VIP Foams

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Smart Foams: Switching Reversibly between Ultrastable and Unstable Foams**

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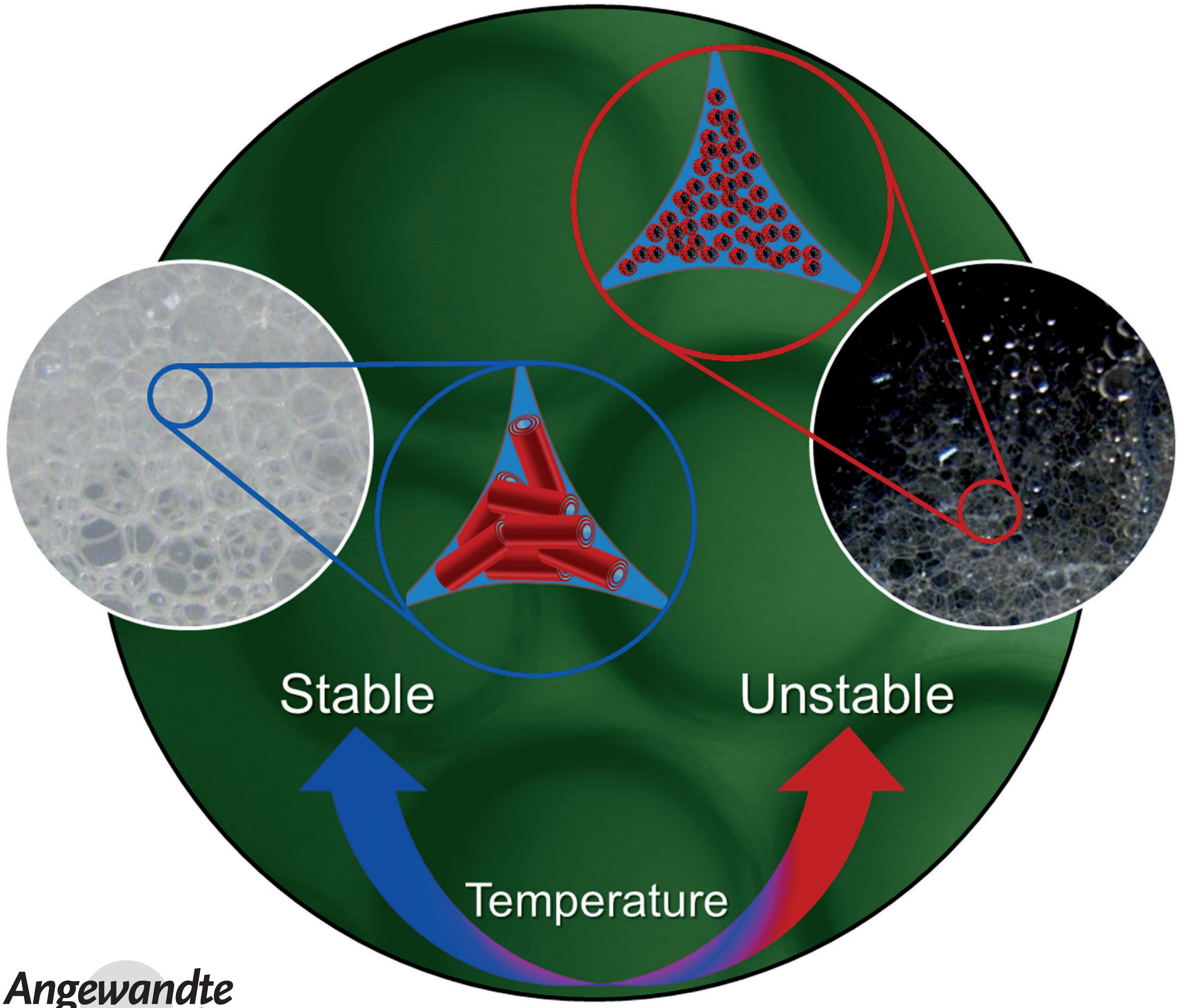

