

Reactive spreading and recoil of oil on water

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Droplets of oil containing oleic acid were observed to spread, then recoil, on an aqueous solution of sodium hydroxide. Surfactant is produced at the interface during spreading, and for reagent concentrations of order $O(1 \text{ mM})$ spreading is observed to be much faster than in the absence of a chemical reaction [radius $R(t) \propto t^\alpha$ with $0.64 < \alpha < 0.89$]. After $t \sim 10 \text{ s}$, drops reach a maximum radius $R_{\text{max}} \sim 3\text{--}5$ times the initial radius. Spreading is faster and R_{max} is larger for higher concentrations of reagents. The drops are then observed to recoil (with apparent power-law behavior $-0.34 < \alpha < -0.14$), due to diffusion of surfactant away from the oil/water interface, with the rate of recoil being controlled by the NaOH concentration. © 2006 American Institute of Physics.
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The literature on spreading of thin films is vast, due to many applications in the fields of medicine, coatings and detergency amongst others.^{1,2} In this paper, we describe an unusual case of surface-tension-driven flow, where changes in surface tension produced by a chemical reaction at an interface drive a nonvolatile liquid droplet to spread into a thin film on a second immiscible nonvolatile liquid. The droplet spreads rapidly, reaches a maximum radius, and then slowly recoils back to a compact liquid lens. Although work has been reported on a great variety of problems involving (im)miscible and/or (non)volatile surfactants spreading and/or retracting (e.g., Refs. 3–10), to the best of our knowledge the spreading and retraction in the same system with nonvolatile immiscible fluids has not been reported.

A sketch of the experimental setup is given in Fig. 1(a). Before each experiment, a polystyrene Petri dish¹¹ was cleaned using distilled water and ethanol. The Petri dish was then filled with a weak aqueous solution of sodium hydroxide (NaOH, 0.5–1 mM) to a depth of $H=2.6 \text{ mm}$. Next, a droplet (approximate volume $0.1 \mu\text{l}$) of white heavy mineral oil¹² containing oleic acid (0.5–1 mM) was placed on the “water” surface using a micropipette. Upon contact of the drop with the substrate, oleic acid at the liquid-liquid interface reacts with the sodium hydroxide in the substrate to create sodium oleate (NaOleate). Sodium oleate is a surfactant that decreases the local oil/water surface tension σ_{ow} [Fig. 1(b)].¹³ This saponification reaction has been used in various pendant-drop and viscous-fingering experiments,^{13–15} and in these systems is known to decrease the oil-water interfacial tension as

$$\sigma_{ow} = \sigma_{ow,\infty} - (\sigma_{ow,\infty} - \sigma_{ow,0})e^{-kt}, \quad (1)$$

with a rate coefficient $k \approx 0.1 \text{ s}^{-1}$ that depends weakly on concentration (cf. Ref. 14). As a result, the spreading param-

eter $S = \sigma_w - (\sigma_o + \sigma_{ow})$ increases, thus providing the driving force necessary for the drop to spread. Spreading does not occur in the absence of the chemical reaction since $\sigma_o = 30.0 \text{ mN/m}$ and $\sigma_{ow} = 63.4 \text{ mN/m}$ (measured with pure oil and water using the pendant-drop method) so that $S = \text{const.} < 0$, and a liquid lens forms.

We observed the oil droplets from below using a charge-coupled device (CCD) camera with typical frame rates of 1–2 fps. Images of the spreading drop were analyzed using edge detection MATLAB software. The error in the drop radius is estimated to be less than 5% (the error is largest for the smallest drops). In each sequence of images, “ $t=0$ ” corresponds to the image *prior* to the first available image in which the micropipette no longer touches the drop; the largest possible error in the time scale is one time step in the video, which is less than 1 s. The initial radius $R(0)=R_0$ was extrapolated from the first six recorded radii by quadratic fitting.

