Experimental Thermal and Fluid Science 86 (2017) 98–101

Contents lists available at ScienceDirect

Experimental Thermal and Fluid Science

journal homepage: www.elsevier.com/locate/etfs

Spreading, fingering instability and shrinking of a hydrosoluble surfactant on water

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ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 1 February 2017
Accepted 2 April 2017
Available online 5 April 2017

Keywords:
Marangoni flow
Spreading film
Fractal dimension
Fingering instability

ABSTRACT

An experimental investigation of spreading and shrinking of a surfactant droplet at the air-water interface with fingering instability appearing at the edge of the droplet stain was reported. It was found that a droplet of a surfactant on the water shows three regimes: spreading, shrinking and resting at the appropriate parameters values. We quantify these regimes by measuring the mean square displacement of the droplet parts, $\langle r^2 \rangle$, with respect to time. Behavior of the fractal dimension of stain in different time intervals also confirms this statement. By defining the angular box-counting dimension, the time variation of the fingerless part of the stain was studied. Three stages: spreading, shrinking and resting were observed again. In the first stage, the result is compatible with the previous works on spreading of the surfactant on a thin water film but the second stage is a novel phenomenon.

1. Introduction

Over the last years, there has been great interest in Marangoni effect due to the wide class of fundamental and applied problems dealt with. Marangoni flow plays a key role in dewetting, spreading and fingering instability [1–7] which can be used for self-propulsion [8] and appears in many natural phenomena, that is, liquid thin films stability [9,10] and movement of insects on water surface [11], and hence has been the subject of extensive investigation.

Marangoni spreading of a surfactant droplet on a thin film and deep liquid layer has been studied widely for decades. Dewetting and fingering instability at the contact line of a spreading surfactant drop and a thin liquid film, and also, instabilities of Marangoni flow on the thick fluid layer are of prime interests to the researchers [12–15].

Continuous injection of an amphiphile on the surface of a centimeter-thick water layer causes a Marangoni flow by the spreading of the hydrosoluble surfactant, and makes the interface to be divided into three flow regions: a source (around the injection point), a transparent zone and the outer zone with structures like Rayleigh-Taylor instability patterns [16].

Spreading and retraction of a trisiloxane surfactant aqueous solutions on the hydrophobic liquids [18], spreading and recoil of surfactant-containing water droplet on alcohol film [19], and spreading and recoil of oleic acid-containing oil droplet over aqueous solution of sodium hydroxide have been reported [20]. Also it has been observed that a smectic liquid crystal domain spreads and retracts at the air-water interface [21,22].

Here the authors aimed to report on axisymmetric spreading of a surfactant drop on a centimeter-thick water layer, fingering instability arising in the spreading front and shrinking of the droplet stain after spreading runs out.

2. Materials and methods

The experiment was carried out in a cylindrical cuvette of 26 cm diameter. The surfactant (butyl glycol-$C_6H_{14}O_2$) drop was carefully released onto the free surface of water, with zero initial velocity. The drop was seeded with tartrazine ($C_{16}H_9N_4Na_3O_9S_2$), rhodamine 6G ($C_{28}H_{31}N_2O_3Cl$) and brilliant blue FCF ($C_{37}H_{34}N_2Na_2O_9S_3$) with the weight percentages of 10%, 7% and 10% respectively to visualize the flow. Droplet's volume (10 μl) was controlled by micro-pipette. The water layer thickness was 1 cm and the experiment was under isothermal condition at a temperature of 22 °C. Surface tensions of the droplet and water at the experimental temperature were 27.7 ± 0.1 mN/m and 72.7 mN/m respectively and our measurements showed that the surface tension change of the droplet after getting dyed, was less than 0.1 mN/m. The experiment was recorded by a photo camera at 240 fps looking from above. Schematic of the experimental setup is shown in Fig. 1.

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http://dx.doi.org/10.1016/j.expthermflusci.2017.04.005

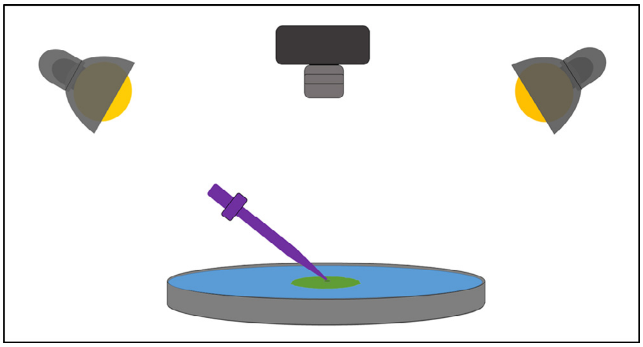

Fig. 1. Schematic of the experimental set-up.

When the droplet was released on the water surface, contact of the droplet and water-air interface triggered the Marangoni flow and spreading began. The colorful stain spread on the surface and part of the droplet was deposited at the bottom of the cuvette (density of butyl glycol at the experiment temperature was $0.93\ g/cm^3$ but, adding the dyes increased the density to $1.16\ g/cm^3$). Whilst the stain was spreading, fingers appeared at the rim of the stain and gradually grew. When the stain reached the maximum growth of the rim, after a short stop, it began to shrink. Shrinking in the rim occurs faster than the fingers and it makes the fingers to get longer. Eventually, shrinking ran out and a stain with long fingers emerged at the rim, diffused slowly and remained on the water surface. So, the whole process can be categorized into three regimes: spreading, shrinking and resting regime (Movie M1 in the Supplementary Material).

