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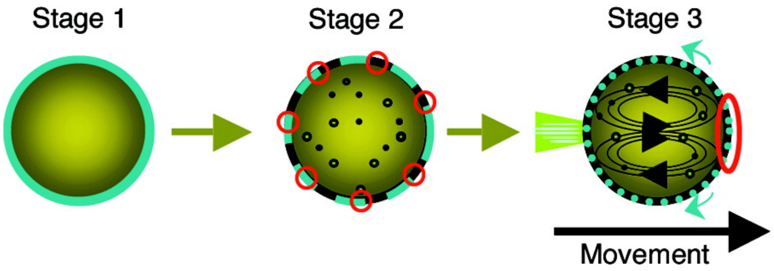

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Fatty Acid Chemistry at the Oil−Water Interface: Self-Propelled Oil Droplets

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Abstract: Fatty acids have been investigated as boundary structures to construct artificial cells due to their dynamic properties and phase transitions. Here we have explored the possibility that fatty acid systems also demonstrate movement. An oil phase was loaded with a fatty acid anhydride precursor and introduced to an aqueous fatty acid micelle solution. The oil droplets showed autonomous, sustained movement through the aqueous media. Internal convection created a positive feedback loop, and the movement of the oil droplet was sustained as convection drove fresh precursor to the surface to become hydrolyzed. As the system progressed, more surfactant was produced and some of the oil droplets transformed into supramolecular aggregates resembling multilamellar vesicles. The oil droplets also moved directionally within chemical gradients and exhibited a type of chemotaxis.

Introduction

Recent enthusiasm for the design and creation of artificial cells through chemistry and physics has focused primarily on the necessary characteristics of replication and metabolism. Here we investigate another essential and perhaps more fundamental characteristic of cells, the ability to move. If we consider a cell in broad terms as an open nonequilibrium chemical system, a supply of fresh material and energy is essential for sustenance of the system. The cell begins to modify its environment by metabolizing resources and producing products and waste. To avoid equilibrium, the system must somehow find new resources to exploit as well as avoid the inhibitory effects of waste products. In this purely chemico−biological sense, we believe that the ability to move will play an important role in avoiding equilibrium in the creation of artificial cellular systems.

Several in vitro models of contemporary cellular movement rely upon the assembly and dynamics of encapsulated protein matrixes.[1−4] The functionality of these models requires intact protein translation machinery and the corresponding metabolism infrastructure. More simplistic physicochemical models of movement have been reported in the past few years.[5,6] Of these, there are a number of works based on self-running oil in water systems containing surfactants.[7−10] For example, Sumino et al.[9] have shown that oil droplets in water can move laterally accumulating surfactant molecules adsorbed to the glass substrate. Toyota et al.[11] have reported that micrometer-sized oil droplets, which can produce membrane molecules by dehydrocondensation with a surfactant, exhibit autonomous swimming movement with vesicles trailing behind in the surfactant solution. In our system we sought to model movement of an oil droplet in a system composed of biologically relevant surfactants that can also undergo phase transitions to produce vesicular structures.

We describe a system of oil droplet movement based on fatty acid chemistry. Fatty acids were chosen because these simple, single-chain amphiphiles exhibit dynamic properties well suited for the synthesis of artificial cells.[12−15] In our two-phase system, the oil containing oleic anhydride precursor is introduced into an aqueous environment that contains oleate micelles. We show that the products produced by hydrolysis of the precursor are coupled to the movement of the oil droplet and the production of vesicles. Externally imposed chemical gradients foster directional motility of the oil droplets.

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Experimental Section

Oleate Surfactant. Neat oleic acid oil (NuChek Prep, Elysian, MN) was added to alkaline water to make 10 mM oleate micelles at pH 11.

Oil Phase. Neat oil of oleate anhydride (Fluka, Italy) was added to nitrobenzene (Fluka) at 0.5 M. As a control, the neat oil of oleic acid was added to nitrobenzene at 1 M. Pure anhydride was used in neat oil form. Anhydride oil stocks were stored away from direct light and under nitrogen.