A typical sequence of images of an oil drop spreading and recoiling is shown in Fig. 2. This particular drop contained 0.5 mM oleic acid, while the substrate contained 1 mM NaOH. As indicated by the length scales in the image, the drop spreads from an initial radius $R_0 \approx 0.4 \text{ mm}$ to R_{max}

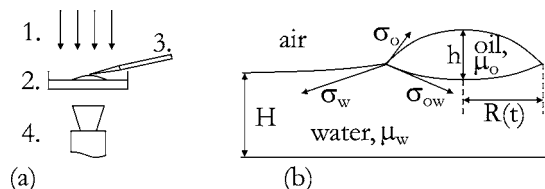


FIG. 1. Sketch of (a) the experimental setup and (b) a liquid lens on a liquid substrate indicating the relevant surface tensions and dimensions. Setup: 1. light source, 2. Petri dish with NaOH solution, 3. micropipette delivering oleic acid in an oil droplet, 4. video camera.

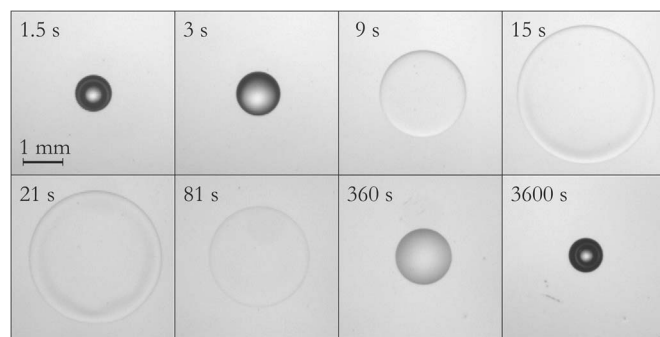


FIG. 2. Images obtained from a typical experiment. A droplet with volume $0.1 \mu\text{l}$ of 0.5 mM oleic acid was placed on 15 ml of 1 mM NaOH (2.6 mm deep). At about $t=15 \text{ s}$ the drop has obtained its maximum size $R_{\text{max}} = 1.75 \text{ mm}$, and a ring-like structure becomes apparent near the outer perimeter of the drop. The drop then recoils over a time on the order of minutes rather than seconds.

$= 1.75 \text{ mm}$, so that the thickness of the drop decreases to $h \approx 10 \mu\text{m}$. The times indicated in the images show how the spreading to R_{max} takes about 15 sec , after which the drop radius begins to decrease monotonically. The drop continues to recoil for many minutes until finally reaching a final radius similar to the initial radius. Note the visible appearance of the rim of the drop when it just reaches R_{max} and is about to start recoiling. The images suggest that recoiling starts at the rim, and creates a “tear”-like structure, which is thicker near the rim and thinner near the center of the drop. Though we have not systematically studied this phenomenon, this type of flow (near the rim only) corresponds to what is typically observed following film rupture.^{16,17} Subsequent images at later times indicate that the teardrop structure is likely a transient one; as viewed from above, the largest part of the recoil appears to occur with a drop shape that resembles a flat pancake (Fig. 2).

The spreading and recoiling data for four experiments with different combinations of the acid/base concentrations are shown in Fig. 3. The top graph shows the data on linear scales while the bottom graph uses logarithmic scales to identify any power-law-like dynamics. From this data we observe that the initial slopes of the spreading curves increase with increasing concentrations. The slowest spreading occurs for 0.5 mM acid on 0.5 mM base, and this also results in the smallest R_{max}/R_0 . The fastest spreading occurs for 1.0 mM acid on 1.0 mM base, and this combination creates the largest maximum radius. The two ‘in between’ cases (0.5 mM acid on 1.0 mM base and 1.0 mM acid on 0.5 mM base) show quite similar spreading dynamics and maximum radii. We comment on the recoiling dynamics below.

