Capillary flow of oil in a single foam microchannel

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When using appropriate surfactants, oil and aqueous foam can be intimately mixed without leading to the destruction of the foam. In this paper, we show that the capillary depression that prevails in foam can even lead to the spontaneous imbibition of foam with oil. We focus on the suction of oil in a single horizontal foam channel, a Plateau border, and show that these liquid capillary tubes can suck up another liquid under the action of capillary forces. The dynamics that we report, is governed by a balance between capillarity and viscosity, which exhibits a scaling law different from classical wicking due to the deformability of the foam channel. It also differs from what is expected in the framework of foam drainage due to the particular geometry of the Plateau borders when swollen with oil.

In various industries, oil is used as an anti-foaming agent to destroy undesirable foam or avoid its formation [7, 14]. Yet, in appropriate conditions, oil droplets can have the opposite effect and increase the stability of aqueous foams [13, 19]. The outcome – stabilizing or anti-foaming – depends on the oil ability to penetrate and spread at the air/water interface [11]. This ability is related to the stability of pseudoemulsion films, comprised between the oil/water and air/water interfaces [5, 11]. Indeed, a high repulsive interaction between the layers of surfactants adsorbed on the two interfaces can hinder the thinning of the pseudoemulsion films, thus preventing the penetration of oil at the air/water interface. In that case, the oil, which is ineffective as anti-foaming agents, is aggregated into oil droplets trapped within the foam network. These can deform this soft porous media and even clog it as solid particles would do, thus limiting the drainage and ultimately stabilizing the foam [16, 22].

Yet, contrary to solid particles, the soft oil droplets are, in turn, deformed by the liquid network of the foam. At equilibrium, the droplets adopt a slender slug shape as recently shown with Surface Evolver simulations [26]. In this letter, we address the dynamics of this situation considering the flow of an oil droplet in a single foam liquid channel, called a Plateau border. These Plateau borders, which are encountered at the intersection of three adjacent bubbles can act as liquid capillary tubes, able to absorb another liquid (oil in our case) under the action of capillary forces. This proof-of-concept experiment demonstrates the ability of aqueous foams to absorb, retain and transport an organic phase, a feature of practical interest in decontamination, soil pollution, detergency or oil recovery.

To obtain stable pseudoemulsion films, we use silicon oils with a viscosity η and ranging from 5 mPa.s to 12 500 mPa.s, and a foaming solution of viscosity η = 1.4 mPa.s, composed of 0.66 %wt of sodium lauryl-dioxynethylene sulfate (SLES ; Stepan Co.), 0.34 %wt of cocoamidopropyl betaine (CAPB ; Evonik) and 0.04 %wt myristic acid (MAC ; Sigma-Aldrich), plus 10 %wt of glycerol [2, 13, 30]. Soap films made with this mixture present rigid boundary conditions [12, 15, 25] and do not break when put into contact with silicon oil, provided that the oil has previously been into contact with the foaming solution. The air/water surface tension of the foaming solution is γ_{aw} = 24 ± 1 mN/m while the air/oil and oil/water surface tensions are γ_{ao} = 20 ± 1 mN/m and γ_{ow} = 5 ± 1 mN/m (measured with the pendant drop.
method).

To form a single Plateau border, we withdraw a triangular prism frame of length 10 cm and side 3 cm out of the foaming solution. Three trapezoidal soap films, which merge in a slender Plateau border parallel to the axis of the prism, thus span on the frame (Fig. [1]). The frame is placed horizontally in a closed chamber with saturated humidity. This reduces evaporation and increases the life-time of the films. Right after taking the frame out of the bath, the Plateau border is large, $r_p = 1010 \pm 20 \mu$m, and drains to a stable value of $r_p = 150 \pm 20 \mu$m in about 20 minutes. Oil is injected with a capillary tube in contact with the upper film to avoid any deformation of the Plateau border. We perform experiments at constant oil flow rate $Q$ and constant oil volume $\Omega$. This latter is illustrated in Fig. [1], where a $\Omega = 1 \mu$L droplet is pushed out of the capillary into the upper soap film. Once the capillary is removed, the oil lens falls in the film under gravity. At $t = 0$, it touches the Plateau border and flows within it forming a slender oil slug of length $\ell$ aligned along the $z$ axis (the center of the slug corresponds to $z = 0$). For constant flow rate experiments, the capillary is placed slightly above the Plateau border and is connected to a syringe pump.

