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Self-Propelled Motion of Micrometer-Sized Oil Droplets in Aqueous Solution of Surfactant

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Additional information is available at the end of the chapter

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Abstract

When an immiscible oil is dispersed in an aqueous solution of a surfactant, emulsions consisting of various-sized oil droplets are generated. Micrometer-sized oil droplets exhibit exotic dynamics such as self-propelled motion in the surfactant solution. Transfer of the surfactant from the aqueous solution phase to the oil droplets through their interface leads to the self-propelled motion in a far-from-equilibrium condition. In this chapter, we demonstrate the observation methods of the self-propelled motion of micrometer-sized oil droplets using phase-contrast, polarized, and fluorescence microscopes and discuss their motion mechanism. Since the generated self-assemblies in micrometer-sized droplet systems are difficult to be identified by spectroscopic methods, the mechanisms of their self-propelled motion have not been clarified. When they are fully understood from nano- to microscale, these findings may be useful to develop not only more stable emulsion systems but also droplet-type analysis systems at the micrometer scale that can carry out reaction, analysis, and detection automatically without the need for an external force.

Keywords: cationic surfactant, chemical reaction, far-from-equilibrium state, interfacial tension, Marangoni effect, micrometer-sized oil droplet, optical microscope, self-propelled motion

1. Introduction

Oil and water are immiscible liquids. When oil is added to water and the mixture is stirred vigorously, oil droplets and water droplets are dispersed in the oil and water phase, respectively. This increases the total area at the oil-water interface; therefore, such an emulsion is unstable. As a result, droplets aggregate and fuse gradually to minimize the contact area between the oil and water phase. To improve the stability of emulsions and utilize those emulsions as

functional capsules in fields of cosmetics, pharmaceuticals, and foods, many physical and chemical approaches have been developed. Therefore, emulsion science and technology is necessary for an improvement in quality of life. In this chapter, we do not describe a stabilization technology for emulsions but rather a research trend in the behavior of micrometer-sized droplets within emulsions in a far-from-equilibrium state. Namely, the phenomena of oil droplets moving three-dimensionally (self-propelled motion) in a ternary system composed of water, oil, and surfactant and the methods to measure this motion are described.

Surfactant molecules form various types of self-assembly in water or buffered aqueous solution [1]. At a relatively low surfactant concentration in water, colloidal self-assemblies, such as spherical, disklike, rodlike, or wormlike micelles, are formed spontaneously. When a small amount of the oil components is added to such a colloidal system, it is solubilized within micelles. An electron microscope is required for the observation of these swelling micelles (microemulsions). They are stable thermodynamically, and this is defined as an equilibrium condition in this chapter. When the oil component is further increased, emulsions consisting of oil droplets with diameters ranging from nanometer to submillimeter are formed. For example, upon the addition of an oil component that was almost insoluble in water, such as *n*-hexane and chloroform, to aqueous surfactant solution of a relatively low concentration, the dispersion became turbid, and, in a short while, it separated into water and oil phase. However, when some specific oil components were dispersed into a similar surfactant solution, the dispersion was not separated into two phases but turned turbid over a week. Interestingly, immediately after the addition of the oil component, it was observed under an optical microscope that oil droplets with diameters ranging from 5 to 100 μm were self-propelled in a dispersion that was partly turbid (**Figure 1**). Self-propelled motion of these spherical droplets had a locomotion speed of above 5 $\mu\text{m}/\text{s}$, which was significantly faster than the random walk of micrometer-sized colloidal particles. In other words, the observed self-propelled motion could be distinguished from Brownian motion. Though the self-propelled motion of these droplets ceased within an hour, the spherical droplets were stable. This phenomenon was observed in a far-from-equilibrium state that gradually approached equilibrium eventually and is of great interest because the micrometer-sized objects moved without the addition of external forces. Note that these observed results depended on the intensity of stirring and composition of emulsion system.

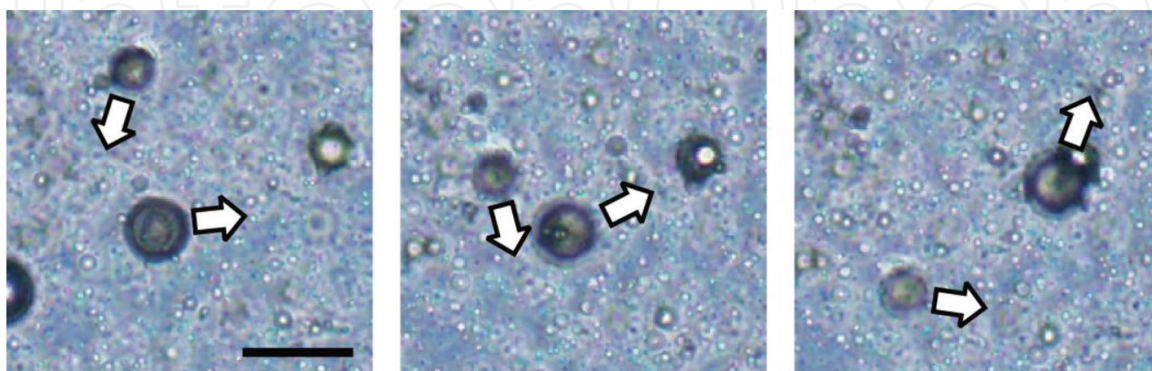


Figure 1. Typical sequential micrographs (time interval = 3 s) of self-propelled motion by micrometer-sized spherical oil droplets in a ternary system composed of water, oil (*n*-heptyloxybenzaldehyde), and surfactant (*N*-hexadecyl-*N,N,N*-trimethylammonium bromide) at room temperature (23–25°C). The arrows indicate the direction of the self-propelled oil droplets. Bar: 100 μm .

