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Flocculation Studies of Granulated Stearyl Alcohol on the Surface of Aqueous Media. III.[1] Changes of Agglomerate Structure in a Two-Dimensional System with Anionic Surface-Active Agent

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Granulated stearyl alcohol was dispersed on the surface of aqueous media in the presence of sodium lauryl sulfate (SLS: 0—0.50 [g/100 ml]). The changes of the shape factors, the average contact numbers and the porosities during flocculation were examined. The particles on the surface of the water without SLS formed more dendric and more porous agglomerates than those on the surface of solutions with SLS (0.25—0.50 [g/100 ml]). The particles on the former surface showed strong hydrophobic bonding (particle/particle bonding) and a higher coefficient of internal friction, measured in the shearing test. So, they were relatively rigid after the initial flocculation. On the other hand, the agglomerate particles adsorbed with SLS on the latter surface showed weak bonding between particles and a lower friction coefficient. So, their agglomerate structure changed with time, forming rounder and more compact agglomerates.

Keywords agglomeration; flocculation; stearyl alcohol; surface-active agent; sodium lauryl sulfate; shape factor; contact number; porosity; internal friction; agglomerate structure

Introduction

Many studies have been designed to elucidate the agglomeration mechanism of suspended particles in pharmaceutical processes. Medalia[2] analyzed the growth of aggregates, using anisometry, with bulkiness and the structure factor as the indexes of aggregate shape. He compared the shapes of simulated flocs with those of actual flocs of carbon black. Meakin[3] characterized the structures of aggregates, obtained in his simulations, by a fractal dimensionality. The value of dimensionality was in good agreement with that found in experiments using metal particles.

The present authors have already studied the kinetics of agglomeration and the micromeritic properties of agglomerates by computer simulation.[4,5] It became apparent that the agglomerate rate constants and the internal packing structures of agglomerates are dependent on the probability coefficient of adhesion. Furthermore, it was noted that the shape factor changed slightly with increase of the agglomeration time. It is preferable to compare these results of simulations with those of practical agglomeration in a two-dimensional system.

In previous papers,[1,6] flocculation in a two-dimensional system of granulated stearyl alcohol was investigated. Anionic, cationic and nonionic surface-active agents were used as aggregating agents. It was shown that the agglomeration kinetics could be represented by a second-order rate equation. The rate constants were determined as a function of the concentration of the surface-active agents. With increasing concentration of agents, these constants varied from a low value (at 0 [g/100 ml] of agents (range I)) to the minimum (in the low range of agent concentration (range II)) and then to a high value with a maximum (in the high range of agent concentration, that is, around or above the critical micelles concentration (cmc) of the agents (range III)). The changes of rate constant with concentration and with kind of surface-active agents are discussed on the basis of the hydrophobic effect of the adsorbed agents, the steric hindrance (of the micelles and the bulky hydrophilic moiety of the adsorbed agents), and the electrorepulsive force. The agglomeration behavior changed with increasing concentration of agent in a similar manner to the rate constant. The particles in these system agglomerated in range I, dispersed in range II and then agglomerated in range III.

In this paper, the shape factors, the contact number and the porosity of the agglomerates in the above system were determined under various conditions. The difference of the agglomeration behaviors mentioned above is discussed on the basis of these determinations.

Experimental

Sample Granulated stearyl alcohol (Kao Co., Ltd.), as described previously,[6] was sieved (Feret's diameter = 1.3 mm). The anionic surface-active agent used was sodium lauryl sulfate (SLS) and the value of cmc was measured by a capillary method.

