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Blebbing dynamics in an oil-water-surfactant system through the generation and destruction of a gel-like structure

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Interfacial dynamical blebbing of an oil droplet on an aqueous solution is reported. The oil droplet and the aqueous solution contain a fatty acid and a cationic surfactant, respectively. When the oil droplet was placed on an aqueous surface, the oil-water interface formed blebs, spherical extrusions on the oil-water interface and circular ones on the edge of the oil droplet. With increase of the concentration of the surfactant and/or the fatty acid, the generated blebs become smaller. Based on the experimental observations together with theoretical considerations, we conclude that the bleb formation is induced through generation and destruction of a gel-like intermediate phase.

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One of the fascinating aspects of living things is spontaneous motion that derives from chemical energy. From a physicochemical point of view, this spontaneous motion is a product of the direct energy transduction of chemical energy into macroscopically ordered mechanical motion, which differs from the mechanism of a conventional thermal engine. Recent progress in biotechnology enables us to grasp the fundamental elements of these energy transducers at nanometer scale, as in actin, myosin, kinesin, and dynein [1]. At larger sizes, from micrometer to millimeter-scale, the most primitive form of energy transduction would be amoeboid motion [2], although the mechanism is still complicated. In amoeboid motion, it is known that cells form a structure called a bleb, which is a quasispherical deformation extruded from the cell surface [3]. A relevant approach toward better understanding bleb formation, we believe, is to construct and analyze a simple physicochemical system mimicking essential aspects of bleb formation.

In this Rapid Communication, we report spontaneous deformation of an oil droplet on an aqueous surface, resulting in spherical extrusions on the oil-water interface and circular ones on the edge of the oil droplet, which resemble blebs on a cell surface. In the following, we use the term "bleb formation" to indicate the deformation observed in this system. The system is composed of an aqueous solution containing a cationic surfactant [stearyltrimethylammoniumchloride (STAC)], and an oil phase containing a fatty acid [tetradecane with palmitic acid]. Upon setting the aqueous solution in contact with the oil phase, the interface between them starts to form blebs spontaneously. Significantly, this system does not contain any biological material such as motor proteins, and even chemical reactions seem to be irrelevant to the process. The only source of energy in the system is the chemical potential energy arising from the initial distribution of chemicals, which is in a far-from-equilibrium condition [4].

STAC and palmitic acid were purchased from Tokyo Chemical Industry Co., Ltd. Tetradecane was available from Wako Pure Chemical Industries, Ltd. Water was purified by a Millipore milli-Q system. As for the aqueous solution, the concentration of STAC, C_s, was varied from 1 to 100 mM, where the critical micelle concentration of STAC is about 0.3 mM. The organic solution was composed of tetradecane and palmitic acid. The concentration of palmitic acid, C_p, was varied from 1 to 20 mM, where 20 mM is slightly lower than the solubility limit of palmitic acid in tetradecane at room temperature. The deformation of the droplet interface was recorded by a charge-coupled device camera at 30 frames per second while the system was illuminated by visible light (cold spot, PICL-NEX Nippon P. I. Co., Ltd). All measurements were carried out at room temperature.

The spontaneous deformation of the oil droplet is exemplified in Fig. 1. Here, a 500-μl oil droplet was added to 2000 μl of the aqueous solution on a plastic plate. Initially, the oil droplet took spherical shape as an ordinary droplet. After a certain induction period (~10 s) the droplet suddenly showed quick spreading and recoiling several times in a second. Then the edge of the oil droplet showed the bleb for-

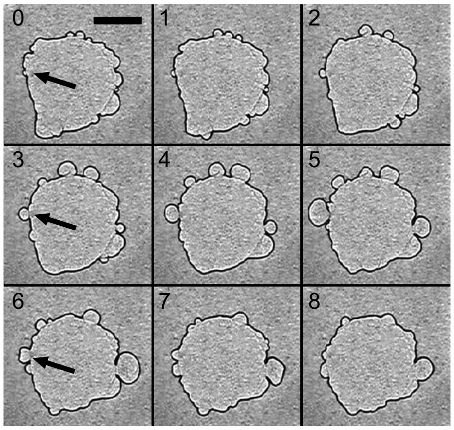

FIG. 1. Snapshots of droplet deformation, where $C_s=10$ mM and $C_p=5$ mM. A 500-μl oil droplet was added to 2000 μl of aqueous solution on a plastic plate. The arrow indicates a bleb that is formed (0–5) and collapses (6,7). The snapshots were taken every 1 s. The scale bar corresponds to 10 mm. See also the movie [5].