Glass Slide Experiment with Phase Contrast Microscopy. Surfactant (100 μL) was added to glass slides with a concave depression (VWR, Milan, Italy) of 1.5 cm in diameter. An oil droplet (0.2 μL) was then added, and movement was monitored using microscopy. Running droplets were analyzed in real time using an inverted microscope with phase contrast optics from Specialty Microscopes with a Panasonic GP-KR222 camera and BTV Pro software.

Fluorescence Microscopy. Samples were analyzed on a Nikon Eclipse TE2000-S with Photometrics Cascade II 512 camera and in-house software. To visualize the origin of the internal oil structures, 10 μM calcein (Sigma-Aldrich, Italy) was added to the aqueous phase. To visualize changes in pH, 10 μM fluorescein (Fluka) was added to the aqueous phase.

Microscopy with DIC. Oil droplets and lipid mixture aggregates produced in the pure oleic anhydride system were visualized using an Olympus differential interference contrast (DIC) microscope, BX51, equipped with a TOSHIBA CCD camera connected to a video-recording system (Sony, WV-DR9).

Stepped pH Gradients. Surfactant (100 μL of 10 mM oleate at pH 11) was introduced to a glass slide with a concave depression of 1.5 cm in diameter. An oil droplet (0.2 μL of 0.5 M oleic anhydride in nitrobenzene) was then added to the surfactant with a pipet. A syringe was loaded with the same concentration of micelles at pH 10, pH 11 (control), or pH 12 and positioned near the oil droplet on the slide. The contents of the syringe were not released manually but were allowed to diffuse out slowly. The oil droplets were observed by phase contrast microscopy.

Size Exclusion Chromatography. The aqueous solution containing 1 mM calcein remaining on the slide after the droplets stopped moving was applied to the top of a 6.5 cm × 1 cm column of Sepharose 4B (Sigma-Aldrich). Water at pH 8 was used to equilibrate the column and elute the vesicles containing the calcein dye.

Results and Discussion

Description of Droplet Movement. When a droplet of 0.5 M oleic anhydride in nitrobenzene was added to the surfactant solution on the glass slide (Figure 1A), the clear oil droplet appeared as a symmetrical sphere (Figure 2A). Immediately, the oil droplet produced jerky movements while at the same time internal structures formed within the oil phase. The volume of the oil droplet typically decreased in this initial stage (compare Figure 2, parts A and B). The oil droplet began to appear turbid due to the accumulation of the internal structures within the oil phase. Initially, the structures appeared to flow within the oil droplet episodically, not continuously. Once the flow in the oil droplet became in phase, convective flow initiated and the oil droplet began to move in a direction commensurate with the direction of the convective flow (Figure 3). The moving droplets expelled lipid material as they moved. Often a droplet was observed with a lipid “tail” trailing behind the droplet (Figure 4). Droplet movement appeared to be directional with the lipid tail attached, and those droplets that have shed the tail moved more erratically. Often the movement of the oil droplet was up the wall of the shallow bowl in the glass slide (Figure 1A) and therefore against gravity. The velocity of the oil droplets decreased over time along with a reduction of the internal movement. Eventually the oil droplets stopped moving but the internal movement continued for many minutes more.