Methods Solutions of SLS, prepared over the range of concentration of 0—0.50 [g/100 ml], were poured into a container (diameter = 14.5 cm). Then granulated stearyl alcohol (1.0 g) was scattered on the surface of the solution, and photographs of the agglomerates were taken at suitable time intervals. The center coordinates of each particle constituting the agglomerates were determined on the photographs and inputted into the computer. The structures of agglomerates were illustrated by the X–Y plotter. The numbers, the diameters and the shape factors of agglomerates were analyzed by using a LUZEX 500 image analyzer (Nireko Co.) on these illustrations.

$$SF(1) = \pi ML^2/4A \qquad (1)$$

$$SF(2) = PM^2/4\pi A \qquad (2)$$

A: the projected area of agglomerate
ML: the longest diameter of agglomerate
PM: the periphery length of agglomerate

The porosities were calculated, on the same illustrations, from the area of a 360-gon inscribed in the periphery of the agglomerates and the projected area of particles.[5] Also, the contact numbers were counted.

Shear Test The relationship between shear stress (τ) and compressive stress (σ) of stearyl alcohol, over the whole range of SLS concentrations, was obtained by the direct shear cell method. The particle–particle cohesive force (C) and internal friction coefficients (μ_i) of stearyl alcohol were determined, based on Coulomb's equation.

$$\tau = \mu_i \cdot \sigma + C \qquad (3)$$

Results and Discussion

Photographs of the agglomeration process were shown in the previous paper.[6] The agglomeration rate changed with the concentration of SLS, and the agglomeration behavior also changed.

The particles on the surface of aqueous media without SLS agglomerated (range I). However, they dispersed at low concentration of SLS (range II), that is, about 0.10 [g/100 ml], and they agglomerated again at high concentration of SLS (range III), that is, 0.25—0.50 [g/100 ml]. This range is around or above the cmc of SLS. From the photographs, it was apparent that the shapes of agglomerates in range I and in range III were very different. This implies that there may be different agglomeration mechanisms operating in the two ranges.

In this paper, the changes of agglomerate shapes with SLS concentration were examined in detail. The structures are illustrated in Fig. 1, based on photographs of the agglomerates. On these illustrations, two shape factors were measured in the SLS concentration ranges where the particles agglomerated (ranges I and III).

