Experimental report

15/09/2016

Proposal: **TEST-2620** **Council:** 4/2016

Title: Hemispherical particles at interfaces

Research area:

This proposal is a new proposal

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Samples: 18-METHYLEICOSNOIC ACID (18-MEA), 18-MEA (d3 deuterated), 19-MEA, CdCl2, CHCL3, NaHCO3, HCL, D2O

Instrument	Requested days	Allocated days	From	To
FIGARO	1	1	12/09/2016	13/09/2016

Abstract:

Aim: To determine whether FIGARO can be used to determine whether self-assembly constraints can cause 3D patterning of the liquid-air interface?

Summary: *In 24 hours of test beam time at FIGARO we were able to successfully perform both specular reflectivity experiments on self-assembly films at the liquid-air interface, and reconfigure the experiment to perform grazing incidence small-angle neutron scattering (GISANS) measurements. The results are encouraging both in terms of providing data to support the hypothesis, and in terms of the successful deployment of GISANS for our system. Approximately 4 more days of beam time would be required to achieve systematic data to provide unambiguous, high impact publishable proof.*

Background: Branched fatty acids form the main component of the lipid barrier on the outer surface of hair (and wool). (On page 2 there is an image a branch at the C19 position). The exact reason for the unusual structure of the fatty acid, and how the two terminal methyl groups arrange at the monolayer interface is still debated. An obvious possibility for why the branched fatty acids are found there is their lower melting temperature than corresponding saturated fatty acids. The alternative natural mechanism to achieve this is through unsaturation (as in omega fatty acids or the lipids in cell membranes) but such molecules are easily oxidized when exposed air, so that route is not available on the hair surface. The chain packing constraints imposed by the methyl group lead to different molecular areas and chain conformations. Other potential explanations for the presence of the branch are bilayer formation inhibition or improved registration of the available area per molecule to the density of cystein residues to which the fatty acids anchor on the underlying macromolecular structure. They have also been proven to possess bacteriostatic properties and there is speculation that the *anteiso* groups affect water structure or adhesion of foreign matter. As part of a *systematic physicochemical study*[1] of the properties of such fatty acids, using a range of techniques including Vibration Sum Frequency (non linear surface) spectroscopy, Langmuir Blodgett film studies and Atomic Force Microscopy it became apparent that deposited films of branched fatty acids formed well defined 2D domains. These domains were NOT observed for unbranched molecules (smooth homogeneous films were formed). The domain size is determined by the position of the branch. We speculate that the reason for domain formation is an intrinsic curvature of the liquid interface driven by the balance between the chain packing and the surface energy of the carboxylate-water contact area.

Previous studies of several person-years of work are summarized in figure1.

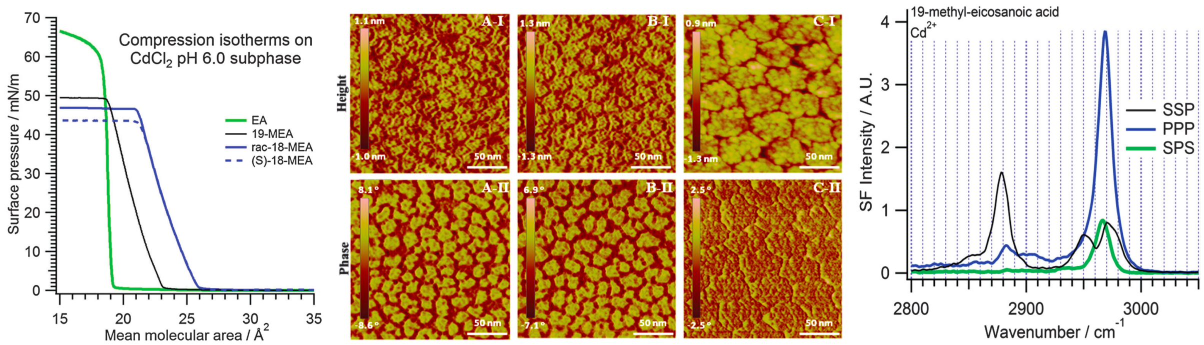

Figure 1. Left: Langmuir Blodgett film studies (pressure-area isotherms). The very different gradient of the pre-collapse regions indicates a very different state of the branched films (blue, black)
Centre: AFM images of branched samples showing domains (not seen for straight chains).