From materials chemistry to soft matter and daily life, foams are substances of outstanding importance. They can be used as sacrificial templates for the production of macroporous materials,[1,2] in food and cosmetics, or for a large variety of other applications.[3–6] Although a strong effort has been made to understand the aging of foams[7] and consequently to increase their stability and properties by their chemical formulation,[8–11] there still is no simple system that would exhibit high foamability together with drastic reductions of the aging processes, leading to long lifetimes. An optimal foam would be made from solutions of foam stabilizers that could move rapidly and readily at the interface (foamability) and subsequently produce an irreversibly adsorbed elastic layer at that interface, which is resistant to compression and thus limits film breaking and gas diffusion (coalescence and coarsening). In addition, those ideal foam stabilizers should also contribute to limit the drainage in the liquid channels that form a continuous network between the bubbles, the so-called plateau borders, kinetically increasing the foam stability. Up to now, it remains difficult to conciliate both the foamability and the resultant foam stability, as optimizing one often reduces the other. For instance, partially hydrophobic solid particles allow the formation of very long-lived foams[12–15] (over weeks) by forming a very solid layer at the interface, which annihilates the foam coarsening. The liquid drainage is usually not stopped in these solid-stabilized foams, though adding more hydrophilic particles could limit the liquid drainage by their accumulation in the plateau borders.[16] However, these solutions of solid particles lead to a limited amount of foam, that is, they exhibit poor foamability. This is mainly because the adsorption dynamic of those solid particles is slow and the adsorption barriers are high. By contrast, low-molecular-weight surfactants can more readily adsorb at the interface. However, they do not give sufficiently solid films and film breaking or coarsening may occur more easily. Common surfactants, such as SDS or CTAB, have a good foamability but produce foams with a stability that does not exceed a few tens of minutes. Protein solutions provide foams in between these two extremes, but often with quite low foamability and fast aging.[17–20] Thus, to find a simple system providing both high foamability and inhibition of aging is a remaining challenge. Moreover, complementary very attractive features of foams would be the possibility of tuning the foam stabilization or destabilization by a simple external trigger. Indeed, in some cases, good foam stability is initially required but the foam should be readily decomposable. This is the case for instance for recovering radioactive materials or in various washing processes. There is abundant literature concerning responsive self-assemblies made of surfactants or gels, however, almost nothing has been reported yet for foams. The first attempt to produce responsive foams has been realized using latex particles[21] and varying the pH value after the foam was formed. Tuning the foamability, but not the foam stability, has been achieved by temperature or UV irradiation.[22] Recently, magnetic responsive foams have been designed.[23] Herein, we report results on a simple and sustainable system that combines a good foamability and an outstanding foam stability, which can then be readily tuned to weak foam stability by changing the polymorphism of the system upon heating. To achieve this goal, we use a fatty acid system made of the 12 hydroxy stearic acid (12-HSA) as foam stabilizer. Fatty acids exhibit low surface tension[24,25] and have promising surface properties.[26] Moreover, the 12-HSA is known to form highly elastic layers at the air/water interface[25] (and even crystalline structures at high surface concentrations) because of strong intermolecular interactions induced by hydrogen bonding between hydroxy groups. Besides, fatty acids are model systems for investigating the properties of insoluble Langmuir interfacial monolayers.[27,28] The use of fatty acids would allow us to significantly increase the foam stability by limiting film breaking and gas diffusion. However, the main problem is that long-chain fatty acids are insoluble or crystallize in water, thus hampering their use as surface active agents.[26] A way to disperse fatty acids in water is to use soluble organic counterions.[29–31] One of our major achievements was to successfully disperse 12-HSA in water using ethanolamine or hexanolamine: under these conditions, one obtains self-assembled multilayer tubes of around 10 μm length and 600 nm diameter.[32,33] We first describe the foamability and the outstanding foam stability of that system at room temperature, hence establishing the link to the supramolecular assembly (tubes) in water. In solution, those tubes melt into micelles at a temperature that depends on the nature of the counterion.[33] Hence, we show that the melting of tubes under micelles upon heating is accompanied by a complete destruction of the foam. This allows us to tune the foam stability with temperature.

