Flocculation Kinetics of the Monodisperse System. Computer Simulation of Flocculation by the Two-Dimensional Geometrical Random Coalescence Model

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The process of the flocculation of monodispersed particles, whose binding strength is assumed to be very strong, had been simulated using the two-dimensional geometrical random coalescence model. The flocculation kinetics and the change mechanism of aggregate shapes were studied. In this simulation procedure, the kinetics were explained to follow a second-order rate equation in agreement with von Smoluchowski's flocculation theory. The morphological parameters, the porosity and the particle diameter of aggregates were indicated to be affected by the number of monodispersed particles and the collision probability, but they converged on one curve under the condition of normalized flocculation time ($t/t_{1/2}$). It was suggested that the change of the aggregate shapes and their enlargement were controlled by the same process, irrespective of the trial conditions. The shape of the aggregate obtained by the flocculation of agglomerated stearyl alcohol beads on the surface of water was similar to that of the simulation. Hence, it was considered that the strength of binding between beads is comparatively strong.

Keywords flocculation; agglomeration; aggregation; computer simulation; aggregate shape; morphological parameter; porosity; particle diameter

Introduction

In pharmaceutical technology, flocculation and granulation are important phenomena for evaluating the stability of a suspension, the control of granulation process, and so on. However, these phenomena have not been studied sufficiently because the required experimental conditions are not easy to control. For this reason, computer simulation techniques have become very useful to the study of these phenomena.[1-10]

In a previous paper,[8] Brownian flocculation processes of mono- and polydispersed particles were simulated using the random coalescence model. In this procedure, it was found that the ratio of effective radii between two collided particles controlled the flocculation process, and the kinetics were in good agreement with the theoretical results of von Smoluchowski and Müller.[11,12] But the shapes of aggregates could not be observed in this model.

In this present study, the flocculation process of monodispersed particles, with the assumption that the binding strength between particles is very strong, is studied using the two-dimensional geometrical random coalescence model. The purpose of this work is to investigate flocculation kinetics and to study the change mechanism of the aggregate shapes.

Experimental

Simulation Procedure A flow sheet of this simulation procedure is illustrated in Fig. 1. A thousand areas with serial address numbers from 1 to 1000, and a two-dimensional coordinate memory to record the shape of an aggregate, were assigned to the computer's memory.

In order to create a monodisperse system at the initial stage of the flocculation process, disks of 1.0 unit in diameter as model particles were positioned in the coordinates of the areas numbered from 1 to N_0, respectively, where N_0 is ranges from 2 to 500. For convenience of calculation, the center of gravity of an aggregate or a particle was arranged on the coordinate origin. Therefore, these coordinates and the address numbers do not express the absolute position of the aggregate in a disperse system, but are used to record the relative locations of particles composing an aggregate and to select an aggregate or a particle randomly.

Two areas with different address numbers were chosen at random by using a computer-generated random number pair (i, j), where i and j range from 1 to 1000. When an aggregate or a particle was found in both areas, a pseudo-random number between 0 and 1 was then generated and compared with the collision probability C_P ($C_P \leqq 1$). If the C_P was larger than the pseudo-random number generated, two aggregates in both areas i and j would approach each other, running parallel with the abscissa, collide and flocculate. The morphological parameters, the porosity and the particle diameter were calculated after the aggregate was rotated at random by a new pseudo-random number between 0 and 2π. The shape of the aggregate was recorded in area i, and the existence of the aggregate in area j was erased.

When one of the areas or neither area with a randomly selected address number did not have aggregates or particles, or the C_P was smaller than the pseudo-random number, it was assumed that they could not collide or flocculate each other, and two address numbers were selected again. It was assumed that one unit of flocculation time went by when 100 pairs of address numbers were called.

The population numbers and other parameters were printed out at suitable intervals. These calculations were terminated when the number of aggregates in all areas became one.

This simulation model was written by optimum FORTRAN 77 on EWS-UX/V (NEC Corporation).