3. Results

To identify the regimes, the mean square displacement of the droplet parts, $\langle r^2 \rangle$, was plotted against time. r is the position of a colored droplet part in the coordinate system fixed at the center of the stain. At each frame of the recorded video the average is computed over the entire colored parts. Reported values in Fig. 2a are for a typical experiment. As seen, in the first regime, $\langle r^2 \rangle$, increased and reached a maximum at $t \approx 1.3$ s. The second regime began with decrease in $\langle r^2 \rangle$ and in the third regime, $\langle r^2 \rangle$ remained constant. At the spreading and shrinking regimes, power law behavior $\langle r^2 \rangle \sim t^{\alpha}$ was observed with exponents of about $\alpha = 0.90$ and $\alpha = -2.61$ respectively.

The fractal dimension of stain (D_b) is close to two, and is constant in the first stage of the experiment. At the end of the first stage, small fingers occurred at the stain margin. The fingers became more lengthy and thin in the shrinking phase. As a result, the fractal dimension of the stain was reduced. In the final stage, the stain is in the resting regime and its shape changes a little and the fractal dimension remains constant again. Fig. 1b illustrates the behavior of fractal dimension in different periods which is in agreement with the results for $\langle r^2 \rangle$.

Radius of the largest circle inscribed in the stain, r_{rim}, as a function of time is an alternative quantity to show three stages: spreading, shrinking and resting. For this purpose, the angular box-counting dimension was introduced. The annulus of stain with the radius r from center and a small width δ can be divided into sectors with the same angle θ as illustrated in Fig. 3a. Each sector that contains a component of the stain is called a filled sector. N (θ) shows the number of filled sectors in the annulus. The angular box-counting dimension of the annulus is defined as:

$$D_\theta(r) = \lim_{\delta\to 0}\lim_{\theta\to 0} \frac{\log N(\theta)}{\log(\theta)} \tag{1}$$

In practice, a fixed value equal to 10 pixels is chosen for δ. D_θ is a value between 0 and 1, it is equal to one for small r and drops from 1 at $r = r_{rim}$. Then, at the onset of the fingers, D_θ decreases. Fig. 3b shows the behavior of D_θ versus r for three time instances.

In Fig. 4, r_{rim} is computed at each time step and plotted against time for a typical experiment. r_{rim} increases and reaches a maximum value at the time t_{max}, then decreases and finally remains constant, and shows the three regimes mentioned above. In this experiment, r_{rim} was found to have a power law behavior $r_{rim} \sim t^{\beta}$. It is shown that the spreading exponent ranges from $\beta = 0.25$ to $\beta = 1$. Exponents around 0.25 correspond to Marangoni-driven flow and exponents around 0.5 are reported for Marangoni spreading in the presence of surfactant supply [2], but surfactant solubility, experiment geometry and layer thickness can influence the spreading exponent [1]. The spreading exponent in this case is about $\beta = 0.44$, which is close to the exponents reported before by other investigators: $\beta = 0.48$ by Hanyak et al. [4], $\beta = 0.5$ by Hernandez-Sanchez et al. [1] and $\beta = 0.6 \pm 0.15$ by Starov et al. [3] for spreading on thin liquid layer. For the shrinking regime of our experiment, the exponent is about $\beta = -1.66$.

The formation of fingers can also be seen in Fig. 3b, the plot of D_θ versus r for three different times of $t_1 = t_{max} - 1$ s, $t_2 = t_{max}$ and $t_3 = t_{max} + 2$ s. At the beginning of the spreading, fingers have not existed yet or are so small; so after corresponding r_{rim}, D_θ at t_1 decreases rapidly. But at t_2 fingers are longer, and at t_3 longest fingers are observed. Hence, decrease of D_θ gets slow and slower respectively for t_2 and t_3. Fig. 5 shows the shape of stain at t_1, t_2

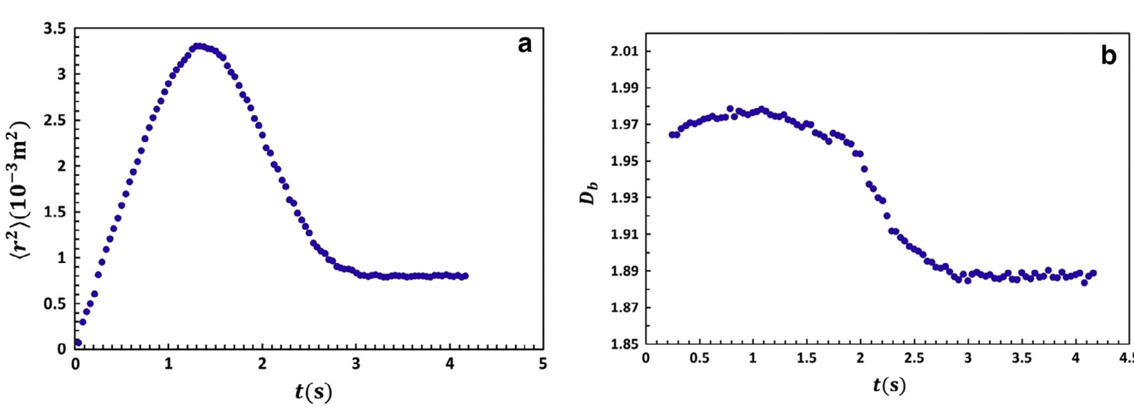

Fig. 2. (a) $\langle r^2 \rangle$ versus time. Spreading, shrinking and resting regimes are explicit in the graph. (b) Fractal dimension (D_b) versus time. D_b regime change times compare well with $\langle r^2 \rangle$.