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Thickness-Dependent Oxidation Kinetics of Coated Films of a Self-Assembled Unsaturated Fatty Acid Aerosol Proxy with Evidence for Inert “Crust” Formation

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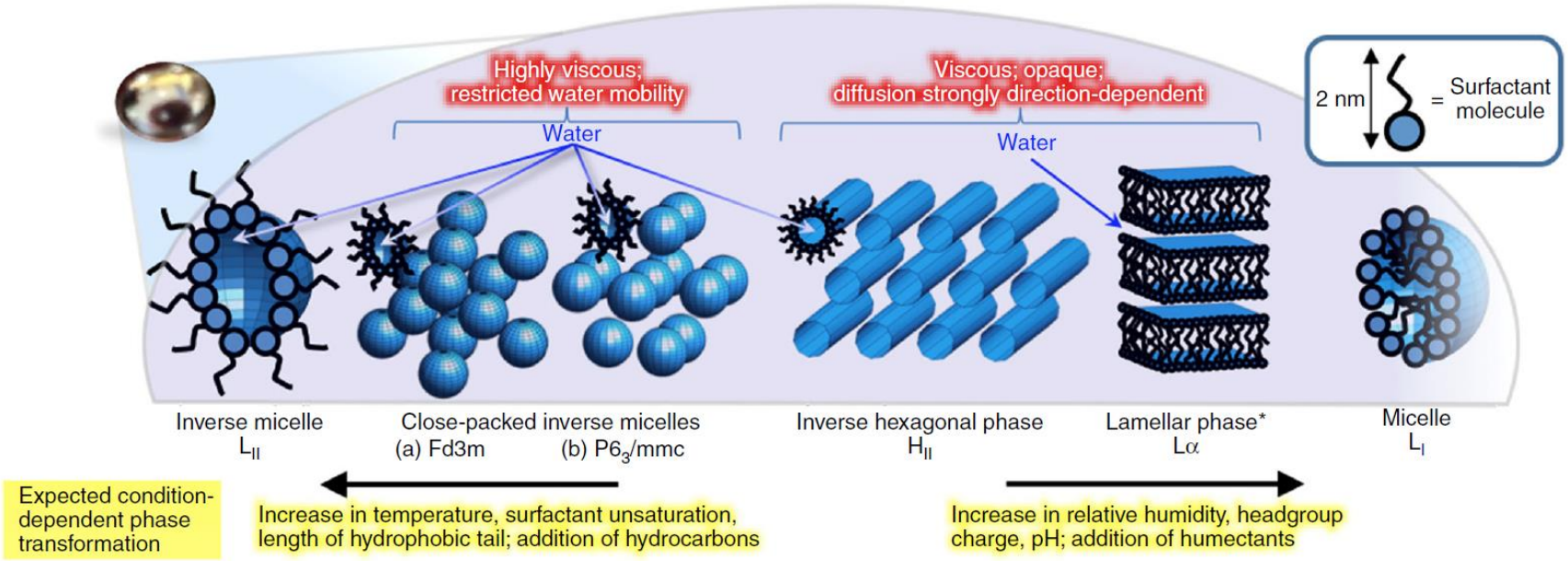
Presentation Materials for EGU2020: Sharing Geoscience Online

Self-Assembly in Unsaturated Fatty Acid Aerosol Proxies



Pfrang et al., *Nat. Commun.*, 2017, **8**, 1724

Previously, self-assembly in an unsaturated fatty acid (oleic acid/sodium oleate) aerosol has been shown to be feasible

These self-assembled liquid crystal phases have different physical characteristics and can significantly effect reactivity and atmospheric lifetime

This study focusses on the lamellar self-assembled phase coated inside a quartz capillary

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Pfrang et al., *Nat. Commun.*, 2017, **8**, 1724

