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How an Extra Terminal Group on Fatty Acids Leads to the Formation of Nanostructured Langmuir Films

A characteristic of fatty acids (FAs) associated with fur and hair are two terminal methyl groups rather than the single methyl group found in simple FAs. When these FAs form Langmuir monolayers, the geometric constraint of the extra methyl group leads to periodic lateral nanostructures, a feature that doesn't appear in simple FAs. To unravel the nature of these nanostructures on aqueous surfaces we use in-situ surface X-ray scattering techniques directly on Langmuir monolayers. Previously, this system has been explored with AFM after transfer to solid supports[1]. In our experiments, we investigate surface films prepared using 19-methyleicosanoic acid (19MEA) at different surface pressures with X-ray reflectivity (XRR) and grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS) methods. Our in-situ results reveal that interfacial 19MEA molecules self-assemble into two-dimensional (2D) hexagonal lattices of objects that resemble squished half hemispheres with a lateral lattice constant that decreases from about 62 to 48 nm with increasing surface pressure. Complementary GIWAXS studies show that the lateral order between the individual hydrocarbon chains is similar to simple FAs. With increasing surface pressure, the lattice constant shrinks and the surface roughness measured by XRR increases from that found for simple FAs to a value which is 3 times larger. We have also measured the phase diagram of mixtures of 19MEA with arachidic acid, a simple FA. With increasing of the arachidic acid composition, we have found a cross-over from a hexagonal to a 1D nanostructure. For a 50:50 mixture the 1D stripe length increases with increasing surface pressure to as large as 150 nm, a longer distance and in the opposite as to pure MEA19 monolayers. A real-space model and a theoretical framework is being developed to explain the self-assembly behavior of the FAs that have two terminal methyl groups. This combined experimental and theoretical work should provide a basis for understanding the unusual nanostructures which form in these simple molecular systems.

[1] Bergendal, Erik, et al. "3D texturing of the air–water interface by biomimetic self-assembly." Nanoscale horizons 5.5 (2020): 839-846.

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Thin films and interfaces in soft matter and materials science

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