SELF ASSEMBLY OF FATTY ACIDS IN AQUEOUS SOLUTIONS

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The use of agricultural resources for industrial purposes will undoubtly be one of the major challenges of the 21 st century. Organic biosynthons used in chemistry should progressively replace those coming from fossil fuels. Our work on dispersions of fatty acids and hydroxylated derivatives forms part of these efforts in that it seeks to demonstrate the potential contribution of fatty acids (which may be extracted from plants) as a new class of surface active agents. Dispersions of fatty acid and their hydroxyl derivatives are thus studied in solution in order to generate a new class of surface active agents for foaming and emulsifying properties.

However, it is known that fatty acids and their hydroxylated derivatives are insoluble in water. Our initial studies thus targeted the physiochemical conditions which would enable dispersion of these compounds. Using commercial fatty acids as model systems, we produced dispersions by using a large variety of counter-ions such as soluble organic amines (ethanolamine, lysine…). These salts made it possible to obtain homogeneous dispersions with considerable polymorphism, which formed micelles [1], vesicles [2], nanotubes [3, 4], cones [5] and torsades [6]. Preliminary studies in foams and emulsions have demonstrated that their stability differs as a function of polymorphism [7].

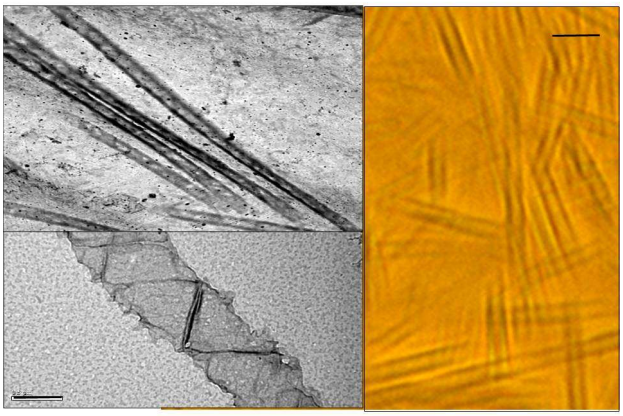

Fig. 1: TEM micrographs (left) (scale bar: 2µm (top) and 500nm (bottom)) and (right) phase contrast micrograph at 52°C of a tube dispersion (scale bar: 10µm)..

Here, we report on the results obtained with the nanotubes made of the ethanolamine salt of 12-hydroxy stearic acid and a novel system of sodium salts of fatty acids in the presence of guanidine chloride and show how small angle neutron diffusion (SANS) help us for the characterization of such systems.

12-hydroxy stearic acid is insoluble in water but forms tubes when combined with ethanolamine as the counter-ion3. The tubes are well visualised by classical microscopy techniques (see Fig. 1). Their external diameter is about 600 nm at room temperature. Those tubes exhibit an incredible temperature behaviour since their diameter varies by a factor ten upon heating [4]. The SANS pattern of such dispersion is depicted at Fig. 2. It shows a strong anisotropic scattering signal and 3 Bragg peaks positioned at Q0, 2Q0 and 3Q0 indicating the formation of stacked bilayers between which water is intercalated. The distance between the bilayers can then be measured from Q0, and is the order of 350 Å at room temperature and slightly decreases with the temperature. One can also measure the bilayer thickness in the Porod regime (not shown) which returns a value of about 40 Å at low temperature and 27 Å at higher. This change indicates a phase transition from a gel to a fluid bilayer.

We now turn on aqueous dispersions made of sodium salts of saturated fatty acids in the presence of guanidine chloride (GuCl). This system was shown to exhibit a broad polymorphism by using microscopy and solid state NMR. Whereas pure sodium salts of fatty acids crystallise at low temperature, the presence of GuCl prevents this phenomenon and yields the formation of a viscous birefringent solution of membranes at low temperature (not shown) and a phase of ‘anastomosis’ is observed (fig. 3) at higher (in press in JCIS). One clearly sees that the fatty acids self assemble into ramified superstructures having a width of tens nm and several microns length, called ‘anastomosis’ which are defined as ‘a network of streams that both branch out and reconnect’ 8.

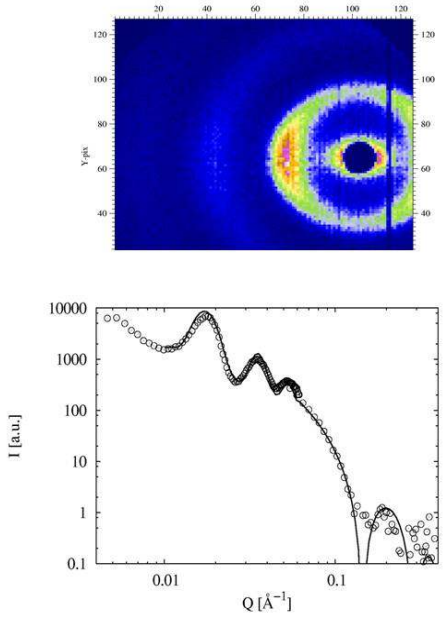

Fig. 2: SANS patterns of a tubes dispersion at room temperature. The anisotropy in the 2D signal (top) arises from the partial alignment of the tubes because of the flow when pouring the solution within the SANS cell.

We shall now investigate this system by using SANS experiments in order to determine the exact structure of those superstructures. If they are composed by nanotubes made of a bilayer of fatty acids, one should obtain oscillations or at least a typical signal in the porod regime that should give us the bilayer thickness. However, if those superstructures are made of a bundle of elongated micelles, the scattering signal should be at a power –4 for low Q.

Unexpectedly, for an alkyl chain containing 20 carbons, the system now forms vesicles (Fig. 3). Clearly, the vesicle membranes are composed by fatty acid bilayers which were characterized by deuterium solid state NMR. We also need to perform SANS experiments on such vesicles for determining the characteristic dimensions. For instance, it is probable that the alkyl chains in the bilayer are interdigitated. This could be easily measured in the Porod regime.

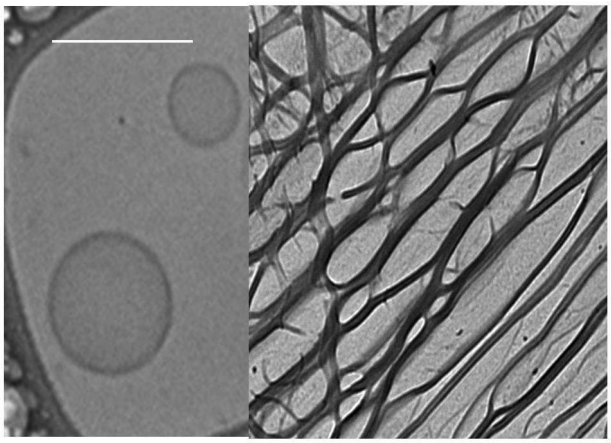

Fig. 3: TEM micrographs of two systems in the presence of GuCl. (left, scale bar 500nm) vesicles made of the sodium salt of arachidic acid (C20) and (right) the phase of anastomosis.

In summary, we have used SANS experiments for characterizing our systems made of fatty acid dispersions. That technique is very useful for determining the polymorphism and structural dimensions of the assemblies.

References:

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Acknowledgements:
We would like to thank L. Noirez, our local contact at the LLB

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