2. Observations of micrometer-sized self-propelled oil droplets

2.1. Optical microscopes for the observations of oil droplets in aqueous solution

A bright-field stereomicroscope can be used to observe micrometer-sized oil droplets in aqueous solutions when oil droplets are thick and their refractive index is significantly different from their surrounding medium (the bulk solution). However, when the difference in refractive index is small and the oil droplets are thin, specific microscopes are required for observation. In this section, the operating principles of polarized, phase-contrast, and fluorescence microscopes, which are used regularly for the observation of soft matter, including oil droplets at the micrometer scale, are introduced briefly.

2.1.1. Polarized microscope

When the surfactant concentration is relatively high in an emulsion system, the nematic and lamellar structures of lyotropic liquid crystal phases are formed. Since the interaction of each phase with light differs because of the different molecular orientation, the structures can be characterized by the texture of polarized microscopy images. In the system of a polarized microscope, the transmitted light through samples, placed on a stage between two polarizers oriented at 90° to the illumination, is observed. Since birefringence occurs because of the optical anisotropy of phase in the sample, the phases within the sample can be identified from the observed textures. For example, to investigate the stability of a ternary system, Abe et al. investigated dimyristoylphosphatidylcholine/water/saturated hydrocarbon, where propanol was added as a cosurfactant, and clarified the composition that generated a stable oil-in-water microemulsion using a polarized microscope [2]. In addition, Ho et al. observed a dispersion prepared by stirring lauryl or cetyl alcohol with a sodium lauryl sulfate aqueous solution using ultrasonication, under a polarized microscope [3]. By varying the alcohol concentration and temperature, various phases such as the schlieren textures of the nematic liquid crystal phase were confirmed. No textures were observed in self-propelled oil droplets under a polarized microscope unless water-insoluble molecules exhibiting a thermotropic liquid crystalline phase were used, indicating that they were not in a liquid crystal phase but an isotropic liquid phase. Self-propelled micrometer-sized droplets comprising thermotropic liquid crystal phases in a surfactant solution have recently gained substantial attention regarding the topological defect of the droplet in self-propelled motion [4].

2.1.2. Phase-contrast microscope

Phase-contrast microscopes are suitable for the observations of transparent specimens, in which their refractive index is similar to that of the surrounding medium (such as living cells and bacteria). Self-propelled motion of micrometer-sized oil droplets in aqueous surfactant solution has also been observed under a phase-contrast microscope. Visualization of transparent specimens with a low refractive index has been achieved by utilizing the diffraction and interference of light. **Figure 2** shows the optical path and operating principle of visualization in this microscope system. A phase-contrast microscope has a ring slit in the condenser, and the objective lens is equipped with a phase-shift plate (**Figure 2A**). The ring-shaped illuminating

light that passes the ring slit in the condenser is focused on the phase-shift plate and is guided to the image plane through an objective lens uniformly. However, in the presence of a specimen between the condenser and objective lens, some of the illuminating light is diffracted by the specimen and separated into two diffraction order beams (the +1 and -1 order) and one remaining light beam, which is unaffected by the specimen (zeroth-order diffracted light), known as the background light. The two diffracted light beams change with the direction of travel and are therefore not focused on the phase-shift plate. On the other hand, the zeroth-order diffracted light beam goes straight ahead and passes the phase-shift plate. Thus, three light beams are focused on the image plane of the objective lens. The image contrast is strengthened by the following two factors: the generated interference between the diffracted and background light rays in the regions of the field of view that contain the specimen and the reduction in the amount of background light that reaches the image plane.

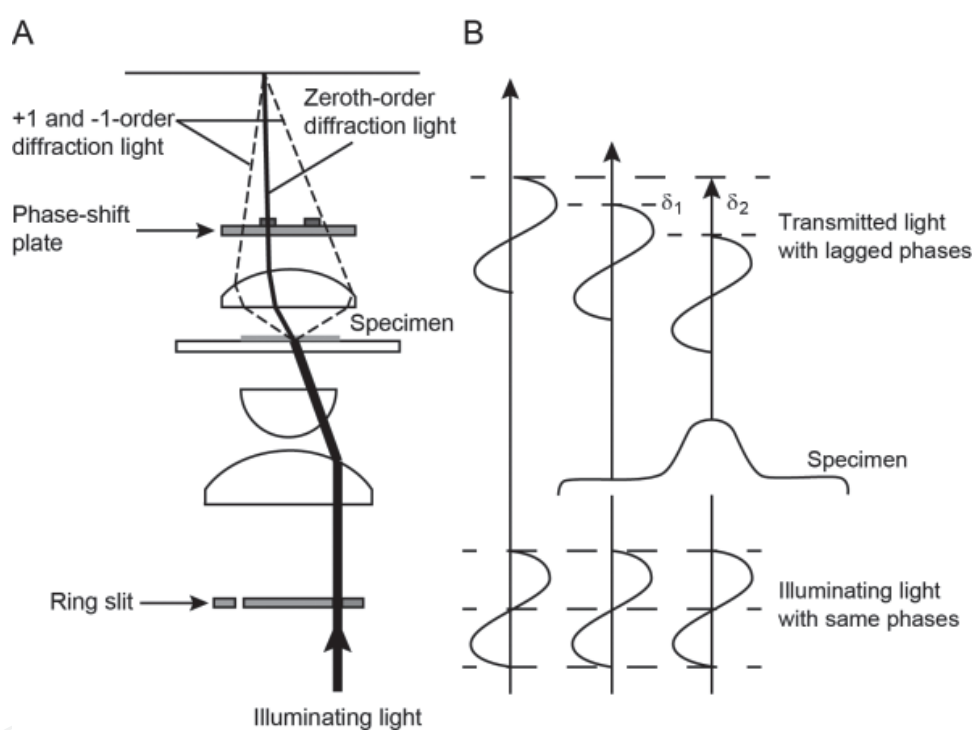


Figure 2. Schematic illustration of optics (A) and operating principle of visualization (B) of a phase-contrast microscope. δ_1 and δ_2 are the lagged phase between the transmitted light rays through the specimen and that of the background, respectively.

