q\mu$ vs. W_c are slightly curved as shown by line (c). It seems that the specific cake resistance at $W_c \sim 0$ kg/m² approximately coincides with that for line (a) and the resistance at $W_c \sim 1$ kg/m² with that for line (b). This implies that the local structure of cake varies as the filtration proceeds; a disordered structure of cake is formed at the beginning of filtration where W_c is small, that is, where q is large, and an ordered structure is formed at the end of filtration where W_c is large, that is, where q is small. Hence it is plausible to assume that the degree of ordering depends on q . This dependence was predicted theoretically by Davis *et al.*⁵⁾ These results enable us to derive a filtration equation in which the

Fig. 4. Three types of relations of $P/q\mu$ vs. W_c . (A) relation for disordered structure; (B) relation for ordered structure; (C) relation for a common structure. (B') asymptote of the line (C) at $q \rightarrow 0$

local cake resistance varies as the filtration proceeds, as follows.

Figure 4 shows schematically three types of relations of $P/q\mu$ vs. W_c given in Fig. 3. If cakes consist of either a disordered or an ordered structure, the relations of $P/q\mu$ vs. W_c for these cakes are given as follows and are illustrated by lines (A) and (B) in Fig. 4.

$$P/q\mu = \alpha_d W_c + R_m \quad (2)$$

$$P/q\mu = \alpha_o W_c + R_m \quad (3)$$

where α_d and α_o are the constant specific cake resistances of disordered and ordered structures respectively. When the cake resistance varies as shown by line (C), it is plausible to assume that line (C) represents as a composite function of Eqs. (2) and (3). Then the equation for line (C) may be expressed as follows:

$$f(q)(P/q\mu - \alpha_d W_c - R_m) + (P/q\mu - \alpha_o W_c - R_m) = 0 \quad (4)$$

where $f(q)$ is the weight function which represents the contribution of disordered phase, and so $ST:TU = f(q_1):1$ in Fig. 4. Since line (C) approaches line (A) as the value of q increases and to line (B'), which has the same slope as the line (B), at $q \rightarrow 0$, $f(q)$ must be a function of q that satisfies these conditions. Here, we employ $f(q) = \beta q$ as the first approximation, where β is a constant. Substitution of $f(q) = \beta q$ into Eq. (4) yields the following relation.

$$P/q\mu = [\alpha_o W_c + R_m - \beta P/\mu + \{(\alpha_o W_c + R_m - \beta P/\mu)^2 + 4\beta P/\mu(\alpha_d W_c + R_m)\}^{1/2}]/2 \quad (5)$$

The values of α_d , α_o and β are determined by fitting Eq. (5) with 100 data points of $P/q\mu$ vs. W_c at $0 < W_c < 1$ kg/m² by a nonlinear least-squares method, the so-called Marquardt method. Fitted lines for the data given in Fig. 3 are drawn as solid curves in the figure. It is clear that the errors of the fitted lines are

very small, so that the data are regarded as properly expressed by Eq. (5).

The weight of cake at the intersection of lines (A) and (B'), W_{cc} , which can be calculated from the values of α_d , α_o and β , may be regarded as a measure to indicate the cake weight above which the ordered structure is predominant.

In the preceding arguments, the degree of ordering is assumed to depend only on the flow rate q ; that is, f is the only function of q in Eq. (5) for a given suspension. To examine the validity of this hypothesis, the local value of cake resistance α , which is given by $\partial(P/\mu q)/\partial W_c$, is calculated and shown for various applied pressures in Fig. 5. The correlations between α and q approximately coincide with each other, irrespective of the applied pressure. Hence the above hypothesis is regarded as valid in the range of this experiment.