We report $\ell$ for various oil viscosities as a function of time both for volume and flow-rate controlled experiments. After a short transitory regime ($t < 1$ s) needed to reach a stationary injection rate, oil slugs fed at constant flow rate spread in the Plateau border with a dynamics $\ell \propto t^{2/3}$ (Fig. [2]), while the volume controlled experiment exhibits two regimes for various oil viscosities (Fig. [3]).

For $t < \tau$, where $\tau$ is the typical time it takes for oil to enter into the Plateau border, $\ell \propto t^{2/3}$. Conversely, for $t > \tau$, $\ell \propto t^{1/3}$ over more than three decades in time. The inset in Fig. [3] also illustrates how the dynamics changes when $r_p$ varies between $150 \pm 20 \mu$m and $1010 \pm 20 \mu$m. For $r_p = 150$ and 210 $\mu$m, the smaller $r_p$, the faster the $t^{2/3}$ dynamics. For $r_p = 520$ and 1010 $\mu$m, this law does not hold: $\ell$ saturates at short time ($10^9 < t < 10^3$) as if converging toward equilibrium, then accelerates at long times ($t > 10^3$). In that case, the Plateau border itself is not at equilibrium at the beginning of the experiment: a water flow concomitant with the oil flow accelerates the dynamics at long times. This is confirmed following the evolution of $r_p$ far from the oil slug: for an initial value of 1010 $\mu$m, $r_p$ is reduced by 50% during the experiment, while for $r_p = 150 \mu$m, it stays within 10% of its initial value.

We now consider the capillary oil flow, induced by the deformation of the air/water and water/oil interfaces. As $\gamma_{aw}/\gamma_{aw} = 0.2 \ll 1$, the contribution of the oil/water interface can be neglected at first order. This suggests a dynamics similar to foam imbibition in the gravity-free case. Solving the complete foam drainage equation for 1D pulsed drainage, Koehler et al. [20] predict

$$\ell \propto \left(\gamma_{aw} \Omega/\eta_0^2\right)^{1/5} t^{2/5},$$

where $\Omega$ is the volume of foaming solution added to an initially infinitely dry foam ($r_p = 0$ for $z > \ell$). How comprehensive it might be, this framework does not precisely describe our experiment: we observe i) an exponent 1/3 significantly different from 2/5 ii) an influence of $r_p$ on the dynamics, while the above scaling law does not. These discrepancies may arise from different geometries of swollen Plateau border. Koehler et al considered swollen Plateau borders with concave triangular cross-sections, as those formed at the intersection between three circles of radius of curvature $r$, with
an area \( A(z, t) = \delta r^2(z, t) \) where \( \delta = \sqrt{3} - \pi/2 \). This is not valid in the presence of an oil drop, as shown by numerical simulation of the equilibrium shape of an oil drop in a Plateau border \(^2\). where swollen cross-sections are convex or flat as sketched in Fig. 1.). We therefore expect \( \delta \) to be a function of \( z \) and \( t \). The full description of the flow and shape variation, which would require a fine analysis of the coupling between deformation, pressure and velocity fields is far beyond the scope of this paper. Yet, to account for our observations, we provide simple scaling arguments in the limit where the capillary suction in the unperturbed Plateau Border is dominant.

At the beginning of the experiment, the droplet inflates the Plateau border and \( r \geq |r_p| \). Yet, as the oil slug elongates, the Plateau border experiences less distortion: \( r \) increases until approaching infinity. For \( \gamma_{\text{av}} / \gamma_{\text{aw}} = 0.2 \), this value corresponds to the equilibrium oil slug shape: a triangle cross section of side length \( r_p \) as calculated in \(^2\) and sketched in Fig. 1 at \( t = 84.10 \text{s} \). This flat shape, which suggests an equilibrium length \( l_{\text{eq}} = 8 \Omega / \sqrt{3} r_p^2 \), is consistent with our experiments. For \( \Omega = 1 \mu \text{s}^{-1} \), we find \( l_{\text{eq}}(r_p = 1010 \mu \text{m}) \approx 5 \text{ mm} \) and \( l_{\text{eq}}(r_p = 520 \mu \text{m}) \approx 2 \text{ cm} \) in agreement with the saturation observed in the inset of figure 1 while \( l_{\text{eq}}(r_p = 150 \mu \text{m}) \approx 20 \text{ cm} \), which explains why we never observe a saturation of \( \ell \) in our decimetric frame for well-drained Plateau borders.

