Broad Polymorphism of Fatty Acids with Amino Organosilane Counterions, Towards Novel Templates

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Lipids are well-known to self-assemble into various supramolecular assemblies[1] among which are micelles, vesicles, cones,[2] tubes,[3] ribbons,[4] discs,[5] and icosahedra.[6] The stability of such structures is governed by the thermodynamics of self-assembly[7] including membrane bending energy, electrostatic interactions between the bilayers, and the way by which the system closes the shape to prevent the formation of edges.[2,5,6] Despite their huge utilization in the industry as soaps, the polymorphism in aqueous solution of long chain fatty acids has been rather poorly described as compared to other lipids. However, it has been well-established that the pH and the occurrence of hydrogen bonds are determinent for the formation of bilayers and vesicles in such systems.[8–19] Recently, long chain fatty acids were shown to form micelles when there are neutralized with a bulky counterion as tetrabutylammonium.[20,21] This opened new avenues for studying the phase behavior of fatty acids in water and determining the physicochemical parameters to be controlled for obtaining homogeneous dispersions in water. Fatty acids could then be used as novel surfactants and, especially in the actual context of green chemistry, as renewable biosurfactants without the need of chemical modifications. Interestingly, surfactants are widely used as templates for the synthesis of mesoporous materials,[22,23] nanoparticles,[24–28] and phase transfer catalysis. In the case of mesoporous silica, the template interacts with the siliceous precursor, generally an organosilane, and plays the role of structure directing agent during the polymerization step. Elimination of the template liberates the porous framework and gives access to mineral or organo-modified mesoporous and nanostructured materials.[23,29] Even though mesoporous siliceous materials were extensively studied over the past decade, the development of such materials is strongly limited by the cost and the nature of the template. Herein, we show that an organosilane bearing an amino group can successfully play as counter ions of fatty acids, forming vesicles in a range of pH from 6 to 9.5 which can be used for stabilizing emulsions, truncated flat lozenges at acidic pH, and thermoreversible gels at basic pH. These thermodynamically stable assemblies already including siliceous precursors are expected to play as novel structure directing agents (templates) and biosurfactants.

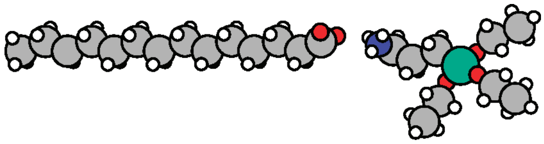

Figure 1. CPK Representation of the APTES salt of myristic acid, the grey, white, blue, red, and green balls stand for carbon, hydrogen, nitrogen, oxygen, and silicon, respectively.

We start with myristic acid (Myr, C14 chain length) in which we incorporated the amino organosilane derivatives which were either aminopropyl-triethoxysilane (APTES; Figure 1) or aminopropyl-methyl diethoxysilane (APMDES). The molar ratio between fatty acid and amino-organosilane is 1 as depicted in Figure 1.

In such salt free systems, the interaction occurs via ion-pairing (neutralization) between the fatty acid and the amino

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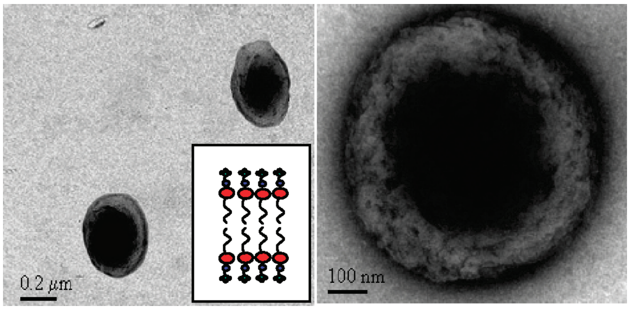

Figure 2. Negative staining TEM images of vesicles made of the myristate salt of APTES in water. (inset) Schematic representation of a bilayer formed by the mixture of myristic acid and the organosilane counterion. The fatty acids (large red ball with tail) form the bilayer and the counter-ions (silicon, hydroxyl, and amine groups are shown in green, red, and blue, respectively) are lying at the surface of both monolayers from ion pairing.