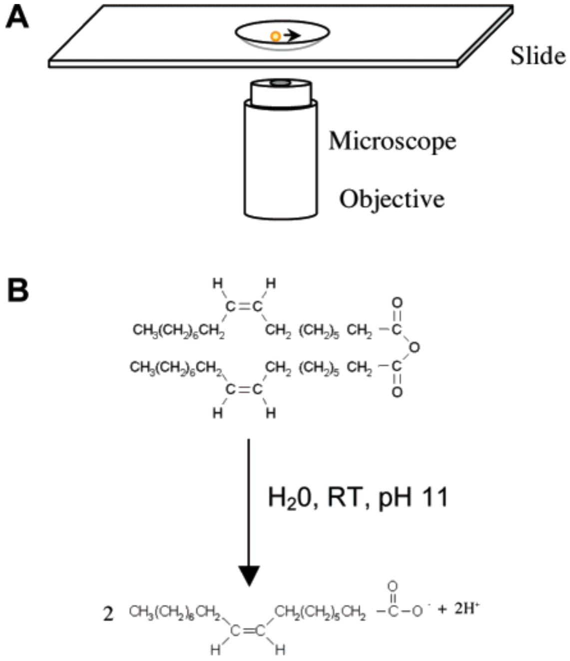

Figure 1. Experimental setup. (A) The concave depression in the glass slide was filled with 100 μL of aqueous solution. A small drop of oil was added by pipet and observed with an inverted microscope. (B) Oleic anhydride was hydrolyzed in the presence of water at high pH and room temperature to form two amphiphiles. Note that at high pH the fatty acids were deprotonated.

Factors Necessary for Lateral Movement of Droplets. A series of controls were performed to investigate the necessary factors responsible for droplet movement. When pure nitrobenzene oil without oleic anhydride was added to water at pH 11 that did not contain surfactant, the oil did not sink. Rather the oil droplet floated at the air−water interface. There was no lateral or internal movement. However, when the same oil drops were added to a solution containing 10 mM oleate, the oil drops sank to the glass−water interface due to the action of the surfactants coating the oil droplet. After many minutes, some droplets developed a few internal structures and slow internal movement within the oil phase was observed. There was no lateral movement.

As another control, oleic acid was mixed with the nitrobenzene oil at 1 M to simulate a case where all of the 0.5 M precursor anhydride has been hydrolyzed. Upon addition to the surfactant solution, these control droplets exhibited some internal and lateral movement as well with shedding of lipid material. But the movement was not sustained. Soon after the oil was introduced, a lipid film formed at the oil−water interface and grew until the droplet was completely encased. As soon as the film formed over the entire oil−water interface (about 1 min) all movement, internal and lateral, stopped (data not shown).

Decanoic acid (C10:0), a short-chain saturated fatty acid, was substituted for the longer chain monounsaturated oleic acid (C18:1) to determine the requirements for the spontaneous movement in the aqueous phase. Decanoic acid does not form micelles at low concentrations.[16] It was found that an oil droplet

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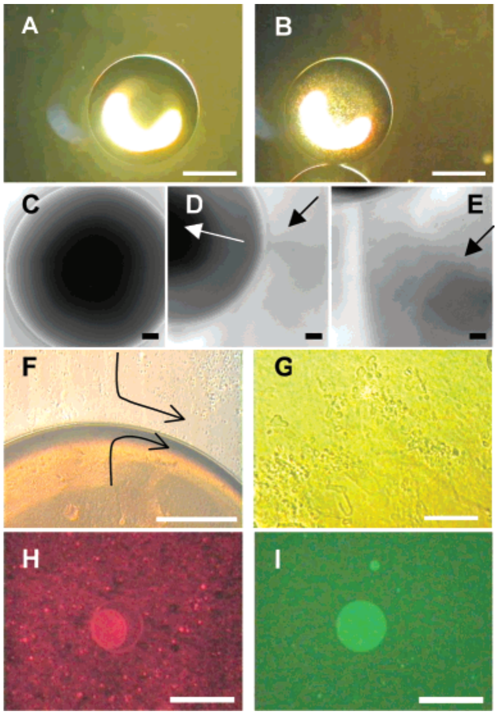

