

Supporting Information

Controlling the interfacial properties and the foam stability by tuning the molar ratio in the myristic acid and choline hydroxide system

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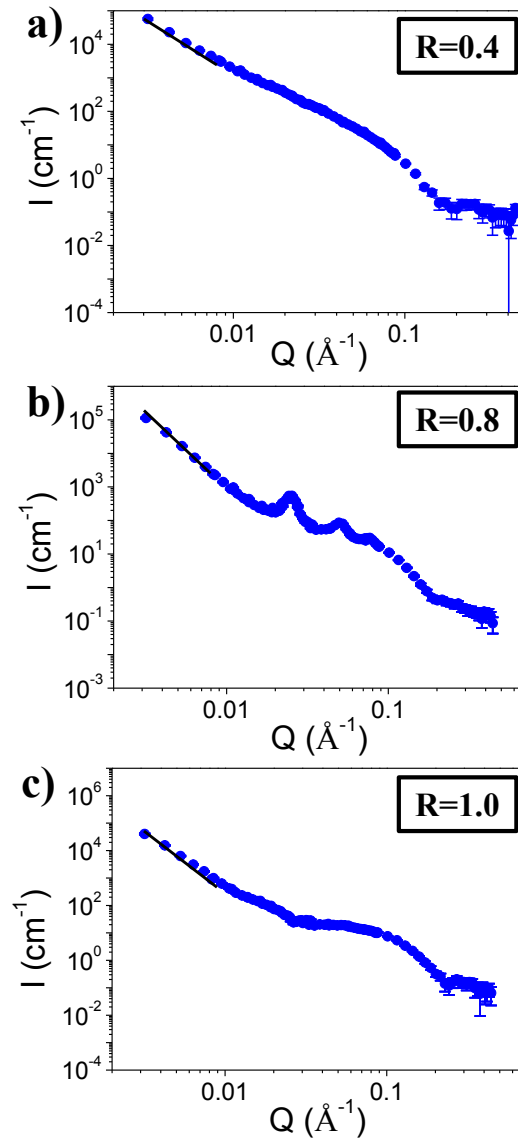


Figure SI.1: SANS spectra of foams for (a) $R = 0.4$, (b) $R = 0.8$ and (c) $R = 1.0$. The black line at low Q corresponds to the best fit obtained using the equation described in the main text to determine the bubbles size.¹

Specular Neutron Reflectivity: demonstrating that facettted vesicles and lamellar phases adsorb at the air/water interfaces

SNR reflectivity is a powerful technique to determine the morphology of the structures formed at the air/water interface in literature for surfactant systems (surfactant monolayers, lamellar phases, multilamellar vesicles and tubes).^{2, 3, 4} We performed SNR experiments at 20°C for two molar ratios R containing self-assembled bilayer structures in bulk: $R = 0.4$ (facettted vesicles) and $R = 0.5$ (lamellar phases). We chose not to study samples containing only micelles since it is known in the literature that pure fatty acid micelles lead to a simple fatty acid monolayer at the interface.⁵ We recorded the evolution of the SNR curves averaged over a period of two hours for sixteen hours (Figure SI.2). The SNR curves remained the same for $R = 0.4$ showing that the structure at the interface was stable, in contrary to the SNR curves for $R = 0.5$ which evolved with time.