counterion in a fashion similar to that in catanionic systems.[5,6,30–34] These stock solutions were heated at 60 °C until the fatty acid melted and all the material remained homogeneously dispersed as a viscous liquid (ionic liquid) at room temperature. Those solutions were kept at 4 °C for several weeks without noticeable alteration because no modification of the turbidity could be observed. The samples were aliquoted in different tubes, and ultrapure water was added at various concentrations ranging between 0.1 and 10%. Samples exhibiting a pH of 9.5 were heated for 12 h or more at 50 °C and vigorously shaken until homogeneous turbid dispersions were obtained. Observation by phase contrast microscopy (see Supporting Information) suggested the presence of vesicles which was further confirmed by transmission electron microscopy (Figure 2). Similar vesicles could be obtained under basic conditions with sodium or potassium salts.[12,13,16]

The vesicles exhibited a diameter of about 400 nm and were highly stable when the sample tube was kept at room temperature for a period of months. They were composed of bilayers in the fluid state as demonstrated by deuterium solid state NMR (see Supporting Information). In water in such experimental conditions, the ethoxy groups are hydrolyzed yielding polar aminosilanols electrostatically bound to the negatively ionized fatty acids providing a sufficiently "small" hydrophilic polar head which facilitates the formation of bilayers and then vesicles (Figure 2) by contrast with a bulkier counterion which induces the formation of micelles.[20] Upon decreasing the pH to 6 with HCl, stable vesicles were still observed but the fatty acids were now embedded in a gel phase (see NMR data in Supporting Information). We believe that such vesicles could be used as templates for the synthesis of polymerized silica vesicles or hollow silica spheres. Interestingly, such above-mentioned supramolecular assemblies have already been reported in the literature in more drastic experimental conditions.[24,26]

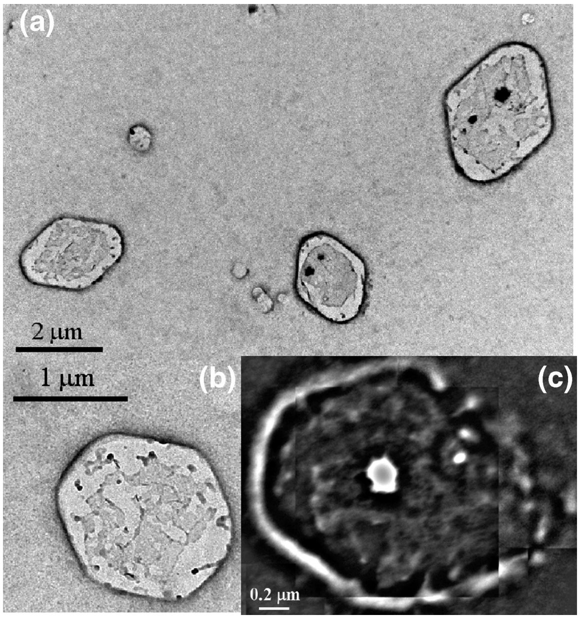

Figure 3. (a, b) Conventional TEM of flat lozenges of the myristate APTES salt at pH 2, obtained by decreasing the pH (with HCl) of a vesicle solution (the roughness of the crystals is better illustrated on the enlargement; b); (c) energy-filtered TEM micrograph at the Si L-edge of a reconstituted image of a lozenge showing the repartition of silicon atoms (white) whereas the crystallized fatty acids (black) were identified by the presence of carbon, oxygen, and azote (see the EELS data).

A further decrease of the pH yielded a bluish solution which did not sediment. This was surprising because fatty acid crystals which form at low pH (un-ionized) are generally known to precipitate. The TEM images revealed the structure of flat truncated lozenges (Figure 3) of about 2 μm length.

Application of energy-filtering TEM for imaging and element analysis[35] provided an appropriate tool for investigating both the internal structural organization of Si atom flat lozenges of the myristate APTES salt at pH 2 (Figure 3c) and coupled-image chemical analysis (see Supporting Information, Figure S2). The Si L-elemental maps of flat particles (Supporting Information, Figure S2) show a bright contrast standing for zones with a high content of Si atoms whereas darker contrast corresponds to weak Si content regions. Then, we can see that Si-rich regions are organized in a fine textured network except for the borderline that appears as a thick Si shell, as well as some nanometer-sized Si bumps. These observations were confirmed by atomic force microscopy (AFM) observation (not shown).