For example, if it is considered that the phase of the zeroth-order diffracted light is directed by the phase-shift plate, the light intensity is zero on the image plane where the three light beams interfere and, thus, the image of the specimen should have dark contrast in the bright field of view. In contrast, when the zeroth-order diffracted light is lagged compared to the other two diffracted light beams, the light intensity becomes maximum because of the interference between the three light beams. Therefore, the image of the specimen with bright contrast is observed in the dark field of view. On the basis of these principles, a transparent specimen, which is difficult to distinguish from the surrounding medium using a bright-field microscope, can be observed by strengthening image contrast.

On observing the self-propelled oil droplets using a phase-contrast microscope, it was found that the interior of the droplets had many small particles and they formed a convective flow. The direction linked with the inlet and outlet of this convective flow was the same as the self-propelling motion direction of the droplets, considering that their motion could be associated with the flow fields within the droplets.

2.1.3. Fluorescence microscope

Dynamics of molecules and particles which are labeled by fluorescent molecules and particles can be traced selectively. Therefore, fluorescence observations have been frequently used in the life sciences. A transparent specimen can be observed under a phase-contrast microscope. By using a fluorescence microscope simultaneously, the specific molecule and its distribution can be visualized in a specimen.

When a substance, which absorbs light energy and emits its energy as light, is illuminated by excitation light, such as X-rays, ultraviolet light, or visible light, the transition of its electrons from the ground state to the excited state occurs. However, because this excited state is unstable energetically, the electrons that absorb energy relax readily to their ground state. In this relaxation process, the emitted light is fluorescence. The relaxation time from an excited state to a ground state is short, below ~10 ms in general, and the luminescence is quenched due to fading of a fluorescent substance under a continuous excited light. Taking this into consideration, the system of a fluorescence microscope has a specific set of operation principles.

In general, if a fluorescent dye has a suitable molecular structure for emitting fluorescence in a specimen, the distribution and migration of a fluorescent dye can be detected easily. The distribution and migration of multiple structures are also observed simultaneously by using multiple fluorescent dyes. In addition, if the background brightness is lowered considerably, the detection sensitivity using a fluorescence microscope is much higher than when using other observation techniques. Therefore, this technique is frequently used for the observation of the dynamic behavior of self-assemblies formed by amphiphiles in aqueous solution. For example, micrometer-sized droplets in a ternary emulsion system composed of water, oil, and surfactant exhibited demulsification triggered by a photoisomerization of the photoreactive surfactant having an azobenzene group [5]. This phenomenon was clarified by fluorescence observations using a hydrophilic fluorescent dye, calcein, and a hydrophobic fluorescent dye, pyrene. In oil droplet systems that exhibit self-propelled motion, the fluorescence microscopy technique is considered to be effective for visualizing the convective flows of the droplets.

2.2. Mechanism of self-propelled motion of oil droplets

2.2.1. Observation of self-propelled motion of oil droplets

Self-propelled motion of micrometer-sized oil droplets has been observed in dispersions composed of specific oils and surfactants as shown in **Figure 3**. For example, in a dispersion prepared by adding a benzaldehyde-type oil component (1) to the aqueous solution of a cationic surfactant having a primary amine group at the end of its molecular structure (2), self-propelled motion of oil droplets accompanied by an internal convective flow was observed

under a phase-contrast microscope. The micrometer-sized structures of closed membranes (giant vesicles) were stripped off at the inlet position of the convection at the surface of this droplet, releasing giant vesicles at the opposite side of self-propelled droplet. In addition, by using a fluorophore with molecular structure similar to **1**, having 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) group, it was confirmed by fluorescence observations that giant vesicles were formed by the production of an amphiphile (**3**) in the droplet. Therefore, the unidirectional motion of self-propelled droplets may be related to not only inner convection but also the evolution of giant vesicles at the opposite side of the droplets [6].

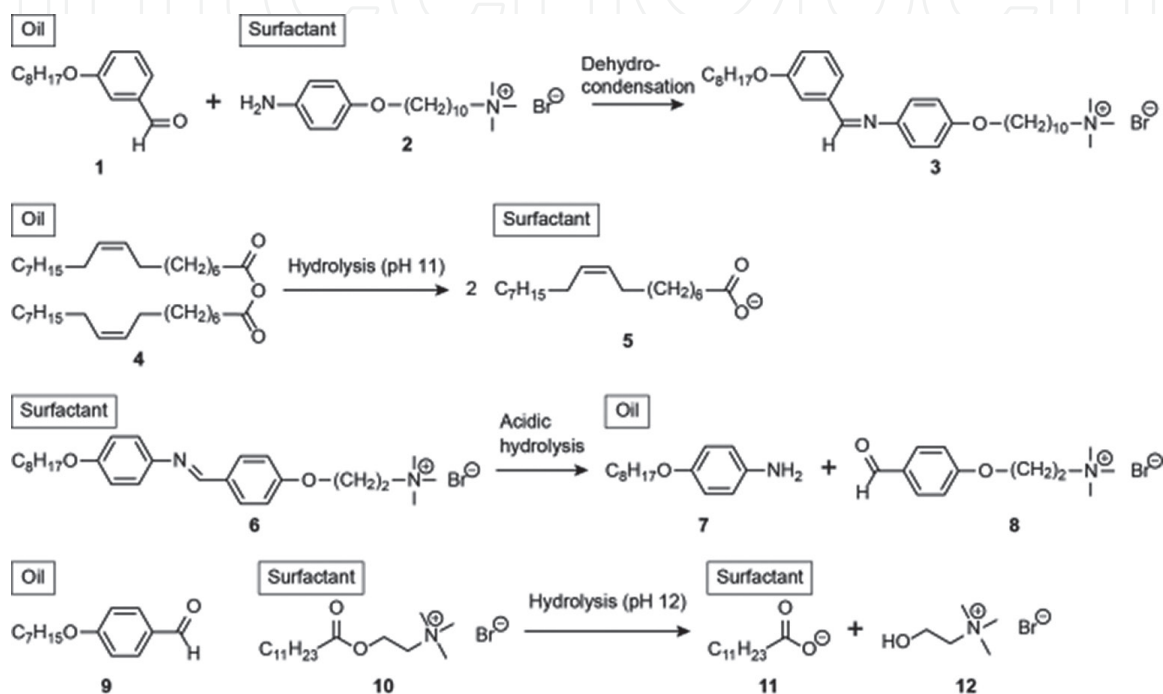


Figure 3. Reaction formula in emulsion systems in which micrometer-sized oil droplets were observed.

