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Flocculation Kinetics of the Didisperse System-Computer Simulation of Flocculation by the Random Coalescence Model

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The process of Brownian flocculation of suspended particles has been simulated based on the random coalescence model for polydisperse systems by using a digital computer. The conformity between von Smoluchowski's and Müller's theories was examined. It was found that the simplifying assumption by which the concept of collision probability is introduced into the theories was adequate. Since no such assumption was necessary in the present model, the model can be applied to more complicated polydisperse systems. Moreover, this model can be used to obtain not only the total number of particles formed but also the particle size distribution at any period in the flocculation process. The results indicate that the process is governed by a layering mechanism such that the flocculation is promoted by a preferential cohesion of small particles to large aggregates.

Keywords——flocculation; agglomeration; computer simulation; random coalescence model; didsperse system; layering mechanism

Introduction

Flocculation and agglomeration are processes that are of pharmaceutical importance. Controlled flocculation, for instance, is a means of avoiding caking in suspension, and flocculation kinetics play a part in both this and in sedimentation kinetics.

This article deals with an investigation of the kinetics of flocculation by computer simulation. Theoretical work in the area of fast coagulation can be roughly separated into the following categories: (a) postulates about the nature of the events and the formulation of equations for the resulting observables; (b) analytical solution to these equations in various degrees of approximation; (c) numerical solution of the equations; (d) computer simulations of the physical processes thought to occur.

This paper falls into the last category. Such simulations were begun by Vold[1-4] and Sutherland,[5] and have been developed by Hutchison *et al.*,[6] Medalia,[7] Sunada and Nakagaki,[8-13] Kausch *et al.*[14] and Meakin[15-17] using two- or three-dimensional models.

Work preliminary to the work presented here has appeared in previous publications.[18-26] In some of these, we approached the problem by a random walk model[18,20,23,26] and in some by a random addition model.[18,21,22,24,25] The former model is advantageous for describing the change in the size and shape of individual agglomerates and the agglomeration kinetics of polydispersed particles. The latter model is useful for simulating the shape and internal structure of an agglomerate in relation to the adhesion behavior of the particles.

In a previous paper,[26] we simulated the agglomeration of mono-sized circles on a two-dimensional plane by using a random "walk" model. In this simulation procedure, the process is one where agglomeration is affected by the frequency of particle collision and the adherence

probability, and, hence, the kinetics are similar to von Smoluchowski's.[27]

The present study deals with the simulation of the flocculation process of suspended particles by means of a random "coalescence" model. The aim of the study was to elucidate the effect of the number and size distribution of the particles at any period in the flocculation process and to check the conformity between von Smoluchowski's and Müller's[28] theories.

Experimental

For the initial stage of the flocculation process, arbitrary numbers of aggregates having a certain size distribution were positioned randomly in areas with locations numbered from 1 to 12000. If the aggregate in a particular area was an i-fold cluster, then the number i was assigned to this area. When there was no aggregate in the area, then the numeral 0 was assigned. The address numbers of the area were used not for indicating the position of aggregates but for randomly selecting aggregates and allowing them to collide.

In accordance with Müller's theory, the collision probability between two particles is minimum when the sizes of the particles are equal and it becomes r_{ij}-times greater when the particles differ from one another in size. The expression for r_{ij} is

$$r_{ij}=(r_i+r_j)^2/4r_ir_j=(1+r_i/r_j)^2/4(r_i/r_j) \tag{1}$$

where r_i and r_j are the "effective" radii of the aggregates of categories i and j. The maximum collision probability ratio $\gamma_{\max_1}$ (which is the ratio of the collision probability of the largest aggregate to the primary particles) can now be introduced into the simulation. The volume of the aggregates having i primary particles is the sum of that of the primary particles. The radius of this aggregate is then given by Eq. 2.

$$r_i=i^{1/3} \tag{2}$$

The address numbers of two aggregates were chosen at random by using computer-generated, random number pairs (x,y), where x and y are between 1 and 12000. When both areas or either area whose address number was selected randomly had the number 0, there would be no aggregates which could collide with each other. At this point, one unit of flocculation time was supposed to have elapsed, that is, the flocculation time was counted. The time for which particles travel until collision or mis-collision occurs in a certain medium can be related to the number of selections of the address numbers by random number generation. A pseudo-random number between 0 and 1 unit was then generated and compared to V_k, the standardized ratio of the two collision probabilities;

$$V_k=r_{ij}/\gamma_{\max_1} \tag{3}$$

where r_{ij} was calculated by Eq. 1, and where obviously $V_k \geqq 1$. When V_k was larger than the generated pseudo-random number, then the two aggregates were considered to have collided and flocculated. The flocculation number $i+j$ was then stored in the area component where the larger of i or j existed previously and 0 was put into the other. If V_k was smaller than the pseudo-random number, then collision was considered not to have occurred and one unit of flocculation time was counted. By proceeding in this manner, the population number of the aggregates decreased as the flocculation time increased, and this functionality could be monitored.