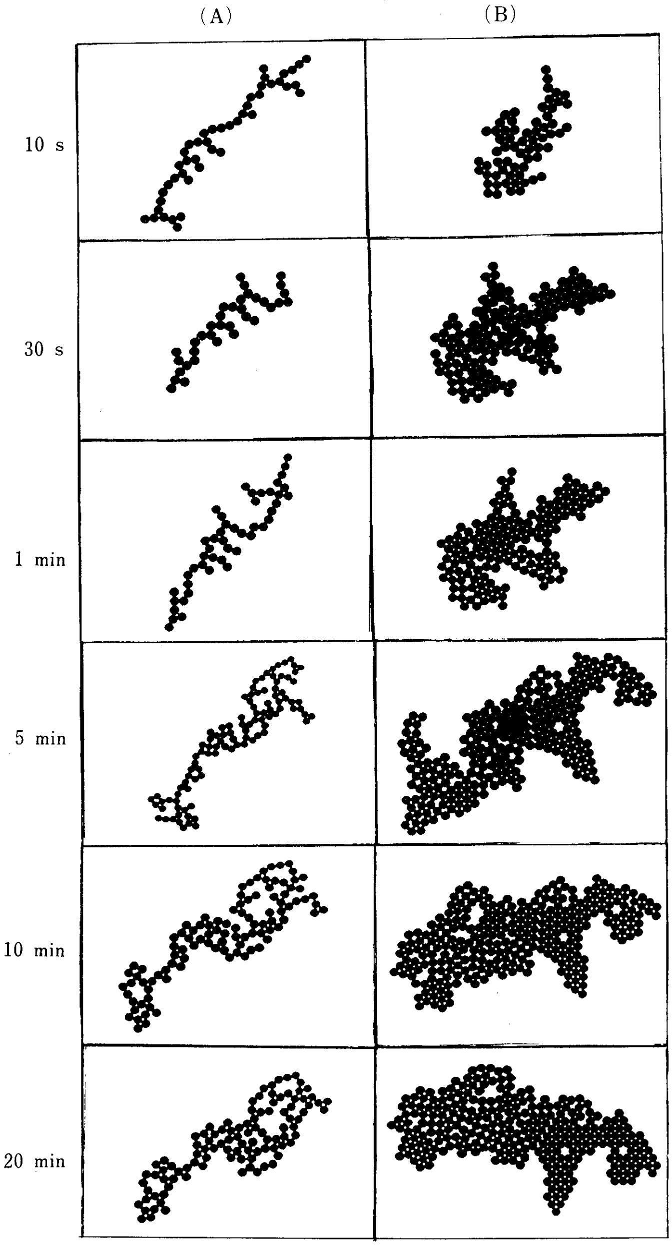

Fig. 1. Illustrations of Agglomerate Structures by X–Y Plotter

Agglomerates on the surfaces of water (A) and of solution with SLS (0.25 [g/100 ml]) (B).

shape factor (1) = (area of circle whose diameter is equal to the longest agglomerate diameter) /(projected area of agglomerate) (4)

shape factor (2) = (periphery length of agglomerate) /(periphery length of circle whose area is the same as the projected area of agglomerate) (5)

Shape factor (1) indicates the roundness of agglomerates. The value of the circle is unity. The smaller the value is, the rounder the agglomerates are. Shape factor (2) indicates their unevenness. The value of the circle is unity. The higher the value is, the more uneven the agglomerates are. Shape factors are shown as a function of agglomeration time in Figs. 2 and 3.

Figure 1 shows clearly the differences of agglomerate shapes in the two ranges. At any stage, the agglomerates in range I (Fig. 1A) are more dendric, and those in range III (Fig. 1B) are rounder and more blocky. The comparison after 20 min of agglomeration makes the differences very clear. In range I, the agglomerates are hollow, that is, closed chains with large intra-agglomerate pores. In range III, they show close packing and partially include the closest packing possible in the two-dimensional system. The agglomerates

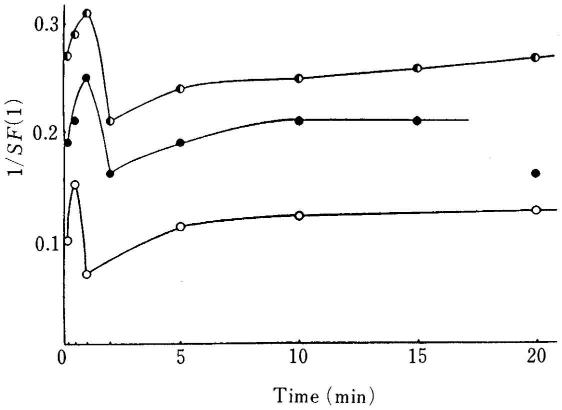

Fig. 2. Shape Factor (1) of Agglomerates as a Function of Agglomeration Time

Concentration of SLS [g/100 ml]: ○, 0; ●, 0.25; ◐, 0.50.

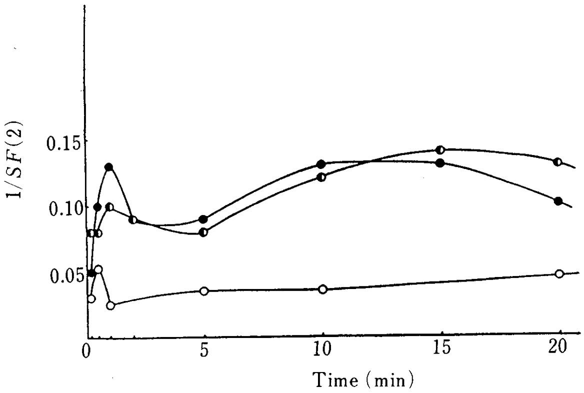

Fig. 3. Shape Factor (2) of Agglomerates as a Function of Agglomeration Time

Concentration of SLS [g/100 ml]: ○, 0; ●, 0.25; ◐, 0.50.