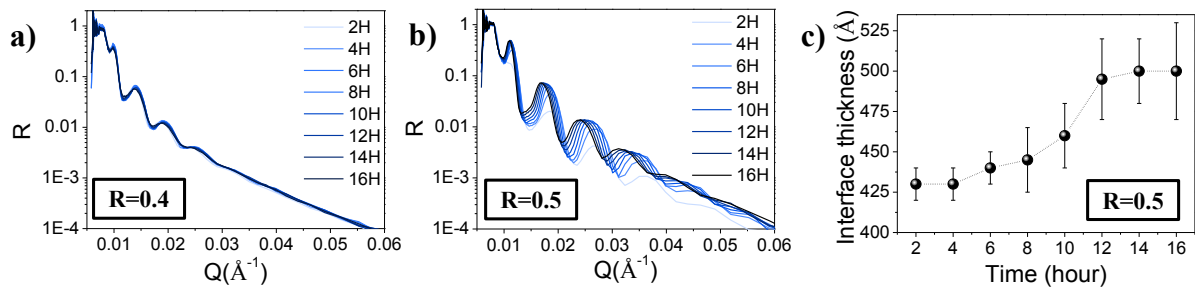


Figure SI.2: Evolution of the SNR curves as a function of time for the samples (a) $R = 0.4$ and (b) $R = 0.5$. (c) Evolution of the interface thickness with time for $R = 0.5$.

In order to describe and to fit the SNR results, we decided to focus only on the SNR curves obtained after two hours of acquisition (Figure SI.3). Please note that it is necessarily only qualitative for $R = 0.5$ as the spectrum is an average over a structure that has evolved during acquisition.

The SNR curves show an overall a Q^{-4} scattering decay coming from the pure air/water interface (Fresnel reflectivity) as well as intense regular interference fringes that come from the presence a thick layer of myristic acid at the interface. Indeed, as they are only two components in the system (myristic acid *versus* D_2O), it is likely that such fringes stem from the presence of lamellar phases of such fatty acids stacked perpendicular to the air/water interface.

Moreover, an overall estimate of the thickness layer d from the d-spacing of the interferences fringes ($d \sim 2\pi/\Delta Q$) gives an order of magnitude that is of the order of the interlayer distance obtained on the lamellar phases in bulk (a few hundreds of Å). Indeed, for $R = 0.4$, the thickness d was around 620 ± 10 Å. For $R = 0.5$, it was around 430 ± 10 Å after two hours, and it increases to reach 500 ± 25 Å after sixteen hours (Figure SI.2).

To fit the SNR data, we considered the two most common possible models that can account for surfactant systems: a single monolayer at the air/water and a multilayer made of layers of fatty acids regularly spaced by layers of water to depict the lamellar phases (Figure SI.3).^{2, 6} The first attempt was a single layer of 16 Å at the air/water interface to account for the monolayer as such thickness corresponds to the length of the alkyl chain of the myristic acid in its extended conformation at the interface. This thickness was too small to obtain interferences fringes in the Q-range probed during the experiment, showing that the structure at the interface was not a simple fatty acid monolayer. The second model tested was a model of lamellar phases in the plane perpendicular to the interface. With this model, we obtained large interferences fringes which correctly described the Q-position of the fringes but not their amplitude, as the fringes are more readily marked in the calculation. The damping of the fringes with respect to the calculation may have several origins: (i) the coverage of the surface by the lamellar phase is not complete; (ii) thermal agitation of the bilayers; (iii) the number of bilayers stacked at the interface is finite.

At $R = 0.5$, the damping is limited. As in this case there are only lamellar phases present in bulk, it is unlikely that the coverage of the surface is not total. It is here difficult to assess if it comes from either thermal agitation, either finite number of bilayers or a combination of both so we refrain ourselves to go deeper in the fitting. However, we are confident that we have lamellar phase at the surfaces. On the contrary, at $R = 0.4$, the damping is large. Since for this R , there is a coexistence in bulk of discs with faceted vesicle, it is possible that there is a coexistence of lamellar stacked at the interface with adsorbed large vesicles. Since these latter will poorly contribute to the SNR (at a given height from the air/water interface, the surface fraction of fatty acids is very low in case of vesicle as they contain mainly water), it will act as a reduction of the surface coverage.