Figure 2. Microscopic images of oil droplets and products. (A and B) Formation of internal structures: (A) an oleic anhydride/nitrobenzene droplet observed 5 s after addition to the surfactant; (B) the same droplet as in panel A 25 s later is reduced in size and contains many internal structures. In this panel another droplet is partially visible having moved next to the droplet under observation. (C−E) Time sequence of moving oil droplet visualized by fluorescence microscopy: (C) A droplet of 0.5 M oleic anhydride in 10 mM oleate micelles was initially still. As the droplet started moving to the left (D) and then upward (E), a trail of decreased fluorescence became evident. The black arrow indicates the trail of low pH, and the white arrow indicates the movement of the oil droplet. Normalized time course: (C) 0 s, (D) 10 s, (E) 11 s. (F) Close-up image of oil droplet (below) and external aqueous volume interface (above). The direction of the internal convective flow and flow of external solution were coupled. Direction of flow is indicated by the arrows. (G−I) Products of the reaction: (G) long tubelike structures and closed circles were observed by phase contrast microscopy; (H) a giant fatty acid vesicle labeled with rhodamine 6 G; (I) the same vesicle as in panel H showing entrapped calcein fluorescence. Bar: 100 μm.

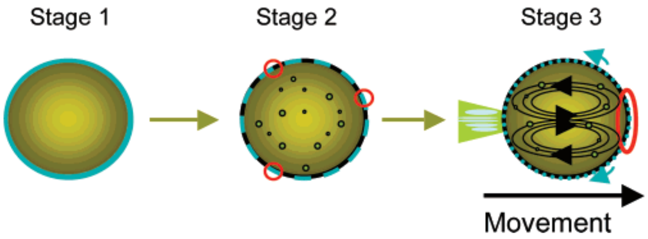

Figure 3. Two-dimensional schematic model of the initial stages in oil droplet movement. Stage 1: A fresh oil droplet (amber sphere) is introduced to the aqueous phase. The droplet appears symmetric and is coated in surfactant (blue line), and the oil phase is clear. Stage 2: Internal structures form within the oil droplet and begin to move as spontaneous oscillations exposing precursor to the water phase. Potential sites of hydrolysis are shown in red. The oil droplet now appears turbid. Stage 3: Symmetry is broken, convection begins (arrows within the oil), surfactant (blue) moves to the anterior pole (blue arrows), and hydrolysis of precursor is localized (red circle). The blue lines behind the droplet represent surfactant coming off the interface. The green zone indicates a zone of low pH. The large single arrow indicates the direction of lateral motion matching the direction of the centerline of convective flow.

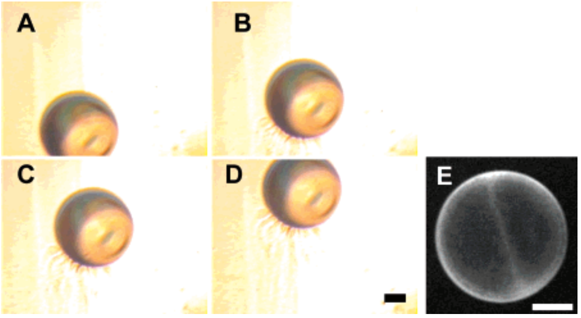

Figure 4. Droplet motion observed by microscopy. (A−D) Time sequence of moving oil droplet visualized by phase contrast microscopy. The droplet moved from the bottom to the top of the viewing area. Each frame was captured at 2 s intervals. There is a “tail” of lipid material attached to the moving droplet. (E) Fluorescent micrograph of an oil droplet with internal convection. The oil droplet was introduced to a micelle solution containing 10 μM calcein. The internal compartments that formed and moved within the oil droplet have incorporated calcein. Bar: 100 μm.

of decanoic acid (10 mM) at pH 11 still exhibited spontaneous motion (data not shown). This indicates that although surfactants are a prerequisite component of the moving system, they do not need to be supplied in a micellar form. On the other hand, oil droplets made of a saturated fatty acid, myristic acid (C14: 1), also moved as long as the temperature of the experiment was maintained above the melting temperature (T_m approximately 55 °C) of myristic acid. Below the melting temperature, the movement stopped (data not shown). This result demonstrates that the surfactant coating the oil droplet must be in a liquid state in order to support the movement. The desorption of surfactants from the interface would influence the convective flow of the interface of the oil droplet, and accumulation of sodium oleate that obstructs the oil−water interface causes the internal convection and lateral motion of the droplet to stop. As demonstrated in the control experiment when oleic acid was substituted for oleic anhydride, the fast accumulation of fatty acid at the interface quickly stops the movement. Therefore, both movements, internal and lateral, require an oil−water interface that is not coated by a thick layer of the product. The surfactants in solution may aid in desorption of fatty acids from the interface.

