Soft Matter

COMMUNICATION

Design of responsive foams with an adjustable temperature threshold of destabilization†

Anne-Laure Fameau, [ID] *[a] Fabrice Cousin,[b] Romain Derrien[c] and Arnaud Saint-Jalmes[c]

Thermoresponsive foams that refer to foams for which the stability can be switched between the stable and unstable state have recently attracted growing interest due to their possible industrial applications. Our approach to design such foams is based on the use of fatty acids, with various counterions and molar ratios. It is the first example of foams with a temperature threshold of destabilization which can be continuously set between 20 °C and 75 °C.

Stimuli-responsive materials have macroscopic properties which can be tuned over a large range on demand in a controlled manner. The desired macroscopic changes can then be triggered either by a change in the environment (pH, ionic strength, *etc.*) or by external stimuli (light, magnetic fields, ultrasounds, *etc.*).[1,2] One of the prerequisites to design smart materials is to understand the fundamentals of molecular interactions at the nanoscale, since they govern the physical properties at all other length scales. Therefore, the challenge is to develop strategies to control these interactions and the targeted macroscopic properties. In this framework, responsive aqueous foams that refer to foams for which the macroscopic stability with time can be switched between a stable and an unstable state have recently attracted growing interest.[3–5] The motivation for foam research is due to their invaluable potential for various industrial applications that encompass cosmetics, detergency, food, fire-fighting and flotation of minerals.[3,4] The optimization of many processes such as washing or material recovery processes requires at the same time the formation of a stable foam, as well as the need to destabilize it in another step of the process. High foam stability is often mandatory during the first part of the process, while a fast and easy foam destabilization is requested at the end. Such ability to rapidly destroy the foam on demand is however a difficult goal to achieve, because the more stable the foam is, the more difficult it is to destabilize.[6] Currently in industry, the way to break the foam is to add chemical defoaming agents, which complicate the process and are often harmful for the environment. In view of the numerous applications, the design of responsive foams is a new and important issue.[7]

Controlling the lifetime of a foam necessitates the adjustement of the rate at which coarsening, coalescence and drainage operate, *i.e.* the three different mechanisms by which it ages. These destabilizing mechanisms are linked together. Designing responsive foams requires that they are all almost arrested and that the stimulus triggers a strong acceleration of at least one of these mechanisms to initiate global foam destabilization. Two main strategies have emerged to modify the foam stability in order to produce responsive foams.[4] The first one is to act directly on the interfacial layers adsorbed at the bubble interfaces. The second one is based on the modification of the bulk properties inside the foam liquid channels between the bubbles. For blocking coalescence and/or coarsening, a possible route is to choose a stabilizing agent which adsorbs almost irreversibly at the air/water interface forming highly elastic interfacial layers.[6] An efficient way to achieve this is the use of particles as foam stabilizers.[8,9] Then, to trigger the destabilization of interfaces, the particles need to be removed from the interface. It requires changing the system composition by adding species to modify the contact angle of particles, *via* chemicals to change the pH,[10–12] additional surfactant[13,14] or organic solvent.[3] A more sophisticated approach to design responsive foams is based on the use of a magnetic field as an external stimulus, which induces the motion of the particles inside the foam liquid channels and leads to the foam film rupture and foam destabilization.[15] However, the foam destabilization is only possible for foams containing a small amount of water. Another drawback with particles as foam stabilizers is their low foamability, *i.e.* the ability to incorporate gas in the foam.[16] Thus, the use of particles is not currently the most suitable approach to design responsive foams. Keeping small molecular weight surfactants as foam stabilizers seems preferable to design responsive foams, because they usually lead to high foamability,

[a] Biopolymères Interactions Assemblages Inra, la Géraudière, 44316 Nantes, France. E-mail: anne-laure.fameau@nantes.inra.fr
[b] Laboratoire Léon-Brillouin, CEA Saclay, 91191 Gif-sur-Yvette CEDEX, France
[c] Institut de Physique de Rennes, UMR CNRS 6251-Université Rennes 1, Rennes, France