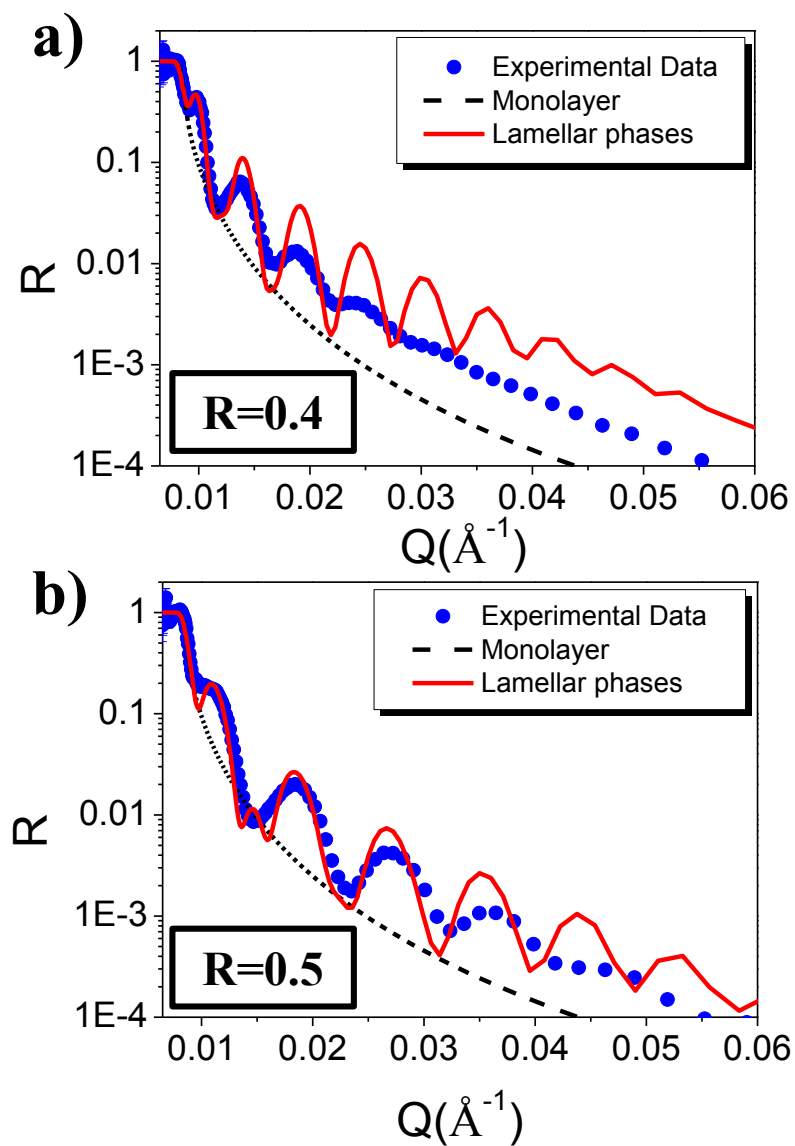


Figure SI.3: Comparison of the SNR results obtained for the myristic acid/choline hydroxide dispersion (circle) with models of a monolayer (dotted line) or lamellar phases structure (straight line) at the air/water interface: **(a)** $R = 0.4$ and **(b)** $R = 0.5$.