Deposited Films: Thickness-dependent kinetics

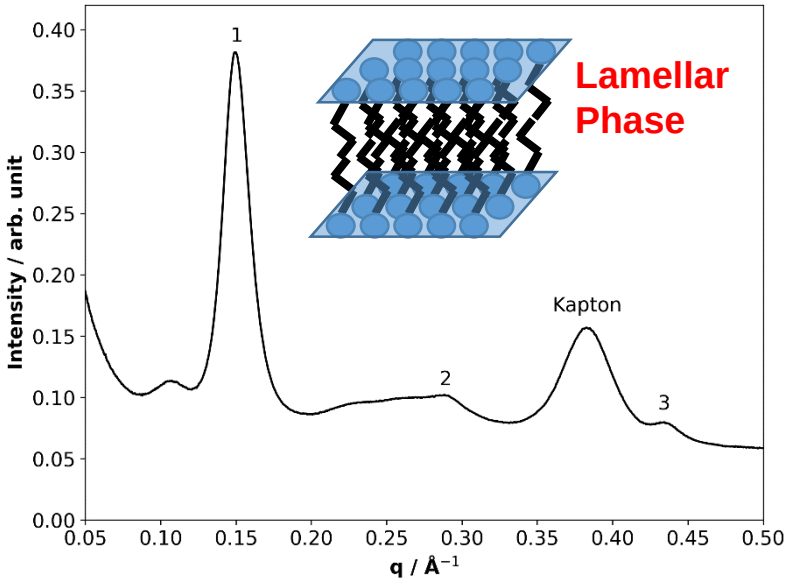

Figure 1. 1D Small-Angle X-ray Scattering (SAXS) pattern of a self-assembled (lamellar) oleic acid/sodium oleate film. Peaks 1, 2 and 3 are associated with the self-assembled phase.

By measuring the decay of the most intense lamellar SAXS peak (peak 1 in the figure), one can quantify the amount of self-assembled phase as a function of time exposed to ozone

Time-resolved SAXS measurements are possible at synchrotron x-ray sources

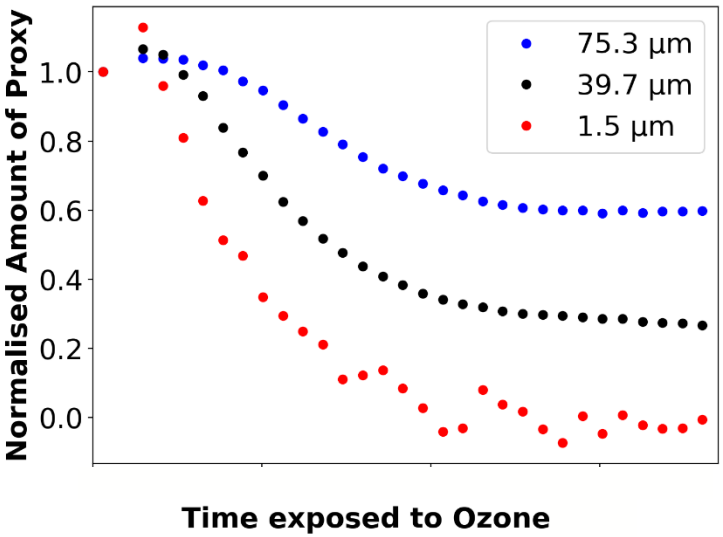

Figure 2. Three representative decay plots for self-assembled oleic acid/sodium oleate films of differing thickness undergoing ozonolysis. A clear thickness-dependent kinetic behaviour is observed. Ozone concentration 77 ± 4.6 ppm.