It has been found that self-propelled motion of oil droplets is caused by generated flow fields induced by the adsorption of surfactant molecules onto the droplet surface in dispersion. Hanczyc et al. reported that oleic anhydride (**4**) droplets containing nitrobenzene exhibited self-propelled motion in a solution composed of sodium hydroxide and sodium oleate (**5**) [7]. In addition, the droplets were self-propelled from a region of lower pH to that of higher pH in a certain gradient field. Thus, it was considered that the surface-active oleate, which was generated by basic hydrolysis of oleic anhydride, got adsorbed to the surface of the droplets, inducing the formation of flow fields. The unidirectional motion of droplets was a result of the flow fields caused by such local adsorption of surfactant molecules. Moreover, in a solution of an imine-containing cationic surfactant (**6**), aniline-derivative (**7**) droplets with diameters of 10–140 μm exhibited self-propelled motion accompanied by the evolution of waste oil droplets with diameters of 1–3 μm on the posterior surface. By tracing the behavior of the droplets using a fluorescence microscope, it was visualized that their dynamics were triggered by the generation of flow at the droplet surface accompanied by the hydrolysis of **6** to produce oil component **7** and electrolyte **8** [8]. Recently, it was also observed that oil droplets composed of *n*-heptyloxybenzaldehyde (**9**) moved autonomously as aggregates formed on their surface in an ester-containing cationic surfactant

(10) solution under a basic condition [9]. This was likely because of the production of lauric acid (11) and electrolyte 12 by the hydrolysis of surfactant 10 and the subsequent neutralization of the fatty acid with sodium hydroxide, forming a cation-anion complex surfactant because of the ionic bonding. These results indicate that the molecular conversion of oil or surfactant component is a key factor, which influences the driving force of droplet motion. In addition, oil droplets composed of benzaldehyde-derivative 9 were self-propelled in a solution of nonreactive surfactants, such as *n*-alkyltrimethylammonium bromide (CnTAB, *n* = 12, 14, 16) or gemini-type cationic surfactants having two hydrophobic and hydrophilic groups [10]. Thus, it is considered that self-propelled motion of oil droplets is strongly associated with not only the molecular conversion but also the molecular interactions between the surfactant and oil molecules.

2.2.2. Proposed mechanism for self-propelled motion of oil droplets

On the basis of the above findings, the mechanism of self-propelled motion of oil droplets is interpreted as follows (**Figure 4**). In a relatively concentrated surfactant solution, self-assembly of surfactant molecules, such as spherical and disklike micelles, distributes heterogeneously [11, 12]. On adding of an oil component into such a surfactant solution, oil droplets with various submillimeter sizes are formed. Surfactant molecules begin to adsorb onto the droplet surfaces, and heterogeneity of droplet surfaces is induced by nonuniform surfactant concentrations, as well as by thermal fluctuations. This causes an imbalance in the interfacial tension between sites with adsorbed surfactant molecules (lower interfacial tension) and bare sites (higher interfacial tension) on the droplet surface. The flow at the oil droplet surface based on the imbalance of the interfacial tension is maintained by Marangoni instability, indicating symmetry breaking [13]. Marangoni flow and subsequent mass transfer are likely caused by relatively strong intermolecular interactions between the surfactant and oil molecules. Furthermore, the momentum between inside and outside of the droplet is exchanged through the Marangoni flow, and the droplet itself is driven in a certain direction. These processes can be considered with regard to interfacial energy: the interfacial energy of the droplet's leading edge (where surfactants are adsorbed) is smaller than that of its trailing edge, inducing a slight movement of droplets including dynamic interfacial fluctuation. The more surfactant the moving droplet takes on, the more the droplet continues to move because of the flux balance between the oil droplet and the bulk solution. At the foreside of self-propelled motion, larger amounts of surfactant molecules adsorb to the droplet surface, and self-propelled motion occurs because of the feedback mechanism caused by the sustainment of flow fields. Thus, self-propelled motion could be affected by both the attractive interactions between the oil and surfactant molecules and the mobility of surfactant molecules at the droplet surface.

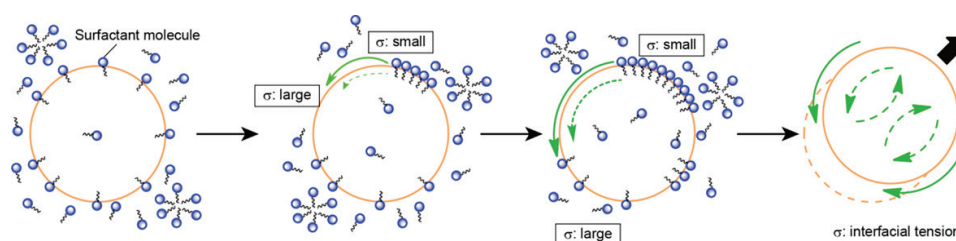


Figure 4. Schematic representation of the proposed mechanism for self-propelled motion of oil droplets. Surfactant molecules are omitted in the fourth image. σ , local interfacial tension of oil droplet surface.