while some of them can also provide highly elastic layers at the interface. To give responsivity to a surfactant layer, one option is to synthesize specific molecules such as photoresponsive surfactants.[2] The adsorption/desorption fluxes of these surfactants at the interface is triggered by light, and the resulting foam can be stabilized and destabilized on demand.[17] A more simple way to design responsive foams based on surfactants is to modify the viscosity of the bulk inside the foam liquid channels in order to tune the drainage rate. Such approach has been used in several responsive foam systems described in the literature: morphological transition of surfactant self-assemblies induced by temperature,[18] by coupling UV and temperature,[19] magnetic field and temperature,[20] and fusion of surfactant crystals above the Krafft transition.[21,22] Up to now, for the temperature-responsive foams already described in the literature, the temperature thresholds of destabilization are specified values depending on the chemical systems used.[3,4] The next barrier to overcome is then to conceive a new class of responsive foam for which the threshold temperature of destabilization can be precisely chosen at will, within a wide range of temperature, and without having to use completely different chemical systems. Together with gaining such an adjustable temperature threshold over a wide range, one must also look for renewable and non-toxic low-molecular-weight surfactants, having high foamability, and long foam lifetime in their stable state.

Here, we demonstrate that the 12-hydroxystearic acid (12-HSA), associated with alkanolamines, successfully fulfills these requirements. First, 12-HSA is a green and renewable surfactant coming from agro-resources and is known as an organogelator.[23,24] Second, at the air/water interface this specific surfactant produces a highly elastic interface close to its pK_a value due to hydrogen bonding.[25] Third, the 12-HSA is known to self-assemble in water into multilamellar micron-size tubes in the presence of alkanolamine as the counterion.[26] In a previous study, we have demonstrated that in the presence of ethanolamine at an equimolar ratio, it enables the production of ultrastable foams.[18] The presence of tubes both jammed in the foam liquid channels and adsorbed at the air/water interface, below a highly elastic monolayer, prevents foam destabilization by reducing drainage, coalescence, and coarsening.[18] Upon heating, the tubes transform into spherical micelles inside the foam liquid channels, leading to a complete and fast destruction of the foam. This transition results from subtle effects linked to fatty acid alkyl chain melting, hydrogen bonding and repulsions between charged headgroups that govern the packing parameter.[27–29] As a consequence, the threshold temperature of the transition (T_t) between the tubes and micelles is directly linked to the molar ratio between the 12-HSA and the counterion, defined as $R = [n_{12\text{-}HSA}]/[n_{12\text{-}HSA} + n_{counterion}]$. Recently, we have broadened our bulk studies and investigated solutions of 12-HSA with alkanolamines differing in the alkyl chain length (from ethanolamine (C2) to hexanolamine (C6)), and also for various R ranging from 0.2 to 0.66 (Fig. S1, ESI†).[30] For all these conditions, multilamellar tubes are present and a transition towards spherical micelles is also always found. The temperature threshold T_t depends strongly on both R and the alkyl chain length of the counterion. If we first focus on the effect
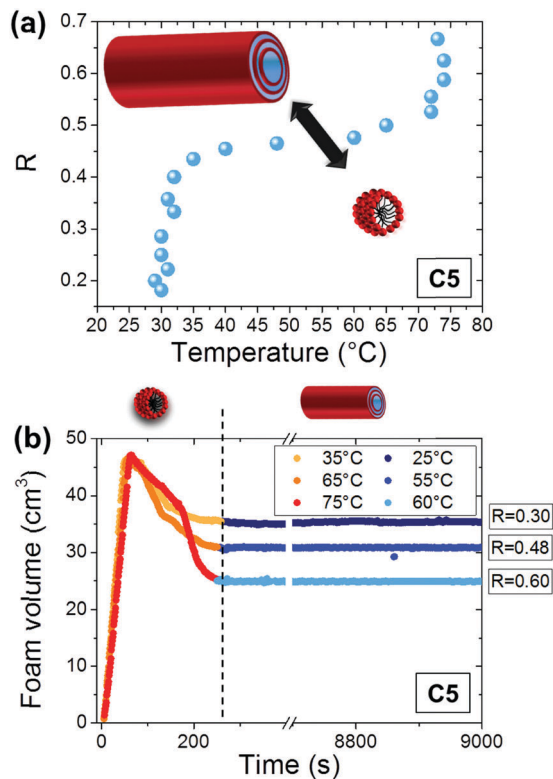

Fig. 1 (a) Evolution of the threshold temperature (T_t) between tubes and micelles as a function of R for C5. (b) Evolution of the foam volume as a function of both time and temperature with the schematic representation of the supramolecular assemblies present in the foam as a function of temperature. Foams produced from C5 with three molar ratios: $R = 0.3$ ($T_t = 30$ °C), $R = 0.48$ ($T_t = 60$ °C) and $R = 0.6$ ($T_t = 74$ °C).