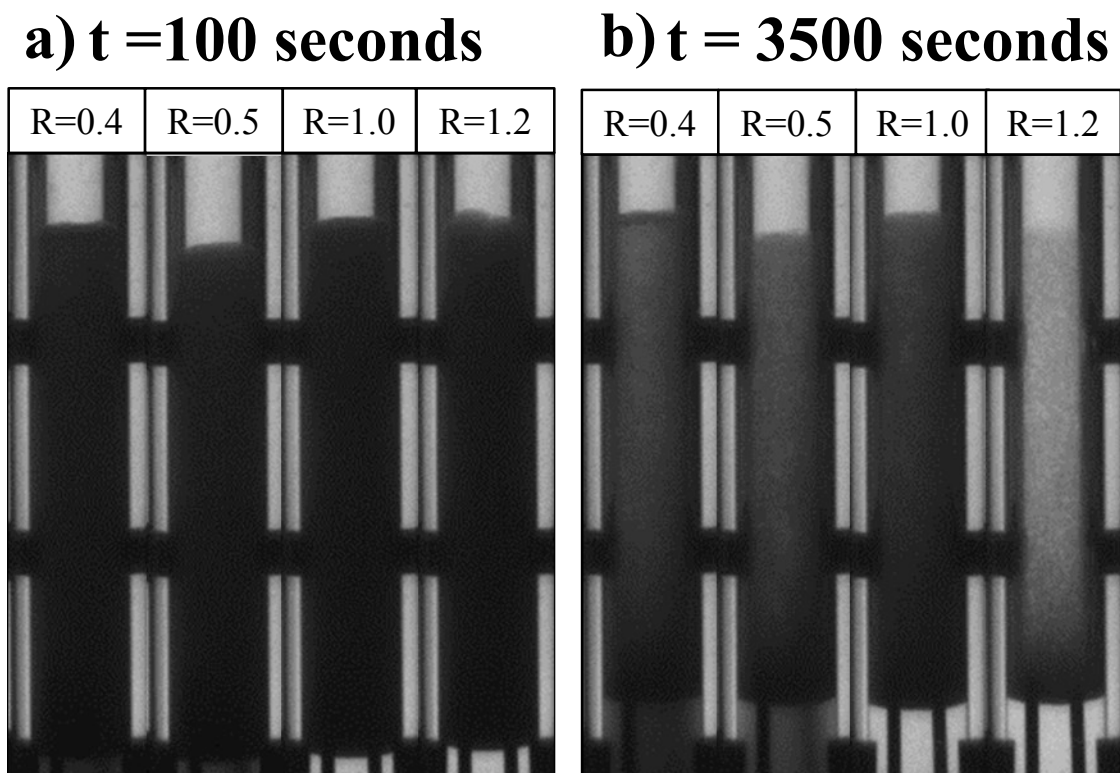


Figure SI.4: Pictures of foams taken by the Foamscan apparatus at 15°C for $R = 0.4$ (faceted vesicles), $R = 0.5$ (lamellar phases), $R = 1.0$ (micelles) and $R = 1.2$ (micelles): **(a)** at $t=100$ seconds and **(b)** $t=3500$ seconds.

Table 1: Values of time in seconds to reach the maximum foam volume fixed at 45 mL as a function of the molar ratio R at 15°C, 25°C and 35°C.

R	0.4	0.5	0.6	0.7	0.8	1.0	1.1	1.2	1.3	1.5	2.0
Time at 15°C (s)	59 ± 3	61 ± 2	61 ± 3	60 ± 5	59 ± 1	60 ± 1	59 ± 3	61 ± 1	57 ± 2	61 ± 4	66 ± 2
Time at 25°C (s)	57 ± 1	55 ± 1	57 ± 1	61 ± 3	57 ± 1	60 ± 4	58 ± 1	52 ± 2	54 ± 2	55 ± 2	64 ± 1
Time at 35°C (s)	53 ± 2	53 ± 1	53 ± 4	54 ± 2	56 ± 4	55 ± 1	55 ± 3	57 ± 4	55 ± 6	57 ± 3	56 ± 5