2.2.3. Visualization of the surrounding and internal flow fields of self-propelled oil droplets

To verify the proposed mechanism of self-propelled motion of oil droplets experimentally, the surrounding and internal flow fields of droplets that were observed under a phase-contrast microscope should be analyzed in detail. These flow fields have been visualized, and their motion speed was analyzed using particle image velocimetry (PIV). This is a method that analyzes velocity and its vector of distinguishable particles (tracers), such as micrometer-sized fluorescent beads, in the flow fields by the following procedure. Firstly, the movement of dispersed tracers in the flow fields is monitored successively at a certain time interval. Secondly, the specified region containing some tracers in the n th image is correlated with a region in the $[n + 1]$ th image. From the comparison of these two images, the velocity and direction of tracers are calculated by the detection of the moving distances between them (**Figure 5**).

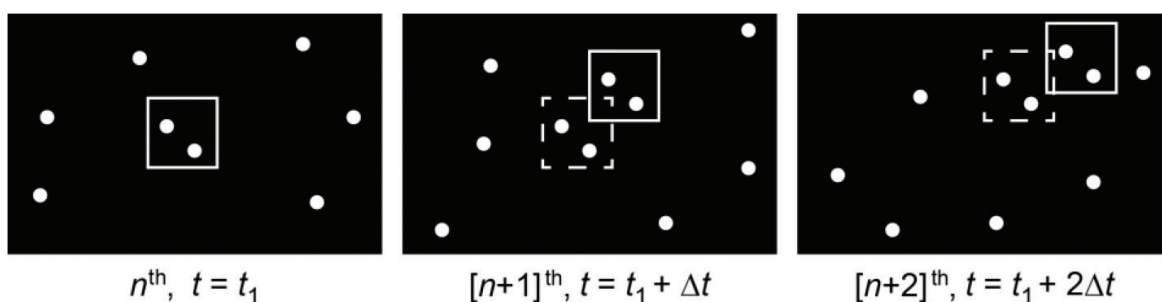


Figure 5. Principle of particle image velocimetry (PIV) measurement. The velocity vector of tracers (white circle) in the square region is calculated by the moving distance for a certain time interval (Δt).

Figure 6A shows the PIV results of self-propelled motion of oil droplets composed of benzaldehyde-derivative (**9**) in 50 mM C16TAB solution using micrometer-sized fluorescent polystyrene beads as a tracer. Hydrophilic fluorescent beads were used for measurements of the surrounding flow fields of the droplets. The surrounding flow fields observed in a pseudo-two-dimensional manner under a fluorescence microscope are shown in **Figure 6A**. The velocity of droplets was constant at ca. 20 $\mu\text{m/s}$. The velocity of the flow fields was accelerated and became maximum when tracers moved in the direction of a self-propelled droplet, which was from the region a to b along the droplet surface. On the other hand, it decreased when tracers moved in the opposite direction from region b to c. These results suggest that Marangoni flow occurred from the leading edge to trailing edge at the surface of the self-propelled droplets.

In contrast, hydrophobic fluorescent beads were dispersed into benzaldehyde derivative **9** for observations of the internal flow fields of the droplets. As a result, some flow fields were confirmed as indicated by white arrows in **Figure 6B**. By tracing the fluorescent bead carefully, it was found that the velocity of flow accelerated at the center (b') and the forward position (c') of the self-propelled droplet. The strong flow at the forward position may be derived from the flow of molecular assemblies composed of mainly oil components near the droplet surface accompanied with Marangoni flow. In addition, flow at the center may be because of molecular assemblies flowing from the backward to the forward position. Even though the PIV technique cannot produce precise information on tracers in terms of time and space resolution in

three-dimensional space, the proposed mechanism was supported by the pseudo-two-dimensional analyses discussed. Therefore, the analysis of flow fields using PIV is highly effective in the investigation of the mechanism of self-propelled motion of oil droplets.

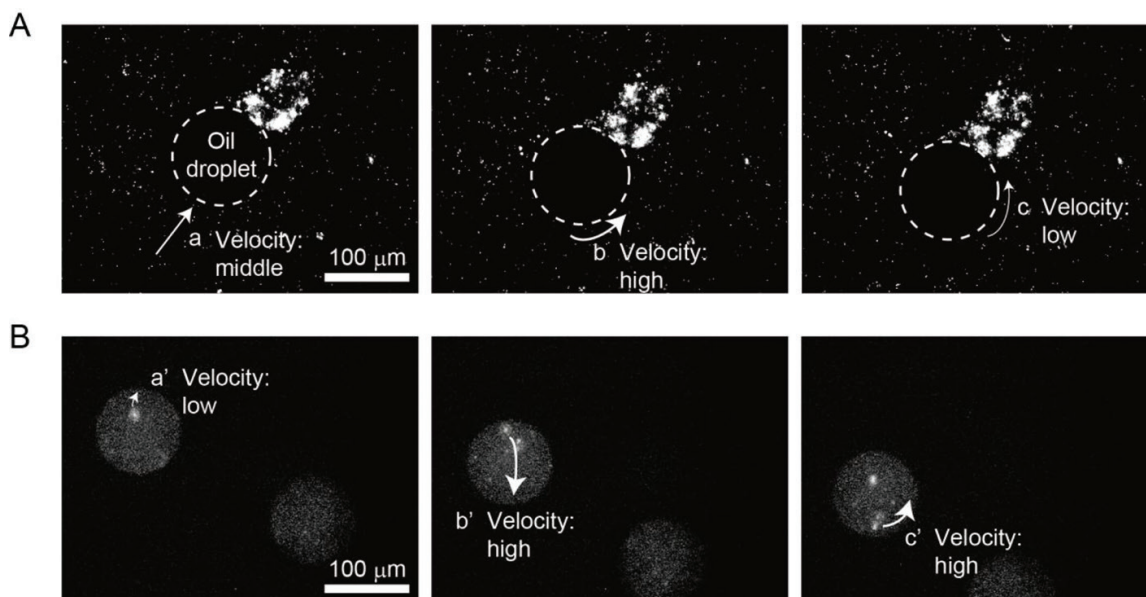


Figure 6. Visualization of the surrounding (A, time interval: 2 s) and internal (B, time interval: 3 s) flow fields of self-propelled oil droplet by using fluorescent beads under a fluorescence microscope.