We produced foams using the multilamellar tubular system (Figure 1) either by shaking by hand (HS-foams) or by using a Foamscan apparatus (F-foams; see the Supporting Information). The stability of HS-foams was evaluated over 6

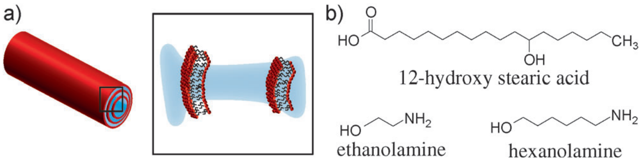

Figure 1. a) Schematic representation of the multilayer tubes and b) chemical structure of the 12-hydroxy stearic acid and the counterions used.

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months by comparing pictures taken at different times (Figure 2a). Foams were shown to be outstandingly stable (over months) and are thus described as "ultrastable" foams. To the best of our knowledge, such foam lifetimes obtained using low-molecular-weight amphiphiles are unprecedented and have up to now only been observed when using solid particles[12,13] or xanthane gelified foams stabilized by proteins.[11]

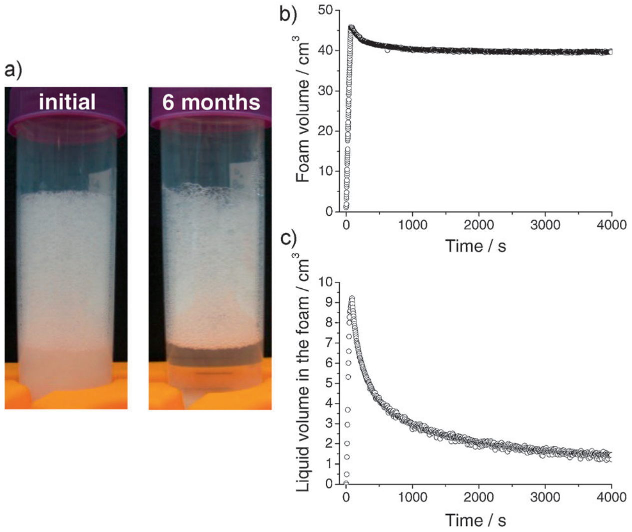

Figure 2. a) Photographs of HS-foams taken at 6 months interval in the system 12-HSA/ethanolamine at 40 mg mL^{-1} fatty acids. The turbid tubular solution that has drained is visible in the lower part of the sample tube. After 6 months, a sediment in the bottom of the tube is apparent. b) Foaming properties as recorded by the Foamscan apparatus in the system 12-HSA/ethanolamine at 10 mg mL^{-1} fatty acids. c) Evolution of the liquid volume in the foam as a function of time determined by conductivity measurement.

The foaming properties were further studied during a shorter period of time, using F-foams (Figure 2b). Producing foams by this procedure provides a quantitative description of the obtained foam in terms of how much foam volume is produced (foamability), how wet it is initially, and how it ages. The foamability was found to be optimal because all the gas was encapsulated in the foam by the end of bubbling (see the Supporting Information). This observation shows that no bubble coalescence occurs, even under short times of bubbling. Interfaces are thus optimally and extremely rapidly covered as in the case of other low-molecular-weight surfactants.

The foam also entrapped a large amount of liquid: at the end of bubbling, the average liquid fraction was around 20%, which corresponds to a relatively wet foam, meaning that the bubble size (in the range of 50 to 100 μm) has remained small and constant during production of the foam (Figure 2c). Once the F-foam is produced, the high stability seen for HS-foam was confirmed, because the foam volume remained constant over the period studied and the bubble size did not change. However, the foam drained within 30 min (Figure 2c). It is worth noting that there remains some liquid within the structure, namely in average about 5% of liquid fraction over the foam column. These foams are thus mainly optimized in terms of inhibited film breaking or coarsening, but less efficiently in terms of drainage reduction.