Several control experiments were conducted to verify that the observed dynamics were indeed caused by the interfacial chemical reaction. In the first control, oil was placed on water (no reagents or surfactant present); the oil spread slowly, eventually reaching an equilibrium drop radius with $R_{\infty}/R_0 \approx 1.25$ (Fig. 3). As a second control, oil was placed on NaOleate-containing water (at various concentrations). With 1 mM NaOleate in the water (this is just below the CMC), droplets of oil were seen to be emulsified rapidly, eventually disappearing from the surface entirely. For significantly

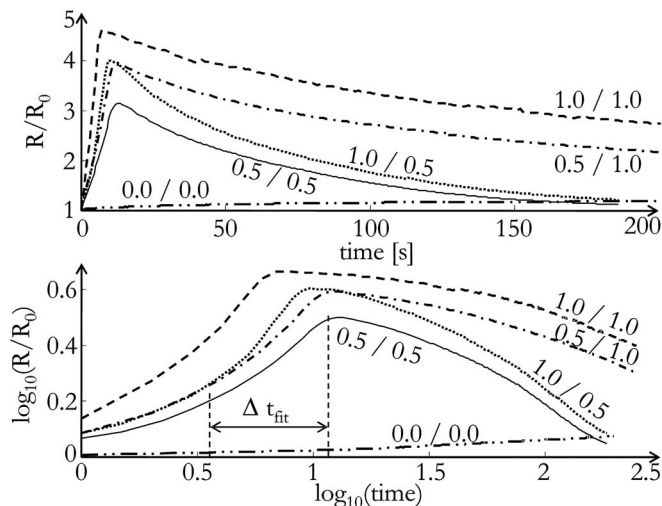


FIG. 3. Typical results for various concentrations of NaOH and oleic acid. Solid line: 0.5 mM acid on 0.5 mM base, dotted line: 1.0 mM on 0.5 mM , dash-dot line: 0.5 mM on 1.0 mM , dashed line: 1.0 mM on 1.0 mM . There were slight variations in the initial radius of these four experiments, $R_0 = 0.58, 0.58, 0.45, 0.55 \text{ mm}$, respectively. The lowest curve (dash-dot-dot) is the control with oil on water. These curves were chosen from a larger data set to represent typical results. Also indicated is Δt_{fit} , the time interval over which a straight line was fitted to obtain α_{spread} for 0.5 mM on 0.5 mM spreading (Table I).

lower concentrations of NaOleate ($\approx 0.05 \text{ mM}$), the drops did not dissolve, and again spread to $R_{\infty}/R_0 \approx 1.25$. Sodium oleate does not readily dissolve in mineral oil, so that it was not possible to perform a control in which NaOleate-containing oil would have been spread on water. In a third control, drops of mineral oil with $0.5\text{--}1.0 \text{ mM}$ oleic acid were placed on pure water and again slow spreading was observed with $R_{\text{max}}/R_0 \approx 1.2$. As a fourth control, pure oleic acid was placed on water; very rapid spreading of a precursor film was observed indirectly using small bubbles as surface markers. Finally, in an otherwise “normal” experiment (such as that in Fig. 3) talcum powder was spread on the substrate surface prior to drop placement. No motion of the talc was observed, indicating that there is no precursor monolayer in this system. It is clear from these control experiments that a drop spreading with $R/R_0 > 2$, and reaching a maximum radius before finally recoiling, are consequences of adding an interfacial chemical reaction to the system.

Plotting the radius versus time on logarithmic scales as in Fig. 3 should reveal possible power-law spreading dynamics, if such dynamics are present. Rather than clear power-law dynamics (i.e., constant slopes for at least an order of magnitude on the time axis), we observe a gradually increasing spreading rate until the maximum radius is achieved. Force balances can be made for specialized spreading problems (e.g., Refs. 1 and 18), and scaling arguments are employed to predict power-law spreading of the form $R(t) \propto t^\alpha$. The physical responses of experimental systems are often more complex and, because of the interplay of various forces, only show power-law-like spreading for finite time intervals. In order to be able to make quantitative comparisons with existing work, we fit power-law curves to our data for finite time intervals during the rapid spreading and slow

TABLE I. Spreading and recoiling coefficients, as well as R_{\max}/R_0 for various combinations of acid/base concentrations. Statistics were collected for 4–6 experiments at each set of concentrations (average \pm standard deviation).