2.3. Unique dynamics of micrometer-sized oil droplets in emulsion

From the proposed mechanism of self-propelled oil droplets based on the heterogeneity in the droplet surface, their motion time, direction, and mode may be controlled and altered by the molecular conversion of oil and surfactant components. Various organic reactions, such as polymerizations [14, 15], enzymatic reactions [16], and synthetic organic reactions [17–19], occur in emulsion systems because of an increase in reagent compatibility, the enhancement of reaction rates, and the induction of regioselectivity. In this section, we introduce the oil droplet system that induces unique dynamics, such as directional motion, division, and deformation, triggered by the molecular conversion of oil and surfactant components.

2.3.1. Guided directional motion

Micrometer-sized objects exhibiting well-controlled motion have drawn much attention because of their potential use as probes or sensors for exploring environmental or biological systems and as carriers for transporting compounds in very small spaces [20–22]. To control the motion time and direction of micrometer-sized oil droplets, gemini-type cationic surfactants containing a carbonate linkage in the linker moiety (**13**), the hydrolytic rate of which can be controlled by pH, have been designed and synthesized [23]. Oil droplets composed of benzaldehyde **9** exhibited self-propelled motion in an aqueous solution of pH 13 prepared by using **13** and sodium hydroxide. Their time of motion was longer than that in a basic solution

of cationic surfactant without a carbonate linkage. Moreover, in a solution of **13**, oil droplets at rest underwent unidirectional self-propelled motion in a pH gradient field toward a higher concentration of sodium hydroxide. Even though they stopped within several seconds, they restarted in the same direction. Gemini-type surfactant **13** was gradually hydrolyzed, accompanied by the evolution of carbon dioxide under basic conditions to produce a pair of the corresponding monomeric surfactants **14**, which exhibit interfacial properties different from **13**. The prolonged and restart motion of the oil droplets was explained by the increase in the heterogeneity of the interfacial tension of the oil droplets. Therefore, this system where a surfactant generates other surfactants with different surface activities from the original, in an aqueous phase, could be one effective strategy for controlling the motion time and direction of oil droplets (**Figure 7**).

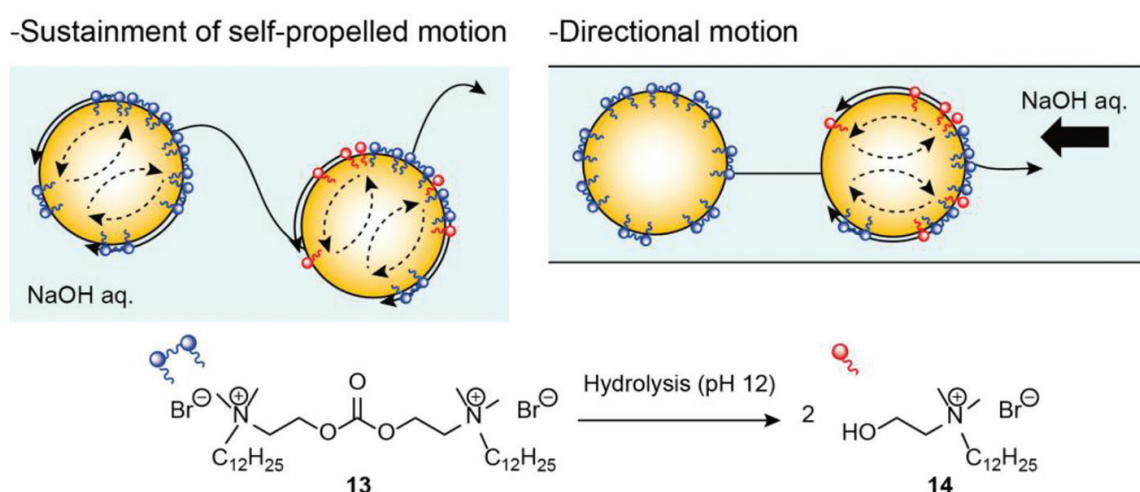


Figure 7. Schematic illustration showing the control of the motion time and direction of oil droplets in the presence of gemini-type cationic surfactant containing a carbonate linkage in the linker moiety under a basic condition.

2.3.2. Division

Even though oil droplets composed of benzaldehyde **9** exhibited self-propelled motion, they slowed down and eventually stopped because the system reached an equilibrium state in which interactions between oil and surfactant molecules were not sufficient for the induction of convective flows. Thus, the division of oil droplets during self-propelled motion is expected to occur through changes in the interaction between the components, such as the dispersion force and the ion-dipole interaction [24]. To induce such changes inside the oil droplet, 1-decanol (**15**) was added to the oil phase of **9**. Under a relatively high acidic condition, such oil droplet (mother droplet) exhibited not only self-propelled motion but also divided in the C16TAB solution. While the larger droplet (older daughter droplet) immediately self-propelled, several dozen smaller droplets (younger daughter droplets) floated in solution for approximately 1 min and then began to move. However, they were self-propelled and eventually dissolved away because of their solubilization in the bulk surfactant solution (**Figure 8A**). The self-propelled older daughter droplet also divided, and then the new older daughter droplet was immediately self-propelled. After the division, these dynamics were

repeated until the older daughter droplet was dissolved away in the solution. In this emulsion, the dehydrocondensation reaction of benzaldehyde **9** and alcohol **15** occurred gradually to produce an acetal molecule, 4-(heptyloxy)-1-didecyloxybenzene (**16**). The oil droplets of **16** were not self-propelled immediately, but several of them began to move after a few minutes in the same acidic C16TAB solution. In addition, acetal **16** was completely hydrolyzed within a few minutes and was not regenerated thereafter in the dispersion. These results indicate that acetal **16** was not the primary component for self-propelled motion and that a sufficient amount of benzaldehyde **9** was required for the induction of self-propelled motion. Therefore, such division during self-propelled motion is owing to the time-course change of the oil droplet component in the reversible reaction system [25].