Definition of Morphological Parameters, Porosity and Particle Diameter Anisometry Q, bulkiness B and structure factor F reportd by Medalia[9] were used as the morphological parameters given in Eqs. 1—3.

$$Q = K_A/K_B \tag{1}$$

$$B = 4\pi K_A K_B/A \tag{2}$$

$$F = (4\pi K_A^2 - A)/A = QB - 1 \tag{3}$$

where K_A and K_B are the principal radii of gyration, which are equal

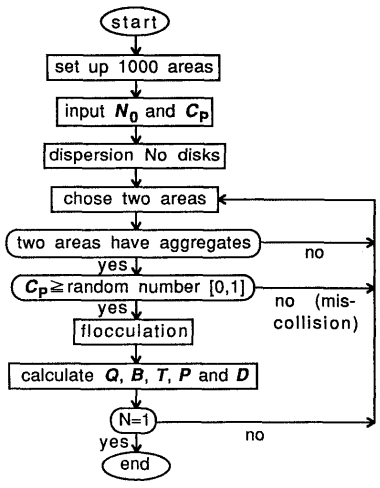

Fig. 1. Flow Sheet of the Simulation Procedure

to the half-lengths of the major and minor axis of the radius-equivalent ellipse, respectively. A is the actual area of the aggregate.

The porosity P, as reported by Kawashima *et al.*,[4] was calculated from the area of a 360-gon inscribed in the periphery of the aggregate and the actual projected area A.

The Feret's diameter D was used as the particle diameter.

Results and Discussion

Analysis of Flocculation Kinetics It is known that the flocculation rate of dispersed particles in this simulation conforms to the second-order rate Eq. 4.[11]

$$N_0/N-1=kN_0t \tag{4}$$

where N is the number of particles at time t, and k is the flocculation rate constant.

Under the condition of constant N_0 and C_P, applicability of Eq. 4 to simulation results is shown in Fig. 2(a) and (b). It is indicated that function $(N_0/N-1)$ is directly proportional to the flocculation time t, and that N_0 and C_P affected the reduction rate of the population.

Von Smoluchowski assumed in his flocculation theory of monodispersed particles that the population number submits to Eq. 5.[9]

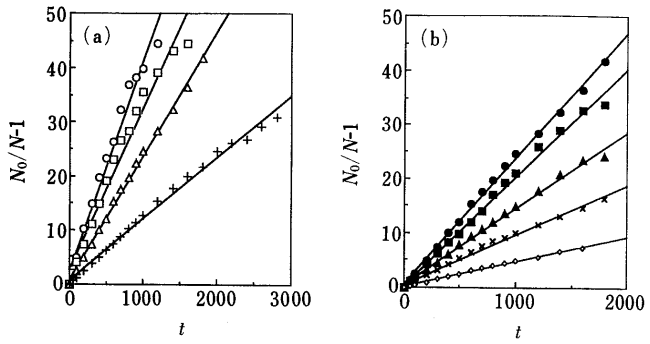

Fig. 2. Applicability of Second-Order Rate Equation of Simulation Results

(a) $N_0=500$: ○, $C_P=1.00$; □, $C_P=0.75$; △, $C_P=0.50$; +, $C_P=0.25$. (b) $C_P=0.50$: ●, $N_0=500$; ■, $N_0=400$; ▲, $N_0=300$; ×, $N_0=200$; ◇, $N_0=100$.

$$N_0/N-1=t/t_{1/2} \tag{5}$$

where $t_{1/2}$ is the half-life period for the flocculation process, defined as the time required to reduce the total number of particles to one-half.

Here $t_{1/2}$ in the case of slow flocculation is defined as Eq. 6 by von Smoluchowski.

$$t_{1/2}=\frac{3\eta}{KTN_0\alpha} \tag{6}$$

where K is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the medium. α is the efficiency of the "effective" collision in flocculation introduced by von Smoluchowski. When $\alpha=1$, Eq. 6 represents $t_{1/2}$ in the case of rapid flocculation. Inserting Eq. 4 in Eqs. 5 and 6,

$$k=\frac{KT}{3\eta}\alpha \tag{7}$$

Because of $\alpha=1$ in rapid flocculation. From Eq. 7,

$$\alpha_o=k_s/k_r \tag{8}$$

where k_r and k_s are the rapid and slow flocculation rate constants, respectively. In this simulation, these constants can be calculated as second-order rate constants from the relationships of Fig. 2, and k_r is the rate constant when the trial condition of $C_P=1$, because there are no miscollisions in this condition. α_O is the efficiency of effective

TABLE I. k Values and α_o with the Various N_0 and C_p

C_p	$k\times10^5$						α_o
	$N_0=500$	$N_0=400$	$N_0=300$	$N_0=200$	$N_0=100$	Mean	
0.25	2.05	2.02	2.02	1.96	2.01	2.01	0.21
0.50	4.65	4.94	4.54	4.55	4.54	4.64	0.50
0.75	7.13	7.40	7.10	7.32	7.32	7.25	0.77
1.00	8.97	9.67	9.20	8.95	10.00	9.36	1.00