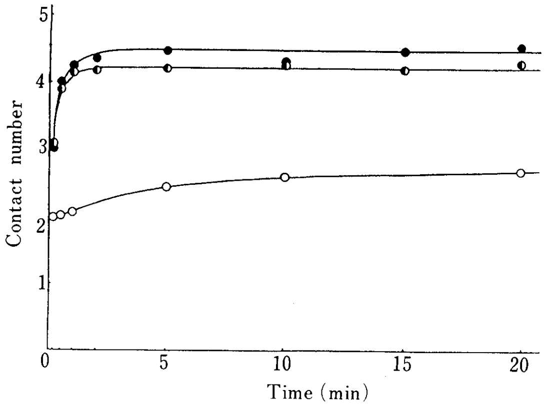

Fig. 4. Average Contact Number as a Function of Agglomeration Time
Concentration of SLS [g/100 ml]: ○, 0; ●, 0.25; ◐, 0.50.

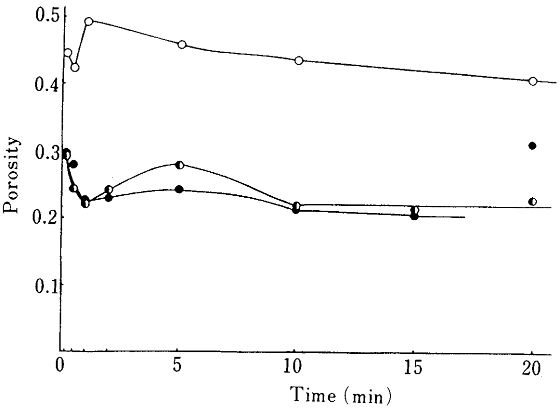

Fig. 5. Porosity as a Function of Agglomeration Time
Concentration of SLS [g/100 ml]: ○, 0; ●, 0.25; ◐, 0.50.

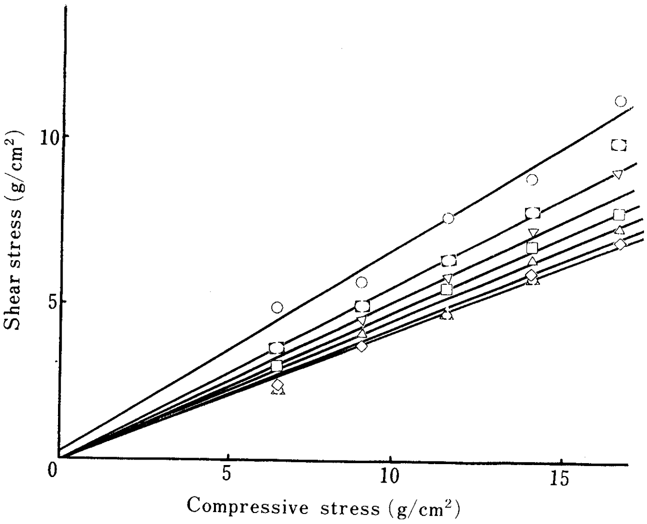

Fig. 6. Relationship between Shear Stress and Compressive Stress
Concentration of SLS [g/100 ml]: ○, untreated particle; ⬚, 0; ▽, 0.50; □, 0.25; △, 0.10; ▲, 0.075; ◇, 0.05.

are larger in range III than in range I.

The measurement of the two shape factors made these differences clearer. The agglomerates in range III show a lower value of shape factor (1) in Fig. 2 (rounder) and a lower value of shape factor (2) in Fig. 3 (less uneven). The differences of agglomerate shape are due to the change of the particle–particle interaction with SLS addition.

