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Less is more: unstable foams clean better than stable foams

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Abstract

Hypothesis: Foamed surfactant solutions can clean surfaces! We hypothesize that the cleaning efficiency depends on the liquid fraction and on the stability of the foam. We also hypothesize that the cleaning efficiency is the better the smaller the average bubble size is.

Experiments: The double syringe technique was used to generate foams with varying liquid fractions but the same, very small bubble sizes with and without perfluorohexane in the gas phase. We performed cleaning tests in which the foams were applied to glass substrates contaminated with a fluorescent oil.

Findings: We found that unstable foams clean better than stable foams. Three cleaning mechanisms were identified: (1) imbibition at low liquid fractions, (2) wiping, i.e., shifting of the contact line between oil, foam and glass, at all liquid fractions, and (3) drainage at high liquid fractions. The change of the liquid fraction and of the foam stability lead to different combinations of these mechanisms and thus to different cleaning results.

Keywords: cleaning with foams, imbibition, perfluorohexane to stabilize foams, cleaning mechanisms

1. Introduction

In the last 20 years colloid and material science have made significant contributions to the development of cleaning processes for sensitive surfaces such as historical surfaces of artistic and cultural assets. Cleaning sensitive surfaces is quite a challenge because a tailor-made cleaning method needs to be developed for each individual surface. As outlined by Baglioni *et al.* [1] the most promising methods for cleaning sensitive surfaces include new “green” surfactant-based self-assembled systems, different types of emulsions and microemulsions, responsive hydro- and organogels, nanoparticle dispersions in apolar solvents, and hybrid organic-inorganic nanocomposite systems [1,2]. Our goal is to develop innovative, foam-based cleaning methods for sensitive surfaces. Foams can be material-preserving and environmentally friendly alternatives for the cleaning of surfaces, especially for those that should not be exposed directly to the cleaning solution. Using foams, one can reduce the amount of surfactant by up to 90 % compared to the use of the respective non-foamed cleaning solution. Furthermore, foam-specific physical mechanisms can make the cleaning process much more efficient than that of the non-foamed cleaning solution. We consider the cleaning process as efficient if (a) no cleaning solution drains out of the foam, (b) contaminations (e.g. oils, soot, pesticides, microbes) are soaked up by the foam, (c) the cleaning process is fast.

Note that foams are commonly considered to have no cleaning effect but to be only a by-product of the cleaning process and an aesthetic add-on for the user [3, 4]. Nevertheless, current research shows that foamed surfactant solutions can clean far more efficiently than the non-foamed ones due to two reasons [3, 5-7]: (1) presence of air-liquid interfaces and (2) imbibition. Both effects are briefly discussed in the following.

(1) That interfaces play a significant role in cleaning processes was demonstrated in two studies. In the first study Andreev *et al.* [5,6] showed a positive influence of the meniscus on the cleaning of silicon wafers contaminated with strongly adhered Si_3N_4 particles in an immersion/withdrawal cell. It was shown in [5] that in the case of non-foamed suspensions the cleaning occurs only in the narrow meniscus region (70 % efficiency), while a foamed particle suspension leads to significantly better cleaning in the bulk of the cell (90 % efficiency) [6]. Jones *et al.* [3] found an improved removal of a model lipid mixture (human sebum) from silicon wafers in the presence of an air-liquid interface and discussed two reasons for this observation. (a) The concentration of surfactant molecules is increased at the interface, allowing impurities / oil to be more easily absorbed into micelles [3]. (b) The sliding of the contact line

over the solid interface (due to wettability defects) is helpful in removing oil and dirt from the solid interface.

(2) The second reason for improved cleaning with foams is capillary imbibition. Mensire *et al.* [8,9] put dry aqueous foams into contact with either a miscible (glycerol containing surfactant solution) or an immiscible liquid (olive or sunflower oil). For both types of liquid, a remarkable ability of the foams to soak up the liquids into the Plateau border network of the foam was observed. For both types of liquid, the imbibition becomes slower as time increases. The authors describe numerically the details of the experimental imbibition process, which is driven by the capillary pressure and resisted by viscous and gravity forces in the Plateau borders [9]. They identify two parameters that control the imbibition efficiency: (i) the ratio between the oil-water and the air-water interfacial tension and (ii) the Bond number $B = g \rho_l R^2 \sigma^{-1}$, which measures the relevance of gravitational stresses $g \rho_l R$ (g - gravity, ρ_l - liquid density) with respect to the capillary pressure σ/R (σ - surface tension)) using the mean bubble radius R as the characteristic length. The first parameter predicts the imbibition strength. The second parameter tells us that the smaller the bubble size the larger is the capillary pressure and thus the imbibed liquid amount. Note that, reducing the bubble size one observes a slowing-down of the imbibition process, since at the same liquid fraction, Plateau borders are smaller and hence viscous dissipation becomes important. The average bubble radius was about 1-2 mm and the liquid fraction ε in the foam did not exceed 0.5 % in the studies carried out by Mensire *et al.*) [8,9].