We have obtained a dataset of kinetic parameters for ~50 film thicknesses

The films are in the range of ~1-75 µm (uncertainty not yet quantified)

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Deposited Films: Reaction Stagnation/Material Remaining after Reaction

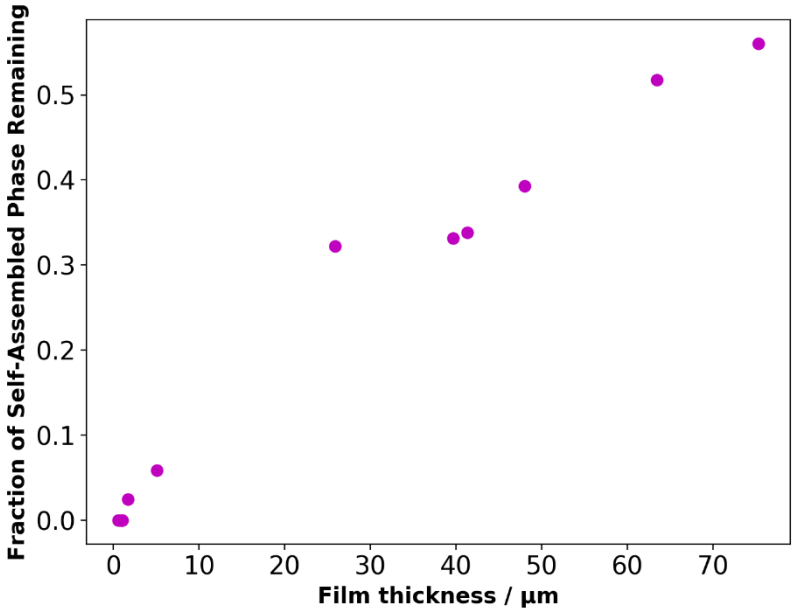

Figure 3. Plot of fraction of self-assembled phase left after ~180 min of reaction with ozone vs film thickness. This plot shows data taken from one capillary coating with varying thicknesses.

The reaction was deemed complete or significantly slowed down by ~180 min.

There is a significant fraction of self-assembled phase remaining at this time and this is proportional to initial film thickness.

This is evidence for an inert "crust" forming on the film, inhibiting further reaction.
(Pfrang *et al.*, *Atmos. Chem. Phys.*, 2011, 11, 7343-7354).

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Quantification of Self-Assembled Effect and Conclusion

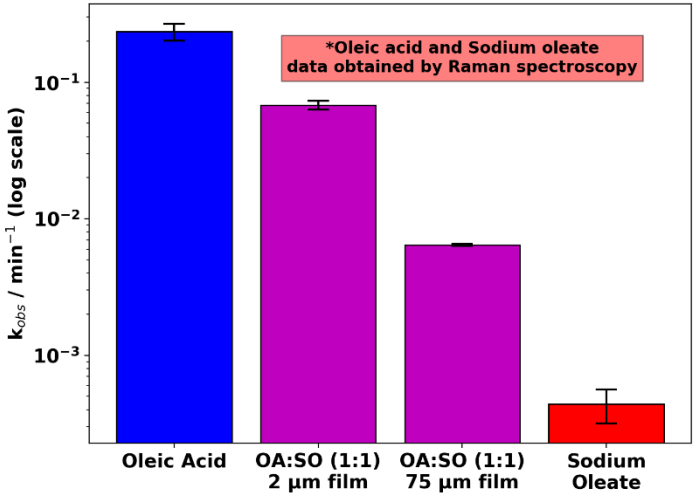

Figure 4. Plot of observed first order decay constant for samples ranging from liquid (oleic acid), semi-solid (self-assembled OA:SO) and solid (sodium oleate). All coated inside quartz capillaries and exposed to 77 ± 4.6 ppm ozone. OA=oleic acid, SO=sodium oleate.

We are now able to show the relative kinetic effect of solid, semi-solid and liquid forms of oleic acid all under the same conditions.

Moving from liquid to solid, there is a marked difference in reactivity.

Combined with the thickness-dependent kinetics, this study represents a significant step towards quantifying the effect of self-assembled/semi-solid phases on organic aerosol lifetime.

KM-SUB kinetic modelling is ongoing to decipher the factors governing this kinetic behaviour.

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