

Experimental report

14/02/2017

Proposal: 9-10-1487

Council: 10/2016

Title: Hemispherical curvature of the water-air interface induced by surface self assembly.

Research area: Chemistry

This proposal is a continuation of TEST-2620

Main proposer: Mark RUTLAND

Experimental team: Mark RUTLAND
Erik BERGENDAL
Georgia PILKINGTON

Local contacts: Richard CAMPBELL

Samples: eicosanoic acid
18 methyl eicosanoic acid
19- methyl eicosanoic acid

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	4	3	10/02/2017	12/02/2017

Abstract:

Films at the liquid air interface are traditionally believed to be flat, however the thermodynamics of self assembly are much larger than gravitational penalties so it is speculated that if a surface active molecule has the right curvature, it will bend and buckle the liquid air interface. Such an observation has not been made before. Indirect evidence for this comes from Vibrational sum frequency spectroscopy, Langmuir Blodgett measurement and AFM imaging of deposited layers. The molecules in question are those found at the surface of hair and wool, and they form the outermost biological barrier. They are implicated in chain fluidity, bacteriostaticity and adhesion. Study of the interfacial self assembly is therefore crucial to understand the hotly debated role of this unique chemistry. Test measurements incorporating both specular reflectivity GISANS deployed on FIGARO were successful and indicate that the experiments are feasible. Further experiments are needed to provide systematic data revealing the length scales and mechanisms.

Challenge: To determine whether self-assembly constraints can cause 3D patterning of the liquid air interface?

Background: The project addresses the vexed question of the surface orientation adopted by the branched fatty acids which form the main component of the lipid barrier on the outer surface of hair (and wool). The exact reason for the unusual structure of the fatty acid, and how the two terminal methyl groups arrange themselves 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 to 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. Such fatty acids moreover have been proven to possess bacteriostatic properties, and this might have implications for the known bacterial resistance of for example wool. It has also been speculated 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 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-air interface driven by the balance between the chain packing and the surface energy of the carboxylate-water contact area.

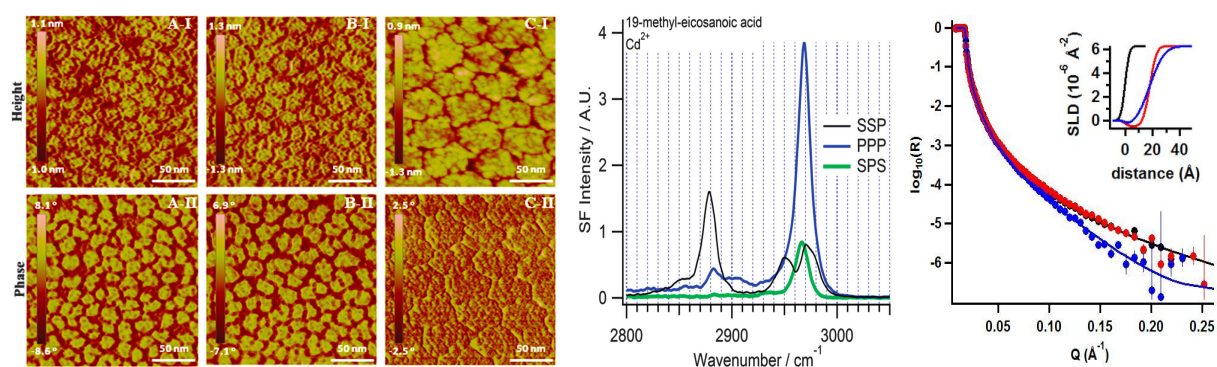


Figure 1. Left: AFM images of branched samples showing domains. Centre: VSF spectrum of 19 –MEA. (It demonstrates more chain disorder than for unbranched molecules). Right: specular neutron reflectivity data (dots) from a test experiment (TEST-2620) shown together with fits (lines) from the SLD profiles in the inset. They indicate that at higher surface pressure ((blue) the topography of the liquid-air interface increases. At low pressure (red) the topography is indistinguishable from pure D₂O.

Results: The FIGARO instrument has been used in a NR study to understand how self-assembly of branched fatty acids perturbs the liquid-air interface, and can potentially be used to pattern it. The measurements strongly confirm the hypothesis, and demonstrate that FIGARO is well suited to study the water curvature. While the experiments must be considered a resounding success and support the hypothesis, the results raise further interesting questions as to how domain size and domain curvature respectively contribute to

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.

the reflectance profiles, and also why there is only measureable interface curvature at higher surface pressures, if self assembly/curvature arguments alone are responsible for the domain structure. These can only be answered (and the results convincingly published) by some follow-up experiments.

