Supporting Information

Design of Responsive Foams with an Adjustable Temperature Threshold of Destabilization

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Figure SI.5: Evolution of the foam volume as a function of both time and temperature. (a) Evolution of the foam volume as a function of both time and temperature. Above the graphs is

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Additional references

SI.1 Materials and methods

Sample preparation

12-hydroxystearic acid (Sigma-Aldrich, 99% purity) was weighed in a sample tube into which ultrapure water was added to reach the fixed concentration of $3.3*10^{-2}$ mol.L⁻¹. Then, we added the desired volume of a 1 M stock solution of the counter-ion to obtain the molar ratio (R) defined as R=n_{12-HSA}/[n_{12-HSA}+n_{counter-ion}], with *n* the molar concentration in mol.L⁻¹. All the counter-ions used are listed Table 1 and purchased from Sigma-Aldrich with the highest purity available. The mixture was heated at 80°C for 15 min until all fatty acid solids were dispersed. Before cooling to room temperature, the samples were vigorously vortexed. Before performing the foaming experiments, each sample was heated at 80°C for 15 min and cooled at room temperature.

Table 1: List of the counter-ions used in this study with their number of carbons and their abbreviations.

Counterion	Number of carbons	Abbreviation
Ethanolamine	2	C2
Propanolamine	3	C3
Butanolamine	4	C4
Pentanolamine	5	C5
Hexanolamine	6	C6

Foam production and characterization

Different techniques were used to produce and study foams. Some foam samples were prepared by vigorous handshaking of cylindrical glass containers (30 mm internal diameter, 120 mm height) containing 15 mL of the 12-HSA dispersion. The mixture was agitated for 30 sec and all foam samples were produced by the same operator.

Foams were also produced with the commercially available FoamScan apparatus developed by IT CONCEPT (Longessaigne, FRANCE). Foam was generated in a round glass column (21 mm in diameter) by sparging N_2 gas through a fixed volume (12 mL) of the aqueous 12-HSA tubes solution *via* a porous disk (pore size 10-14 µm) located at the bottom of the glass column. The flow rate was fixed at 35 mL/min. The FoamScan uses image analysis to monitor the foam formation and stability with a CCD camera (Sony Hexwave HAD). In all our measurements, a foam volume of 45 mL was generated. The temperature of the glass column was controlled by a water bath.

We also used a home-made apparatus, which is more versatile than the FoamScan. We measured both the overall foam volume and the amount of liquid inside the foam. With this setup, the foams were also made by bubbling gas into the solution through a frit, but we could change the frit porosity and the gas injection rate. This allowed us to test the foaming and stability as a function of the bubble size and initial foam wetness (the higher the gas rate, the higher the initial liquid fraction). Moreover, our foam column (35 cm high) was vertically equipped with electrodes - every 2 cm – so that we could follow the liquid fraction at any height in the foam as a function of time. The liquid fraction was inferred from the electrical conductivity thanks to a calibration curve.¹



SI.2 Phase diagram of the 12-HSA/counter-ion system

Figure SI.1: Phase diagram of the 12-HSA/counter-ion system as a function of temperature and molar ratio R showing the temperature transition (T_t) at which tubes transformed into limpid solution containing micelles. The schematics represent the chemical structure of the counter-ions. The grey color corresponds to the carbon atom, the blue to the azote, the white to the hydrogen and the red to the oxygen. Adapted from ref².

SI.3 Foam stability with time

To check the ultrastability character of these foams, we produced foams by handshaking below T_t for all counter-ions and for various molar ratios. In every case, neither the foam volume nor the macroscopic aspect of the foam changed during the conservation after 4 months showing the ultrastability of these foams. The stability of foams was evaluated by visual inspection over 4 months by comparing pictures taken just after foam formation (10 minutes) and after different times of conservation below T_t . The Figure SI2 shows the stability of foams based on C6 below T_t . However, at a temperature above T_t , the foams were still able to be easily produced but were unstable as the foam volume quickly decreased with time. For all systems, we noted that the foam destabilisation rate was faster for temperatures above 45°C than between 25-40°C. At high temperatures, the gas transfer between bubbles is faster than at lower temperatures and coalescence events occurs more frequently. These results confirm that the presence of tubes is a prerequisite to obtain ultrastable foams, whereas micelles lead to unstable foams.