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1 Self-assembly of long chain fatty acids: effect of a methyl branch. Liljeblad, JFD, Tyrode, E; Thormann, E; Dublanchet, AC; Luengo, G; Johnson, CM; Rutland, MW. Physical Chemistry Chemical Physics 2014, 16 (33) 17869-17882.

Right: VSF spectrum of 19–MEA. (It demonstrates more chain disorder than unbranched molecules).
At the FIGARO instrument a test experiment was granted (**TEST-2620).** In 24 hours of beam time allocated we performed two sets of experiments: Firstly, specular neutron reflectivity (NR) measurements were performed using the Langmuir trough and a completely deuterated subphase to examine changes in the vertical composition of the water-fatty acid interface. Moreover, we did a GISANS experiment with twofold purpose: On the one hand, to determine what modifications, if any need to be made to reproducibly perform GISANS experiments of fatty acids at the liquid-air interface at FIGARO and to establish the required data acquisition times in this scattering geometry for our system. On the other hand, to probe the fatty acid monolayers in order to look for evidence of lateral ordering displayed by domain arrangement. In the test experiment we used the fatty acid molecule in figure 2.

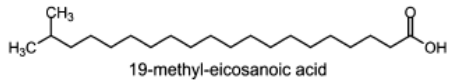

Figure 2. Molecule used in the NR and GISANS study of the air-liquid interface.

<u>Specular reflectivity</u>
Firstly, specular reflectivity was measured on the neat deuterated water surface. Next, 54 µl of 1.0 mg/ml solution of 19-MEA in chloroform was added to the Langmuir trough surface with a subphase of 0.1 mM in both $CdCl_2$ and $NaHCO_3$. This led to an area per molecule of ca 26 Å^2. The molecules were compressed analogously to the isotherm in figure 1 (black). Specular reflectivity measurements were performed at pressures of 1.3 and 35 mN/m. The NR data together with fits to determine scattering length density (SLD) profiles are shown in figure 3.

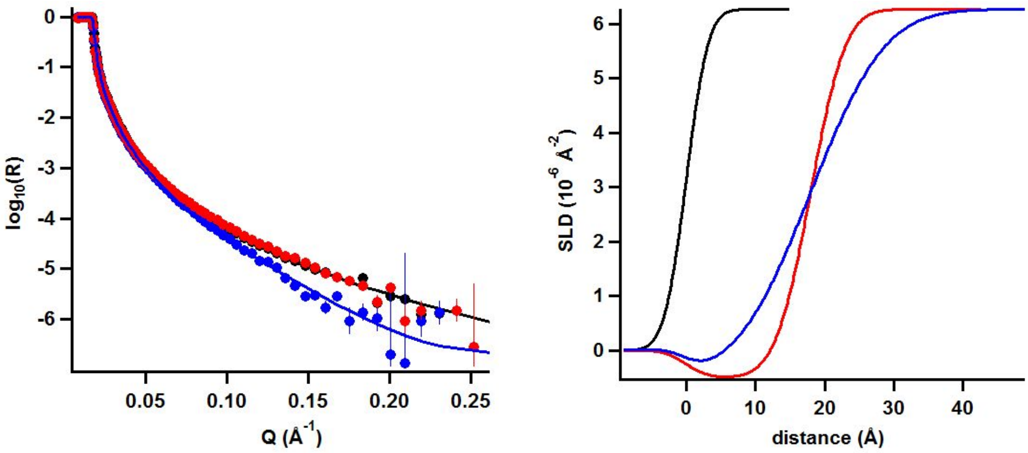

Figure 3. Left: Specular neutron reflectivity data (dots) shown together with fits (lines) for pure D_2O (black), a branched fatty acid monolayer on D_2O at pressure of 1.3 mN/m (red) and of 35 mN/m (blue). Right: SLD profiles originating from the fit to the NR data.

The specular reflectivities reveal two vital pieces of information for the project. Firstly it is apparent that there is very little difference in the data when the fatty acid is added at a low surface pressure; the fitted roughness of the interface remained unchanged. At 35 mN/m, however, the data are very different and the fitting indicates that this is due to a 10-fold increase in the interfacial roughness. This change far exceeds that expected from capillary waves as a result of the lower surface free energy of a laterally homogenous surface, but instead should be construed as indicative of a 3D topography being induced at the interface. Until now, the 3D structures observed using AFM (figure 1 center) had been observed only following transfer of the films to a solid substrate. This result from FIGARO therefore provides the first direct evidence that in fact the self-assembly properties DO influence the fluid water interface, and represents strong support for the underlying hypothesis of the work.