At this stage, one needs to determine the origins of this outstanding stability, and how it is connected to the supramolecular assemblies. The presence of tubes in the foam was first confirmed by confocal microscopy using a hydrophobic fluorescent probe inserted into the multilamellar tubes (Figure 3a and b). This observation shows that although some tubes unfolded upon foam formation giving free monomers that moved at the interface, they are still present in the foam liquid channels. The length of the tubes is reduced by a factor of around two in the foam compared to the bulk solution (see the Supporting Information). Small angle neutron scattering (SANS) experiments were carried out on the foam to provide local scale information. The results were compared with those obtained for the initial tube solution (stock solution) and for the drained solution recovered at the bottom on the foam after drainage (Figure 3c). The three azimuthally averaged spectra were clearly similar with Bragg peaks at the same Q position. Those peaks stand for the multilamellar arrangement of the fatty acid bilayers within the tubes[32] and confirm the presence of tubes in the foam. The only difference in the case of the foam is the Q^{-4} scattering decay at low Q, which accounts for the Porod surface scattering of the large bubbles of the foam. Although their length may have changed in the foam, the tubes are still composed of multilamellar fatty acid bilayers that exhibit similar structural parameters as in the stock solution.

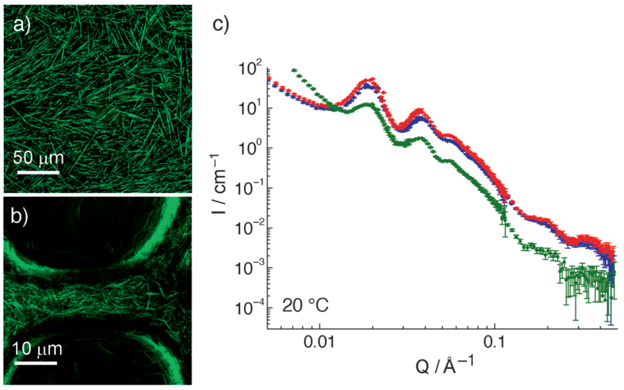

Figure 3. Confocal microscopy images of a) a bulk solution of tubes and b) a foam that was deposited on glass lamellae and was further covered with a glass plate using a spacer ensuring a fixed volume of 25 μL. c) SANS data recorded for the foam (green), the stock solution (blue), and the drained solution (red). In the case of foams, it was first checked by contrast variation experiments that the recorded signal corresponded to SANS scattering and not to neutron reflectivity[36] (see the Supporting Information, Figure S1).

Another important information on the foam structure is at the local scale in the thin lamellae separating two bubbles that are in contact. Elucidating the mechanisms governing the stability of these thin lamellae is crucial for explaining why bubbles do or do not coalesce and how gas diffuses from small to large bubbles (coarsening). To this end, we performed experiments on a single film with a "thin-film balance" apparatus[34] (see the Supporting Information, Figure S2). In the single film a thin central part with thicknesses of a few tens of a nm was observed, which is then called a "black film"[34,35] and implies that tubes are expelled from this film. The thin central part also exhibits a small area and is surrounded by a large meniscus that is much more extended than what is usually found for other surfactants. This result suggests that tubes accumulate and are jammed within that surrounding meniscus. By analogy in the foam, we expect the tubes to be expelled in the plateau borders and to be absent from the lamellae that separate the bubbles. This specific structure of the lamellae that separate the bubbles turns out to be quite efficient for reduction of the foam aging.