Figure 6 shows the dependence of α_o and α_d on P for deionized suspensions of $\phi_p = 0.025$. It is clear that α_o and α_d are constant irrespective of P ; that is, $\alpha_o \approx 1.5 \times 10^{-13}$ m/kg and $\alpha_d \approx 0.9 \times 10^{-13}$ m/kg. This indicates that the relation of $P/q\mu$ vs. W_c is successfully expressed by Eq. (5). Figure 7 shows the dependence of α_o and α_d on ϕ_p for deionized suspensions. It is clear that the same values of α_o and α_d as above are obtained independently of the particle concentration and the validity of Eq. (5) is thus confirmed. Figure 8 shows the values of α_o and α_d for various electrolyte concentrations C_e . When $C_e < 3 \times 10^{-4}$ mol/l, the same values of α_o and α_d are obtained as before. However, when $C_e \geq 3 \times 10^{-4}$ mol/l, the values of α_d can be determined but those of α_o cannot. This means that the relation of $P/q\mu$ vs. W_c is represented by a straight line and that all the cake structure is randomly close-packed in this region.

The dependence of W_{cc} on P for the suspensions discussed in Fig. 6 is shown in Fig. 9. Here the value of W_{cc} is physically meaningful in the range of $0 < W_{cc} \leq 1.0$ kg/m², since the filtration is terminated at $W_c = 1.0$ kg/m². It is clear that W_{cc} and $(1 - W_{cc})$ kg/m² respectively represent the weights of cakes in which the disordered structure is predominant and cakes in which the ordered structure is predominant. As P increases, q increases and so the particle flux increases. Figure 9 shows that the fraction of disordered structure increases with increasing P and the ordered structure disappears completely at $P > 700$ kPa. The reason why the structure is disordered at a high particle flux is considered to be as follows; the supply of particles to the cake surface is so fast that the ordered phase of particles above the cake surface cannot be formed.

The dependence of W_{cc} on ϕ_p for suspensions discussed in Fig. 7 is shown in Fig. 10. It is interesting to note that W_{cc} has the minimum at $\phi_p = 0.04$. When

Fig. 5. Dependence of α on q for various applied pressures when deionized suspensions of $\phi_p = 0.025$ are filtered

Fig. 6. Dependence of α_o and α_d on P for deionized suspensions of $\phi_p = 0.025$

Fig. 7. Dependence of α_o and α_d on ϕ_p for deionized suspensions at $P = 290$ kPa

$\phi_p > 0.04$, W_{cc} increases with increasing ϕ_p . This disordering with increasing ϕ_p is probably due to the high flux of particles. On the other hand, the disordering with decreasing ϕ_p at $\phi_p < 0.04$ is considered to be due to the fact that particles near the cake surface are not concentrated enough for the ordered phase to be formed.

The dependence of W_{cc} on C_e for suspensions discussed in Fig. 8 are shown in Fig. 11. For

Fig. 8. Dependence of α_0 and α_d on C_e at $\phi_p=0.025$ for various applied pressures. The data for deionized suspensions are shown as a reference.

Fig. 9. Relation between W_{cc} and P for deionized suspension of $\phi_p=0.025$

Fig. 10. Relation between W_{cc} and ϕ_p at $P=290$ kPa for deionized suspensions

any applied pressure, W_{cc} gradually increases with increasing C_e and leaps upward at $C_e \approx 3 \times 10^{-4}$ mol/l, above which the value of α_0 cannot be determined and the cake structure is disordered everywhere. This disordering is attributable to the compression of electric double layer thickness around the particle surface.

The relations between the ordering and experi-

Fig. 11. Relation between W_{cc} and C_e at $\phi_p=0.025$ for various applied pressures. The data for deionized suspensions are shown as a reference.

Fig. 12. Correlation between cake structure and the experimental conditions. X represents the zone where the transition of a dispersed phase to an ordered phase takes place.

mental conditions are summarized in Fig. 12. Figure 12(a) shows an ordering condition. When the flux of depositing particles is high, as obtained by increasing either the flow rate (Fig. 12(b)) or the particle concentration (Fig. 12(c)), the particle supply is too fast for ordering to take place above the cake surface, and the cake structure becomes disordered as illustrated in the figures. When a suspension is diluted, as illustrated in Fig. 12(d), the flux is

sufficiently small but particles are not concentrated enough for the ordered phase to be formed. When the electrolyte concentration is high enough, as illustrated in Fig. 12(e), the electric double-layer thickness becomes thin and the interparticle repulsive force is not strong enough for ordering to take place.