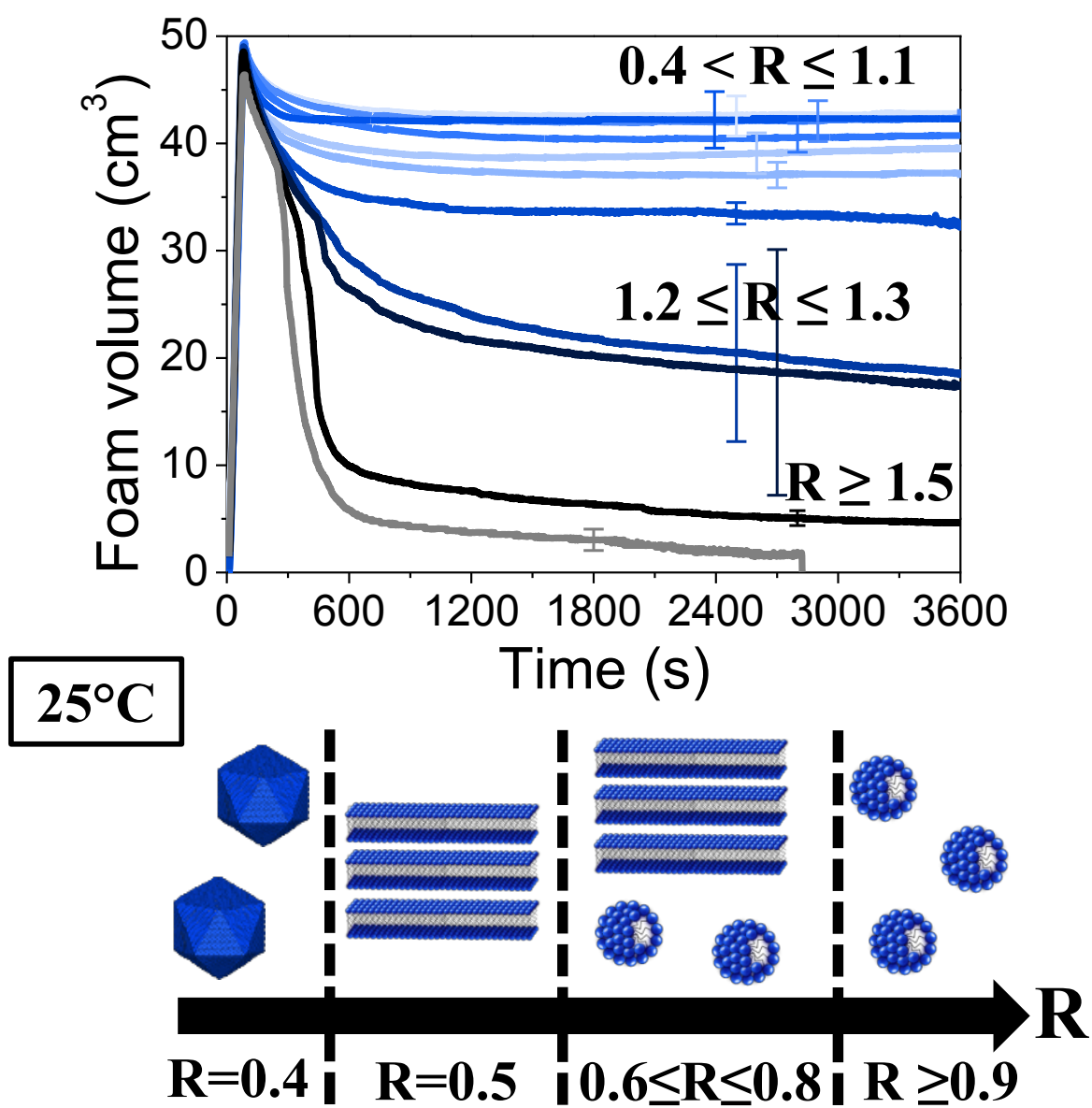


Figure SI.5: Evolution of the foam volume as a function of time for foams produced by bubbling gas for various molar ratios (R) at 25°C. The schematics represent the self-assemblies present in bulk as a function of both R and the temperature.