Firstly, the thin central part of the lamellae is made of two repulsing interfacial layers on which only free monomers of 12-HSA are adsorbed. These layers are most likely within a condensed-like state with the alkyl chains in close packing. It is well known that the presence of fatty acids adsorbed at an interface provides interfacial layers of high dilational moduli, E easily reaching hundreds of $\mathrm{mN\,m^{-1}}$[25,27,28] as the molecules are insoluble. Moreover, it is also known that 12-HSA can pack at interfaces even more efficiently than common fatty acids.[25] Such high dilational moduli (or low compressibility) are indeed the main reason why coarsening is almost stopped: the Gibbs criterion states that coarsening stops if $E > \gamma$, where γ is the surface tension. In fact, if the bubble interfaces cannot be continuously compressed, the smallest bubbles cannot vanish towards the largest ones, and coarsening is blocked.[4,6,7]

Secondly, coarsening and lamellae ruptures are also limited because the area of the thin contact part between bubbles (through which most of the gas diffusion occurs) is small, because of the presence of the tubes in the surrounding menisci that make them thicker and wider than usual. Adding the fact that the tubes can be jammed within the plateau borders (at least at the latest stages of drainage, when the borders are already well shrunk) completes the picture that rather well explains the surprising long lifetimes of these foams. We thus have here the first surfactant system that foams easily and that, because of an optimal arrangement of monomers and tubes within the foam structure, does neither coarsen nor collapse.

Foams were further heated and their stability was monitored. As mentioned previously (see above), the multilamellar tubes melt into micelles at a temperature denoted T_m, which depends on the nature of the counterion.[33] HS-foams made with the ethanolamine salt ($T_m = 70\,°C$) were still remarkably stable up to two weeks at 60 °C. A similarly high stability was observed for the hexanolamine salt ($T_m = 60\,°C$) at 50 °C (see the Supporting Information, Figure S3). This high stability was quantitatively evidenced below T_m on the F-Foams (Figure 4a). SANS data obtained at these temperatures were also similar for the foam, the stock solution, and the drained solution (see the Supporting Information, Figure S4). This result shows that at $T < T_m$, tubes are always present in foams and exhibit the same behavior as in bulk solution. However, at a temperature $T > T_m$, a foam could still be produced but was no longer stable as the foam volume quickly decreased with time (Figure 4a). In the case of the HS-foams (using the hexanolamine salt, $T_m = 60\,°C$), destabilization occurred in only 15 min in an oven at 60 °C (see the Supporting Information, Figure S5). This effect is dramatic since the destabilization passes from weeks to a few minutes over only a few degrees. This event occurs exactly at the tube/micelle transition in both foams made of the ethanolamine and hexanolamine salts. The SANS data obtained above that transition temperature show that micelles (that have replaced tubes) are indeed present in solution but also in the foam (Figure 4b).

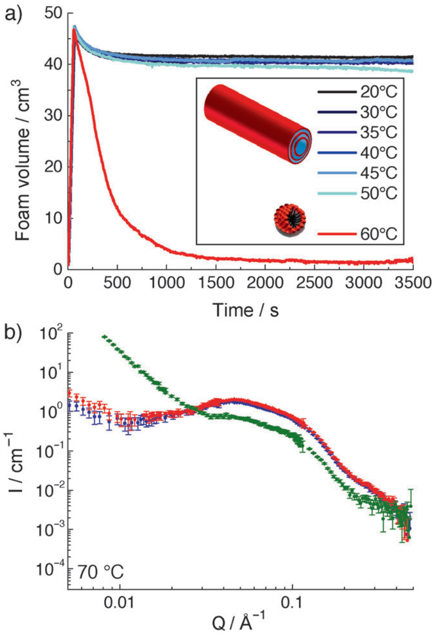

Figure 4. a) Evolution of the foam volume as a function of time in F-foams at different temperatures for the 12-HSA/hexanolamine system ($T_m = 60\,°C$). b) SANS data at 70 °C (in the 12-HSA/ethanolamine system, $T_m = 70\,°C$) showing that micelles are formed at that temperature in the foam (green), the stock solution (blue), and the drained solution (red).