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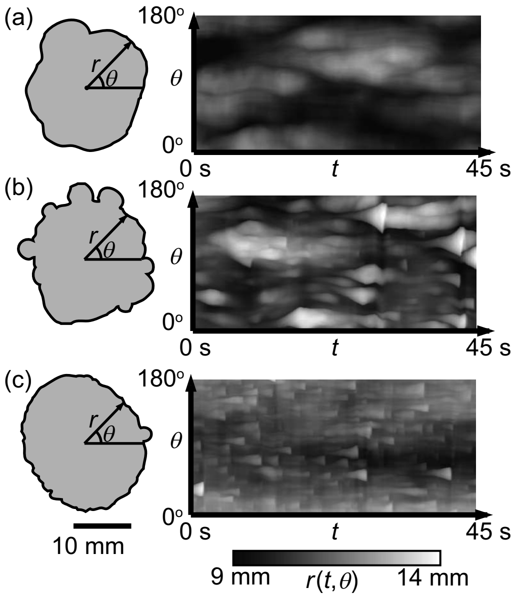

FIG. 2. Spatiotemporal plot of droplet deformation at different C_p: (a) 1, (b) 5, and (c) 10 mM. A 500-μl oil droplet was added to 2000 μl of the aqueous solution ($C_s = 10$ mM). The position of the edge of the oil droplet was measured in cylindrical coordinates $r(t,\theta)$ every 0.1 s. In the right diagram, $t = 0$ corresponds to ca. 1 min after the addition of the oil droplet to the surface of the aqueous solution. Note the bleb size decreases as C_p increases.

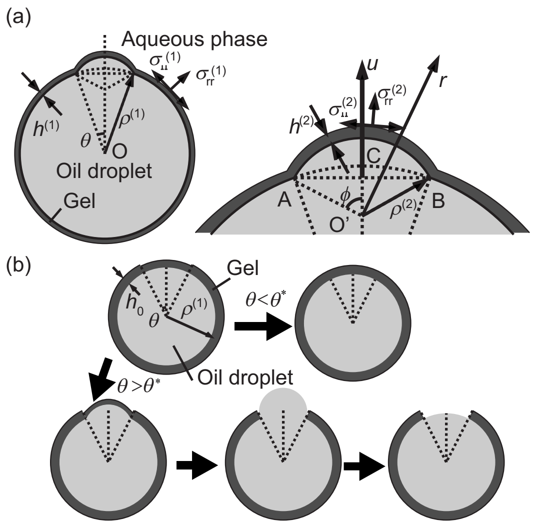

FIG. 3. (a) Geometrical configuration of the theoretical model. It is assumed that the droplet exhibits a small deformation on its periphery. (b) Mechanism of bleb formation. The oil droplet, with a radius $\rho^{(1)}$, is covered with the gel whose steady-state thickness is h_0. From $-\theta$ to θ, the gel thickness is perturbed to be slightly thinner than h_0. If $\theta < \theta^*$, the perturbation is stabilized, whereas for $\theta > \theta^*$ the bleb forms until the gel disappears. After the disappearance of the gel, the bleb shrinks quickly due to the increased interfacial energy between the oil and the water.

mation. The induction period gets longer for a larger air-water interface area. We suppose that the induction period corresponds to the time for palmitic acid to cover the air-water interface. In fact, once a droplet starts bleb formation, another new oil droplet on the same air-water interface, regardless of the distance from the preexisting droplet, does not require the induction period. This evidence suggests that the induction period is the time required for the spreading of palmitic acid on the water surface. The shape of the blebs is always circular, implying that the instability is caused by a volume force, such as higher internal pressure, as the primary factor. We can consider that an interfacial instability, such as Marangoni flow, would exhibit a secondary effect on the observed phenomena.