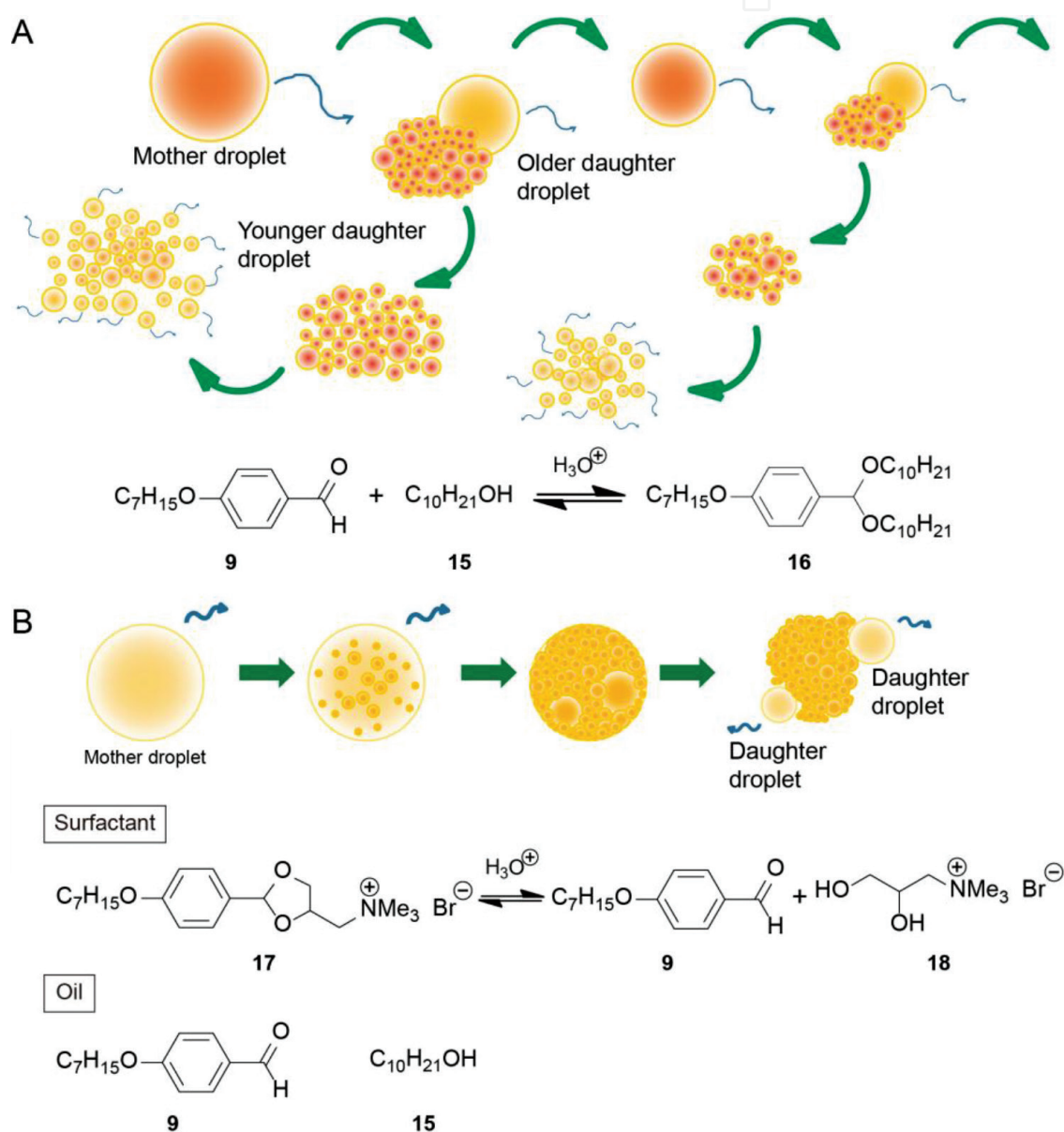


Figure 8. Schematic illustration of division during self-propelled motion of oil droplets induced by the reversible reaction of benzaldehyde **9** and alcohol **15** (A) and the hydrolysis of surfactant **17** to feed “fresh” benzaldehyde **9** into the self-propelled droplets (B).

A different division mode from the above system was also investigated using a cationic surfactant having a five-membered acetal moiety (**17**) that is hydrolyzed and affords a “fresh” benzaldehyde component (**9**) for the self-propelled oil droplets composed of benzaldehyde **9** and alcohol **15** (**Figure 8B**). In a solution composed of C16TAB and **17** containing HCl, the self-propelled motion of the initial oil droplet (mother droplet) continued until the droplet began to slow down, stopped, and then divided to release a small oil droplet (daughter droplet) which immediately self-propelled. Subsequently, other small oil droplets (daughter droplets) began to self-propel, and the daughter droplets continued in self-propelled motion. Surfactant **17** was hydrolyzed rapidly to produce benzaldehyde **9** and electrolyte **18**. On the other hand, acetal **16** was not generated under these acidic conditions. The molar fractions of **9**, **16**, and **17** did not show any change and almost reached equilibrium when the self-propelled oil droplets typically exhibited their division (ca. 10 min after the preparation of the emulsion solution), implying that the division of the self-propelled oil droplets was primarily derived from the supplied **9** and **18** (with C16TAB). Thus, the mechanism for division dynamics was proposed as follows. Self-propelled oil droplets took up the fresh benzaldehyde component (**9**) fed into them through hydrolysis of surfactant **17**, which led to the hypertrophy of oil droplets within themselves. Then, as the daughter droplets grew to reach a size that was sufficient for exhibiting the same self-propelling properties, they were released from the mother droplet [26].