This observation offers us a versatile and simple way to produce temperature-tuneable foams. The triggering of the foam stability by temperature is illustrated in Figure 5. An initial stable foam made with the hexanolamine salt ($T_m = 60\,°C$) at 20 °C has a given constant foam volume that markedly decreases when the temperature is raised up to 60 °C (Figure 5a). The foam is dramatically destabilized at that temperature in consistency with our previous experiments (Figure 4a). Remarkably, decreasing the temperature to 20 °C is accompanied by a sudden stop of the decrease of the foam volume that becomes constant again as a function of time. If the foam is initially produced at $T > T_m$, it is not stable as evidenced by the quick decrease of the foam volume (Figure 5b). However, here again lowering the temperature below T_m, that is, 55 °C, a temperature at which the tubes are reformed, enabled us to recover a very stable foam. Additional curves are shown in the Supporting Information, Figure S6. Altogether, tubes are reformed in the foam upon cooling, as observed in the bulk when crossing the tube–micelle transition, thus allowing recovering the stabilization

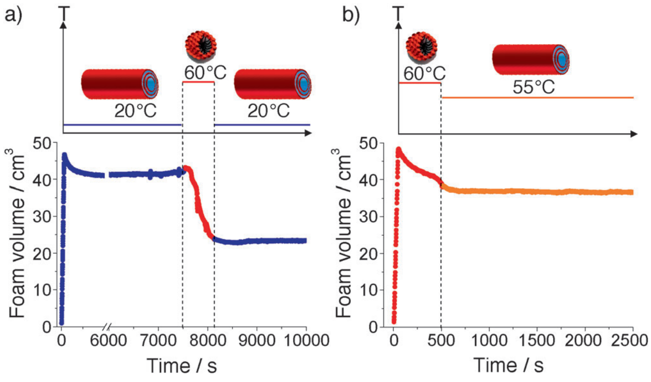

Figure 5. Two examples showing the evolution of the foam volume as a function of time and temperature (in the 12-HSA/hexanolamine system, $T_m = 60\,°C$). On top of each graph the schematic representation of the supramolecular assemblies (not true to scale) present in solution and in the foam are shown as a function of the temperature.

of the foam. This almost instantaneous phenomenon leads to a complete reversibility of the system. Moreover, the foam can also be regenerated (when it has been destructed at high temperature) by a simple reinjection of gas into the column below the temperature at which tubes melt into micelles. Herein, we can only speculate on the origins of foam destabilization. Many effects that can lead to lamellae rupture and foam collapse can occur, as listed below. Lamellae and foams are fragile and brittle architectures, especially if the interfacial layers are solidlike as expected here. So when the temperature is raised, interfacial flows, changes in the shape of the lamellae and menisci around them must be triggered easily leading to the lamellae rupture. We also believe that above the tube/micelle transition temperature, the interfacial layers become softer and less condensed also because fatty acids become more soluble (increasing the monomer concentration) at high temperatures. Moreover, the exchange of monomers between the interface and the micelles is expected to be faster than between the interface and the tubes.

Then, we have shown that in terms of foam stability, this system made of multilamellar tubes of 12-HSA combines the advantages of both the solid particles and the low-molecular-weight amphiphiles, because those fatty acids readily and quickly move to the interface but also produce solid layers that cannot be indefinitely compressed. In addition, the tubes lead to large menisci surrounding the lamellae, and reduce the drainage flows. Of particular interest is that the reversible phase transition of tubes into micelles upon heating leads to reversible fast foam destabilization. This system is unique compared to other amphiphile-forming tubes that generally melt into vesicles.[37] 12-HSA is a generic molecule that results from the hydrogenation of a sustainable material, i.e., ricinoleic acid and is available in large amounts at low cost. As the tube/micelle transition can be tuned by the nature of the counterion[33] or the physic-chemical parameters,[38] one could design similar systems, leading to foams that could be destabilized at any desired temperature.

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