Self-organization of Multilayered Oil Droplet in Water

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Dynamic behavior of initially sessile droplets of oleic acid with sodium oleate was investigated in an aqueous buffer solution. The interface of droplet highly fluctuated at pH 9.0 and concomitantly grew a multilayered structure inside of the droplet. Volume change of the droplet suggested the existence of three independent mass-transport processes. This phenomenon was observed under specific conditions of pH and oil composition.

It is known that dynamic instability is induced at the interface between two immiscible liquids (e.g., oil and water) in the presence of surfactants.[1,2] The locomotion of oil droplets is propelled by mutual mass transport across the oil–water interface,[3–5] and self-reproduction of vesicles is driven by chemical reactions.[6,7] In this letter we report a new class of dynamic instability in an oil–water system. It is the formation of multilayered structures inside of a droplet of (*Z*)-9-octadecenoic acid (oleic acid). This phenomenon was found under specific conditions of pH and the composition of the oil and was associated with strong fluctuations at the interface. Experimental results suggest the reaction-free, transport-driven reproduction of interface.

All chemicals used in experiments were of analytical grade purchased from Wako Pure Chemicals Co. and were used without further purification. Sodium oleate was dissolved in oleic acid by heating (<350 K) under inert atmosphere. Oil droplets on a glass plate[8] were in contact with a 200 mM *N*,*N*-bis(2-hydroxyethyl)glycine (Bicine) buffer solution (pH 6.2–10.7). The volumes of the oil and the aqueous phase were 5 and 200 μL, respectively.[9] The oil droplets (diameter ≈30 μm) were monitored under a phase-contrast optical microscope (Olympus IX-70) at 22.0 ± 0.5 °C.

Figure 1 shows the change in a sessile droplet of sodium oleate–oleic acid (1:2) in water at pH 9.0. Figure 1a illustrates by snapshots the growth of a multilayered structure inside of the droplet. The gray color at $t = 0$ means[11] homogeneous hydration of oil droplet. The edge became sharp at 10 min, and at 30 min it appeared a layered structure inside of the droplet. At 90 min, the multilayered structure had well developed. This growth of multilayered structure was a gradual process associated with the fluctuations of interface.

The space–time diagram (Figure 1b) supplements the continuous image for the growth of the layers inside of the droplet; this diagram was composed of the time sequence of the single-line images along the vertical diameter of droplet. The dark edges after 10 min suggest the increase in the curvature of the hydrated droplet. These edges became gradually hazy after 30 min, which can be interpreted as a result of fluctuations. The increase in the phase contrast after 30 min implies the three-dimensional change of the droplet.

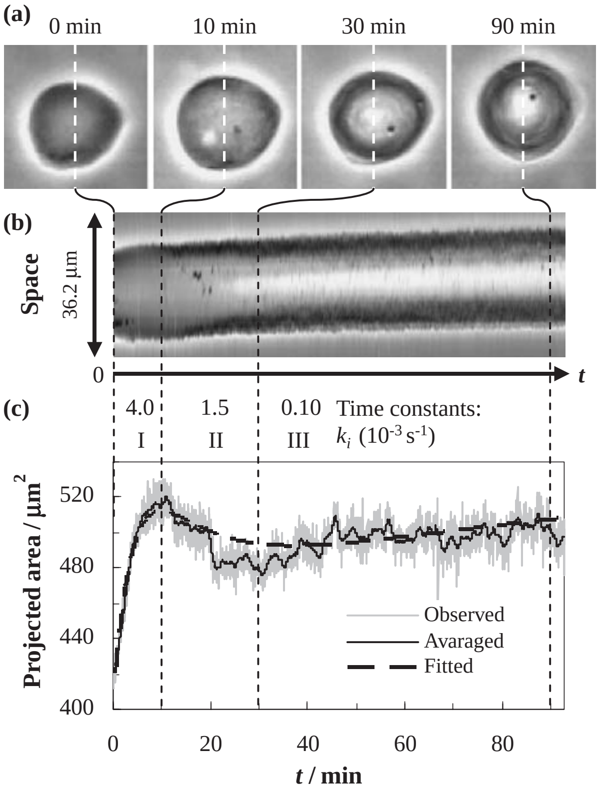

Figure 1. Formation of multilayered structure in a sessile oil droplet of sodium oleate–oleic acid (1:2) in a 200 mM Bicine buffer solution (pH 9.0). (a) Phase-contrast images of the oil droplet (size: 36×36 μm^2). (b) Space–time diagram constructed from the image sequence recorded by 30 flames s^{-1} along the white broken lines. (c) Change in the area of the droplet. Gray line: observed; solid line: moving average taken for every 30 s; broken line: the curve fitted by eq 1.

Figure 1c illustrates the change in the area of the droplet. Here, the change in every second (gray line) appears as strong fluctuations. The moving average for 30 s (solid line) suggests the existence of periodical events after 30 min, whose period increases with time from 5 to 10 min. The profile of the moving average is composed of the following three phases: the initial increasing phase (0–10 min, phase I), the decreasing phase (10–30 min, phase II), and the gradual reincreasing phase (30–90 min, phase III). Assuming that these processes coexist, we curve-fitted this profile by the following equation:

$$f(t) = C_0 - c_1 e^{-k_1 t} + c_2 e^{-k_2 t} - c_3 e^{-k_3 t} \qquad (1)$$

The broken line in Figure 1c indicates the result given by eq 1, where $C_0 = 560$; $c_1 = 180$, $c_2 = 130$, $c_3 = 90$ (in μm^2); $k_1 = 4.0$, $k_2 = 1.5$, $k_3 = 0.10$ (in $10^{-3}\,s^{-1}$). This good result implies that the change in the projected area is induced by three independent processes: the fast increasing process (process 1, characterized by the time constants $k_1 = 4.0 \times 10^{-3}\,s^{-1}$), the decreasing process (process 2, $k_2 = 1.5 \times 10^{-3}\,s^{-1}$), and the slow increasing process (process 3, $k_3 = 0.10 \times 10^{-3}\,s^{-1}$).