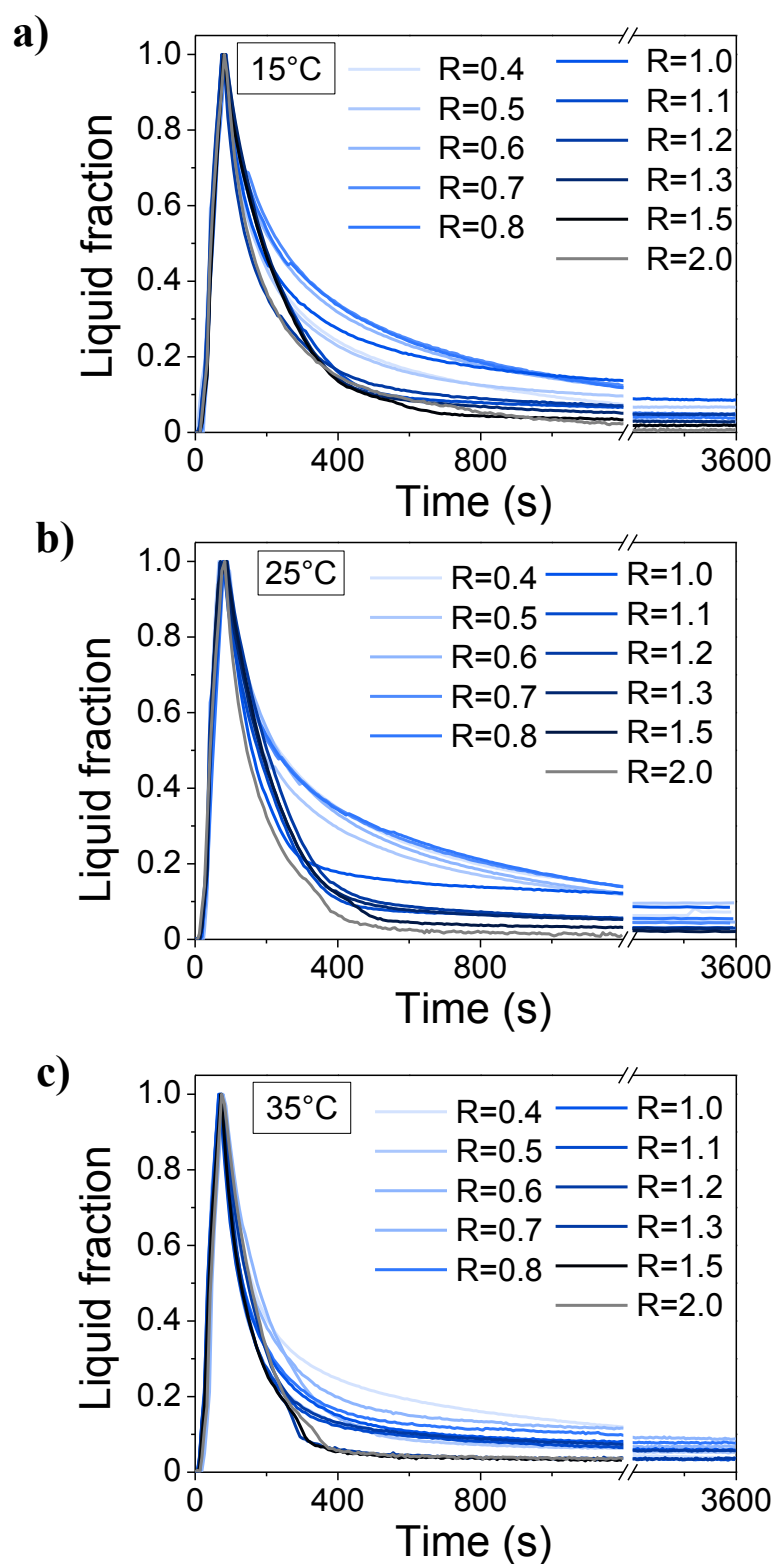


Figure SI.6: Time evolution of the normalized liquid fraction for foams produced by bubbling gas for various molar ratio (R) at: **(a)** 15°C, **(b)** 25°C, and **(c)** 35°C.