acid/base		0.5 mM	1.0 mM
0.5 mM	α_{spread}	0.64 ± 0.06	0.81 ± 0.07
	α_{recoil}	-0.34 ± 0.09	-0.14 ± 0.04
	R_{\max}/R_0	3.09 ± 0.44	3.88 ± 0.45
1.0 mM	α_{spread}	0.88 ± 0.06	0.89 ± 0.06
	α_{recoil}	-0.22 ± 0.10	-0.14 ± 0.08
	R_{\max}/R_0	3.78 ± 0.36	4.16 ± 0.62

recoiling stages. In particular, we take only the data from half a decade in the time interval preceding t_{\max} (the time corresponding to $R=R_{\max}$) and fit this data with straight lines (Fig. 3). We find that the average exponents are $0.64 < \alpha_{\text{spread}} < 0.89$, with α_{spread} being smaller for low concentrations of reactants (Table I). We can contrast this result with power-law spreading of a drop on a thin film, where the drop acts as a source of constant concentration,¹⁹ for which $R(t) \propto t^{1/2}$.

For recoil, taking just the data from t_{\max} to half a decade later in time and fitting as a power law shows that the average exponents are $-0.34 < \alpha_{\text{recoil}} < -0.14$ (Table I). Note the fairly large standard deviations in α_{recoil} , indicating that some caution is necessary when drawing general conclusions about the recoiling process. Nevertheless, the data suggest that the qualitative recoiling behavior is correlated to the concentration of the base in the water phase and is typically faster in experiments with lower concentrations of NaOH.

We observe three separate stages of the experiment to be discussed: (i) spreading, (ii) recoil, and (iii) the final equilibrium size of the lens. We explain the observed spreading dynamics as follows. When the droplet is first placed on the NaOH/air interface, only a few oleic acid molecules are near the interface and readily react with the NaOH to produce the surfactant, NaOleate. As a result, the oil/water interface tension decreases, the spreading parameter S increases but remains negative, and the drop spreads to a new (instantaneous) equilibrium radius. These first stages of spreading correspond to a quasistatic process which maintains equilibrium at the triple line. Balancing the surface tensions at the contact line and assuming that the droplet takes the shape of two spherical caps as in a liquid lens, gives an exact relationship between drop radius and σ_{ow} . Using (1) and expanding the resulting relationship for early times, we obtain $R(t) - R_0 \propto V^{1/3}kt$, which gives spreading rates of order 0.1 mm/s when $k \approx 0.1 \text{ s}^{-1}$, in qualitative agreement with our experiments. Note that since the droplet is much more viscous than the water phase ($\mu_o/\mu_w \approx 10^2$), and despite the substrate being shallow,²⁰ order of magnitude estimates²¹ show that dissipation is dominated by viscous *stretching* of the oil droplet. Consequently, the dissipative stress is of order $O(\mu_o u/R)$, and weak during early stages of spreading, in agreement with the quasistatic spreading model.

This quasistatic process then proceeds, gradually reacting away all the oleic acid in the drop and increasing its

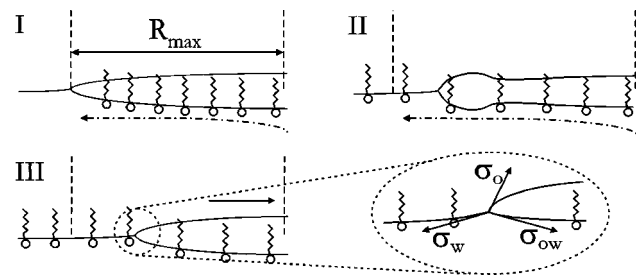


FIG. 4. Sketch of the suggested mechanism for recoiling: I. Reaction goes to completion and the drop reaches a maximum radius; II. Surfactant diffuses beyond the maximum radius of the drop; III. $\sigma_w \approx \sigma_{wo}$ and so the spreading parameter reduces to $S \approx -\sigma_o$, and the drop recoils.