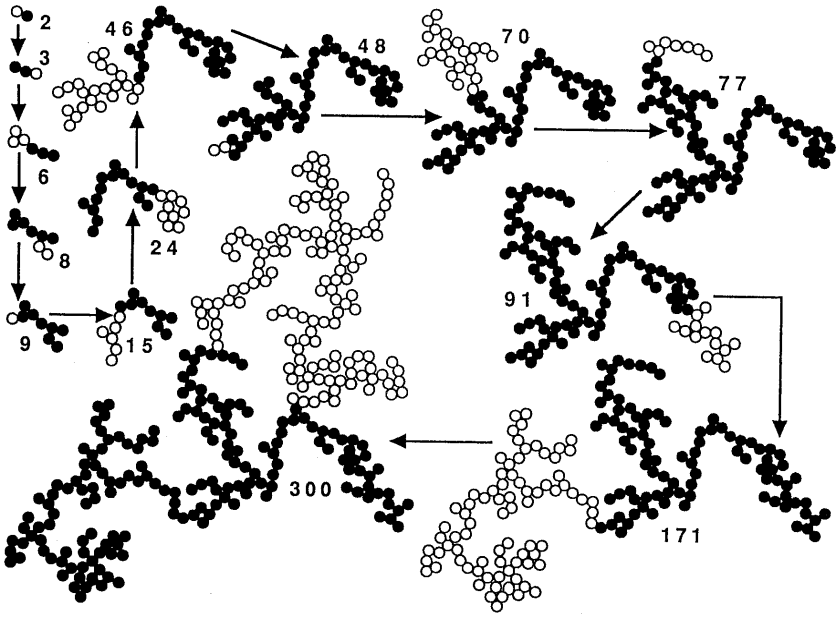

Fig. 3. Simulation Result for the Growth of Aggregates ($N_0=300$, $C_P=1.00$)

Clusters of closed and open circles represent previous and newly added aggregates, respectively, and numerals are the number of particles composing an aggregate.

collisions observed from simulation trials.

Results in Table I indicates that the flocculation rate constants are independent of N_0 as represented in Eq. 7, and the increase with the enlarging of C_P. And α_0 is nearly equivalent to C_P established in this simulation.

From these results, the flocculation process of this simulation was found to be in good agreement with second-order kinetics and flocculation theory by von Smoluchowski.

Change Mechanism of Aggregate Shapes A typical case of the enlargement process of aggregates is given in Fig. 3 for $N_0=300$ and $C_P=1.00$. In this figure, it was found that aggregates had been growing into larger aggregates which had multi-branching structures created by the sequential collision between particles and/or small aggregates in the early stage of flocculation and by large ones in the final stage. This structure was formed by permanent maintenance of particle bindings, *i.e.* no-rearrangement of particles in an aggregate. It was considered that the aggregates obtained by this procedure matched for ones which had very strong particle bindings under actual flocculation.

The variation in mean bulkiness, as one of the morphological parameters, at time t is shown in Fig. 4(a) and (b) under the condition of constant N_0 and C_P. These results indicate that N_0 and C_P affects the change rate of the mean bulkiness as the function $(N_0/N-1)$.

When the bulkiness data was regulated as a function of the normalized flocculation time $(t/t_{1/2})$, it converged on one curve, independently of N_0 and C_P (Fig. 5).

These tendencies are observed in other parameters, such as the mean of anisometry, structure factor, porosity and particle diameter, as shown in Fig. 6. It is suggested that the shape change and the growth process of aggregates in this simulation has the same tendency as under normalized flocculation time, and the value of $t_{1/2}$ affects the change rates of these parameters.