As just mentioned, foams with low liquid fractions and small bubble sizes are needed to maximise imbibition, i.e. to optimise the cleaning process. Furthermore, the smaller the bubbles the more interfaces and meniscii are created in contact with the solid surface which further improves the cleaning process. The double-syringe technique is an ideal tool for generating well-controlled, small-bubble foams (see Section 2.3.). With this technique foams with bubble sizes as small as 10-20 μm and liquid fractions of 3-30 % can be generated [10]. In contrast to other methods, the liquid fraction of the foam can be varied without impacting the bubble size. The aim of our study is to understand how the structure and stability of foams affect the cleaning efficiency of a foamed surfactant solution. For this purpose, we carried out cleaning tests in which foams with different liquid fractions but same bubble size were put on glass substrates contaminated with a fluorescent oil. Cleaning foams with predefined liquid fractions were produced with the double-syringe technique. For foams with different liquid fractions both the dynamics of the cleaning process and the oil imbibition ability were studied. The same experiments were carried out with perfluorohexane-containing foams to avoid Ostwald ripening during the cleaning process [11-15]. We will show and discuss that three different mechanisms,

namely imbibition, shifting of the contact line (wiping), and drainage contribute to the cleaning process with foams and how a wise choice of the foam properties leads to an optimum interplay between the three effects and hence to optimal cleaning.

2. Materials and Methods

2.1. Chemicals

The surfactant Glucopon 215 UP was donated by BASF and used as received without further purifications. Glucopon 215 UP is an alkyl polyglycoside with alkyl chains between 8 and 10 carbons and a head group composed of 1.5 glycoside units. Citric acid (Aldrich, 99 %), ammonia solution 25 % (Merck) and perfluorohexane (Aldrich, 99 %) were used as purchased. The sunflower oil was purchased from supermarket (brand name JA). Double distilled water was used for the preparation of the aqueous solutions. We synthesised Pigment Yellow 101((1,1'-((1E, 1'E)-hydrazine-1,2-diylidenebis(methanylylidene))-bis(naphthalen-2-ol)) according to Noshiranzadeh *et al.* [16]. Pigment Yellow is a fluorescent oil-soluble dye. Fluorescence spectroscopy was used to determine the adsorption wavelengths of 365 nm (UV light) and 460 nm (blue light) and the emission wavelength of 520 nm.

2.2. Sample Preparation

Surface and Interfacial Tension Measurements: The critical micelle concentration (cmc) of Glucopon 215 UP was determined by surface tension measurements using the Du Noüy ring method and a STA1 tensiometer from *Sinterface Technologies* (Figure S1 in the *Supporting Information*). A *Profil Analysis Tensiometer PAT-1* from *Sinterface Technologies* was used to measure the surface tension of the Glucopon 215 UP solution at a concentration of $c = 10$ cmc. The surface tension was measured against air and again against air enriched with perfluorohexane (PFH). The interfacial tension between the surfactant solution ($c = 10$ cmc) and the sunflower oil (without and with PFH) was measured with the *Spinning Drop Tensiometer SVT 15* from *Data Physics*.

Cleaning Solution: For the foam generation an aqueous solution of Glucopon 215 UP with a concentration of $c = 90$ cmc ($\text{cmc} \sim 0.9 \text{ g l}^{-1}$) was prepared. As the pH of the aqueous surfactant solution is between 11.5 and 12.5, the pH of the solution was buffered to a value between 8 and 8.5 by adding citric acid (10 g l^{-1}) and ammonia solution (a higher pH value can damage historical surfaces).

Sample Preparation for Cleaning and Imbibition Tests: The round glass plates used for the cleaning tests have a diameter of 8 cm. The samples with Pigment Yellow were prepared by placing 0.1 ml of a saturated solution of Pigment Yellow in sunflower oil centrally on the glass plates. Figure 1 (right top corner) shows a fluorescing sunflower oil droplet on a glass plate under UV-light observed from below. The cleaning foam was placed on top of the oil for the cleaning tests.