To clarify the effect of the chemical components, we observed the deformation of the oil-water interface in the same setup while changing C_p with constant $C_s = 10$ mM. The typical size of the blebs ranges from 0.1 to 10 mm depending on C_p. When C_p is small, the bleb is large (Fig. 2 and movie [5]). For small C_s, the size of the blebs also increases (data not shown). It is noteworthy that the shrinkage of the blebs is much faster than their growth. Bleb formation typically takes about 10 s, whereas bleb shrinkage takes about 1 s (Fig. 2 and movie [5]).

While observing the interfacial deformation, we noted that a gel-like structure is formed during bleb formation. The gel-like structure was formed spontaneously through the mutual contact between the aqueous phase and the organic phase in a bottle at room temperature though the formation process took quite a long time (~ several hours) and was suspended when the whole oil-water interface was covered with the gel-like structure. To see the character of this gel-like structure, a mixture of the ingredients with $C_s = 10$ mM and $C_p = 10$ mM was mixed well and sonicated for 3 h at 50 °C, kept still at room temperature for 20 h, and treated with a centrifuge at 2500 G for 6 h. After the treatment, an intermediate phase between the organic and aqueous phases was observed. On inclining the bottle, the intermediate phase exhibited an apparent yield stress, as a gel-like phase. The gel-like phase was stable at room temperature for several months.

From our experimental observations, it was suggested that the gel-like structure is generated when the system approaches thermal equilibrium. Because palmitic acid is slightly soluble in the aqueous phase, we can hypothesize that the generation of the gel-like structure is limited to occur only close to the oil-droplet surface. In order to understand the mechanism of bleb formation, here we discuss it theoretically, assuming that the elastic material, the gel, is generated on the oil-droplet surface.

We consider a two-dimensional model that is appropriate for the instability of the edge of a flat oil droplet, whose size is larger than the capillary length. The model is schematically depicted in Fig. 3(a). We separate the droplet periphery into an unperturbed part and a perturbed part. The perturbed part is spanned by the angle 2θ. Here θ is kept constant and the volume conservation is ignored. The unperturbed part of the oil-droplet periphery, which has a radius $\rho^{(1)}$ and center O, is covered with the gel with a uniform thickness $h^{(1)}$, whereas the perturbed part of the droplet has a curvature radius $\rho^{(2)}$ and a gel thickness $h^{(2)}$. Hereafter, $i = 1,2$ implies the variable at the unperturbed and the perturbed parts, respectively. The stress of the gel in the angular direction is denoted as $\sigma_{\perp\perp}^{(i)}$. The center of the circle that fits the deformation is set as O'. The position of the center of the deformation, O', is indicated by the coordinate u, whose origin is C and outward direction is set as positive. The point C is the intersection of the lines OO' and AB, which is the line connecting the sides of the bleb. The angle of the perturbed part seen from the center is 2ϕ, as shown in Fig. 3(a). From these conditions, we can obtain $\rho^{(2)}=\sqrt{u^2+(\rho^{(1)}\sin\,\theta)^2}$, and $\phi=\arccos(-u/\rho^{(2)})$.

