

## Fingering Instability in Thin Wetting Films

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We report on a new hydrodynamic instability which occurs at the spreading edge of a thin wetting film. A drop of aqueous surfactant solution placed on a glass surface moistened with a thin layer of water spreads by propagating fingers, whose velocity and shape depend on the thickness of the ambient water layer and on the surfactant concentration. The two fluids are miscible and show negligible viscosity difference, ruling out a Saffman-Taylor instability. We propose that the Marangoni effect, which is fluid flow induced by gradients in surface tension, drives the instability.

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Studies of the dynamics of wetting, which is the displacement of one fluid by another, and the associated movement of the contact line, where the two fluids and solid meet, are beginning to widely gain attention.<sup>1</sup> Most investigations have focused on the forced or spontaneous movement of a straight or circular contact line over a solid surface. We report results on a new hydrodynamic instability at the spreading edge of thin films which leads to wetting by fingered growth. We find that certain aqueous surfactant solutions (and other liquids to be discussed), spreading on a glass surface premoistened with water, wet the surface by propagating fingers from the nominal contact line. Surface coverage proceeds much more quickly than in ordinary spreading. The velocity and shape of the fingers depend on two parameters: the thickness of the preexisting water film and the surfactant concentration which, when increased, reduces the surface tension of the drop with respect to the ambient water film. The fingers undergo shielding, spreading, and tip splitting; processes also observed in other fluid-flow instabilities. We note, however, that the fluids we use (pure water and aqueous surfactant solution with less than 0.1% surfactant by weight) are miscible and show negligible viscosity difference. In addition, the experiments are performed in an *open-cell* geometry with no external pressure gradient forcing movement of the liquid-liquid interface. These two features rule out the presence of a Saffman-Taylor instability.

Fingering in surfactant solutions was first observed by Marmor and Lelah.<sup>2</sup> Contrary to their reports, we find that no fingering occurs when a drop of aqueous surfactant solution is placed on a dry surface. We have demonstrated, for the first time, the strong dependence of the rapid spreading and fingering on the thickness of the ambient water film and on the surfactant concentration, and we propose that the mechanism responsible for the instability derives from the presence of the Marangoni effect, first described correctly by Thomson.<sup>3</sup> The effect refers to flow produced by variations in surface tension. Surface-tension gradients, here produced by

gradients in surfactant concentration, cause a shear stress at the air-water interface (in the direction of increasing surface tension) which induces motion in the interface and the adjoining liquid layers.

A schematic of the experimental setup is shown in Fig. 1. Dry nitrogen is blown into a flask of water whose temperature is controlled by immersion in a heat bath. (All the water used in the experiments is purified and doubly distilled.) The water moisture is forced into a sealed humidity chamber and condenses onto a 5 by 5 cm<sup>2</sup> clean glass slide mounted on the inside bottom of the chamber. The relative humidity in the chamber, which can vary between 85% and supersaturation, is monitored through a hygrometer and a thermocouple which measures the temperature in the chamber close to the slide. In this study, we estimated the thickness of the preexisting water film from the work of Derjaguin and Churaev.<sup>4</sup>

To observe the spreading drop, which quickly becomes too thin to be visible, we illuminate it from above with a fiber-optic lamp fitted with condensers to collimate the light. The shadow of the drop rim is focused onto opal glass which acts as a projection screen for the light refracted from the spreading liquid. This fingering rim is highly visible in the transmission geometry. The shadow is reflected from a mirror into a high-resolution camera (MTI 680X) and videotaped with a S-VHS JVC recorder. For this experiment the video images were frozen every frame (i.e., every  $\frac{1}{30}$  sec) and photographed with a 35-mm camera. Slide projections of the fingered border were traced by hand and digitized using a standard image processing package.<sup>5</sup>

The common criterion used to determine the cleanliness of the glass is that a continuous water film form on the slide when placed in the chamber and that uniform interference fringes be visible. We clean our glass slides by washing them in Micro detergent and immersing them in a 1% nitric-acid solution at 80°C for 2 h. The slides are repeatedly washed with water to remove any final traces of acid and they are then dried in a stream of