The imbibition tests were carried out in a glass cuvette (28 ± 0.2 mm light path, $h = 35$ mm, $w = 35$ mm, $d = 32$ mm) with sunflower oil containing the fluorescent oil-soluble dye Pigment Yellow. The oil layer had a height of $h_{\text{oil}} \approx 4$ mm in the absence of the foam. Subsequently, the foam was placed on top of the oil. For the drop tests, an oil drop with a volume of ~ 0.1 ml was added to the foam in the glass cuvette.

Figure 1: Experimental optical set-up for studying the cleaning process via fluorescence imaging.

2.3. Double-Syringe Technique

The double-syringe foaming technique (see Figure S2 in the *Supporting Information*) was investigated in detail by Gaillard *et al.* [10]. It is ideal to generate reproducibly small-bubble foams with bubble sizes of $\langle r \rangle \approx 10 - 20 \mu\text{m}$ and well-defined liquid fractions ϵ . The liquid fraction of the foam can be calculated from the volume of gas (in this case air) V_G and the volume of the surfactant solution V_L .

$$\varepsilon = \frac{V_L}{V_L + V_G} \quad (1)$$

To generate the foam, we fill one syringe (60 ml) with the surfactant solution and air corresponding to the required liquid fraction ε . The filled syringe (60 ml) was connected to a syringe of the same volume using a Luer-Lock connector. The piston of the second syringe is in fully closed position.

By pushing the pistons of the connected syringes by hand for 20 times, a foam with the volume $V_F = V_L + V_G$ is generated. For the study at hand, foams with liquid fractions of $\varepsilon = 5 \%$, 7% , 10% , 15% and 20% were formed. To produce foams with perfluorohexane in the gas phase, one syringe was filled with the required volumes of air and liquid. A drop of perfluorohexane taken from the ice bath (liquid, but extremely volatile at room temperature) was added into the other syringe before connecting both syringes. If the liquid content is very low, not all the gas is included in the foam and the syringe is therefore not completely filled with foam at the end of the foaming process. In this case the initial liquid fraction does not correspond to the final liquid fraction of the foam [10]. The precise value of this lowest attainable liquid fraction depends on the formulation. In our case it was 5% . Due to the formation of very small foam bubbles a huge gas/solution interface is formed which is why a high surfactant concentration ($c = 90 \text{ cmc}$) is required to prevent depletion [17].

2.4. Optical Home-made Set-up for Studying the Cleaning Process

To monitor and analyse the cleaning process, the home-made set-up shown in Figure 1 was used. The equipment consists of an aluminium box with a round window at the top and a digital camera at the bottom (Figure 1). On top of the window a contaminated round glass plate ($\varnothing = 8 \text{ cm}$) was fixed and exposed to UV light by six UV-light-LEDs with an average wavelength of 375 nm . A dichroic filter was used as a beam splitter. As the cleaning foam was placed on the contaminated glass plate the *ToupTec* digital camera (model EP3CMOS06300) was switched on to monitor the cleaning process and keep records of its dynamics. The camera objective is provided with long pass filter GG-495 (3 mm) which transmits light with a wavelength above 495 nm . It hence blocks the UV-light allowing only the fluorescence response of the foam to be monitored by the camera. The home-made set up was turned by 90 degrees to perform the imbibition and drop tests. The glass cuvette was placed in front of the round window and exposed to UV light. The foam was placed in the oil-filled cuvette or the oil drop in the foam-

filled cuvette. The processes taking place were recorded by the digital camera. The Camera software *Toupsky* and the commonly used program *Fiji* (*ImageJ*, <https://imagej.net/Fiji>) were used to edit and analyze the photographs. The editing of the photographs is described in more detail in the *Supporting Information*.

3. Results and Discussion

3.1. Cleaning of Glass Plates with PFH-free and PFH-containing Foams

The cleaning tests were carried out with foams with different defined liquid fractions ($\varepsilon = 5\%$, 10% , 15% , 20%) to study the influence of ε on the cleaning efficiency. We used round glass plates contaminated with sunflower oil which contained the fluorescent oil-soluble dye Pigment Yellow. PFH-free cleaning foams were produced with the double-syringe technique (see Section 2.3.) and deposited on the round glass plates. The cleaning tests were repeated with foams with the same liquid fractions but with PFH in the gas phase (PFH-containing foams). The resulting osmotic pressure inhibits coarsening of the foam bubbles [14]. All cleaning tests were repeated at least 3 times for each liquid fraction. During the cleaning tests, we investigated the evolution of the bubble size and of the contact area between oil and glass plate.