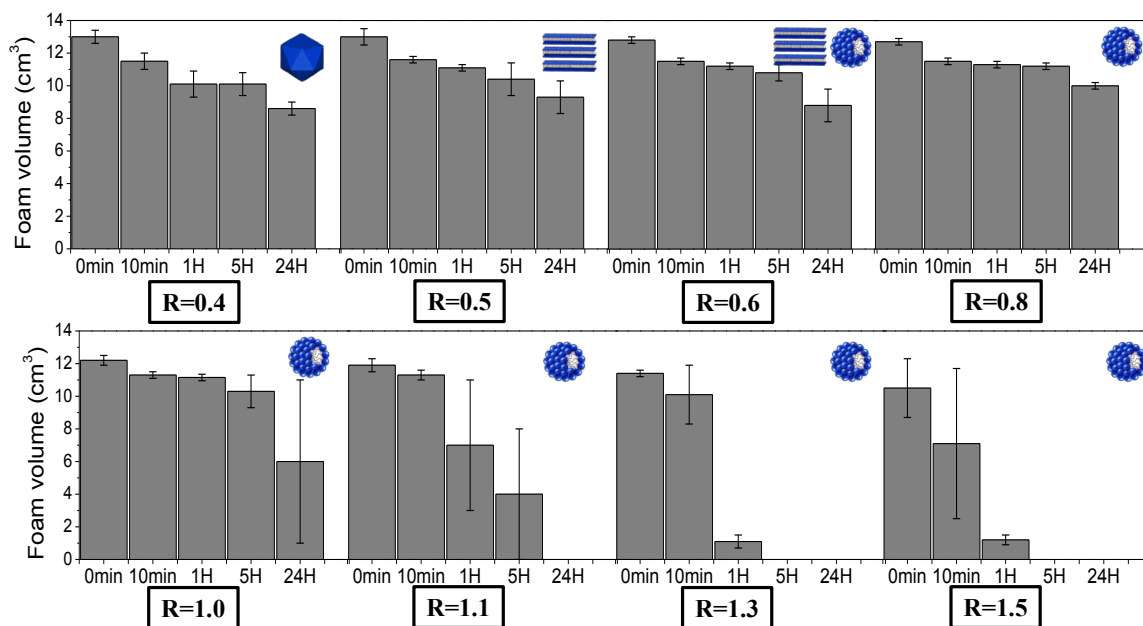


Figure SI.7: Evolution of the foam volume as a function of time for foams produced by hand-shaking for various molar ratios (R) at 25°C. The schematics represent the self-assemblies present in bulk as a function of both R and the temperature.

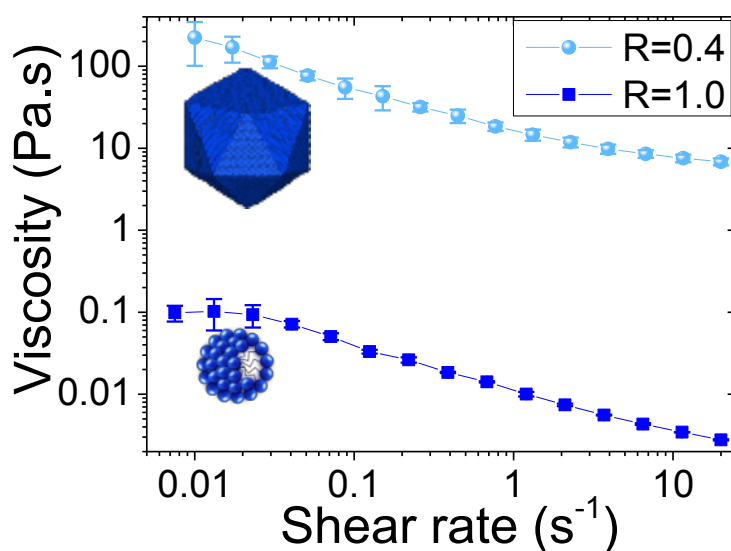


Figure SI.8: Evolution of the viscosity as a function of the shear rate for dispersions at 25°C containing faceted vesicles (R = 0.4, light blue circle) and spherical micelles (R = 1.0, blue square).

References

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