Figure SI.2: Photographs of foams taken: (a) just after foam formation (10 minutes) and (b) 4 months after foam formation and conservation at 15°C (below T_t), for a sample based on C6 with R=0.25 and T_t = 23°C.

SI.4 Evolution of the liquid fraction and effect of the bubbles size

By using our home-made setup to produce and study the foams, we recorded the evolution of the liquid fraction with time for different systems above and below T_t (Figure

SI.3). With this set-up, we investigated the role of the initial bubble diameter on the foam stability. We produced bubbles from 0.3 mm to 2 mm in diameter. We observed that the transition between stable and unstable foams remained the same and was directly linked to the presence or absence of tubes whatever the bubbles size. For a foam based on C2 for R = 0.4, we studied the evolution of the liquid fraction as a function of time for $T < T_t$ (Figure SI.3.a). The foam with the smallest bubbles (0.3 mm in diameter), had an initial liquid fraction of 0.15, but after drainage, the liquid fraction at late time (30 min) was around 0.1. For the largest bubbles (2 mm in diameter), after drainage, the liquid fraction was slower around 0.02. In the presence of tubes for $T < T_t$, the foam volume was always stable, however the drainage was stronger and faster for larger bubble sizes, as already observed in the literature.³ Below T_{t_t} the liquid fraction slowly evolved with time in the first 20 minutes and finally stopped to decrease, allowing the foam to survive for months (Figure SI.3.b). For $T > T_t$, the local liquid fraction of the foam sharply failed within minutes, as a consequence of the simultaneous foam collapse (Figure SI.3.b).



Figure SI.3: Foam based on C2 for R = 0.4. (a) Evolution of the normalized liquid fraction in the middle of the glass column for $T < T_t$ as a function of time for two different bubbles size: diameter of 0.3 mm (•) and 2 mm (•). (b) Evolution of the liquid fraction in the middle of the glass column as a function of time for $T < T_t$ in blue (•) and for $T > T_t$ in red (•).

SI.5 Effect of the molar ratio on the foam volume as a function of both time and temperature



Figure SI.4: (a) Evolution of temperature of transition (T_t) between tubes to micelles as a function of R for C4. **(b)** Evolution of the foam volume as a function of both time and temperature. Foams produced from C4 with three molar ratios: R=0.3 (T_t =33°C), R=0.48 (T_t =60°C) and R=0.6 (T_t =77°C).

SI.6 Reversibility of the systems between stable and unstable foams

Four examples of smart foams are shown Figure SI.5. To illustrate further the reversibility of these systems, we produced foams by bubbling gas with a Foamscan apparatus at R=0.45 with C6 (T_t = 28°C) and with C3 (T_t =38°C) (Figure SI.5.a-b). The foam was produced at 20°C for C6, and we observed a constant foam volume over time (Figure SI.5-a). When the temperature was raised up to 35° C (T > T_t), the foam was progressively destabilized with time leading to a foam volume decrease of roughly 25 mL in 30 minutes. By decreasing the temperature back to 20° C (T < T_t), the foam volume became constant again. The same trend was observed for the foam produced from C3 (Figure SI.5.b). The initial foam was unstable at 50°C (T > T_t), but became stable again by decreasing the temperature below T_t and completely destabilized by increasing again the temperature above T_t (Figure SI.5.b). Additional curves are shown to illustrate the versatility of the 12-HSA tubes systems (Figure SI.5.c-d). In all cases, foams kept at $T>T_t$ led to unstable foams since the foam volume decreases quickly. Decreasing the temperature to a temperature below T_t was accompanied by a stop of the decrease of the foam volume, *i.e.*, a stabilisation of the foam. The foam remains stable over long period if the temperature was not further re-increased above T_t. The temperature could be varied several times and the same effect above and below Tt was observed. Note that sometime the decrease of the temperature could be accompanied by a decrease of the foam volume, not because of a loss of the foam stability but because of a change of the gas pressure within the bubbles upon cooling.



Figure SI.5: Evolution of the foam volume as a function of both time and temperature. (a) Evolution of the foam volume as a function of both time and temperature. Above the graphs is shown the schematic representation of the supramolecular assemblies (not at scale) present in the foam as a function of the temperature. (a) Foam produced from C6 with R=0.45 (T_t =28°C). (b) Foam produced from C3 with R=0.45 (T_t =38°C). (c) Foam produced from C3 with R=0.35 (T_t =38°C). (d) Foam produced from C5 with R=0.43 (T_t =35°C).

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