Figure 2a shows the two evolutions without (left) and with (right) PFH. All foams have an initial mean bubble radius of $\langle r \rangle = 50\text{--}70\ \mu\text{m}$ at the beginning of the experiment. However, the bubble size of the PFH-free foams grows rapidly after generation and deposition on the glass plate. For all liquid fractions, the bubble size increases roughly by a factor of five in 30 min (Figure 2a, left). This growth is due to coalescence and coarsening [18-20]. On the contrary, the bubble size of the PFH-containing foams remains roughly constant at $50\text{--}70\ \mu\text{m}$ (Figure 2a, right), with a slight increase for the lower liquid fraction. Hence, coarsening in PFH-containing foams is negligible over the time scales of the experiments.

Figure 2: (a) Mean bubble radius $\langle r \rangle$ as a function of time of foams with different liquid fractions without (left) and with (right) PFH in the gas phase. (b) Average change of the oil area on the glass plates in percent including error bars during the cleaning tests with PFH-free (left) and PFH-containing (right) foams of different liquid fractions. The fact that some error bars include values for $A_{oil} > 100\%$ is explained in the *Supporting Information* in Section S3.

Figure 3a shows photographs of the oil area with PFH-free foams with a liquid fraction of $\varepsilon = 5\%$ (top) and $\varepsilon = 20\%$ (bottom) at different times during the first twelve minute (photographs of cleaning tests with foams with liquid fractions of $\varepsilon = 7\%$, 10% , and 15% as well as with $\varepsilon = 5\%$ over longer time interval are shown in the *Supporting Information* (Figures S4.1 and S4.2)). The photograph at time $t = 0$ min shows the soiled glass plate from below directly after application of the foam. In all cleaning tests the area of the fluorescent oil visible on the glass plate decreases with time.

Figure 3: Photographs of the cleaning tests with (a) PFH-free and (b) PFH-containing foams, respectively, with $\varepsilon = 5 \%$ and 20% right after the application, after 4 min, 8 min, and 12 min.

Looking at Figure 3a (top) one sees that the borders of the oil area are rather jagged during cleaning at low liquid fractions ($\varepsilon = 5 \%$): the oil seems to be sucked into the foam. Comparing the photographs for $\varepsilon = 5 \%$ and $\varepsilon = 20 \%$, one sees a change in the cleaning process. For $\varepsilon = 20 \%$ the initial drop splits into many smaller drops with fairly round borders (Figure 3a, bottom). It seems that only the distribution of the oil on the plate is changed, without oil being sucked into the foam. This observation indicates that different, ε -dependent mechanisms are involved in the cleaning process, which will be discussed in Section 3.3.

Figures 3b shows the photographs of the cleaning tests with PFH-containing foams during the first twelve minutes with a liquid fraction of $\varepsilon = 5 \%$ and $\varepsilon = 20 \%$ (photographs of the cleaning tests with foams with $\varepsilon = 10 \%$ and $\varepsilon = 15 \%$ during the first twelve minutes and with foams with all liquid fractions over longer time intervals are shown in the *Supporting Information*

(Figures S4.3-S4.5)). As already mentioned, the PFH-containing foams are more stable and no significant change of the bubble sizes is observed (Figure 2a). Although a cleaning effect can be seen in all photographs it must be mentioned that this effect is very small and very slow for foams with $\varepsilon = 5 \%$, 10% , and 15% . At a liquid fraction of $\varepsilon = 5 \%$, the oil drop does not change its position on the glass substrate during the entire experiment (Figure 3b, top). Only a small removal of the oil from the plate is visible. The cleaning effect becomes more effective with increasing liquid fraction, i.e. the foam with the highest liquid fraction ($\varepsilon = 20 \%$) has the best cleaning effect. The borders of the oil drop become rounder and the drop is split by the foam into smaller drops (Figure 3b, bottom). In addition, the oil area stops evolving after only 12 minutes which is much faster than with the lower liquid fractions at which the oil area evolved over much longer times (~ 60 min, see Figures S4.4 and S4.5 in the *Supporting Information*). This observation again indicates that different, ε -dependent mechanisms must be involved in cleaning as will be discussed in Section 3.3.

Comparing the photographs of the cleaning tests with PFH-free (Figure 3a, top) and PFH-containing (Figure 3b, top) foams with $\varepsilon = 5 \%$ clear differences can be seen. With the unstable PFH-free foams an efficient cleaning effect can be seen, i.e. the oil area becomes rapidly smaller (Figure 3a, top). With the stable PFH-containing foam almost no cleaning effect is visible at the same liquid fraction. Obviously, cleaning is more efficient with the unstable foam at low ε -values. This holds true for all ε -values except for $\varepsilon = 20 \%$. In this case, both the stable and the unstable foam clean efficiently. However, in the first case (PFH-free) the oil droplet is split into much smaller drops compared to the second case (PFH-containing). We have here another indicator for different cleaning mechanisms – this time not ε -dependent (see Section 3.3 for an explanation).