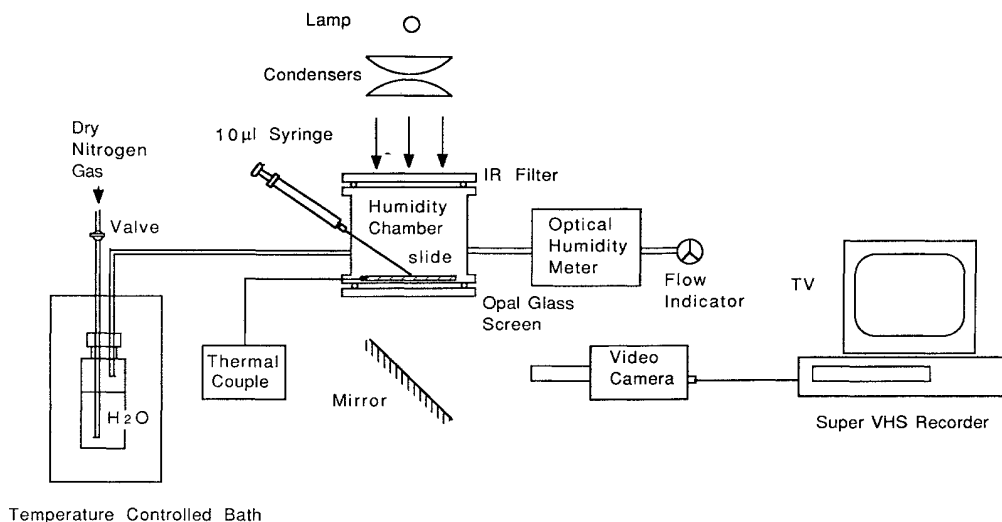


FIG. 1. Schematic of experimental setup.

dry nitrogen and placed in the sealed humidified chamber.

The experiment is performed by gently placing a 2- $\mu$ l drop of an aqueous solution of surfactant AOT [sodium *bis*-(2-ethylhexyl) sulfosuccinate], in the concentration range 0.01–10 mM, onto the surface of a water-moistened smooth glass slide. Our measurements indicate that a 1-mM AOT solution has a surface tension of 40 dyn/cm, significantly lower than that of the ambient water film (73 dyn/cm). The Marangoni force pulls liquid from the drop along the surface of the water with a spreading rate on the order of 1 cm/sec. For comparison, a drop of pure water spreading on the moist slide travels at a speed of about 0.1 cm/sec (see Fig. 3). The surfactant drop does not spread as a uniform circular disk of liquid, as usually seen in ordinary wetting. It spreads by immediately forming fingers propagating from the nominal contact line.

Different patterns are observed as the thickness of the preexisting water film is varied and the AOT concentration is held fixed. Figure 2 shows the time development of two drops of 1-mM AOT spreading on an ambient water film of different thicknesses. From Ref. 4 we estimate that the water film thickness in Fig. 2(a) is about 0.1  $\mu$ m, while that in Fig. 2(b) is close to 1  $\mu$ m. Spreading on the thicker water film creates fingers which are broader and more rounded at the tips. Spreading on the thinner water film leads to narrow, sharply tipped, and very ramified fingers. There is an observable dependence of the wavelength of the instability on the thickness of the ambient water film; an increase in the film thickness of about an order of magnitude leads to an approximate doubling of the finger width.

In all the surfactant cases we have studied, the fingers, in trying to maintain a preferred finger width, undergo tip splitting. When the fingers become too wide, they bifurcate, and the process continues. Our image analysis

indicates that screening also occurs. Most of the finger growth occurs at the tips, with little growth at the base of the regions between the fingers. In the late stages of spreading, the fingers can coalesce, but the final patterns remain stable with no retraction evident; retraction of the drop<sup>2</sup> only occurs when evaporation effects are not brought under control.

We have measured the growth rate of the fingers by defining the length  $R(t)$  to be the difference between the radius of the circular envelope circumscribing the majority of fingers and the initial radius of the drop. Figure 3 is a plot of the finger length  $R(t)$  for spreading on the thick and thin films. In either case,  $R \sim t^\alpha$ , where  $\alpha = 0.70$  and 0.66 for the thick and thin films, respectively. The difference between the two exponents lies within experimental error. The proportionality constant is larger for spreading on the thicker water film since viscous dissipation effects are smaller.

When a drop of AOT solution is placed on a dry slide, no fingering occurs because there is no ambient water to establish the surface-tension gradient. In the study by Marmur and Lelah,<sup>2</sup> which was carried out in an open environment, no effort was made to control condensation from the atmosphere onto the glass surface and it is most likely that a thin undetected film of water led to the fingering seen. As we have shown, a film much less than 1  $\mu$ m can initiate the instability.