It was otherwise assumed that the unit flocculation time had elapsed when the address numbers had been called 10000 times. The population number and average radius of the aggregates were printed out every five unit.

These calculations were terminated when the population number of the aggregates became less than 1/10 of the initial number or when r_{ij} exceeded $\gamma_{\max_1}$, which corresponds to the fact that the agglomerates of larger size than max might be broken.

Results and Discussion

von Smoluchowski assumed in his theory of rapid flocculation that the ratio of the number of aggregates N_m of m single particle at any time to the total original number N_0 is given by the expression

$$N_m/N_0=(t/t_{1/2})^{m-1}/(1+t/t_{1/2})^{m+1} \tag{4}$$

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.

A typical case is given in Fig. 1 for $\max=2\times10^6$ with 10000 primary particles having a uniform radius of 1.0. In this figure, the total number of particles and the number of each

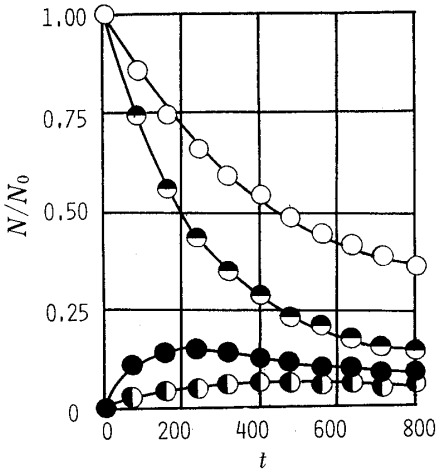

Fig. 1. von Smoluchowski Plots of Simulation Data in a Monodisperse System, ($N_0=10000$ and $r_1=1.0$)
○, N; ◓, N_1; ●, N_2; ◐, N_3.

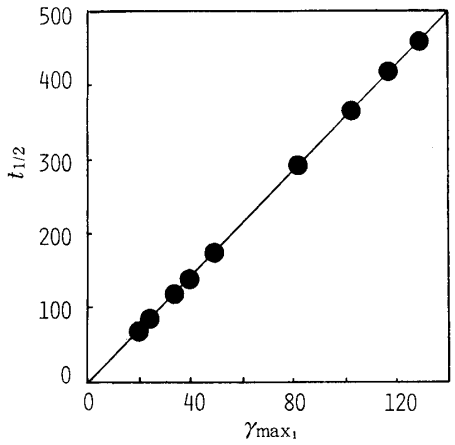

Fig. 2. Relation between $t_{1/2}$ and γ_{max_1} ($N_0=$ 5000, 7500 and 10000)

TABLE I. $t_{1/2}$ and k Values with Various r_i

r_i	$t_{1/2}$	$k\times10^6$
1.0	465.94	0.2170
3.0	465.95	0.2170
7.0	465.94	0.2170
10.0	465.94	0.2170
20.0	465.94	0.2170
30.0	460.91	0.2170
40.0	456.85	0.2189
50.0	458.00	0.2184

$N_0=10000$, max$=2\times10^6$.

TABLE II. $t_{1/2}$ and k Values with Various N_0

N_0	$t_{1/2}$	$k\times10^6$
10000	66.90	1.4948
7500	89.58	1.4886
5000	134.27	1.4908

$r_i=1.0$, max$=2\times10^6$

species up to triplet are shown as a function of time. Theoretical curves calculated by Eq. 4, where $t_{1/2}$ was calculated from Eq. 5, are represented by solid lines.

$$t_{1/2}=Nt(N_0-N) \tag{5}$$

It was found that this model is in good agreement with von Smoluchowski's theory.

Table I shows the values of $t_{1/2}$ and the flocculation rate constant at various sizes of the primary particle under the condition of constant γ_{max_1} and N_0. It was indicated that these values are not affected by the primary particle size.

Table II indicates that the flocculation rate constant is independent of N_0, when r_i is kept constant. It is clear from Fig. 2 that γ_{max_1} is in direct proportion to $t_{1/2}$ which varies inversely to N_0 in a monodisperse system ($t_{1/2}=3.58\gamma_{max_1}$, $N_0=10000$; $t_{1/2}=4.77\gamma_{max_1}$, $N_0=7500$; $t_{1/2}=7.16\gamma_{max_1}$, $N_0=5000$). Thus the following empirical formula was obtained.

$$t_{1/2}=35800\gamma_{max_1}/N_0 \tag{6}$$

This equation was used for obtaining $t_{1/2}$ values.