The average contact numbers (Fig. 4) and porosity (Fig. 5) of agglomerates were calculated on the same illustrations to examine the internal structure in more detail. For comparison with the simulation results,[5] the calculation of porosity was carried out from the area of a 360-gon inscribed in the periphery of the agglomerate and the projected area of particles. This calculation method takes into consideration that the agglomerates in practical pharmaceutical processes behave as though the points on the outermost surface are linked. Similarly, Medalia[2] considered the volume swept out by an aggregate as it rotated in connection with the actual dynamic behavior of aggregates. In range I, the average contact number is about 2.0 to 2.7, and the porosity is about 0.4 to 0.5. In range III, they are about 4.5 and about 0.2, respectively. These values are in fair agreement with the simulated values.[5] The values in range-I coincide with those when the probability coefficient of adhesion is large (that is, the *k*-value is large).[5] On the other hand, the values in range III coincide with those when it is small. When the above-mentioned coefficient is large, the particle–particle bond is strong in practical agglomeration. So it is apparent that the agglomerates in range I showed much stronger particle–particle bonding than those in range III.

The shapes of simulated agglomerates[5] do not agree with the shapes of practical agglomerates (Fig. 1), whereas the above-mentioned two values were in good agreement with the simulated values. The agglomerates in range I are linear and, on the whole, slender (Fig. 1A). The simulated agglomerates, *e.g.* when the *k*-value is 100,[5] branch off radically, and are round, on the whole. In this system, the agglomeration process on the surface of water (range I) may be summarized as follows: (1) linear agglomerates form, composed of several particles (2) these small agglomerates contact each other at the heads (3) the larger, dendric and slender agglomerates are formed. On the other hand, the simulation does not consider the contacts between agglomerates. It seems that the agglomerate–agglomerate contact should be considered in the agglomeration simulation.

In Fig. 6, the relationships between shear stress and compressive stress are shown. The relationships are linear at any concentration of SLS. Thus, Coulomb's equation (Eq. 1) can be applied.

$$\tau = \mu_i \cdot \sigma + C \qquad (6)$$

τ : shear stress

σ : compressive stress

μ_i: coefficient of internal friction

C: cohesive force

The C-values showed little change with concentration of SLS. The relationship between μ_i and the concentration of SLS is shown in Fig. 7. The μ_i-value shows the minimum in the SLS concentration range II, where the particles on the surface of the aqueous media are dispersed. The value in range I is higher than that in range III. This means that the particle–particle friction is higher in range I. The agglomeration mechanism may be as follows. The particles of agglomerates on the surface of water without SLS are

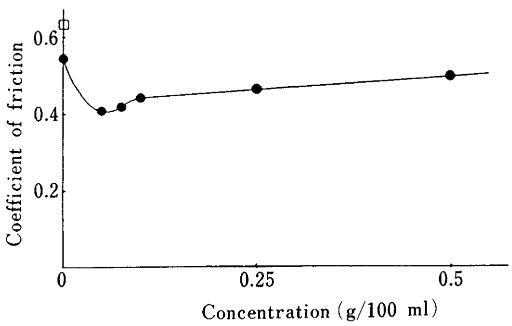

Fig. 7. Relationship between Coefficient of Internal Friction and Concentration of SLS

●, treated particle; □, untreated particle.

difficult to move. So their dendric and porous structure is retained. However, on the surface of aqueous media with SLS, they move with time to positions of lower potential energy. Then they become more closely packed and rounder. This change of agglomerate structure with time corresponds to the compaction described by Kawashima *et al.*[5)]

The effects of SLS on the agglomerate structure can be summarized as follows. (1) On the surface of aqueous media without SLS, the particles agglomerate owing to hydrophobic particle–particle bonding. Because this bonding is strong, the particles after they agglomerate can not move with respect to each other. Thus, dendric and porous agglomerates can be obtained. Those agglomerates contact each other, and form more dendric and porous agglomerates. (2) When SLS is added, the adsorbed SLS make the particle surface hydrophilic. Around the concentration of SLS where the wettability is highest, the particles on the surface disperse. (3) With increase in the concentration of SLS, the particles agglomerate again owing to the hydrophobic interaction between the SLS molecules at the surface of the solution and adsorbed on the particles. In this region, SLS can act as a lubricant of the particle–particle surface. The particles after agglomeration can move toward the center of the agglomerate. Thus, flexible agglomerates are formed on the surface of aqueous media at high concentrations of SLS, and then change to more closely packed and rounder agglomerates with time.

References and Notes

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