The molecules shown in fig 2 have been used to study the effect of branching on the surface self-assembly structures. The Langmuir trough set-up of FIGARO was employed with a deuterated subphase to increase contrast against the hydrogenous fatty acids and thereby probe the structure of fatty acids at the water-air interface. The D₂O subphase was prepared with 0.1 mM Cd²⁺ to increase the compression of the monolayer and the pD of the subphase was buffered with 0.1 mM HCO₃⁻ and adjusted with DCl to 5.6 (effectively pH 6). Sweeping over the whole compression range with short measurements was done to calibrate the area of interest between intermediate to high surface pressures. This region was then studied with small increments of surface pressure and longer counting times. Measurements were conducted over the full Q-range at the lowest and highest surface pressures recorded while a systematic series of data was acquired only over the Q-range 0.05–0.25 Å⁻¹ at intermediate pressures.

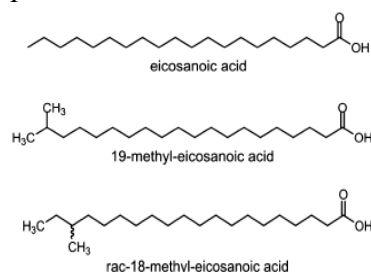


Figure 2. Molecules. Larger *domains* are expected with the 19 branch. Higher *curvature* is predicted for the 18 branch. Intermediate behaviour was expected with mixtures.

Specular NR measurements provided information on the structure of the films along the surface normal. A series of steps along the pressure isotherm have been taken to follow how the scattering length density (SLD) profile emerges with surface confinement (increased pressure). Clearly, (see figure 3) higher pressures lead to an increase in buckling of the water-air interface induced by fatty acids. The buckling is proven because the data from EA alone result in a minimal change in the reflectivity profiles where the interfacial roughness values used in the model are consistent with capillary wave theory (i.e. 2.5–4.5 Å). In the case of 18-MEA, 19-MEA and the 18MEA:EAmixtures the values rose to 11 Å at 45 mN/m surface pressure, which is far outside what can be rationalized with capillary wave theory.

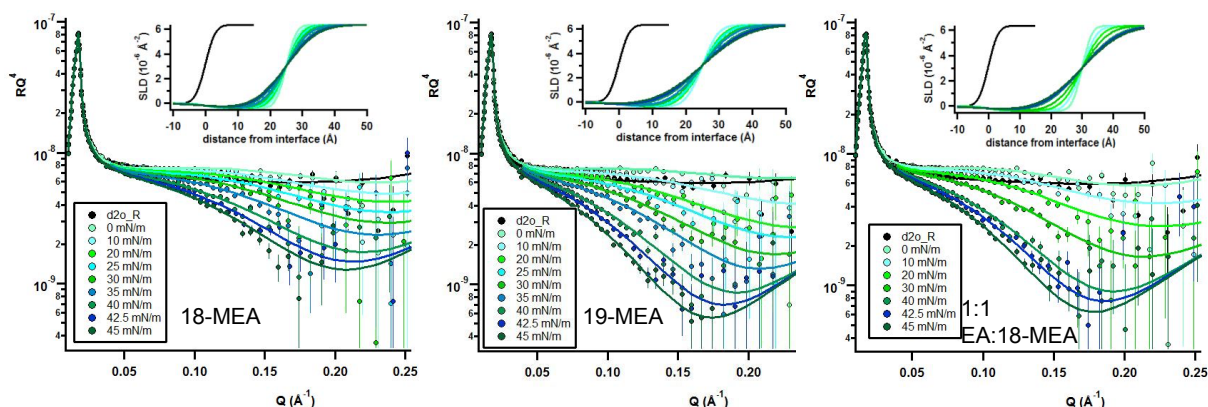


Figure 3. L to R: NR profiles for 18-MEA, 19-MEA and a 50:50 mixture of 18-MEA:EA. In each case the inset shows the fitted SLD profiles for the D₂O-air interface, (black) and the corresponding profiles in the presence of the fatty acid.