Figure 3 shows that the number of small particles diminishes more rapidly in the presence of large ones. The Müller equation gives the variation of population numbers of total particles and the small particles with time

$$N=\frac{N_1}{1+t_{1/2,1}}\left\{1+\frac{\lambda}{(V_n\lambda+1)(1+t/t_{1/2,1})^{\lambda-1}}\right\} \tag{7}$$

$$N_s = N_1(1+t/t_{1/2,1})^{2\lambda/(\lambda+1)} \frac{V_n\lambda^2}{\{(V_n\lambda+1)(1+t/t_{1/2,1})^{\lambda-1}\}^2} \quad (8)$$

where $\lambda=(V_r^2+1)/2V_r$, $V_r=r_1/r_s$ and $V_n=N_1/N_s$, r_1, r_s, and N_1 and N_s are the radii and the population numbers of large and small primary particles, respectively; $t_{1/2,1}$is the half-life of large particles in the monodisperse system. The solid lines show the theoretical population density of total large and small particles calculated by means of the above equations. In the initial stage, a larger flocculation velocity was observed compared to the theoretical curves in the monodisperse system of the large particles. On the other hand, during the latter period, the data were in accordance with von Smoluchowski's equation. It seems reasonable to assume

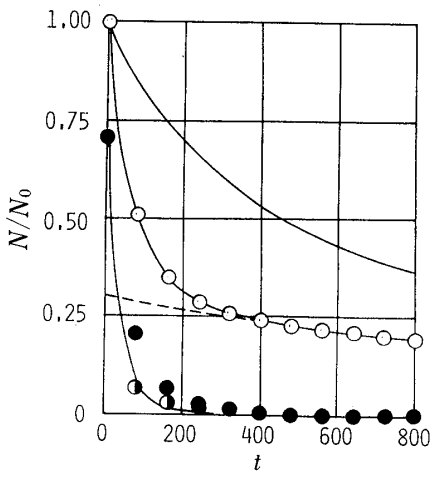

Fig. 3. N_1/N_0, N_s/N_0 and N/N_0 as a Function of Time for a Didisperse System, ($r_1=40$ and $r_s=1$; $N_1=3000$, $N_s=7000$ and $N_0=10000$)

——, von Smoluchowski's plot ($N_0=10000$); – – – –, von Smoluchowski's plot ($N_0=3000$); —○—, Müller's plot (total number of particles); ◑, Müller's plot (number of large particles); —●—, Müller's plot (number of small particles).

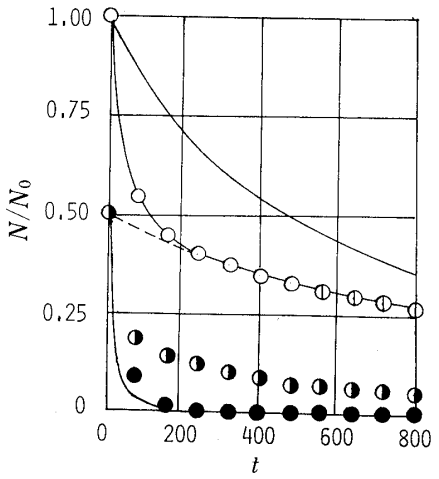

Fig. 4. N_1/N_0, N_s/N_0 and N/N_0 as a Function of Time for Didisperse System, ($r_1=40$, $r_s=1$ and $N_1/N_s=1$; $N_1=5000$, $N_s=5000$ and $N_0=10000$)

——, von Smoluchowski's plot ($N_0=10000$); – – – –, von Smoluchowski's plot ($N_0=5000$); —○—, Müller's plot (total number of particles); ◑, Müller's plot (number of large particles); —●—, Müller's plot (number of small particles).

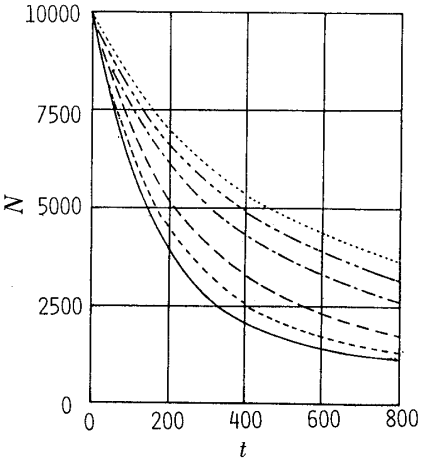

Fig. 5. N as a Function of Time, V_r is Taken as a Parameter and V_n is Maintained Constant, ($=1000/9000$; max$=2\times10^6$)

------, monodisperse; – – – –, $r_1/r_s=5.0:1.0$; – – – –, 10.0 : 1.0; ——, 20.0 : 1.0; – – – –, 30.0 : 1.0; ——, 40.0 : 1.0.