In Figure 2b we summarize the results of all cleaning tests which we obtained during 15 min for the PFH-free and during 60 min for the PFH-containing foams. We define the area of the fluorescent oil visible at $t = 0$ min as the reference area corresponding to $A_{\text{oil}} = 100 \%$. We plotted the average change of the oil area A_{oil} on the glass plates as a function of time t for PFH-free (Figure 2b left) and PFH-containing (Figure 2b right) foams with different liquid fractions. The experimental time was limited to 15 min for PFH-free foams since the foams decayed very quickly (Figure 2a left). Extending the cleaning time up to 30 min one sees significant better cleaning at $\varepsilon = 5 \%$ only, namely a further reduction of A_{oil} down to 15% (see Figure S4.2 in the *Supporting Information*). At all other liquid fractions, the oil area stayed approximately the same at $t > 15$ min. We extend the measurement time up to 60 min for PFH-containing foams since the cleaning process was very slow in these cases. As already discussed, the following

trends are clearly seen: (1) Oil removal from soiled glass plate is significantly slower for PFH-containing foams than for PFH-free foams for all liquid fractions. (2) With the exception of $\varepsilon = 20\%$, oil removal is less efficient for PFH-containing foams even with an extended cleaning time of 60 min. (3) Increasing the liquid fraction in PFH-containing foams one observes an increase of oil removal, while for PFH-free foams the area of oil which remains on the glass surface after 15 min goes through a maximum at $\varepsilon = 7\%$.

3.2. Oil Imbibition Ability of PFH-free and PFH-containing Foams

It is known that foams can absorb certain liquids in the Plateau borders. The driving force for this “imbibition” are capillary forces [9,21], arising from the reduction of the water-air interface in the foam, whereby the total energy of the system decreases [8, 22]. In the case of non-miscible liquids such as sunflower oil, in addition to reducing the water-air interface, a new oil-water interface is formed in the Plateau Borders, which requires energy. Thus, the influence of the newly formed water-oil interface must be included in the foam energy [8-9]. Assuming a low liquid fraction foam, one can show that the drainage behaviour of this hybrid foam is similar to that of an ordinary foam with an effective interfacial tension of [8-9],

$$\gamma_{\text{eff}} = \sigma_{\text{gas/solution}} \left(1 - 3 \frac{\gamma_{\text{oil/solution}}}{\sigma_{\text{gas/solution}}} \right), \quad (2)$$

where $\gamma_{\text{oil/solution}}$ is the interfacial tension between the oil and cleaning solution and $\sigma_{\text{gas/solution}}$ the surface tension of the cleaning solution. If γ_{eff} is positive and the liquid fraction of the foam small enough, spontaneous imbibition of the oil occurs since it is energetically favourable. To calculate the effective interfacial tension for our system, we measured the interfacial tensions of the different interfaces with a pendant drop and a spinning drop tensiometer, respectively. The resulting interfacial tensions are listed in Table 1. For the PFH-containing system the surface tension $\sigma_{\text{gas(PFH)/solution}}$ between cleaning solution and PFH-containing air and the interfacial tension $\gamma_{\text{oil(PFH)/solution}}$ between PFH-containing oil and cleaning solution was measured.

Table 1: Interfacial tensions of the different interfaces involved in the cleaning process measured with a pendant drop and a spinning drop tensiometer, respectively.

Interface		Interfacial Tension / mN m^{-1}	Technique
Air / Cleaning Solution	$\sigma_{\text{gas/solution}}$	27.5	Du Noüy
Air with PFH / Cleaning Solution	$\sigma_{\text{gas(PFH)/solution}}$	22.0	Pendant Drop
Oil / Water	$\gamma_{\text{oil/water}}$	28.7	Pendant Drop
Oil / Cleaning Solution	$\gamma_{\text{oil/solution}}$	2.5	Spinning Drop
Oil with PFH / Cleaning Solution	$\gamma_{\text{oil(PFH)/solution}}$	2.6	Spinning Drop