GISANS

Here the neutron beam was decreased in width in the horizontal direction and an additional GISANS slit was added (5-mm width). Moreover, the direct and refracted neutron beams were shielded from the detector to avoid the presence of these very strong signals and to gain a pure GISANS signal. The GISANS measurements were done at the branched fatty acid monolayer on D_2O at a pressure and of 35 mN/m, as at high pressures a highly ordered lateral structure had been found in AFM measurements (figure 1 center).

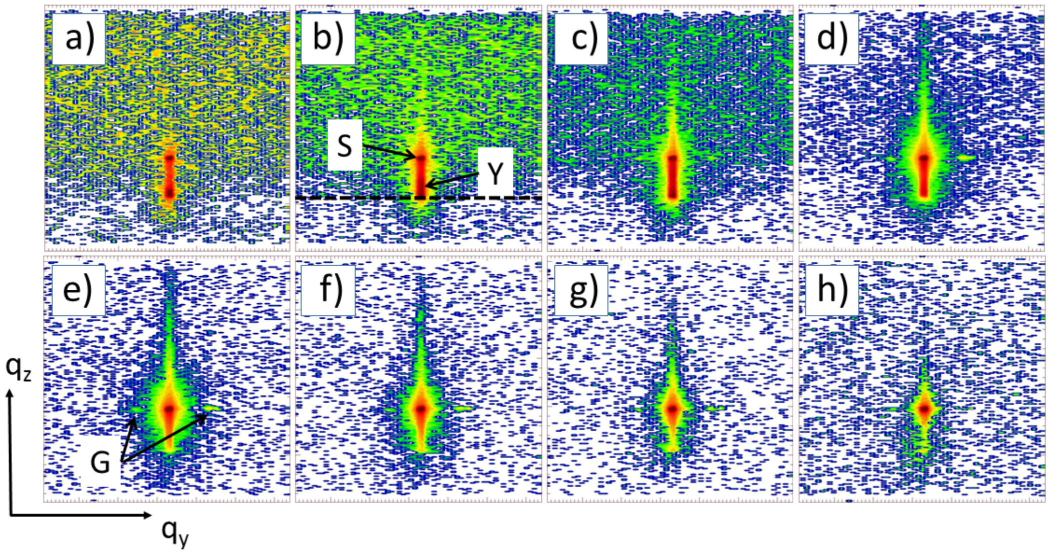

Figure 4. 2D GISANS data integrated for parts of the wavelength band of the FIGARO instrument: a) 1.8 to 3.6, b) 3.6 to 5.4, c) 5.4 to 7.2, d) 7.2 to 9.0, e) 9.0 to 10.8, f) 10.8 to 12.6, g) 12.6 to 14.4 and h) 14.4 to 16.2 Å. The specular peak is indicated with S, the Yoneda peak with Y, ghost peaks with G and the horizon with the dashed line. Intensity is shown on logarithmic scale with white for the lowest and black for the highest intensity.

Figure 4 shows examples of 2D GISANS data cut from the complete time-of-flight (TOF) data set for a wavelength band as indicated. The images in the top row are from wavelengths below the critical wavelength, i.e. for neutrons penetrating into the sample, whereas the images in the bottom row are from wavelength above the critical wavelength, i.e. for totally reflected neutrons. The specular and the Yoneda peak are well visible. Unfortunately, ghost peaks also appear left and right of the specular peak. As they were also found in the direct beam, we conclude that they originate from unwanted reflections in the neutron guide. We had reduced these ghost peaks by narrowing down the width of the slits 2 and 3, which reduced their intensity significantly, but did not successfully completely remove them. The instrument responsible has undertaken to work on reducing their effects this autumn. Nevertheless, the test experiment was successful and demonstrated the great potential of the system and the FIGARO instrument to resolve the effects on the Yoneda peak from the 2D ordering of the interface as a result of the hierarchical assembly of branched fatty acids.

Future work required!

i) A systematic study of the effects of area per molecule (or surface pressure) on the degree of buckling can be accessed through a correlation with the interfacial roughness using specular NR. The relationship between intrinsic curvature and molecular density is not yet clear.
ii) GISANS measurements at AT LEAST two difference surface pressures are required to see whether there is a pressure dependence of the domain size, and complementary measurements using a subphase contrast matched to air are required to determine whether the domains are two or three dimensional – i.e. to see whether the liquid surface is systematically buckled.