So, using energy-filtered TEM and electron energy-loss spectroscopy (EELS), we were able to determine that the truncated lozenges are made of both crystallized fatty acids and the organosilane. Interestingly, flat truncated lozenges are also known to form in the crystallization of various polymers[36] and their composition; that is, the coexistence

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of organosilane and lipids can be related with diatoms, unicellular organisms which developed later in the earth's history.[37]

Upon increasing the pH of a vesicle dispersion of Myr-APTES at a concentration of 1% in water, the solution became immediately clearer and even isotropic when heating to homogenize the sample. Micelles formed at 60 °C as confirmed by both solid state NMR (isotropic line, not shown) and preliminary small angle neutron scattering data (see Supporting Information). Surprisingly upon cooling, the solution became slightly turbid and a gel formed. The thickening is so efficient that a gel as dilute as 0.05% in a 1 cm diameter test tube can be turned upside down without any flow. This value is comparable to that obtained with Gemini surfactants which were shown to be good low molecular weight gelators of water.[38] However, in our case, the gel is disrupted in organic solvents such as chloroform and ethanol. A gel was also obtained when using APMDES; however, the thickening was less efficient at low concentration.

The gel was perfectly thermo-reversible; that is, micelles reform upon heating. It exhibits a broad transition at around 35 °C as illustrated by differential scanning calorimetry (see Supporting Information). This shows that the gel occurs because of an intrinsic property of the system and is not due to the polymerization of siliceous precursors as in silica gels.[29,39,40] The gel was formed by elongated (>100 μm) entangled fibers of crystallized fatty acids of about 100 nm width as revealed by TEM (Figure 4), scanning electron microscopy (SEM), small-angle neutron scattering (SANS), and NMR (see Supporting Information).

Vesicle dispersions can be used to formulate emulsions by adding oil and energy.[41] A dispersion of Myr-APTES was used to produce an emulsion (see Supporting Information). The emulsion droplets exhibited a micrometric size and therefore remained stable at room temperature without noticeable coalescence or creaming after days (not shown). Upon increasing the pH of the emulsion it did not jellify as was previously observed with vesicles. This suggests that all the fatty acid salts were embedded on the surface of the emulsion droplets. However, upon addition of a basic dispersion of Myr-APTES to that emulsion and after manual shaking, a gel formed after several minutes. We can then conclude that the droplets are entrapped within the fibers which suggests interesting applications for the encapsulation of drugs. Moreover, that gel is also thermo-reversible because a liquid emulsion reforms upon heating.

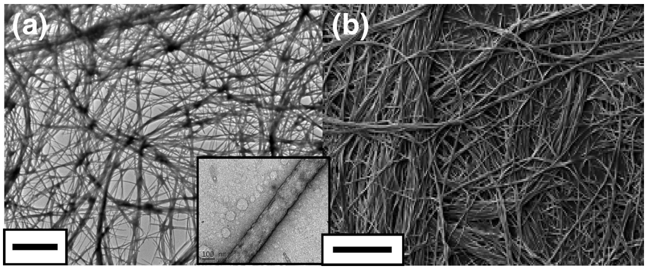

Figure 4. Electron microscopy investigation of a 1% Myr-APTES gel diluted 10 times. (a) TEM images after negative staining; (b) Low-voltage SEM image. Scale bars are 10 μm for TEM and SEM and 100 nm for the TEM inset.

Thus, we reported preliminary data on the amino-organosilane derivative salts of myristic acid and show that it exhibits a broad polymorphism producing supramolecular assemblies in water such as vesicles, flat truncated lozenges, emulsions, and fibers. These findings are of particular importance in our course for determining the physicochemical parameters for homogeneously dispersing fatty acids in water and studying their potential role as biosurfactants. Moreover, we expect these novel systems to find applications as surfactants and for the synthesis of novel materials.

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Supporting Information Available: Phase contrast microscopy, DSC, NMR, SEM, SANS, emulsion formulation, TEM details, and EELS data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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