Considering that the gel is generated on the droplet surface, we take into account the effect of elasticity of the generated gel based on a "stacked rubber band model" [6]. We suppose the stress depends linearly on the strain, and the gel growth is limited by the stress [6]. We consider the situation where the gel is generated only at the droplet interface, and as a result the gel is pushed into the aqueous phase while it grows. The radial stress of the gel in the outward direction from the oil droplet is denoted as $\sigma_{\mathrm{rr}}^{(i)}$. Because the deformation of the gel is faster than the rate of gel generation, the tangential stresses in the gel are given as $\sigma_{\perp\perp}^{(1)}=B(r-\rho^{(1)})/\rho^{(1)}$ and $\sigma_{\perp\perp}^{(2)}=B(r\phi-\rho^{(1)}\theta)/\rho^{(1)}\theta$, where r is the length from the center of the curvature radius, and B is the Young's modulus of the gel. From the balance equation of the stress, $\partial(r\sigma_{\mathrm{rr}}^{(i)})/\partial r-\sigma_{\perp\perp}^{(i)}=0$, and with the boundary condition of radial stress at the gel-water interface $\sigma_{\mathrm{rr}}^{(i)}|_{r=\rho^{(i)}+h^{(i)}}=0$, we can calculate the radial stress on the gel-oil interface as

$$\sigma_{\mathrm{rr}}^{(1)}|_{r=\rho^{(1)}}=-B(h^{(1)})^2/2(\rho^{(1)})^2 \tag{1}$$

and

$$\sigma_{\mathrm{rr}}^{(2)}|_{r=\rho^{(2)}}=-\frac{B}{\rho^{(2)}}\left(\frac{\phi[2\rho^{(2)}h^{(2)}+(h^{(2)})^2]}{2\rho^{(1)}\theta}-h^{(2)}\right). \tag{2}$$

The inclusion of the Laplace pressure, the pressure just inside the oil-gel interface, gives $p^{(i)}=\gamma/\rho^{(i)}-\sigma_{\mathrm{rr}}^{(i)}|_{r=\rho^{(i)}}+p_0$, where p_0 is the pressure in the aqueous phase and γ is the effective oil-gel-water interfacial energy. As we suppose that the pressure inside the droplet quickly reaches mechanical equilibrium, i.e., $p^{(1)}=p^{(2)}$, the dynamics of the bleb formation is described through the time evolution of $h^{(i)}$ as

$$\partial h^{(i)}/\partial t=k_1-k_2\exp(\,\beta\sigma_{\perp\perp}^{(i)}|_{r=\rho^{(i)}+h^{(i)}}), \tag{3}$$

where k_1, k_2, and β are positive constants that represent the rate of generation of the gel on the oil-droplet interface, the breaking rate of the gel in the stress-free condition, and the effect of the stress on the gel breakage, respectively. In this model, the radial stress $\sigma_{\mathrm{rr}}^{(i)}$ increases the internal pressure of an oil droplet and the tangential stress $\sigma_{\perp\perp}^{(i)}$ promotes the breakage of the gel.

Assuming that h_0 is the steady solution of the unperturbed part [Eq. (3) $(i=1)$], bleb formation occurs for a perturbation given on $\theta>\theta^*$ according to the linear stability analysis of [Eq. (3) $(i=2)$] [7], where

$$\theta^*=\frac{1}{h_0}\sqrt{\frac{6\gamma\rho^{(1)}}{B}} \tag{4}$$

under the condition $\theta\ll 1$.

The result of the theoretical consideration is schematically depicted in Fig. 3(b). Under the condition $\theta>\theta^*$, the slight decrease in thickness of the gel in the perturbed area induces deformation of the oil droplet, and the deformation results in an increase in tangential stress in the gel that induces further thinning of the gel. By contrast, the gel thickness recovers and blebs cannot be formed when $\theta<\theta^*$ [Fig. 3(b)]. Note that the system must adopt a low interfacial energy as compared with the stress from the gel in order to have a small θ^*. This equation also predicts that, for large h_0, the size of the instability onset of the bleb (θ) becomes small. For large C_{s} and C_{p}, we can say qualitatively that generation of the gel is promoted so that large h_0 is realized. Thus, this result indicates that smaller blebs are generated for the higher C_{s} and C_{p} values. This prediction corresponds to the experimental results (Fig. 2).

