Smart Foams: Switching Reversibly between Ultrastable and Unstable Foams

Anne-Laure Fameau, Arnaud Saint-Jalmes, Fabrice Cousin, Bérénice Houinsou-Houssou, Bruno Novales, Laurence Navailles, Frédéric Nallet, Cédric Gaillard, François Boué, Jean-Paul Douliez

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From materials chemistry to soft matter and daily life, foams are edifices 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 [13-16]. Although a strong effort has been made for understanding the aging of foams[7] and consequently for increasing their stability and properties via their chemical formulation [8-10], there still does not exist a system which would exhibit high foamability in parallel with drastic reductions of the aging processes, leading to huge lifetimes. It must be mentioned however that the stability can be increased alternatively but by using gelator within the foam stock solution [11]. An optimal foam would be made from solutions of foam stabilizers which could move rapidly and readily at the interface (foamability) and subsequently produce an irreversibly adsorbed elastic layer at that interface, resisting to compression and thus limiting 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 which 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-living foams [12-15] (over weeks) by forming a very solid layer at the interface, which annihilate 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 via their accumulation in the Plateau borders [16]. However, these solutions of solid particles yield the production of a limited amount of foam, i.e., they exhibit poor foamability. This is mainly because the adsorption dynamic of those solid particles is slow and that the adsorption barriers are high. Solid particles also present the strong inconvenience that they aggregate in water and the foaming stock solution is not stable in time. By contrast, low molecular weight surfactants can more readily adsorb at the interface. However, they do not yield sufficiently solid film and film breaking or coarsening may occur more easily. For instance, SDS, CTAB or lauryl ether sulphate, which are the most common used surfactants 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 still low foamability and aging [17-20]. Thus, it remains to find a simple system providing both high foamability and arrest of aging. Moreover, complementary very attractive feature of foams would be the possibility of tuning the foam stabilisation/destabilisation by a simple external trigger. Indeed, in some cases, good foam stability is initially required but the foam should be finally voluntarily destructed. This is the case for instance for recovering radioactive materials or in various washing processes. The first attempt to produce responsive foams have been realized using latex particles [21] increasing the pH by dropping diluted NaOH on the foam. However, such a drastic destabilizing procedure has the strong disadvantage that foams cannot be longer re-formed, except if one further re-decreases the pH of the solution what may not be satisfactory in many applications. Tuning the foamability (but not the foam stability) has been achieved by the temperature or UV irradiation [22]. If some results start to be collected on responsive self assemblies made of surfactants or gels (with reversible effects) [23], almost nothing has been found yet with foams.

Here, we report results on a simple and sustainable system which gathers 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 as foam stabilizer a fatty acid system made of the 12 hydroxy stearic acid (12-HSA). 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 an air/water interface [25] (and even crystalline structures at high surface concentrations) because of strong intermolecular interactions induced by hydrogen bonding between hydroxyl groups. Besides, fatty acids are the model systems for investigating the properties of insoluble Langmuir interfacial barriers.
The structure of the supramolecular assembly of fatty acids at the local scale within the foam was probed by Small Angle Neutron Scattering (SANS). The experiments were carried on the foam and the results were compared with those obtained for the initial tube solution (stock solution) and for the liquid solution recovered at the bottom on the foam after drainage (drained solution), figure 3c). The three azimuthally-averaged spectra were clearly similar. They show Bragg peaks at the same Q-position. Those peaks stand for the multimellar arrangement of the fatty acid bilayers within the tubes [29] and confirm the presence of tubes in the foams. 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 multimellar fatty acid bilayers exhibiting similar properties than in the stock solution.