The results show that the surface tension of the cleaning solution is reduced in the presence of PFH vapour, as is known from literature [23-25]. This reduction is caused by the adsorption of the very hydrophobic PFH molecules on the water surface [25]. According to Equation (2), the effective interfacial tension of our system without perfluorohexane is $\gamma_{\text{eff}} \approx 20.0 \text{ mN m}^{-1}$, while $\gamma_{\text{eff}} \approx 17.7 \text{ mN m}^{-1}$ with perfluorohexane. Thus $\gamma_{\text{eff}} > 0$ for both systems. Based on this result imbibition should occur at a liquid fraction of $\varepsilon = 5 \%$ in both foams. Since the effective interfacial tension is a bit lower in the presence of PFH, the imbibition should be slightly weaker for the PFH-containing foams. To show this experimentally, imbibition tests were performed with both systems. For that purpose, the fluorescent oil was filled into a glass cuvette reaching an initial height of $h_{\text{oil}} = 4 \text{ mm}$. Subsequently foams with different liquid fractions were placed on top of the oil. Figure 4a shows photographs of imbibition tests with PFH-free foams at liquid fractions of $\varepsilon = 5 \%$ (top) and $\varepsilon = 20 \%$ (bottom) (photographs of the imbibition tests of foams with $\varepsilon = 7 \%$, 10% , and 15% are shown in the *Supporting Information* (Figure S5.1)). The first photograph (Figure 4a, left) shows the fluorescing oil on the bottom of the glass cuvettes. The following photographs (Figure 4a) show the cuvette 4 min, 8 min, and 12 min after the foam was placed on top of the oil. Note that the oil-free foam is barely visible in UV light. The photographs taken for $\varepsilon = 5 \%$ (Figure 8, top) show that the fluorescent oil was drawn into the foam (imbibition). In contrast to this, for $\varepsilon = 20\%$ (Figure 4a, bottom) the fluorescent oil floated on the drained cleaning solution.

Figure 4: Photographs of the imbibition test before (oil without foam) as well as 4 min, 8 min, and 12 min after the application of the (a) PFH-free and (b) PFH-containing foam, respectively, with $\varepsilon = 5 \%$ and 20%

Figure 5a shows zoomed photographs of the imbibition test with $\varepsilon = 5 \%$ (left) and $\varepsilon = 20 \%$ at $t = 8 \text{ min}$ corresponding to the white boxes in Figure 4a.

Figure 5: (a) Zoomed photographs of the imbibition test 8 minutes after having placed the PFH-free cleaning foam with $\epsilon = 5\%$ (top) and $\epsilon = 20\%$ (bottom) on top of the oil layer, corresponding to the white boxes in Figure 4a. h_t is the total height of the oil and the liquid that has drained under the oil, i.e. $h_t = h_{oil} + h_{solution}$. (b) Time evolution of the oil height h_{oil} (circles) and the total height h_t (dotted lines) in the glass cuvette during the imbibition tests for foams of different liquid fractions without PFH.

Looking at Figure 5a (top) one sees that the oil is sucked into the foam. Imbibition is stopped at a certain height in the foam due to gravity and the beginning foam decay. In our case, imbibition stopped after ~ 6 min. At longer times, the process may actually revert, since the bubbles become bigger with time (Figure 2a, left) and imbibition strength decreases with increasing bubble size [9]. At higher liquid fractions almost no imbibition takes place (Figure 4a (bottom) and Figure S5.1 in the *Supporting Information*), which is expected, since the driving capillary forces are much weaker. Moreover, at high liquid fractions, drainage is visible [26]: the liquid running out of the foam flows under the oil and the oil floats on the liquid (Figure 5a (bottom)). This is clearly visible in Figure 5b, where we plotted the time evolution of the oil height h_{oil} during the imbibition tests for all liquid fractions. It can be seen that in all cases h_{oil} first decreases slightly, but then increases again or remains constant. One observes that the oil is sucked into the foam initially, but flows back during foam decay. At higher liquid fractions the oil phase starts to float upon the drained cleaning solution. The dotted lines (Figure 5b) show the total height of the oil and the liquid that has drained under the oil, i.e. $h_t = h_{oil} +$

h_{solution} . In other words, it shows the distance between the bottom of the cuvette and the foam. As expected, drainage increases with increasing liquid fraction [27].

