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Flocculation Studies of Granulated Stearyl Alcohol on the Surface of Aqueous Media. II. Flocculation–Deflocculation Mechanism in a Two-Dimensional System

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The flocculation–deflocculation mechanism of granulated stearyl alcohol dispersed on the surface of aqueous media in the presence of surface-active agents was examined. The flocculation rate was estimated on the assumption of a second-order rate process. The flocculation rate decreased at first, and then increased to the maximum value with increasing concentration of the surface-active agent. Thereafter, the flocculation rate decreased, and reached an almost constant value. The profiles of change of the flocculation rate with concentration of surface-active agent in the systems containing various kinds of surface-active agents were similar. However, taking account of the critical micelle concentration, the profiles could be classified into two patterns. One reason for the difference between the profiles was supposed to be the difference in structure of the surface-active agents. The flocculation behavior is discussed in relation to the effects of hydrophobic interaction, electrorepulsive force and steric hindrance.

Keywords——flocculation; granulated stearyl alcohol; surface-active agent; two-dimensional system; second-order rate process; wettability; contact angle; flocculation mechanism

Introduction

There have been several reports on simulations of the shape of flocks made by attaching particles to a fixed particle from several directions or attaching flock to flock.[1] We have calculated the changes of particle number and shape in the flocculation process for various model particles by simulation.[2] Granulation in a two-dimensional system was also simulated and could be explained well in terms of a second-order process. The flocculation behavior of granulated stearyl alcohol on the surface of solutions of ionic surface-active agents has already been reported,[3] and in this paper, we deal with the flocculation behavior in the presence of nonionic surface-active agents and the flocculation mechanism in a two-dimensional system, taking the concept of a slow coagulation process[4] into account.

Experimental

Sample——Sieved, granulated stearyl alcohol (Kao Co., Ltd.) was used for dispersing samples as described in the previous paper (Feret's diameter = 1.3 mm).[3] Nonionic surface-active agents used as the flocculating agent were tetraoxyethylene dodecylalcohol (TED, 0.0227 mM), hexaoxyethylene dodecylalcohol (HED, 0.0364 mM) and octaoxyethylene dodecylalcohol (OED, 0.0455 mM) (Nikkol, Nikko Chemicals Co., Ltd.). The values following the abbreviations are the values of critical micelle concentration measured by a capillary method at 25 °C.

Measurements of Flocculation–Deflocculation——Measurements were carried out as described in the previous paper.[3] A suitable amount of a solution of the nonionic surface-active agent was poured into a container (diameter = 14.5 cm), and the granulated stearyl alcohol (1.0 g) were scattered on the surface of the solution. The number of particles and the state of flocks were analyzed by measurements on photographs of particles and flocks on the surface, and by using a LUZEX 500 image analyzer (Nireko Co.).

Measurement of Wettability——Wettability was measured as described previously.[3] The granulated stearyl alcohol (1 g) was compressed at a pressure of 1 ton on a multipurpose compressor (type TCM-5000C, Shinko Tsushin) to make a tablet (diameter = 2.0 cm, and thickness = 0.5 cm). The height and diameter of a droplet (10 μl) of the solution on the tablet was measured, and the contact angle (as an index of wettability) was evaluated by the method described by Bikerman.[5]

Results and Discussion

Flocculation Rate Constant

The flocculation behavior on the surface of a solution of surface-active agent was evaluated as described previously[3] by the application of a second-order rate equation expressed by Eq. 1:

$$1/N - 1/N_0 = kt \qquad (1)$$

where t is the time, N_0 and N are the numbers of particles at time 0 and t, respectively, and k is the flocculation rate constant.

Applicability of Eq. 1 to the flocculation behavior in a two-dimensional system was tested, and the results at characteristic states of the systems are shown in Fig. 1. The values of k for all the systems, obtained from the slopes of the $1/N - 1/N_0$ *vs.* t plots, are shown in Fig. 2.

The value of k decreased with increasing concentration of the nonionic surface-active agents, and the minimum value appeared before the critical micelle concentration (cmc) was reached. Then the value of k increased and reached an almost constant value after passing through the maximum value far above the cmc. The concentration where the k value showed the minimum or maximum value increased with increasing chain length of the polyoxyethylene. Also, the shorter the polyoxyethylene chain length, the sooner the k value shifted from the minimum to the maximum value. Thus, the flocculation behavior might depend on the molecular size of the surface-active agent.