Thus, at long times, \( r \gg r_p \) and the pressure difference between the center and the edge of the slug is dominated by the depression in the Plateau border downstream of the oil: \( \Delta P = P(\ell/2) - P(0) = -\gamma_{\text{aw}}(1/r_p + 1/r) \sim -\gamma_{\text{aw}}/r_p \). Then, we evaluate the pressure gradient using a first order approximation: \( \nabla P \sim -\gamma_{\text{aw}} / (r_p \ell) \).

We now consider the dynamics of the slug, given by \( \ell \) the mean axial velocity, which results from a coupling between capillary suction and viscous dissipation in the oil. Using Stoke’s equation gives:

\[
\dot{\ell} \sim -\frac{A}{K \eta_o} \nabla P \sim -\frac{A}{K \eta_o} \frac{\gamma}{r_p \ell} \tag{1}
\]

\( K \), the flow resistance factor for slender channels, has been calculated for various channel sections. In the limit of rigid boundaries, achieved with surfactants such as those considered herein, \( K = 8 \pi \) for circular section and \( K = 50 \) for Plateau border’s section \(^2\) \(^2\).

For constant flow rate experiments, we combine Eq. \(^{1}\) with the continuity equation \( Q t \sim A \ell \):

\[
\frac{\ell}{(Q T)^{1/3}} \sim \left( \frac{1}{K} \right)^{1/3} \left( \frac{t}{T} \right)^{2/3} \tag{2}
\]

Here, \( T = \eta_o r_p / \gamma_{\text{aw}} \) is the characteristic visco-capillary time. Plotted in dimensionless coordinates \( \ell / (Q T)^{1/3} \) and \( t/T \) (Fig. 2), all the data for constant flow rate experiments \((\eta_o = 5, 20 \text{ and } 100 \text{ mPa.s} \text{ and } Q \text{ ranging from } 50 \text{ to } 1440 \mu \text{l/h}) \) collapse on a curve of slope \( 2/3 \) as predicted by Eq. \(^2\).

For constant volume experiments and early times \((t < \tau)\), the oil is still flowing from the soap film to the Plateau border, thus the constant volume condition is not yet fulfilled. Assuming a constant flow rate from the soap film to the Plateau border: \( Q \sim \Omega / \tau \) and using Eq. \(^2\), we find:

\[
\frac{\ell}{(\Omega / \tau)^{1/3}} \sim \left( \frac{1}{K} \right)^{1/3} \left( \frac{t}{\sqrt{\tau T}} \right)^{2/3} \tag{3}
\]

For each experiment, \( \tau \) is estimated by measuring the falling velocity, \( v \), and the radius, \( r_o \), of the oil lens while it is confined within the soap film \((\tau = r_o / v)\). We find \( \tau \sim 1 \text{ s} \), a value almost independent of \( \eta_o \), as \( \tau \) only increases by a factor 5 while the viscosity is multiplied by 2500 (inset of Fig. 4). Eq. \(^3\) is confirmed by the good collapse of Fig. 4 where we report the data of Fig. 3 plotted in the dimensionless coordinates \( \ell / (\Omega / \tau)^{1/3} \) and \( t / \sqrt{\tau T} \).

Once the oil has completely entered the Plateau border \((t > \tau)\), the volume of oil is constant \( \Omega \sim A \ell \). Combined with Eq. \(^1\), this gives:

\[
\frac{\ell}{(\Omega / \tau)^{1/3}} \sim \left( \frac{1}{K} \right)^{1/3} \left( \frac{t}{T} \right)^{1/3} \tag{4}
\]

Eq. \(^4\) accounts for the \( l^{1/3} \) dynamics observed at long time (see Fig. 4). Since \( \tau \) is almost independent of \( \eta_o \), the scaling laws \(^3\) and \(^4\) exhibit the same dependency with the oil viscosity \((\ell \propto \eta_o^{-1/3})\). This explains why we obtain a collapse for both regimes in the dimensionless coordinates of Fig. 4. Moreover, the collapse of additional data corresponding to \( \Omega = 1.4, 2.3, 3.4 \) and 4.3 \( \mu \text{l.s}^{-1} \) confirms the \( \Omega^{1/3} \) volume dependency in \(^3\) and \(^4\).