Internal Structures in the Oil Phase. Before movement, small internal structures began to form within the oil droplet. By the time lateral movement initiated many of these structures were present, and they flowed within the oil droplet convectively. To understand the nature of these structures, oil droplets containing 0.5 M oleic anhydride were placed in a micelle solution containing 10 μM calcein. If the internal structures formed from water entering the oil phase, then the internal structures would be fluorescent. With fluorescence microscopy, we observed that the internal structures in the oil phase glowed with the fluorescent signal from the aqueous calcein as shown in Figure 4E. The image also shows that the majority of internal structures are located at the surface of the oil droplet with one distinct line of structures flowing through the center of the oil droplet. The structures moved convectively from the outer surface of the droplet to the posterior end, through the center of the droplet, and out to the front. Given that these internal structures are aqueous and large enough to see with a low-power objective, it is likely that they have a structure similar to large reverse micelles with the surfactant acting as the boundary.

Even when pure nitrobenzene was added to the surfactant, some droplets were observed that contained a few internal structures. This could be explained by the mass transfer of sodium oleate to the interface, the formation of reverse micelles, and the dynamics of surfactant adsorption/desorption as seen in similar oil/water/surfactant systems.[17,18] The increase of water content within nitrobenzene oil due to the mass transfer of salts from the aqueous phase to the oil droplet has been investigated previously[19,20] in nitrobenzene/surfactant systems[21] and expressed theoretically by Yoshikawa and Matsubara.[22,23] Formation of water pockets within the oil phase would drastically increase the effective surface area of the oil−water interface and may serve as a repository for the sodium oleate. The existence of these structures may prevent stalling or termination of the convection when the local concentration of the product on the surface of the droplet becomes high.

Self-Generated pH Gradient. Interestingly, not only the lateral movement and the internal flow, but also the flow of aqueous solution surrounding the droplet contributes to the spontaneous movement. The direction of water flow is coupled with the direction of internal convective flow (see Figure 2F). This flow of water toward the leading edge may indicate the primary site of hydrolysis since water is consumed in the reaction. The water then flows around the droplet to the trailing edge.

Hydrolysis of the precursor produces two oleic acids, but at the high pH of the surrounding solution the products would quickly become deprotonated (Figure 1B). We investigated whether a zone of differential pH is generated proximal to the oil droplet during the movement. In order to monitor local changes in pH, oil droplets were added to 10 mM oleate micelle solution at pH 11 with the addition of 10 μM fluorescein. The fluorescence intensity of fluorescein is dependent upon pH and decreases when the pH passes below 7. As the droplet moved, a zone of low pH became apparent at the trailing edge of the droplet (Figure 2C−E). This zone of low pH was aligned with the centerline of the convective flow and correlated with the direction of the convection as well as the direction of lateral movement. As the droplet changed direction, the flow of low-pH solution from the trailing edge also changed being aligned with the centerline of the convection. Therefore, due to the chemistry in the oil droplet, a local pH gradient was self-generated of roughly four pH units from the leading to trailing edge.

If the movement of the oil droplets is governed by a self-generated pH gradient, then the droplets may respond to externally imposed pH gradients. Figure 5 shows a still droplet that was manipulated by the creation of local pH gradients. When oleate micelles at pH 10 were introduced through a syringe to the oil droplet in a micellar solution at pH 11, the internal convective flow became active and the droplet moved away from the low-pH solution (Figure 5, parts A and C). On the other hand, when oleate micelles at pH 12 were then introduced to the same oil droplet, the opposite response was achieved: the internal convective flow started toward the high-pH solution, resulting in the movement of the droplet into the higher pH solution (Figure 5, parts B and D). There was no response when micelles at pH 11 were added to the droplet as a control.