2.3.3. Deformation

Although the above oil droplets maintained spherical morphology during self-propelled motion, there have been no reports on micrometer-sized self-propelled oil droplets mimicking amoeboid motion in aqueous solution. Similar to white blood cells, amoeboid motion of amoebae such as *Dictyostelium discoideum* [27] is one mode of cell locomotion associated with variations in body shape. Hence, micrometer-sized self-propelled oil droplets exhibiting such deformation could be applied as underwater carriers or probes in very narrow spaces and through many obstacles, similar to white blood cells invading blood vessels to attack tumors beneath the vessel.

To construct an oil droplet system exhibiting deformation, a mixture of two miscible compounds having similar molecular structure, fatty aldehyde **19** and fatty alcohol **15**, were used. The attraction between **19** and **15** is expected to induce spatial heterogeneity in the oil droplets. In addition, these compounds can generate acetal **20** under acidic conditions. Therefore, when these oil droplets were dispersed in a C16TAB solution, the heterogeneity resulted in differences in the adsorption and/or dissolution of the surfactant molecules at the surface and core of the oil droplets. When the molar ratio of aldehyde **19**/alcohol **15** was 60/40 mol%, self-propelled motion of the oil droplets was observed, and their shapes changed autonomously as shown in **Figure 9**. By using water-dispersed fluorescent microspheres with a diameter of 1 μm , the flow fields around self-propelled oil droplets exhibiting deformation were visualized, and their velocity was analyzed. The fluorescent microspheres at the back of the oil droplet flowed in the direction opposite to that of the oil droplet motion and approximately three times faster than those at the front of the oil droplets. The individual oil components, **19** and **15**, were liquid; however, their mixture at the molar ratio used became solid several minutes after mixing. This was likely owing to the strong attractive and non-covalent bond

forces between aldehyde **19** and alcohol **15**, such as hydrogen bonding and dispersion forces. On the other hand, though acetal **20** was produced in C16TAB solution containing 0.001–0.1 M HCl, its high production inhibited the induction of deformation dynamics. Therefore, there were two factors contributing to the deformation during self-propelled motion of oil droplets. These were the formation of a precipitous gradient field of interfacial tension at the back of the droplet surface and the localization of convective rolls inside the droplet caused by both the localized interfacial tension gradient and the spatiotemporal switching of intermolecular interactions among the surfactant and oil molecules [28].

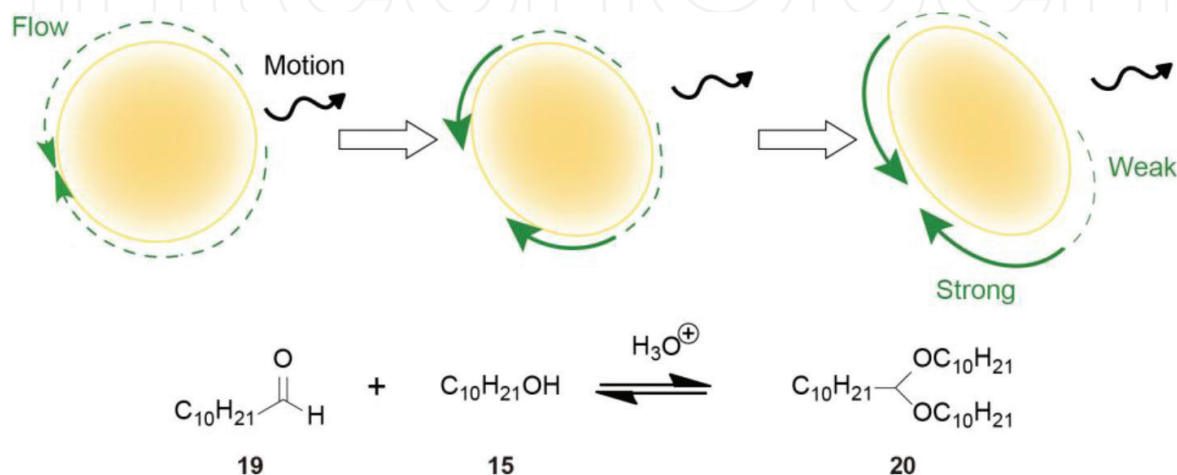


Figure 9. Schematic illustration of deformable self-propelled oil droplets composed of a fatty aldehyde and an alcohol.

3. Conclusions and future remarks

In this chapter, we demonstrate the observation methods for the self-propelled motion of micrometer-sized oil droplets using phase-contrast, polarized, and fluorescence microscopes and discuss the mechanism of motion. Since it is visible to human eye, self-propelled motion of the millimeter-sized oil droplets on the surface of aqueous solutions has been reported by many researchers [24, 29–35]. Recently, their divisions, fusions, and morphological changes have also been described. For example, Sumino et al. reported, with small-angle X-ray diffraction, that the gel phase formed spontaneously around millimeter-sized self-propelled oil droplets exhibiting “blebbing” [35]. However, since the generated self-assemblies in micrometer-sized droplet systems are difficult to identify by spectroscopic methods, the mechanisms of their self-propelled motion have not been clarified. When the mechanisms are fully understood at the nanometer to micrometer scale, the described findings will be useful to the development of more stable emulsion systems. In addition, such systems could be utilized for the reaction (microreactors) and transportation (microcarriers) of biomolecules and low-molecular-weight organic compounds [36, 37]. Furthermore, microchannel technology combined with the self-propelled droplet system is expected to lead to the development of droplet-type analysis system at the micrometer scale that can carry out reaction, analysis, and detection automatically without the need for an external force. We envisage that such automatic reaction field and analysis systems will be helpful for the improvement of novel emulsion technology.

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