The finger width and velocity also depend on the surfactant concentration of the emplaced drop, a result we are presently investigating. Aqueous AOT solutions below 0.03 mM do not spread by fingering, but spread circularly and slowly. At this concentration, surface-tension difference between the AOT solution and pure water is negligible. One must establish a sufficient difference in surface tension in order to initiate the instability. Slow spreading with no fingering also occurs in cases where the water film condensed onto the glass was

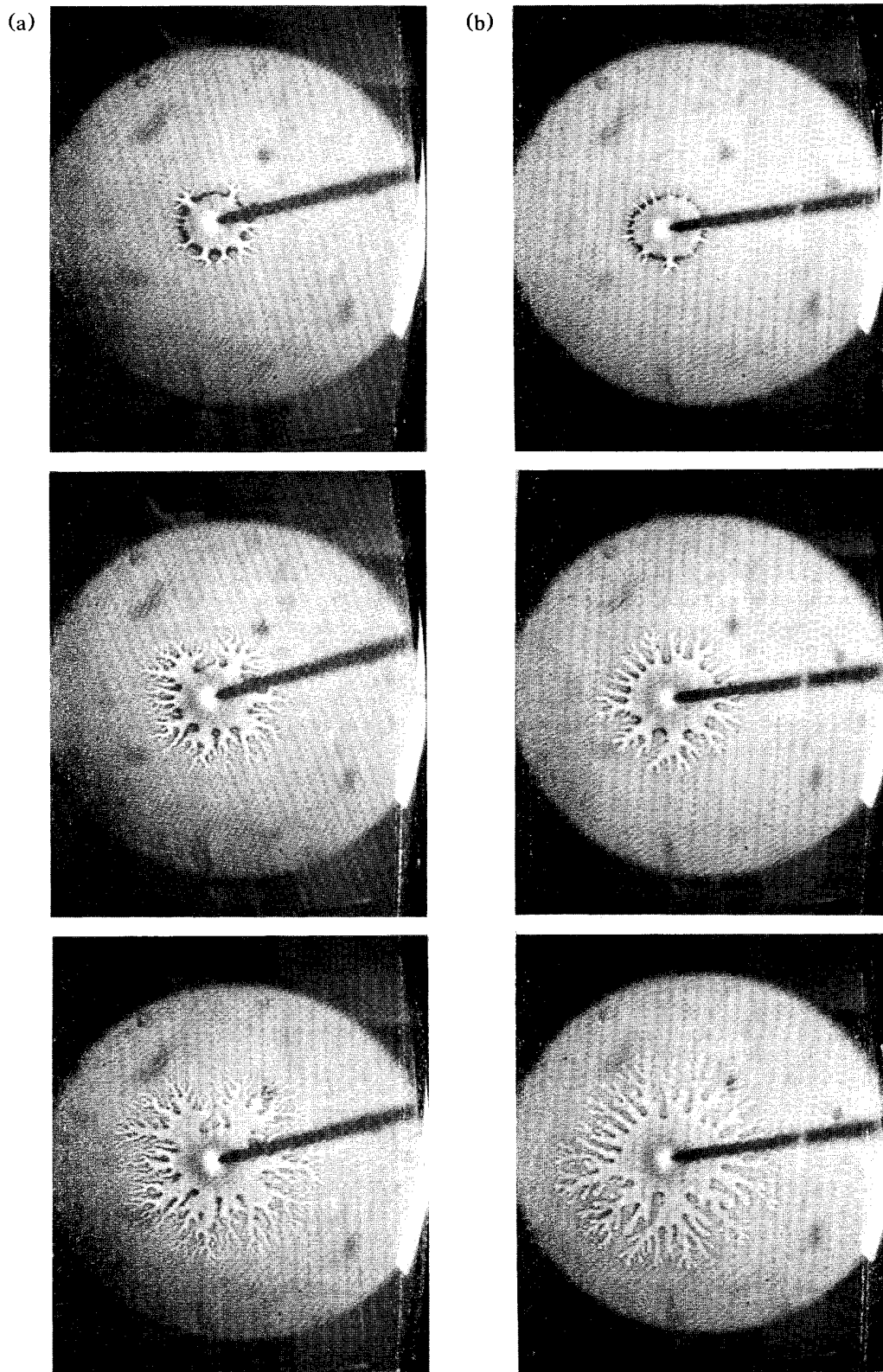


FIG. 2. Photographs of droplet spreading and fingering. (a) Spreading on a thin water layer ( $\approx 0.1 \mu\text{m}$ ) and (b) spreading on a thick water layer ( $\approx 1.0 \mu\text{m}$ ). The time sequence is 0.1 sec (top), 0.5 sec (middle), 1 sec (bottom). The inner drop radius in the top photograph is approximately 4 mm.

