Accelerated Dissolution of Fatty Acid Particles at the Oil–Water Interface

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We found self-motion and accelerated dissolution of a fatty acid particle at the oil–water interface. The dissolution time at the interface was 15–20 times shorter than that in the oil phase. The driving force of the self-motion and the accelerated dissolution is the Marangoni flow induced by the spatial heterogeneity of a fatty acid layer at the oil–water interface.

The dissolution of solid particles is the important unit operation of chemical engineering.[1] In general, solution rates are controlled by heating or agitating disperse mediums. We have focused our attention on the acceleration of the dissolution at the oil–water interface. The self-motion and the dissolution of solid particles and liquid droplets at liquid surfaces are known in some systems.[2–6] The particles move around on the surfaces and dissolve into the liquid phases owing to the Marangoni flow induced by chemical or thermal gradients on the surfaces.[2] Non-homogeneous distribution of surfactant molecules around the solid particle induces a gradient in the surface tension which acts as the driving force of the self-motion and the accelerated dissolution. This acceleration phenomenon is interesting from the viewpoint of chemical engineering, because this acceleration is achieved without heating or agitating.

In the present study, we evaluate the effect of the Marangoni flow on the dissolution time of a fatty acid particle at the silicone oil–water interface.[7–9] The fatty acid and the silicone oil are the ingredients used widely in pharmaceutical and cosmetic products.[10] The influences of viscosity of the silicone oil and addition of a silicone surfactant are also investigated to elucidate the governing factor of the accelerated dissolution.

The dissolution of the fatty acid particle is drastically accelerated at the silicone oil–water interface. When a particle is deposited at the interface between silicone oil, polydimethylsiloxane with 250 in molecular weight, and water as shown in Figure 1, the particle moves around at $17 \pm 1\,\mathrm{mm\,s^{-1}}$ on the interface and is completely dissolved in the dissolution time per unit weight $t = 144\,\mathrm{s\,mg^{-1}}$. In many cases, the particle motion is random and continuous, whereas intermittent motion, i.e., alternation between rest and motion, is observed with probability 0.2. On the other hand, the particle immersed in the silicone oil does not move around and t is $2500\,\mathrm{s\,mg^{-1}}$. The dissolution time at the interface is 17 times shorter than that in the oil phase. The degree of the acceleration depends on the amount of the fatty acid in an oil/water binary system when the fatty acid particle is added after another. When the number of the particle $n \leq 6$, t is almost constant value, ca. $200\,\mathrm{s\,mg^{-1}}$ as shown in Figure 2. On the other hand, when $n \geq 7$, t increases with n and attains above $1000\,\mathrm{s\,mg^{-1}}$. Interestingly, the dissolution time correlates to the self-motion of the particle. The particle moves around at $10–20\,\mathrm{mm\,s^{-1}}$ in the region of $1 \leq n \leq 6$, whereas that stays in one position on the interface in the region of $n \leq 20$. The velocity of the self-motion decreases with increasing n. This result predicts that the increase of the self-motion velocity promotes the dissolution of the fatty acid crystals.

The addition of a silicone surfactant, poly(oxyethylene)–methylpolysiloxane copolymer, prevents the accelerated dissolution. The silicone surfactant having 14.5 in HLB is efficiently adsorbed at the oil–water interface.[11] Three silicones whose molecular weights are 250, 600, and 700, respectively, are mixed to control their viscosity. Figure 3 shows the ratio of the dissolution times R against the concentration of the silicone surfactant in water, c. Here, R is given by $R = t_\mathrm{O}/t_\mathrm{O/W}$ where $t_\mathrm{O/W}$ and t_O are the dissolution time at the oil–water interface and that in the oil phase, respectively. The ratio R decreases with the increase of c but does not depend on the viscosity of the oil phase. Moreover, the self-motion of the particle is not observed when $c = 0.01\,\mathrm{wt\,\%}$. These results predict that the adsorption of the

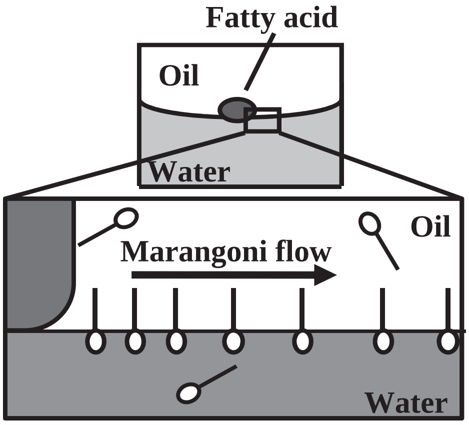

Figure 1. Schematic illustrations of the oil–water interface adsorbing a fatty acid crystal and molecules.