Let us now look at Figure 4b, which shows photographs of imbibition tests with PFH-containing foams for $\varepsilon = 5\%$ and 20% at different times (photographs of imbibition tests with $\varepsilon = 10\%$ and 15% are shown in the *Supporting Information* (Figure S5.2). Again, the first photograph shows the oil on the bottom of the glass cuvettes, while the following show the cuvette 4 min, 8 min, and 12 min after the PFH-containing foams were placed on top of the oil. Despite the positive effective surface tension, no imbibition is visible at either liquid fraction. The experiments with foams with liquid fractions of $\varepsilon = 5\%$, $\varepsilon = 10\%$, and $\varepsilon = 15\%$ only show how the oil moves upwards on the wall between foam and glass. For this reason, the time evolution of the oil height (in analogy to Figure 5b) could not be determined.

When comparing the imbibition tests with and without perfluorohexane, it seems as if only in PFH-free foams oil is imbibed by the foam. This is surprising, because in both cases (with and without PFH) the foams fulfil the necessary conditions for imbibition [8-9]. Since the bubble size of the PFH-containing foams is very small, we suspect that the light scattered by the foam may be too strong to detect the oil in the Plateau borders. To prove or disprove this suggestion, we monitored the imbibition of an isolated fluorescent oil drop (0.1 ml) which we placed in the center of a PFH-containing foam with $\varepsilon = 5\%$ (see Figure 6). Due to the high yield stress of the foam, the drop remains at its initial position. This allows optimising the camera settings without the overruling influence of the large oil volume at the bottom of the cuvette. Looking at Figure 6, one sees that the oil droplet spreads due to imbibition. The oil approaches the front wall of the glass vial, hence increasing the detected light intensity. In the case of PFH-containing foams this process is very slow, because the imbibition speed slows down with decreasing bubble size [8,9]. We can thus conclude that imbibition takes place, but is slow and not easily detectable due to the strong light scattering of the foam.

Figure 6: Zoomed photographs of an oil drop spreading in the center of a PFH-containing foam at a liquid fraction of $\varepsilon = 5\%$ immediately after adding the drop ($t = 0$ min), after 4 min, 8 min, and 12 min. The photographs were converted to black and white and the contrast was intensified.

In summary, we can conclude that all foams (with and without PFH, different liquid fractions) have the tendency to reduce the amount of oil spread on a glass plate. However, we see clear differences in the cleaning behaviour for foams with different liquid fractions and stabilities. In Section 3.3 we will discuss these observations.

3.3. Involved Cleaning Mechanisms

Combining our observations with those reported in the literature on related systems, we propose that three main mechanisms play simultaneously a role in foam-based cleaning. These three mechanisms are sketched in Figure 7. Depending on the liquid fraction and foam stability, the relative importance of each of these mechanisms differs.

Mechanism I (see top of Figure 7, orange arrows) is classic imbibition of oils with positive effective surface tension. In this mechanism, the oil is sucked into the Plateau borders of the foam by capillary forces [8,21]. This mechanism is strongest for foams with small liquid fractions and small bubbles [8]. Yet, the smaller the bubbles the slower is the oil uptake due to viscous dissipation in the narrow Plateau borders [8]. In the ideal case - as sketched in Figure 7 - all oil is sucked up by the foam. However, for this to happen, the oil needs to be detached from the solid surface. For such a detachment the oil/water contact line of the drop boundary must be moved along the surface, which is known to be difficult due to contact line pinning. This contact line pinning is visible by the ragged form of the boundary of the oil zone, as can be seen e.g. in the top row of Figure 3a. To overcome the strong pinning forces, one commonly uses mechanical wiping.

This is exactly where **Mechanism II** comes into play (middle row of Figure 7). An unstable foam is continuously in motion. Multiple bubble re-arrangements occur with characteristic time

scales of milli-seconds, leading to violent wiping motions between the foam and the interface. This wiping moves very thin wetting films and bubble meniscii rapidly along the surface, exerting strong shear stresses, whose cleaning efficiency has already been proven for individual menisci [3]. In a stable foam, however, there is little motion and this mechanism is thus much less efficient. The characteristic time of Mechanism II is directly related to the foam ageing time (causing the bubble re-arrangements), which is exactly what one observes when comparing unstable (without PFH) and stable foams (with PFH).

At higher liquid fractions, a third **Mechanism III** comes into play (bottom of Figure 7): drainage. If the foam is higher than $l_c^2/\langle r \rangle$, where $l_c^2 = \gamma/\rho g$ is the capillary length [28], the capillary forces of the foam are not sufficient to retain all the liquid. Consequently, the liquid drains and accumulates underneath the foam (see Figures 4-5). The draining liquid can also “flow” under the oil film thereby lifting it off the surface. At the same time, if capillary forces are not strong enough to maintain the foaming liquid, they will not be able to imbibe oil either. Hence, once the conditions of drainage are reached, oil will only be pushed together on the surface. A rough calculation assuming that the oil film is pushed together into one hemispherical drop predicts a final surface coverage of 13% in either case (with or without PFH). Looking at the results for the highest liquid fractions in Figure 2b, one sees that this calculation is indeed a good approximation.