As the pressure increases, in every case the interface becomes “thicker” – *ie* the topography of the D₂O-air interface becomes larger due to the fatty acid self assembly structures perturbing the water-air interface. It is a little surprising that the 3 D topography is almost nonexistent at low pressure.

Figure 4 shows how the “roughness” (the *de facto* measure of the D₂O interface topography and/or thickness) varies with pressure for the different systems studied, and also how the thickness (at the highest pressure) varies as function of the film composition.

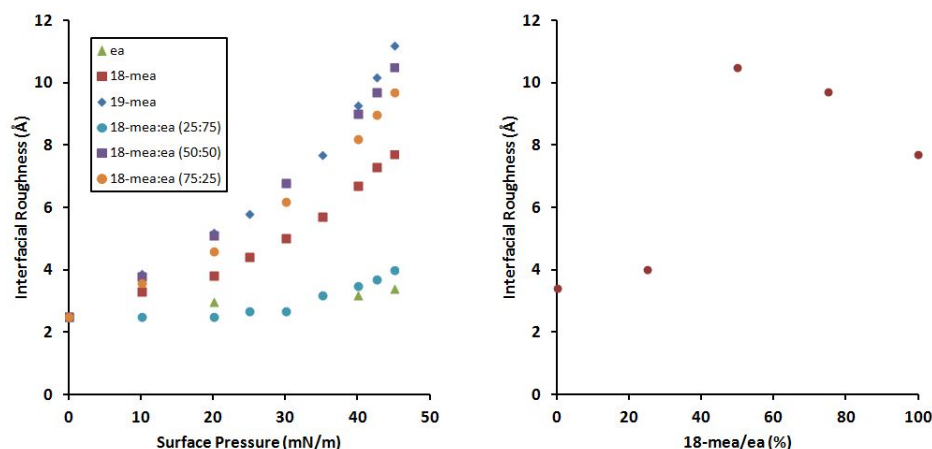
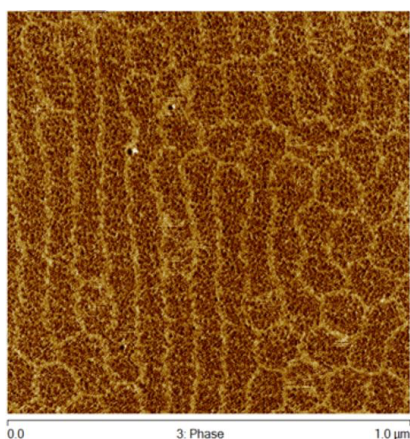


Figure 4 Left: variation of the “roughness” with pressure for the different systems studied, and (Right) how the thickness (at the highest pressure) varies as function of the film composition.

The unbranched EA demonstrates the least topography as expected from the observation of continuous (flat) films in the AFM images. The curvature of the molecule packing is larger for 18-MEA than for 19-MEA (leading to the smaller aggregates in plane) but the topography of the layer appears *least* for this molecule. The height of the spherical cap represented by the domain is thus probably not limited by the gravitational penalty of raising the water interface to accommodate the molecular curvature, but by the energy penalty of the “edge effects” (hydrophobic contact of hydrocarbon with water) in relationship to the gain (smaller headgroup area within the aggregate).

The mixed 18-MEA:EA system (ie mixtures of branched and unbranched molecules) is extremely rich in new information. Firstly it is clear that there is NOT phase separation of the molecules. In this case the roughness would be expected to be linear with the composition and bounded by the two extremes. Instead the system displays a highly synergistic behaviour.



At 25% 8-MEA the monolayer appears to behave essentially as EA – the branch is accommodated and does not lead to curvature imposing roughness. At 50% however the roughness is the highest (almost exactly the same as the 19-MEA). This nonlinear behaviour is initially surprising but supports the arguments made above. The lower curvature leads to a larger domain in the XY plane and the edge effects become proportionally smaller so that in addition to the large XY extent, the spherical cap has a larger Z variation. The recent AFM image of the 50:50 composition shows that spherical (cap) domains can also grow into more cylindrical structures (analogously to micelles)

Figure 4 AFM image of 1:1 EA-MEA deposited film. 1μmx1μm

Unexpectedly, there was no surface topography observed at very low film pressures, an important finding which is, hard to explain using the current model. Gaining sufficient insights to unambiguously publish these findings will be only possible through further NR studies to map the region between 25 and 50% in Figure 4b).