The profiles of change of the k value for the system of ionic surface-active agents have been reported[3] and are shown in Fig. 3 for comparison. The value of k decreased and reached a minimum with increasing concentration of the anionic surface-active agent. Then, the value of k increased and attained a maximum around the cmc. On the other hand, in the system of cationic surface-active agent, the value of k decreased rapidly and remained small until the

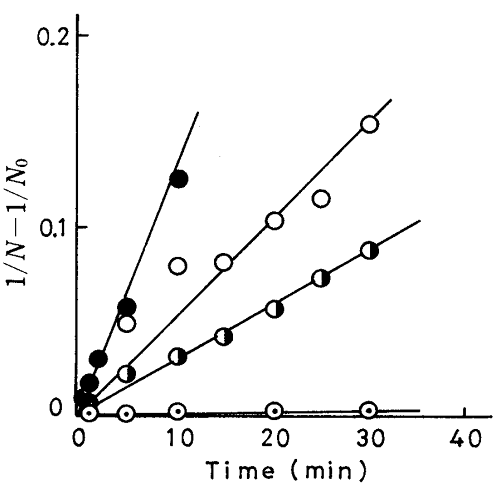

Fig. 1. Applicability of A Second-Order Rate Equation to Flocculation Behavior in a Two-Dimensional System

Concentration of HED (mM): ○, 0; ⊙, 0.022; ●, 0.222; ◑, 0.444.

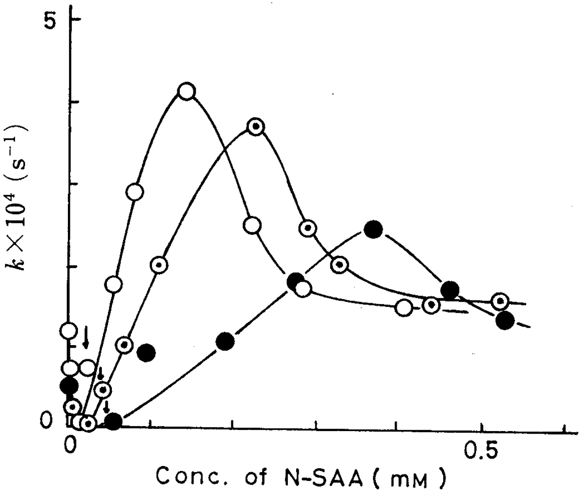

Fig. 2. Relationship between Flocculation Rate Constant (k) and Concentration of Nonionic Surface-Active Agent (N-SAA)

○, TED; ⊙, HED; ●, OED; ↓, cmc.

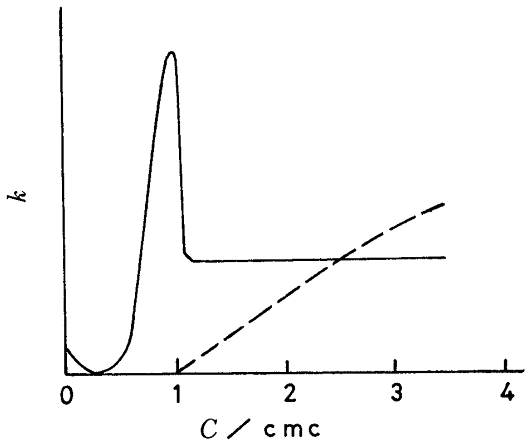

Fig. 3. Schema of Relationship between *k* and Reduced Concentration (*C*/cmc) for Anionic and Cationic Surface-Active Agents[3)]

——, A-SAA (sodium lauryl sulfate); ----, C-SAA (benzalkonium chloride).

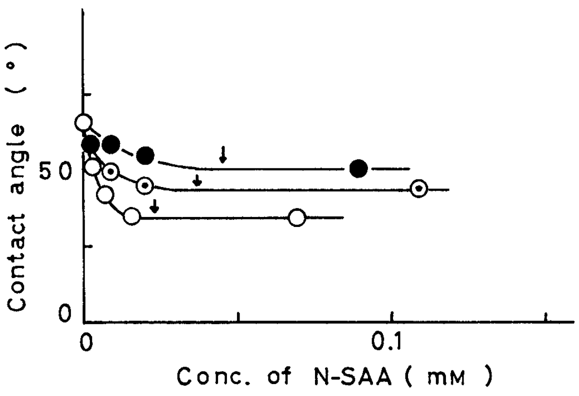

Fig. 4. Relationship between Contact Angle and Concentration of N-SAA

○, TED; ⊙, HED; ●, OED; ↓, cmc.

concentration reached the cmc. Then, the value of *k* increased with increasing concentration of the cationic surface-active agent. Thus, a similarity in the flocculation–deflocculation behavior can be seen in the systems of cationic and nonionic surface-active agents used in this study, since the maximum value of *k* did not appear within the concentration range from 0 to the cmc.

Wettability

The contact angles measured with the nonionic surface-active agents are shown in Fig. 4. The contact angle decreased with increasing concentration of the nonionic surface-active agent, and reached an almost constant value above the cmc. This is similar to the results in the systems of ionic surface-active agents reported in the previous paper.[3)]

As the surface-active agent is adsorbed on the granulated stearyl alcohol by hydrophobic interaction, an increase in the amount of the surface-active agent adsorbed might make the particles hydrophilic. Therefore, it was thought that the surface was covered by a saturated monolayer of the surface-active agent so that the contact angle showed an almost constant value above the cmc.