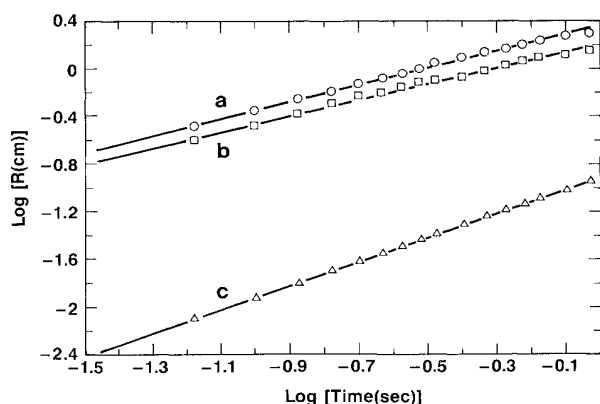


FIG. 3. Finger length  $R(t)$  for 1-mM drops of aqueous AOT. Curves *a* and *b* represent spreading on the thick and thin water films, respectively. Curve *c* represents the radius of a uniform circular drop of pure water spreading on an ambient water film about  $1 \mu\text{m}$  thick. The slopes obtained from the linear fits are the following: *a*, 0.70; *b*, 0.66; and *c*, 0.99.

produced at a relative humidity less than 90%, even for a drop with AOT concentration as high as 10 mM. In this case, large viscous dissipation in the spreading thin film is expected to slow down movement of the nominal contact line, thereby inhibiting the instability. At high surfactant concentrations ( $\approx 10$  mM), we again observe spreading with a uniform circular edge. In these cases, transport of excess surfactant from the bulk to the surface of the spreading fluid may inhibit the formation of large surface-tension gradients, thereby preventing any sustained Marangoni flow.

Our observations suggest that there exists a "primary," surfactant-rich film which spreads out circularly ahead of the fingering front. Although it is difficult to visualize any flow ahead of the fingers, we base this claim on an experiment in which the AOT solutions were colored with naphthol blue-black dye. A pale blue disk of dye spreads out a few mm ahead of the apparent contact line. Behind the disk, a sharp depression in liquid height occurs leading to a fairly long area of very thin fluid, into which the fingers grow and spread.

For a uniform, steady-state front subject to a Marangoni force, the fluid surface velocity is directly proportional to the local height and surfactant concentration gradient.<sup>6</sup> A mechanism which will enhance the local concentration gradient at the finger borders will lead to an unstable spreading front. We assume that the bulk of the drop maintains a fairly constant surfactant concentration. On the other hand, our observations indicate that the primary film establishes a surfactant concentration gradient in the thinned film region. If most of the concentration gradient occurs in the thinned region, then

the gradient increases as the length of the thinned region decreases. Since the length of the thinned region ahead of the finger decreases locally, the concentration gradient in front of a protrusion is larger, thereby increasing the local fluid velocity. As the bulk of the drop spreads, therefore, any perturbation causing a local protrusion of the contact line should be amplified.

We have created fingering patterns that do not undergo tip splitting when using drops of alcohol or alcohol-water mixtures spreading on an ambient water film. The alcohols are almost completely miscible with the water (unlike the surfactants we have studied) and can be chosen to have the same surface-tension difference with the water as the surfactant case. Williams produced fingers similar to our AOT patterns when performing experiments with alcohol in an alcohol-saturated environment.<sup>7</sup> We expect a fingering instability to be present in many other thin-film systems subject to surface-tension gradients.