According to the preceding arguments, the conditions for ordering are summarized as follows. (1) The flux of depositing particles is sufficiently small. (2) The particle concentration above the cake surface is sufficiently high. (3) The electric double-layer thickness around the particle surface is thick enough. These conditions imply that the transition of a dispersed phase to an ordered one, like the Alder transition, takes place in the zone X in Fig. 12(a) before particles deposit on the surface. Hence, if the above conditions are always satisfied during the filtration, a cake of completely ordered structure will be formed. However, as we can see in Fig. 9, about 10% of the cake near the filtration medium is disordered even though the magnitude of P is sufficiently small. We presume that this is due to the disturbance of the flow at the beginning of filtration. The size distribution of particles is also an important factor in the formation of ordered structure. It is known that rather strict monodispersity is necessary for the ordering of suspended particles⁶⁾. But it may be possible to gain an ordered structure composed of monodispersed particles of two different sizes, because Sanders found the such a structure is the microstructure of natural opal⁹⁾.

Conclusion

Suspensions of monodispersed PSL particles of $0.5\mu\text{m}$ diameter were filtered and the data were analyzed by using a filtration equation in which the dependence of packing structure on flow rate was taken into account. The following conclusions were reached.

1. A cake of ordered close-packed structure is obtainable under the following conditions; (1) The flux of depositing particles is sufficiently small. (2) The particle concentration above the cake surface is sufficiently high. (3) The electric double-layer thickness around the particle surface is thick enough.

2. Cakes obtained under common experimental conditions of constant-pressure filtration are composed of both disordered and ordered domains whose specific cake resistances are 0.9×10^{13} and 1.5×10^{13} m/kg respectively.

3. It is suggested that the transition of a dispersed phase to an ordered one, like the Alder transition, takes place above the cake surface before particles deposit on the surface.

4. The proposed filtration equation is applicable to cakes composed of ordered and disordered cakes.

Nomenclature

C_e	= electrolyte concentration	[mol/l]
P	= applied pressure	[Pa]
q	= flow rate of filtrate	[m/s]
R_m	= resistance of filtration medium	[1/m]
s	= mass fraction of solid in suspensions	[—]
s_c	= mass fraction of solid in cake	[—]
t	= time	[s]
v	= volume of filtrate through unit area	[m]
W_c	= weight of cake deposited on unit area	[kg/m ²]
W_{cc}	= value of W_c at boundary between ordered and disordered cake	[kg/m ²]

<Greek Letters>

α	= specific cake resistance	[m/kg]
α_o	= specific cake resistance of ordered cake	[m/kg]
α_d	= specific cake resistance of disordered cake	[m/kg]
β	= coefficient for filtration equation	[s/m]
μ	= viscosity of filtrate	[N·s/m ²]
ρ	= filtrate density	[kg/m ³]
ϕ_c	= packing density of solid in cake	[—]
ϕ_p	= volume fraction of particles in suspension	[—]

<Subscripts>

c	= cake
d	= disorder
e	= electrolyte
m	= medium
o	= order
p	= particle

Literature Cited

- 1) Alder, B. J. and T. E. Wainwright: *Phys. Rev.*, **127**, 359 (1962).
- 2) Barringer, E. A. and H. K. Bowen: *J. Am. Ceram. Soc.*, **65**, C-199 (1982).
- 3) Bensley, C. N. and R. J. Hunter: *J. Colloid Interface Sci.*, **92**, 448 (1983).
- 4) Bridger, K., M. Tadros, W. Leu and F. Tiller: *Separation Sci. Tech.*, **18**, 1417 (1983).
- 5) Davis, K. E. and W. B. Russel: *Adv. Ceram.*, **21**, 573 (1987).
- 6) Emmett, S., S. D. Lubetkin and B. Vincent: *Colloids Surfaces*, **42**, 139 (1989).
- 7) Hachsu, S., Y. Kobayashi and A. J. Kose: *J. Colloid Interface Sci.*, **42**, 342 (1973).
- 8) Monovoukas, Y. and A. P. Gast: *J. Colloid Interface Sci.*, **128**, 533 (1989).
- 9) Sanders, J. V.: *Phil. Mag. A*, **42**, 705 (1980).
- 10) Scott, G. D. and D. M. Kilgour: *J. Phys.*, **D2**, 863 (1969).