Mechanism of the Flocculation–Deflocculation in a Two-Dimensional System

The flocculation behavior in a two-dimensional system of granulated stearyl alcohol in various kinds of surface-active agents (SAA) showed similar patterns. However, as described before, the minimum and maximum values of *k* appeared in the concentration range between 0 and around the cmc with the anionic surface-active agent (A-SAA). On the other hand, with the cationic and nonionic surface active agents (C-SAA, N-SAA), the minimum value of *k* appeared in the same region as in the case of A-SAA, but the maximum value did not appear in that concentration range. Thus, when the cmc is taken into account, the flocculation behaviors in this study can be classified into two patterns independently of the ionic property of the SAA.

The surface tension of SAA solution decreases with increasing concentration of SAA and shows an almost constant value above the cmc. Hence, it was supposed that the change of surface tension itself can not account for the difference in the flocculation behaviors in these systems. Also, as changes in viscosity with the concentration of SAA are small below the cmc, viscosity might not play an important role in the flocculation behavior when the concentration of SAA is low. Judging from the change in contact angle, the amount of SAA adsorbed on the surface of the particle increases with increase in the concentration of SAA. As far as molecular structure is concerned in these systems, N-SAA and C-SAA have a bulkier structure than A-SAA has. Thus, it was thought that the steric character of SAA might play an important role in the flocculation process, besides the electrorepulsive force and hydrophobic interaction of adsorbed SAA.

The flocculation–deflocculation behavior in the A-SAA system was considered as follows. The amount of SAA adsorbed on the granulated particle (Γ_p) and the amount of SAA adsorbed on the surface of the aqueous medium (Γ_s) increase with increasing concentration of SAA. The effect of the molecules adsorbed on the surface of SAA solution on the flocculation behavior might be small because of the small Γ_s when the concentration of SAA is low, so the granulated particles made hydrophilic were less able to flocculate, and the value of k decreased at the initial stage. The increase in Γ_p and Γ_s with increasing concentration of the SAA made the particles tend to flocculate because of the hydrophobic interaction between the SAA molecules adsorbed on the surface of the solution and on the particles. Here, considering the lower steric hindrance in the A-SAA system, the particles have better access to each other and flocculate at small Γ_p and Γ_s. As a result, the minimum value of k appeared at a lower value of C/cmc in the A-SAA system compared with those in the other SAA systems, *i.e.*, N-SAA and C-SAA systems. The hydrophilic part of SAA adsorbed on the particle remains in the solution, and interactions between the hydrophilic part of adsorbed SAA and micelles might take part in the flocculation process when the concentration of SAA reaches the cmc. The micelles of ionic SAA are supposed to make the particles keep away from each other because of their steric hindrance and electrorepulsive force. Thus, the particles in the A-SAA system seem to be less able to flocculate, and the maximum value of k might appear around the cmc in this system. In the region where the concentration of micelles is high enough to restrict the movement of particles, the value of k should show an almost constant value as is the case in Fig. 3.

The difference in flocculation behaviors between the A-SAA system and the C-SAA and N-SAA systems might be explained as followed. Large Γ_p and Γ_s might be required for the particles to have access to each other and flocculate by hydrophobic interaction between the adsorbed SAA molecules in the C- and N-SAA systems, when the steric hindrance of the bulky hydrophilic moiety is taken into account. Therefore, the value of k is still small around the cmc in the C- and N-SAA systems. When the concentration reaches the cmc, the particles are covered by a saturated monolayer of adsorbed SAA. In the case of the N-SAA system, the particles have access to each other, and flocculate by hydrophobic interaction. Hence, it is thought whether the particles flocculate or deflocculate around the cmc probably depends on the electrorepulsive force, because the particles in the N-SAA system where the electrorepulsive force may be negligible behave in a different way from that in the A-SAA system. In the case of C-SAA, the electrorepulsive force might be effectively diminished by the bulky hydrophobic moiety. Thus, C-SAA is expected to behave in the same way as N-SAA in the flocculation process. In such a case, the factors which affect the movement of particles might be the surface viscosity, the steric hindrance of micelles and so on because of the weak or negligible electrorepulsive force of C-SAA and N-SAA. As a result, the value of k would increase with increasing concentration of C-SAA and N-SAA around the cmc where k showed almost the maximum value in the A-SAA system. As the concentration of micelles increases, the movement of particles is gradually interfered with, and they become less accessible to each other. Thus, the maximum value of k is reached. After that, the value of k decreases until the micelles control the movement of particles as can be seen in Figs. 2 and 3. Since the concentration of SAA is very high, there is a possibility that the viscosity affects the flocculation behavior, too. In the case of C-SAA shown in Fig. 3, the value of k keeps on increasing above the cmc, but the value of k should be fixed in the higher concentration region of C-SAA, as in the other SAA systems, whether or not a maximum value appears.

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