Although the Marangoni effect has been studied for some time, most of the work was focused on an explanation of the uniform front flow<sup>6</sup> or on the instability which gives rise to roll cells along the interface between two bulk fluids.<sup>8</sup> The instability we are studying arises at the edge of the spreading fluid. For a uniformly spreading front of constant height, the length  $L$  of the spreading film grows as  $t^{1/2}$ .<sup>6</sup> Our results show that the fingering front grows at a faster rate. One of the difficulties in applying this analysis to the present case is that the height of the spreading fluid is changing (a true free-boundary problem) and these changes alter the local concentration gradients which in turn induce flow. Such problems do not arise in viscous fingering, for example, and it will be interesting to investigate further the surfactant system to find connections with such other flow instabilities.

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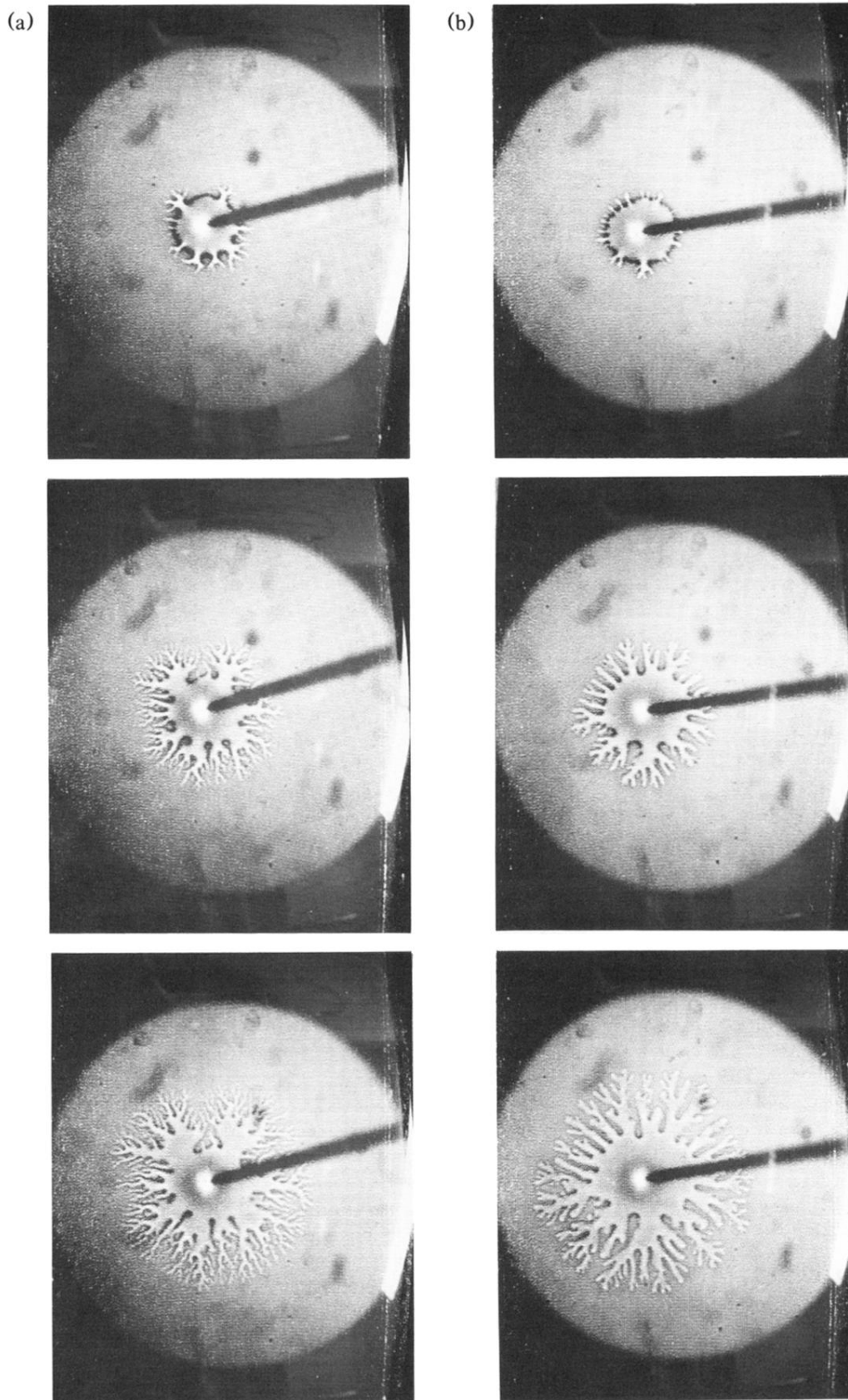


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