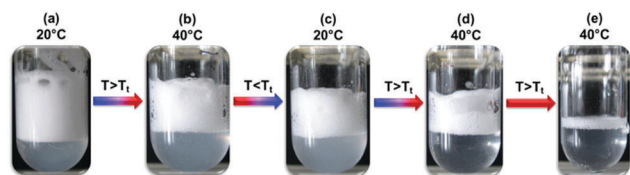of R, we observe the same qualitative behaviour for all counterions: T_t is almost constant at low R, then it increases sharply to reach a plateau at high R for which T_t is again constant (Fig. 1a and Fig. S1, ESI†).[30] Only the temperature range varies when changing the counterion. By increasing the chain length of the counterion, T_t is shifted toward lower values. Consequently, T_t can be precisely tuned from 20 °C to 75 °C. Below T_t all the solutions are always highly viscous (viscosity >1000 mPa s^{-1}). Around T_t, the viscosity decreases by more than three orders of magnitudes within a few degrees. Here, we study if and how these thermally-driven supramolecular and bulk transitions are transposed at the scale of the foam, for all R and counterions in order to produce temperature-tuneable foams for a wide range of temperatures.

First, we produced foams by setting the temperature below T_t for all counterions and for various R to be in the presence of tubes before foaming (Fig. 1 and Fig. S1, ESI†). We used two methods of foam production to vary the initial bubble size: handshaking or bubbling methods. In every case, when tubes were present in bulk, the foamability was good and ultrastable foams were obtained whatever the bubble size (Fig. S2 and S3a, ESI†). However, at a temperature above T_t, the foams were still able to be easily produced from the micellar solution but were then unstable in time. The liquid fraction of the foam sharply fell within minutes, as a consequence of the simultaneous foam
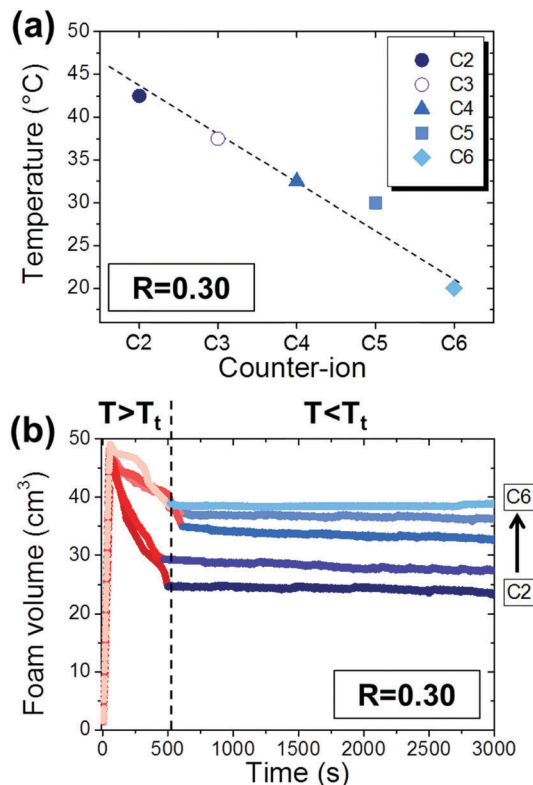
collapse (Fig. S3b, ESI†). The presence of tubes is a prerequisite to obtain ultrastable foams whatever the nature of the counterion or R. Otherwise, once the 12-HSA molecules are assembled into micelles, they cannot efficiently stabilize the foams, neither prevent a fast drainage due to low viscosity and/or film ruptures. The two regimes of tubes (associated with high viscosity) and micelles (associated with low viscosity) are thus respectively linked to high and low foam lifetimes. We present below other proof of these links, illustrating that they remain valid whatever the values of R, the alkyl chain length of the counterion, and the foam's initial bubble size.