There are three possibilities to induce the interfacial fluctuations under the present conditions: the reaction (dissociation) of oleic acid at the interface, the mass transport across the interface, and the mutual interaction between them. We, therefore, examined the contribution of the reaction by changing both the composition of oil and the pH of the buffer solution in order to construct a phase diagram. Though the surface composition of oil is determined by the dissociation constant of oleic acid (pK_d) and pH of the surrounding buffer solution under equilibrium conditions, this composition may be different from that of equilibrium if the renewal of oil surface occurs continuously. Therefore, the composition at the dynamic interface is an issue of nonequilibrium thermodynamics. Assuming that the composition of regenerated oil surface ($X \equiv$ [sodium oleate]/[oleic acid]) is proportional to that of the *initial* bulk oil, we derive the following relation:

$$\Delta = \mathrm{pH} - \mathrm{p}K_\mathrm{d} = 2.303 \ln(X) \qquad (2)$$

where Δ is the thermodynamic force of the dissociation reaction of oleic acid and is proportional to the distance from the equilibrium. This relation appears as a diagonal line on a $\Delta - \ln(X)$ plane.

The results are plotted in Figure 2. The thick diagonal line corresponds to the equilibrium where $\Delta = 0$ at $X = 1$. There are two noteworthy things: Firstly, the internal growth of multilayered structure (◆) appeared under very restricted conditions, only where the strong interfacial fluctuations (as shown in Figure 1) were observed. Secondly, the multilayered-structure formation is independent of the distance from the equilibrium, as it is independent of the diagonal line **A** for any value of X. These results suggest that the dissociation reaction of oleic acid has little influence on the strong fluctuations of the oil–water interface. Further experiments for higher value of X could not be conducted because of the limitation of solubility of sodium oleate in oleic acid.

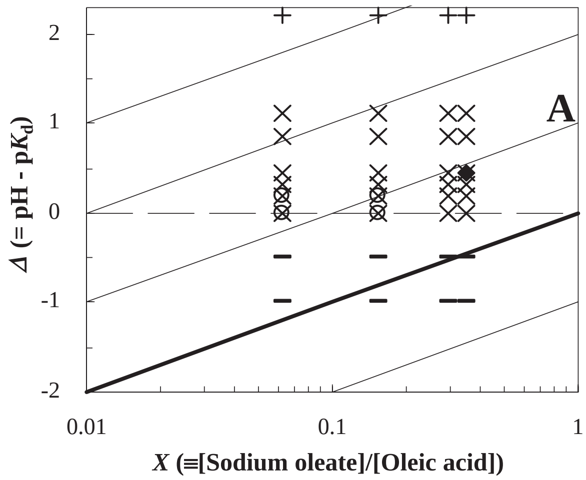

Figure 2. Phase diagram of the morphology of oleic acid–oleate droplet. X: 0.062, 0.153, 0.298, 0.354. Δ: −0.98, −0.49, 0.00, 0.20, 0.32, 0.45, 0.85, 1.12, 2.22. Symbols: oil (—); myelins or hydrated droplet (×); droplet covered with gel-like ripples (○); multilayered droplet (◆); micelles (+). For the diagonal lines, see text.

As the contribution of reaction is negligible, the strong continuous fluctuations at the interface must be induced by mass transport across the interface. Now we consider the overall scenario of multilayer formation based on solely mass transportation, by attributing the three independent processes elucidated from Figure 1 as follows:

Process 1: transport of water into the oil (hydration).
Process 2: dissolution of oil components into water.
Process 3: transport of water into the oil.

The mechanisms of water transport in processes 1 and 3 are different because the time constant of process 1 is 40 times larger than the other. We may, therefore, reasonably think that the strong fluctuations observed at the late stage (phase III) is correlated to the slow transport of water into the oil, most probably phagocytically as reverse micelles or w/o emulsions. Since both of them are associated with cooperative detachment of amphiphilic molecules from the interface, they induce the Marangoni instability[5,7] that is observed as the intermittent deformation of the interface. This cooperative transport increases the volume fraction of water at the vicinity of the interface of the hydrated oil. Finally, it results in the phase separation of water and oil along the interface, which may be detectable through the phase-contrast microscope. We propose this scenario as a probable explanation for multilayered structure formation inside of the oleic acid–oleate droplet. Further investigation is in progress by changing the buffer concentration.

References and Notes

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8 Glass plates were cleaned in 2% v/v Extran MA-02/water, rinsed with ultrapure water, and immersed in 2 M NaOH/ethenol for overnight. They were then treated four times with ultrasonic cleaning in ultrapure water for 20 min. Surface moisture of the glass plates was blown out by airflow before use.
9 This composition corresponds to an 80 mM solution of oleate and oleic acid (if they dissolve completely). As the critical micelle concentration (cmc) of sodium oleate–oleic acid falls in the range of 0.7–1.4 mM at pH 8.5,[10] we may regard that most of them in aqueous phase exist as micelles under present experimental conditions.
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11 The data acquisition was started 3 min after the oil droplets were in contact with the buffer solution.

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