Finally, we stress that the collapse is less satisfactory for \( \eta_o = 5 \) and 20 \( \mu \text{Pa.s} \). These light oils spread easily into the films, making the measurement of \( v \) and \( r_o \) more difficult and yielding an uncertainty over \( \Omega \).

In this simple analysis, we did not consider any dissipation associated to water flow. This is justified by the following observations showing that water is stagnant and "unzips" around the oil slug: i) the interference pattern of the soap films barely changes during an experiment, suggesting quiescent soap films ii) experiments performed with a frame twice shorter (5 cm) yield similar dynamics even though the dissipation associated to water flow is diminished iii) a bubble placed downstream in the Plateau border remains static while the oil flows towards and around it iv) for well drained Plateau borders, there is no variation of the Plateau border cross section downstream, as would be logically expected if water was indeed flowing \(^2\).

In the classical imbibition dynamics of undeformable pores of radius \( b \), the driving capillary pressure gradient, \( \gamma / \ell b \), is also a decreasing function of \( \ell \). There, the typical gradient of velocities occurs on \( b \) leading to a viscous dissipation in \( \eta \ell / b^2 \), which gives the well-known \( l^{1/2} \) dynamics of Washburn’s law \(^4\) \(^2\) \(^3\) observed in solid
porous media and capillary tubes. In our case, the gradient of velocities occurs on a self-adjusted length due to the ability of the channels to deform. This length, set by volume conservation $\sqrt{\Omega / \ell}$, gives a viscous dissipation in $\eta \ell / \Omega$ and the observed $t^{1/3}$ dynamics.

Remarkably, at the end of the experiment, $\ell (r_p = 150 \mu \text{m}) \approx 10 \text{ cm}$, with an aspect ratio $\ell / r \simeq (\pi \ell^3 / \Omega)^{1/3} \sim 1000$ without breaking into droplets as could be expected from the Plateau-Rayleigh instability. Various physical effects, such as confined geometries, internal or external flows, viscosity contrast or even optical or acoustical wave guiding can affect the propagation of surfactant-driven instabilities [6, 8, 9, 13, 17, 24, 29]. In that case, we expect subtle coupled flows between the oil, the aqueous phase and the interface as can be observed on core flows [18] or in drainage of aqueous foams [10].

In our case, the stabilization can be attributed to the non-axisymmetric cross-section of the Plateau border. This statement is strengthened by the following observation: when one of the soap film is broken, the liquid (water + oil) is rapidly transferred from the Plateau border to the sole soap film left. This sudden change of topology is instantaneously followed by the fragmentation of the oil slug. For $\eta_w / \eta = 50$, the typical wavelength of the fragmentation $\lambda$ is $1.4 \text{ mm}$, a value consistent with theoretical calculations for the breakup of an infinitely long cylindrical thread in an ambient fluid [29]. Moreover, $\lambda$ increases with oil viscosity as predicted by theory.

Our local scale experiments highlight the remarkable ability of foam to suck and displace an immiscible liquid as an individual continuous stream. Imbibition of oil through the microchannels of an aqueous foam with rigid interfaces exhibits unusual imbition dynamics in $t^{1/3}$ and $t^{2/3}$ compared to Washburn’s dynamics in $t^{1/2}$ that classically prevails in solid pores. This fast velocity of spreading at short time, which is due to the deformability of the foam’s channels, can be enhanced using more soluble surfactants. In that case, we expect subtle coupled flows between the oil, the aqueous phase and the interface as can be observed on a larger scale in core-annular flows [18] or in drainage of aqueous foams [10].

A crucial point in the context of enhanced oil recovery is whether our predictions persist at the global scale of an aqueous foam. In the affirmative, aqueous foams may reveal as promising active pumping materials.

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