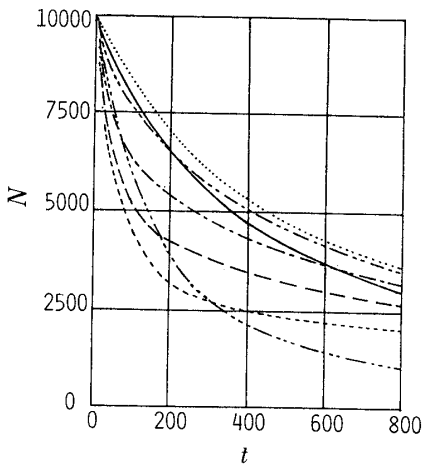

Fig. 6. N as a Function of Time; V_n is Taken as a Parameter, and V_r is Maintained Constant ($=40/1$; max$=2\times10^6$)

------, monodisperse; – – – –, $N_1/N_s=9000:1000$; – – – –, 7000 : 3000; – – – –, 5000 : 5000; ——, 3000 : 7000, – – – – – –, 1000 : 9000; ——, 100 : 9000.

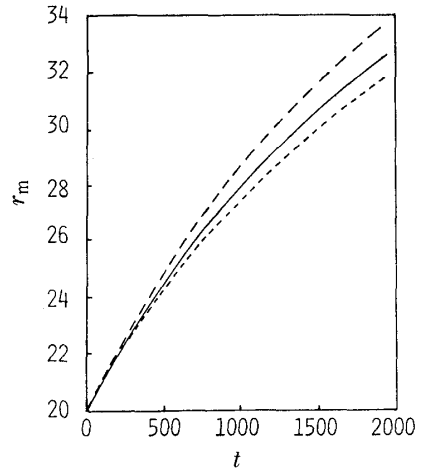

Fig. 7. r_m (Mean Radius) as a Function of Time

Standard deviation (S.D.) is taken as a parameter; mean radius = 20.0; ----, S.D. = 0.0; ——, S.D. = 3.0; — —, S.D. = 5.0.

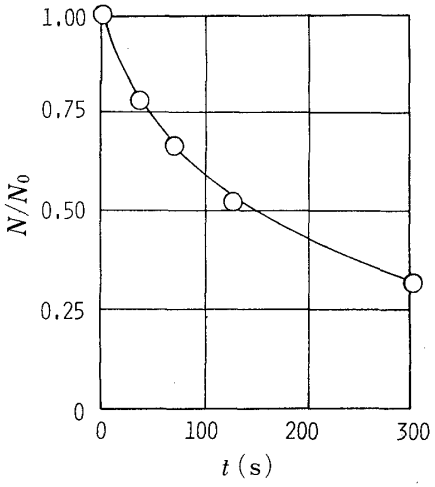

Fig. 8. Comparison of the Experimental Results of Tourila with the Simulation Results

Actual system, $V_r = 598/283$, $V_n = 6.01 \times 10^8/6.01 \times 10^8$, $n = 0.01\,\mathrm{g\,cm^{-1}\,s^{-1}}$, $T = 290.8\,\mathrm{K}$, $t_{1/2} = 310.84\,\mathrm{s}$; simulation system, $V_r = 5.33/2.52$, $V_n = 5000/5000$, $t_{1/2,1} = 916.48$, $\max = 2 \times 10^6$; transformation coefficient = 0.339 s.

○, actual system; ——, simulation.

that the process was governed by a layering mechanism[29] and that the flocculation was promoted by a preferential cohesion of small particles to large aggregates.

Figure 4 shows the results for didispersions containing the same number of small and large particles. The layering mechanism can also be considered to hold in this system. Figure 5 shows the total population number N as a function of t in a didisperse system, when V_r is taken as a parameter and N_n is maintained constant. It can be seen that the flocculation velocity increases as V_r increases.

The influence of the ratio V_n on the flocculation velocity is shown in Fig. 6 under conditions of constant V_r. It is clear from these results that the population number increases as V_n increases during the initial stage of the flocculation but the situation becomes complicated during the latter stage. Hence, if a polydisperse system behaves like a didisperse system, the Müller model holds well.

Further simulations were carried out to investigate the application of Müller's theory to a polydisperse system. Figure 7 shows the results for the system of primary particles having a large standard deviation. Flocculation occurred rapidly in accordance with the model based on a layering mechanism.

It is important to obtain the relationship between actual flocculation phenomena and the simulation. One way to do this is to use time transformation, *i.e.*, real time in actual flocculation to unit time in the simulation. A typical example is given in Fig. 8, which shows the flocculation of Au-Sol with NaCl reported by Tourila[30]; 0.339 s was used as the transformation coefficient. It was found that the results of simulation were in good agreement with the experimental results, and it is concluded that this model may be very useful for the simulation of Brownian flocculation.

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