An other important information on the foam structure is at local scale in the thin lamella separating two bubbles which are in contact. Figuring out the mechanisms governing the stability of this thin lamella is crucial for explaining why bubbles coalesce or not and how gas diffuses from small to large bubbles (coarsening). For this, we have performed experiments on a single film with a ‘thin film balance’ apparatus [32](see supporting information, figure S2). One observed in the single film a thin central part, with thickness of a few tens of nm, what is then called a “black film” [32] and implies that tubes are expelled from this film. That thin central part also exhibits a small area and is surrounded by a large meniscus much extended than what is usually found for other surfactant foams (see the details in the S2 picture). This shows that tubes are collected and jammed within that surrounding meniscus. By analogy in the foam, we expect the tubes to be expelled in the Plateau borders and absent from the lamella separating the bubbles. This specific structure of the lamella separating the bubble turns out to be quite efficient for the huge reduction of the foam aging. First, the thin central part of the lamella 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 provide interfacial layers of high dilational moduli E reaching easily hundreds of mN/m [4, 6, 7] as the molecules are insoluble. Moreover, it is also known that hydroxylated fatty acids can pack at interface even more efficiently than usual fatty acids [25]. Such high dilational moduli (or low compressibility) is indeed the main reason why coarsening is almost stopped: the Gibbs criterion states that coarsening stops if E > γ, where γ is the surface tension. In fact, if the bubble interfaces cannot be continuously compressed, the smallest bubble cannot vanish towards the largest ones, and coarsening is blocked [4, 6, 7].

Secondly, coarsening and lamella ruptures are also limited because the area of the thin contact part between bubbles (through which most of the gas diffusion occurs) is small, due to the presence of the tubes in the surrounding menisci which 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 which explains rather well the surprising long lifetime of these foams. We have thus here the first system which foams easily and which does not coarsen nor collapse because of an optimal arrangement of monomers and tubes within the foam structure.

Foams were further heated and their stability was monitored. It must be recalled that the multimellar tubes melt into micelles at a temperature denoted Tm which depends on the nature of the counterion [23]. HS-foams made with the ethanolamine salt (Tm = 70°C) were
still remarkably stable up to two weeks at 60°C. A similar high stability was observed for the hexanolamine salt (Tm = 60°C) at 50°C (see supporting information, S3). That high stability was quantitatively evidenced below Tm on the F-Foams (figure 4a). SANS data at those different temperatures were also similar in the foam, the stock solution and the drained solution (see supporting information S4). This shows that at all temperatures below Tm, tubes are always present in foams and exhibit the same behaviour as in bulk solution. However, at a temperature above that of the melting of the tubes, a foam could still be produced but was no longer stable as the foam volume quickly decreased with time (see figure 4a). Destabilisation occurred in only 15 minutes as observed on the HSP drainage flows. Of particular interest is that the reversible phase transition of tubes into micelles upon heating yields reversible fast destabilisation. This system is unique compared to other amphiphile-forming tubes which generally melt into vesicles \[33\]. Moreover, the multilamellar tubes can survive to various changes of physico-chemical parameters \[34\]. 12-hydroxy stearic acid is a generic molecule that results from the hydrogenation of a sustainable material, i.e., ricinoleic acid. It is available in large amount at low cost. Because the tube/micelle transition can be tuned by the nature of the counter-ion \[31\], one could design similar systems, leading to foams being destabilized at any desired temperature.

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Figure 3. Confocal microscopy images of a bulk solution of tubes (a) and of a foam (b) which was deposited on glass lamellae and further covered with a glass plate using a spacer ensuring a fixed volume of 25 µL. (c) SANS data recorded for the foam (+), the stock solution (∗) and the drained solution (●). 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 [35] (see Supporting Information, figure S1).

Figure 4. Evolution of the foam volume as a function of time in F-foams at different temperatures for the 12pHSA/hexanolamine system. SANS data at 70°C (in the 12pHSA/ethanolamine system) showing that micelles are formed at that temperature in both the foam (+) and the aqueous solutions (drained (●) and stock (●)).

Figure 5. Two examples showing the evolution of the foam volume as a function of time and temperature (in the 12-HSA/hexanolamine system). On the top of each graph is shown the schematic representation of the supramolecular assemblies (not at scale) present in solution and in the foam as a function of the temperature.

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Entry for the Table of Contents

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Smart Foams: Switching Reversibly between Ultrastable and Unstable Foams

Smart foams: Ultrastable foams with an optimal foamability have been obtained using hydroxyl fatty acids tubes. The stabilization results from the adsorption of monomers at the air-water interface preventing coalescence and coarsening and from the presence of tubes in the Plateau borders limiting the drainage. Upon heating, tubes transit to micelles, which induces foam destabilization. Such foams are thus the first to have a temperature tunable stability.