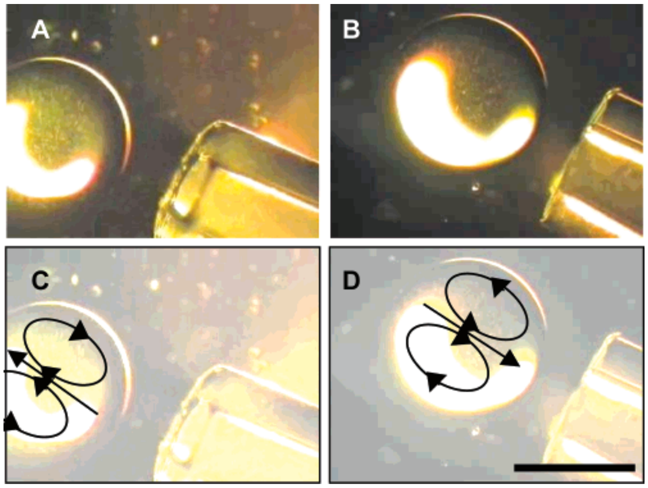

Figure 5. Control of oil droplet movement with imposed pH gradient. Micellar solutions at pH 10 (panels A and C) or pH 12 (panels B and D) were introduced locally to a still oil droplet at pH 11. The internal convective flow responds to the pH change by moving away from the low-pH solution and toward the high-pH solution as indicated by the arrows in panels C and D, respectively. Bar: 1 mm.

Products in the Aqueous Phase. Oil droplet movement produced a visually turbid aqueous solution containing many long tube-shaped structures and closed circles, that appeared to be vesicles (Figure 2G). To determine whether these vesicle-like structures act as proper compartments to retain solutes, 1 mM calcein was included in the micelle solution of a typical moving oil droplet reaction. Capture of calcein by the resulting vesicle-like structures was determined by fluorescence microscopy after size exclusion chromatography. The majority of structures produced in the oil droplet experiment contained the fluorescent dye, indicating that these structures represent typical fatty acid/soap vesicles with a trapped aqueous internal volume as shown in Figure 2, parts H and I.

When the carrier oil, nitrobenzene, was excluded from the system, the oil droplets of pure oleic anhydride also moved showing the internal and lateral motion, shedding tubular vesicle-like structures. The droplets proceeded through a similar series of stages as described above with the mixed oil system. However, some of the large oil droplets (with diameters of several dozen micrometers) underwent a phase transition to produce large aggregate structures as shown in Figure 6. This transition usually occurred when the droplets moved into an environment already containing many vesicle structures. The other oil droplets continued moving and generating vesicles in close proximity to the oil−water interface until each droplet completely was consumed.

The oleate produced through hydrolysis of the precursor is shed from the oil droplet as evidenced by the loss of volume of the oil droplet over time as well as the streams of lipid-like material expelled from the droplet. The thick membranous structures originating from and trailing behind the moving oil droplets may be primarily sodium oleate, which is the deprotonated product of hydrolysis, associated with the counterion in the solution. Surface convection on the droplet moves the surfactant toward the trailing pole where it accumulates if the mass transfer rates are slower than the surface convective flux.[24] Much of this material is then converted to vesicles as revealed

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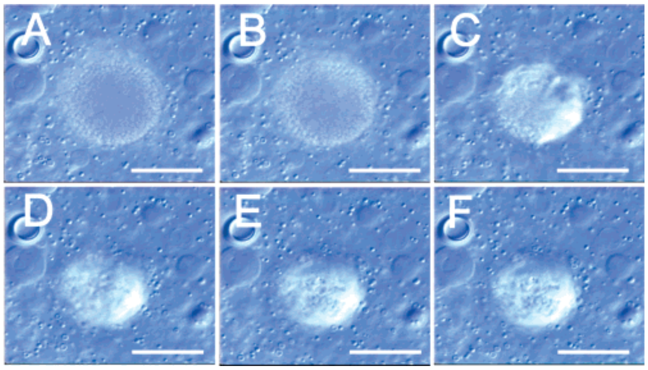

Figure 6. Sequential micrographs of a phase transition of a pure oleic anhydride droplet by DIC microscopy. Each frame (A−F) was captured at 0.2 s intervals. Bar: 50 μm.

through microscopic analysis of the aqueous phase (Figure 2, parts H and I).