Second, we studied the foam stability for 12-HSA tubes obtained with the same counterion but with varying R, and for temperatures between 20 °C and 75 °C (Fig. 1b and Fig. S4, ESI†). For example, Fig. 1b shows the results for the foams obtained by bubbling at $T > T_t$ for C5 at three molar ratios: T_t ($R = 0.3$) = 30 °C; T_t ($R = 0.48$) = 60 °C and T_t ($R = 0.6$) = 74 °C. Under such conditions, micelles were present in the solutions under foaming, for all R. In this setup, once the foam volume has reached 45 mL, the bubbling is stopped, and we can monitor the evolution of the foam volume as the foam ages. We observed that for all R, none of the foams were stable, as the foam volume started to decrease once the gas flow was stopped. However, once the temperature decreased below T_t, in every case, the destruction of the foam was completely stopped. At the molecular scale, the tubes were reformed inside the foams leading to their stabilization. Similar results have been obtained with C4 at three molar ratios (Fig. S4b, ESI†). Therefore, thermoresponsive foams, which can be switched between stable and unstable states, can be obtained with T_t varying over a wide range, for a given counterion and just by modifying R.

To illustrate the reversibility of the stabilization/destabilization phenomena, we performed experiments with C5 at $R = 0.30$ ($T_t = 30$ °C) and photographs are presented in Fig. 2. The foam was produced at 20 °C by handshaking, and we observed a constant foam volume over time, thanks to the presence of tubes. When the temperature was raised up to 40 °C ($T > T_t$), the foam started to get destabilized within a few minutes with a fast foam volume decrease due to coalescence events between the bubbles visible with the naked eye (Fig. 2b). Simultaneously, more liquid had also drained out of the foam. Before all the foam disappeared, it is possible to stop the foam ageing by

Fig. 3 (a) Evolution of the transition temperature (T_t) as a function of the counterion for $R = 0.30$. (b) Evolution of the foam volume with time for all the counterions for $R = 0.30$ above and below T_t.

decreasing the temperature back to 20 °C ($T < T_t$). We observed that the foam regained stability. By increasing again the temperature above T_t, the foam quickly destabilized to almost disappear in less than ten minutes (Fig. 2d and e). Above T_t, the drained solution became completely transparent showing the presence of micelles (Fig. 2d and e). Other examples can be found in the ESI† (Fig. S5).

Finally, we fixed the value of R and changed the counterion to expand the temperature range for which responsive foams can be obtained. For example, for $R = 0.30$, T_t was shifted from 42.5 °C for C2 to 20 °C for C6 (Fig. 3a). We suppose that this shift could be explained by a difference in the pK_a value between the counterions.[30] For all counterions, we produced foams above T_t where micelles were present, and a fast foam destabilization was again observed in few minutes. As previously observed, when the temperature was decreased below T_t, the foam destabilization stopped due to tube recovering (Fig. 3b).

In conclusion, the profound link between foam stabilization/destabilization and the presence of 12-HSA micron-size tubes or nanometric micelles inside the foam liquid channels is clearly demonstrated by our experiments. This study on different molar ratios and counterions shows the robustness of this effect: whatever the temperature ranges required for having tubes or micelles, these are always linked to long or short foam lifetime, respectively. We show here that we have been able to produce responsive foams which can be stabilized/destabilized at any given temperatures between 20 °C to 75 °C. Combining a proper choice of R and of the counterion chain length enables to set the

Fig. 2 Photographs showing the stabilization/destabilization phenomena with temperature for foam produced from C5 with $R = 0.30$ ($T_t = 30$ °C). (a) Stable foam at 20 °C ($T < T_t$). (b) At 40 °C ($T > T_t$), foam destabilization started occurring. (c) By decreasing the temperature back to $T < T_t$ (20 °C), the foam became stable again. (d and e) Upon increasing the temperature to $T > T_t$ for a second time, the foam destabilization could again be observed and the foam was destroyed.

temperature threshold over a range that almost covers the one for which water is liquid. It is the first time that, using the same surfactant, responsive aqueous foams are made with a transition temperature varying over such a wide range of temperatures.

From applied perspectives, this study extends the application scope of this system.[18] The multilamellar tubes can be obtained by various counterions and especially using green counterions such as choline hydroxide.[19] Therefore simple, green, and low-cost responsive foams can be easily obtained based on 12-hydroxystearic acid. These features make it interesting for a wide range of applications where stabilization and controlled destabilization of foam is desired from low to relatively high temperatures, such as: textile, petrochemical, washing, and material recovery processes.[4] This technology is not patented. From a fundamental point of view, the approach used here to modify the foaming properties by tuning the molar ratio between the surfactant and the counterion could be extended to many surfactant systems, and especially for the ones already described in the literature to produce thermoresponsive foams.[21]

Conflicts of interest

There are no conflicts to declare.

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