surface area. If, after some time, the spreading parameter becomes positive, then there is no equilibrium radius and a stress balance with dissipative mechanisms is needed to find the spreading rate. If we assume that the quantitative results from Ref. 14 and (1) approximately hold for this system, we expect S to become positive after $t \approx 5 \text{ s}$. For these longer times a different approach is then necessary, in which there is a balance of the driving and dissipative stresses acting on the drop. The main driving stress for spreading is surface tension [of order $O(S/R)$], provided no precursor monolayer develops.²¹ The gravity [of order $O(\rho_o gh)$] and capillary stresses [of order $O(\sigma_o h/R^2)$] are much weaker, since the drop height is always smaller than the capillary length (of order 1 mm) and the drop is generally quite flat. However, it is clear that more work is required to fully characterize the system in all spreading regimes. In particular, whether the spreading parameter stays negative at all times (with $R=R_{\max}$ when $|S|$ is smallest) or whether $S > 0$ for some period of time (with $R=R_{\max}$ when S crosses through zero the second time) is an open question.

In any case, at a certain time almost all the oleic acid in the drop will have reacted. As a result, a maximum radius is reached, and as diffusion overcomes the rate of production of surfactant at the interface the surface tensions in the neighborhood of the contact line are modified, breaking mechanical equilibrium and causing the drop to recoil. A tentative mechanism for the recoiling is sketched in Fig. 4. After spreading to $R=R_{\max}$, we assume that most of the NaOleate is “trapped” at the oil/water interface [Fig. 4I]. Next, NaOleate diffuses to the air/water interface [Fig. 4II], possibly assisted by weak advection due to a Marangoni flow that persists in the substrate until chemical equilibrium is reached. We estimate that the timescale for NaOleate to diffuse through the substrate (diffusivity in bulk water: $10^{-5} \text{ cm}^2/\text{s}$), a distance comparable to the maximum radius of the drop, is of order 10^3 s which compares favorably with the time scales in Figs. 2 and 3. Diffusion of surfactant effectively decreases σ_w and increases σ_{ow} , thus tending to equalize σ_w and σ_{ow} . As a result, mechanical equilibrium at the triple line is broken, and the drop recoils under the tension provided by σ_o [Fig. 4III]. This diffusive mechanism is consistent with the observation that the surface tension of an oil/water interface, which has been treated with surfactant, can *increase* with time due to migration of surfactants away

from the interface.¹⁵ We suggest that the role of the concentration of NaOH on the recoiling dynamics (Fig. 3) lies in the fact that the Debye length decreases upon increase of the NaOH concentration. When fewer ions are present in the substrate, the polar heads of the NaOleate molecules repel each other more strongly at a given molecular spacing than when more ions are present to screen the charged heads. Hence, the diffusion of surfactant away from the oil/water interface is enhanced by the intermolecular repulsion the strength of which increases with lower concentrations of NaOH.

Finally, it may be surprising that the final equilibrium radius of the lens is about equal to the initial radius (Fig. 2), despite the presence of surfactant in the system. Given a drop volume of $0.1 \mu\text{l}$ and concentration of 1 mM acid, we expect on the order of 10^{13} surfactant molecules. If these are evenly spaced at the oil/water interface, then given typical values of R_{max} we expect intermolecular spacings of about 1 nm (i.e., smaller than the Debye length). Once the surfactant is spread out evenly over the entire surface of the Petri dish, however, the intermolecular spacing increases to roughly 30 nm. At such low surface concentrations, the surfactant hardly influences the surface tensions of the system, and we expect the final drop radius to be close to the initial radius.

To summarize, we have observed drops of oil spreading on water with an interfacial chemical reaction which altered the spreading dynamics such that (a) the rate of spreading is much faster than what is expected for surfactant spreading on a liquid; (b) this spreading rate depends on the concentrations used in the interfacial reaction, being faster for larger concentrations; (c) a maximum radius is reached 3–5 times the size of the initial drop radius; and finally (d) the drops recoil back to their initial radius over a much longer period of time than the time it takes to spread. We present arguments to provide a qualitative understanding of the physical mechanisms, but further modeling of this system is necessary for a full understanding of the complex interplay of various spreading and dissipation mechanisms.

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