The hydrolysis reaction often continues to completion. A small volume of clear nitrobenzene oil remains after many hours in the mixed oil experiments, and the phase transition and complete consumption of pure oleic anhydride occurs in the pure anhydride droplet experiments. However, in the mixed oil experiments complete hydrolysis often occurs long after the droplets stop moving with the continuation of internal flow. Lateral movement may require a certain degree of surface tension differential as the products of the reaction interact with the aqueous environment. In addition, the external water phase becomes acidic which likely slows the hydrolysis rate. If the rate of hydrolysis and thus the production of fatty acid slows, then the droplet will not move even though hydrolysis still proceeds slowly to completion.

As the precursor is hydrolyzed, the concentration of surfactant in solution increases and the pH of the solution decreases. If the pH of the solution is in the range of 7−9, oleic acid/oleate vesicles will form since the pK_a of the carboxyl head group in the membrane is approximately 8.5.[12] Therefore, it is not surprising that vesicles are produced by this system since the conditions support the formation and stability of lamellar structures.

We have also observed that the oil droplets consisting of oleic acid and not the oleic anhydride precursor can also move. Therefore, the hydrolysis reaction itself is not necessary for movement to occur, but rather the presence of the product of hydrolysis is necessary. However, in contrast with the anhydride system, the movement of the oil droplets with oleic acid is brief and not sustained.

Interpretation of Self-Propelled Oil Droplets. For a completely symmetric oil droplet to begin to move directionally, first symmetry must be broken. In our system we can detect four asymmetric processes: convection in the oil phase, water rushing into the leading edge, accumulation and expulsion of lipids from the trailing edge, and the self-generated pH gradient. The initial symmetry-breaking event may be caused by random oscillations at the interface. During an oscillation both surfactant at the interfacial boundary and the oil flow due to fast adsorption of surfactants to the interface followed by a slow desorption process.[21,25−30] When a patch of fresh oil becomes exposed to the water during a local oscillation, the Marangoni effect causes a flow of material at the interface toward the zone of high surface tension. This flow then causes the movement of fresh oil from the interior to move to the interface. Local seeds of product aggregation begin to form at the interface affecting the interfacial tension of the system. Stirring disrupts these oscillation events providing evidence that local gradients and dissipative dynamics play critical roles in the oscillatory behavior of the system.[22,23] When the sites of oscillation at the interface occur near one pole of the oil droplet, this triggers flow of oil due to a surface tension differential. This flow then becomes reinforced due to the initiation of internal convection. The localization of oscillation to one pole may be influenced by the self-organization of surfactant into lamellar structures along the interface, causing the flow of material at the interface, and internal flow becomes in phase. By in phase we mean that the oil droplet as a complete unit transforms into a convection cell and all the above-mentioned asymmetric processes can occur simultaneously. During this symmetry-breaking event, the release of product occurs at the opposite site to where the surfactant is dissolving into the naked oil droplet. In this way fresh oil is continually being exposed to the water phase forming a positive feedback loop that allows for continuous hydrolysis and convection (see Figure 3).

We have observed that the droplets self-generate a pH gradient in the solution proximal to the droplet, and this may affect the interfacial tension of the oil−water boundary with increased tension at the trailing edge. This would cause a flow of material from the leading to the trailing edge to compensate for the difference in interfacial tension. Such difference in the interfacial tension creates the convection flow coincident with the directional movement. A difference in interfacial tension due to pH effects may or may not play a role in the initial symmetry-breaking event but likely is responsible for continuous and sustained motion of the oil droplet.