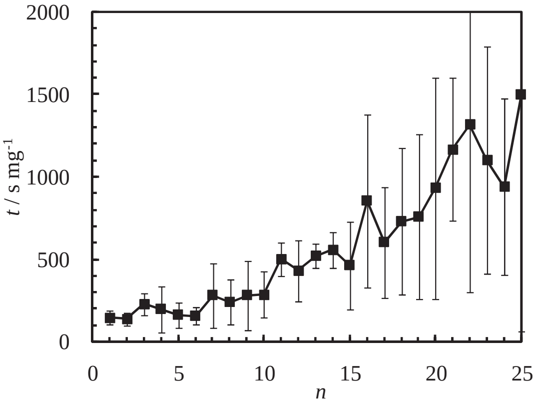

Figure 2. The dissolution time of the fatty acid particle at the oil–water interface, t, against the number of the particles, n.

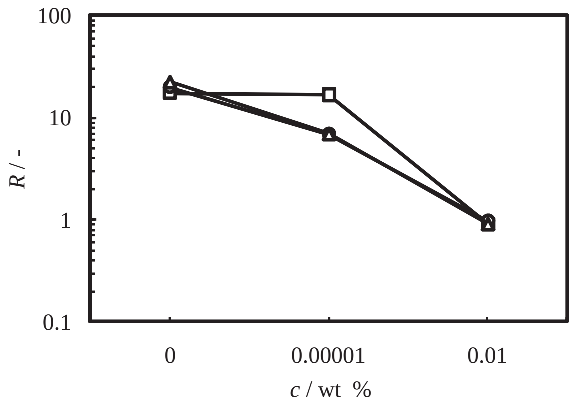

Figure 3. The ratio of dissolution times R against concentration of silicone surfactant in water, c. The viscosities of silicone oils are 1.1 mPa s (○), 2.1 mPa s (□), and 3.2 mPa s (△), respectively.

surfactant at the oil–water interface prevents the accelerated dissolution. On the other hand, the viscosity of the oil does not change R drastically in the present systems.

The experimental results demonstrate that the self-motion of the fatty acid particle is caused by the Marangoni flow at the oil–water interface. As mentioned above, locomotion of the particle at the interface depends on the concentration of the surface-active materials, i.e., fatty acid and silicone surfactant. This result shows that a gradient in the packing density of the surface-active materials induces the liquid flow near the oil–water interface. These dependences are common in the particle/droplet motions induced by the Marangoni flow.[5,12] Bekki et al. showed that the velocity of the self-motion induced by the Marangoni flow is proportional to $(C_S/C - 1)^{1/2}$ and $(1/\rho)^{1/2}$ where C is solute concentration, C_S the solute concentration of its saturated solution, and ρ the viscosity of the medium.[12] Such liquid flow around the particle accelerates the dissolution of the fatty acid. Based on the Nernst–Noyes–Whitney equation, the dissolution rate of the particles is inversely proportional to the thickness of a diffused layer on the particle surface.[1] The Marangoni flow decreases the thickness and accelerates the dissolution. The efficiency of the Marangoni flow on the accelerated dissolution is remarkable compared with other acceleration procedures. When the particle is in the oil phase, t decreases with rising temperature and attains $160\,\mathrm{s\,mg^{-1}}$ at 313 K. This result means that the efficiency of the Marangoni flow is appropriate to temperature rising of 15 K in the present system.

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7 The fatty acid (lauric acid, lunac L-98, Kao Co.), silicone oils (polydimethylsiloxane, KF96A(1CS), KF96A(2CS), and KF96A(6CS), Shin-Estu Chemical Co., Ltd.), and silicone surfactant (poly(oxyethylene)–methylpolysiloxane copolymer, KF-6011, Shin-Estu Chemical Co., Ltd.) were commercially available and were used as received. The fatty acid is a white powder with a high fluidity. The size and weight of the fatty acid particle are 1.02 ± 0.10 mm, 0.4 ± 0.1 mg, respectively. KF96A(1CS), KF96A(2CS), and KF96A(6CS) have a molecular structure of $(CH_3)_3$–$SiO[Si(CH_3)_2O]_nSi(CH_3)_3$, a specific gravity of 0.82, 0.67, and $0.93\,\mathrm{g\,cm^{-3}}$ at 298 K, and molecular weights of 250, 600, and 700, respectively.
8 The dissolution times of the fatty acid crystals were obtained as follows. The fatty acid particle was floated on the silicone oil (2 g)/water (2 g) interface in an annular glass container whose diameter is 10 mm. The area of the oil/water interface is $79\,\mathrm{mm^2}$, whereas the depth of the oil and water phases is 24 and 26 mm, respectively. All of the experiments were performed at 299 K. The shape and the motion of the particle at the interface were checked to measure the dissolution time. The dissolution time of the fatty acid in the silicone oils were also examined. The fatty acid particle was immersed in the silicone oil (2 g) under the same conditions.
9 Viscosity measurements were carried out by a CVJ5000 viscometer at 298 K. The movement of the fatty acid particle was monitored with the digital camera OLYMPUS SP560UZ whose minimum time-resolution is 1/15 s.
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