All three mechanisms depend on the liquid fraction and the stability of the foam. The lower the liquid fraction, the more efficient are Mechanisms I and II. The less stable the foam, the more efficient Mechanisms II and III. The interplay between the different mechanisms leads to a complex cleaning efficiency of foams. Not only do unstable foams clean more efficiently than stable foams (due to the importance of the wiping, i.e. Mechanism II), but even for unstable foams, the cleaning efficiency depends on the liquid fraction of the foam. Depending on the desired outcome, it is advisable to work either with foams at low liquid fractions ($\epsilon < 5\%$) or with foams at high liquid fractions ($\epsilon > 10\%$). In the first case, cleaning is slow, but has the advantage that the oil is soaked up by the foam due to imbibition, i.e. Mechanism I. In the second case, the oil is rapidly detached from the surface due to drainage, but remains underneath the foam together with a lot of liquid, which may not be practical. At intermediate liquid fractions, cleaning is less efficient.

Mechanism I (Imbibition)

- > low ϵ
- > all foams

Mechanism II (Wiping)

- > all ϵ
- > only PFH-free

Mechanism III (Drainage)

- > high ϵ
- > all foams

Figure 7: Schematic drawing of the three different mechanisms taking part in the cleaning process with PFH-free and PFH-containing foams for different liquid fractions ϵ .

4. Conclusions

In this study cleaning tests with foams with different liquid fractions and different stabilities were performed to understand the role of foams in cleaning processes. We have shown that under certain conditions foams can be very efficient cleaning tools, which we explained by an efficient interplay of three mechanisms. Mechanism I is imbibition, i.e. oil is drawn into the foam due to capillary forces [8-9, 29]. Imbibition occurs most efficiently in foams with low liquid fractions and small bubble sizes. Mechanism II is wiping - the movement of the contact line between oil, glass, and foam - which is caused by the dynamics of the foam's decay processes. This mechanism acts at all liquid fractions. Mechanism III is drainage of the cleaning solution at higher liquid fractions ($\epsilon \geq 10\%$). Thus, the cleaning process is dominated by imbibition (I) and wiping (II) for low liquid fractions and by wiping (II) and drainage (III) for higher liquid fractions. The importance of the wiping mechanism leads to the main result of this

research, namely that unstable foams clean more efficiently than stable foams. However, even for unstable foams, an optimum liquid fraction needs to be found. Foams with low liquid fraction ($\epsilon < 7\%$) and with high liquid fraction ($\epsilon > 10\%$) seem to be efficient cleaners after inspection of Figure 2b in terms of the evolution of the surface covered by the oil. However, both limits follow completely different cleaning mechanisms: in foams with low liquid fractions, the oil is efficiently sucked into the foam, while with high liquid fraction foams, the oil is merely pushed together underneath the foam by the draining cleaning solution.

To sum up, **less is more**. The best cleaning result is achieved with a foam with a **low liquid fraction** ($\epsilon \leq 5\%$) and **small bubble sizes** with **limited stability**. In comparison to previous work, where static foams have been studied [29], our results emphasise the importance of the “wiping” action of the foam bubbles on the surface. As such, our insights combine what is known for static foams with recent understanding of the efficiency of meniscus dynamics in the cleaning process [3]. While we used a specific model system having in mind an environmentally friendly cleaning process, all proposed mechanism are general enough to be easily transferred to other surfactants and oils, as long as the effective surface tension remains sufficiently low (Equation (2)) and the foam stability is “intermediate” (high enough so that the foam remains on the surface during the cleaning process and low enough to ensure bubble dynamics).

While this work has put light on some fundamental cleaning mechanisms of foams, many detailed questions remain to be answered. While we explored the influence of foam stability and liquid fraction, the precise role of the bubble size needs to be elucidated. Having a very different impact on the three mechanisms, it is likely that there is an optimum bubble size for efficient cleaning. It will also be important to optimise the surfactant concentration and to understand the cleaning of non-imbibing oils and solid soils. In order to improve the cleaning efficiency, one may also consider adding particles to the foaming solution [5-6]. It will be important to consider more realistic surface contaminations, including soot particles, waxes, resins, dust, or pesticides. Last but not least, a way to upscale significantly the production of foams with small bubbles and low liquid fraction must be found to use this cleaning approach for larger surfaces.

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