Fatty acid multilayer tubes with temperature tuneable diameter: a bulk structure remains intact at the air/water interface?

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Fatty acids are surfactants of particular interest in the present context of green chemistry since they can be extracted from agricultural resources. They are well known to self assemble into various supramolecular structures in water. Here we report on the formation of multilayer tubular structures made of 12-hydroxy stearic acid (Figure 1) [1]. The ethanolamine salt of that fatty acid exhibits two interesting but unexpected properties: (i) the outer diameter of tubes $D_{tube}$ is temperature-dependent and varies from 600nm to 5µm; (ii) foams made with these tubes are very stable.

To understand the temperature dependence of $D_{tube}$, we studied the effect of the nature of the counter-ion. We used various hydroxyalkylamines and obtained in all cases tubes with a temperature tuneable diameter, but the dependence is different for each counter-ion. We systematically measured the structural parameters (the bilayer thickness, the interlayer repeat distance) at different scales and thermodynamical parameters by coupling phase contrast microscopy, DSC and SANS as function of the temperature. The temperature influences the elastic fluctuations in the lamellar stack, which tunes $D_{tube}$ at the micron scale. However, surprisingly, the structural evolution does not follow the thermodynamical phase transitions. In order to understand why such systems yield extremely stable foams, we studied the behaviour of the multilayer tubes at the air/water interface by neutron reflectivity that provides the bilayer thickness and interlayer spacing. Remarkably, our results show that the multilayer tubes are adsorbed at the interface and the same temperature dependence of the $D_{tube}$ as in bulk is observed.

In summary, although the mechanisms responsible for the increase of the tubes diameter remain yet to be understood, our exhaustive study allows us to obtain multilayer tubes with desired sizes, at a given temperature, by a simple change of the nature of the counter-ion. This can be done either in bulk or at an interface.

Figure 1: Structure of the tubes in bulk and at the air/water interface as a function of the temperature.