Figure 7 shows the mean of the anisometry at the number of particles S in various aggregates. This figure shows that the anisometry of primary particles was equal to one. On the other hand, it was indicated that the anisometry of the aggregates containing more than two particles became approximately two on the average, and this value was independent of S. From these results, the characteristic pattern of the anisometry shown in Fig. 6 was suggested to be caused by the following. The rapid increase of the mean anisometry in the early stage of flocculation is based on the reduction of primary particles $(Q=1)$ and the increase of aggregates $(Q\fallingdotseq 2)$. When primary particles

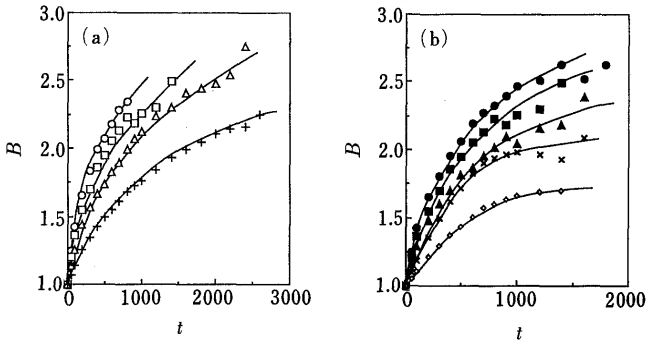

Fig. 4. Bulkiness as a Function of Flocculation Time

(a) $N_0=400$: ○, $C_P=1.00$; □, $C_P=0.75$; △, $C_P=0.50$; +, $C_P=0.25$. (b) $C_P=0.75$: ●, $N_0=500$; ■, $N_0=400$; ▲, $N_0=300$; ×, $N_0=200$; ◇, $N_0=100$.

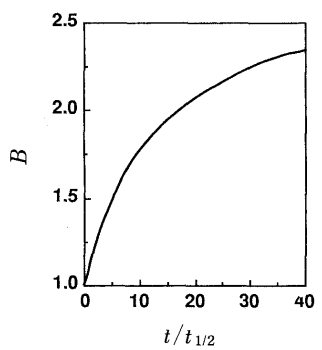

Fig. 5. Bulkiness as a Function of Normalized Flocculation Time

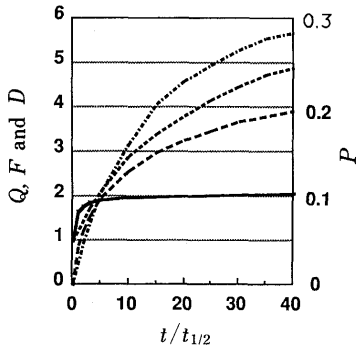

Fig. 6. Anisometry, Structure Factor, Particle Diameter and Porosity as a Function of Normalized Flocculation Time

——, anisometry; – – –, structure factor; ------, particle diameter; —·—, porosity.

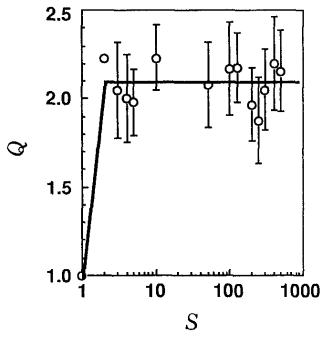

Fig. 7. Anisometry as a Function of the Number of Particles Composing an Aggregate

Each value represents the mean ± standard error of 10 aggregates.

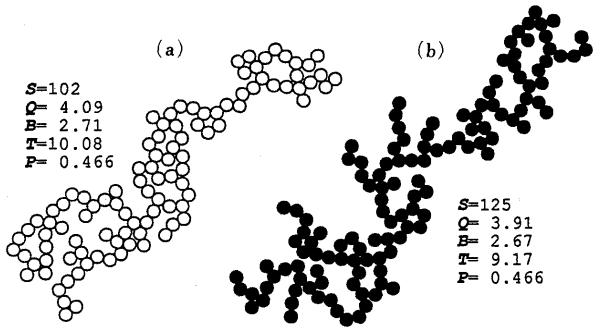

Fig. 8. Comparison of the Experimental Aggregate Shape (a) with the Simulation Results (b)

Simulation condition is $N_0=125$, $C_P=1.00$.

were almost consumed, the flocculation was only carried out between aggregates, and the mean values of the anisometry become constant. This result was in agrreement with that observed in Fig. 3.

It is very important to explain the relationship between the actual flocculation phenomena and the simulation. One way is to compare aggregate shapes from both procedures. As a real flocculation model, the two-dimensional aggregate which was observed in flocculation studies of agglomerated stearyl alcohol beads on the surface of water[13] was chosen as the model by which to evaluate the simulation. A typical example is given in Fig. 8. This figure shows that both aggregates have multi-branching structures, and their shapes and their morphological parameters resemble each other. It was suggested that the binding strength between beads is comparatively strong and that the binding strength was caused by direct hydrophobic bonds.

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