Indeed Marangoni instability may explain not only the convection within the oil phase of the droplet but also the movement of the droplet. Theoretically, the Marangoni effect may spontaneously initiate motion and allow for self-sustained autonomous movement of a droplet in a surfactant-rich environment with enough force to create movement.[31,32] Observationally, the direction of lateral movement and the direction of convection are correlated with concomitant change in the direction of convective flow as the droplet changes trajectory. The above results suggest that the convection significantly increases both the rate of mass exchange in liquid/liquid extraction[33] and the rate of surface chemical reactions.[34] In our case, Marangoni convection would enhance the transport of the precursor to the interface, affecting the concentration of reaction products at the interface,[34] and if so, the rate of the reaction

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may become a primary parameter in modulation of the surface tension differential.

Significance of the Oil Droplet Systems. Simple chemical systems composed of moving oil droplets may fall into three categories. In the first category, thermal gradients within the oil phase produced asymmetrically by laser light resulted in floating oil droplets that moved. Here, the application of heat causes a difference in surface tension at the surface of the oil droplet resulting in the movement of the droplet along the air−water interface. This is driven by a thermocapillary or Marangoni convection-driven surface tension gradient.[10] This is similar to our system in that difference in surface tension create convection that produces movement of the oil droplet. However the thermal asymmetry system does not include a positive feedback loop and therefore does not produce autonomous sustained movement working only under external application of a thermal gradient. A thermal differential may also play a role in our system since the mixture of the fatty acid products with basic aqueous solution is exothermic and would produce heat. In addition the presence of a monolayer of oleate at the oil−water interface may serve as an insulator effectively prolonging the dissipation of any thermal gradient.[35]

In the second category, oil droplets move autonomously along a glass surface coated with amphiphiles.[7−9] The movement of the oil droplet depends upon differences in surface tension between the leading and trailing edge of the oil droplet. A surface tension difference results in differing contact angle between the oil droplet and the glass substrate as mediated by the surfactants in the aqueous phase. The initial movement and direction of the oil droplets moving along a surfactant-coated glass may be governed by thermal fluctuations that change the contact angle of the droplet with the glass. Once the droplet moves in a direction the movement is propagated by this difference in contact angle with the glass from the leading to trailing edge. If the glass surface is treated such that it eliminates surfactant adsorption, the droplets will not move. Movement in this system is dependent upon the adsorption of surfactants to a surface and the interaction of the oil with the surfactants. In our system, the glass substrate may not be important given that our droplets move on untreated (net negative charge at high pH) and polylysine-coated positively charged glass (data not shown). We do not observe any specific interaction with the glass surface and no shape distortion which would indicate difference in contact angle.

We place our system in a third category in which autonomous oil droplet movement is coupled to a chemical reaction. Movement is mediated through the surface tension differences at the interface brought about by a self-generated pH gradient. Motion is sustained due to a Marangoni instability causing convection that continuously exposes fresh precursor to the water phase allowing the chemistry to continue through a positive feedback mechanism. Motion can also be controlled with chemical gradients that impose a pH differential on the system. If the mechanism of droplet movement described here relies primarily on the production of acids within a basic environment, then many other chemical systems should also be capable of movement with the essential factors being an oil phase for the introduction of acids, the aqueous phase at high pH, and the presence of surfactant to mitigate the surface tension between the oil and the water.

Conclusion

We have demonstrated a self-propelled oil droplet system based on fatty acid chemistry. This system exhibits symmetry breaking with four characteristics: directional internal convective flow, directional external water flow, directional product release, and a self-generated pH gradient. The simple ingredients—oil with acid-producing precursor and alkaline water with surfactant—work in concert to produce sustained autonomous motion. The supramolecular structure itself contains the chemistry that fuels its movement. The system produces not only more surfactant but protons resulting in acidification of the environment immediately surrounding the oil droplet. The droplet successfully moves away from this waste product into fresh unmodified alkaline solution and even displays a primitive form of chemotaxis. Although this mechanism of movement is unlike mechanisms of motility employed by natural cellular life, directed motion by convection may be useful in an artificial cell context in the avoidance or delay of chemical equilibrium.

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Supporting Information Available: Movies that show the lateral movement of oil droplets with phase contrast microscopy and the internal convective flow with fluorescence microscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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