As a summary of the theoretical considerations, the bleb formation occurs in a system where (1) generation of the gel-like structure is mainly limited by the periphery of the fluid droplet; (2) generation of the gel-like structure is slow compared with the deformation; and (3) the effective interfacial energy is low enough compared with the stress from the gel-like structure. The conditions 1 and 2 are satisfied if the component of the gel-like structure is separately dissolved into two fluids which comprise the interface. These criteria are satisfied in our system, as palmitic acid, one of the presumed components of the gel-like structure, dissolved in tetradecane is not well soluble in the aqueous phase. In relation to the condition 3, many reports have indicated that different types of gels are generated [8–11], whose typical elastic constant $B\sim 10^2-10^3$ Pa and an ultralow interfacial energy can be achieved in an oil-water-surfactant systems, such as systems generating microemulsions [8,12] whose effective interfacial tension could be small as $\gamma\sim 10^{-6}$ N/m. To have $\theta^*\sim 1$, with $B\sim 10^2$ Pa, $\gamma\sim 10^{-6}$ N/m, and $\rho^{(1)}\sim 10^1$ mm, h_0 must be on the order of 10^{-5} m, which is a reasonable value. Thus, the theory implies that the bleb formation could be a general phenomenon for oil-water-surfactant systems in chemically far-from-equilibrium conditions.

The quick shrinkage of the bleb can be explained under the same framework. According to the above-mentioned model, the thickness of the gel decreases with growth of the bleb. As the thickness of the gel approaches zero, the interfacial energy between the oil phase and the aqueous phase changes from γ to γ_{ow}, which is the interfacial energy of the direct oil-water interface. We may suppose that γ_{ow} is much larger than γ [8]. Such drastic increase in the interfacial energy results in destabilizing the bleb. As a result, the bleb shrinks.

As another interesting situation, a floating oil droplet shows splitting as well as bleb formation, when C_{s} is small. Here, the spontaneous deformation of the oil droplet is exemplified in Fig. 4, where $C_{\mathrm{s}}=1$ mM and $C_{\mathrm{p}}=10$ mM. A 1000-μl oil droplet was added to 100 ml of the aqueous

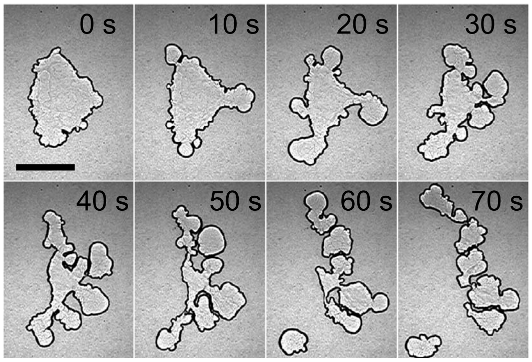

FIG. 4. Snapshots of droplet deformation, where $C_s = 1$ mM and $C_p = 10$ mM. The scale bar corresponds to 20 mm. See also the movie [5].

solution in a Petri dish with a diameter of 12 cm. The induction period for this situation was about 1 min. It was observed that some of the blebs grew large enough to induce fission of the droplet. Gradually, the oil droplet broke up into smaller droplets ($\sim$10–100 μl) (Fig. 4, and movie [5]). Considering that the gel-like structure is generated on the surface of the oil droplet and induces higher internal pressure, the basic mechanism of the droplet motion could resemble the motion of the real slime mold [13].

It is also interesting to note that bleb formation is a new type of instability in oil-water-surfactant systems, where the Marangoni instability is often observed [14,15]. In this sense, it is expected that the cooperative instability of bleb formation and the Marangoni instability would be widely observed in a variety of oil-water-surfactant systems.

Our research on this purely nonbiological system demonstrates basic characteristics of bleb formation that will be useful in understanding the complicated biological phenomena. This system allows us to easily tune the parameters of bleb formation at a greatly reduced cost compared with systems using biological materials. Overall, this study not only helps us to understand the physicochemical mechanism of bleb formation in biological systems but also should inspire research on the dynamics of soft condensed matter in far-from-equilibrium conditions, especially as a model system of energy transduction in living organisms.

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