Supplement of Atmos. Chem. Phys., 24, 13571–13586, 2024
https://doi.org/10.5194/acp-24-13571-2024-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Experimental observation of the impact of nanostructure on hygroscopicity and reactivity of fatty acid atmospheric aerosol proxies

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S1 Kinetic data

Observed pseudo-first order decay constants (k_{obs}) were measured in the same way as described in Milsom *et al*. – where the SAXS peak area was followed as a function of time (Milsom et al., 2021). Taking the natural log of each peak area normalised to the initial peak area, and plotting this against time, afforded a linear plot with the gradient being k_{obs}; this approach is valid where the reaction is pseudo-first order.

The key points are: (i) k_{obs} was measured at the fastest point of the reaction – where the decay was pseudo-first order (see Fig. 7 in the main text); (ii) these k_{obs} values are a measure of the rate of decay of oleic acid *in that nanostructure* – it is clear from the Raman decay (Fig. 6-7(f)) that oleic acid remains in the film after the destruction of the initially observed ordered phases.

Nanostructure	***wt % fructose***	***k_{obs} / x 10^{-2} min^{-1}***	***k_{obs} (uncert.) / x 10^{-2} min^{-1}***	***Thickness / µm***
Liquid	0	23	3	50
Inv. Mic.	20	31	7	95
Inv. Mic.	50	45	10	95
Ord. Inv. Mic.	33	18	2	83
Lam.	0	7	5	0.59
Lam.	0	0.64	0.01	73
Solid	0	0.04	0.01	50

Table S1. Kinetic data with measured pseudo-first order decay constants (k_{obs}) and corresponding nanostructure, composition and film thickness data. The "liquid" and "solid" nanostructures correspond to oleic acid and sodium oleate on their own, respectively – these were measured using Raman spectroscopy as described in Milsom et al. (Milsom et al., 2021). *All data with 0 wt % fructose are taken from Milsom et al.*(Milsom et al., 2021).

S2 The inverse micellar phase formed at high humidity without the addition of fructose

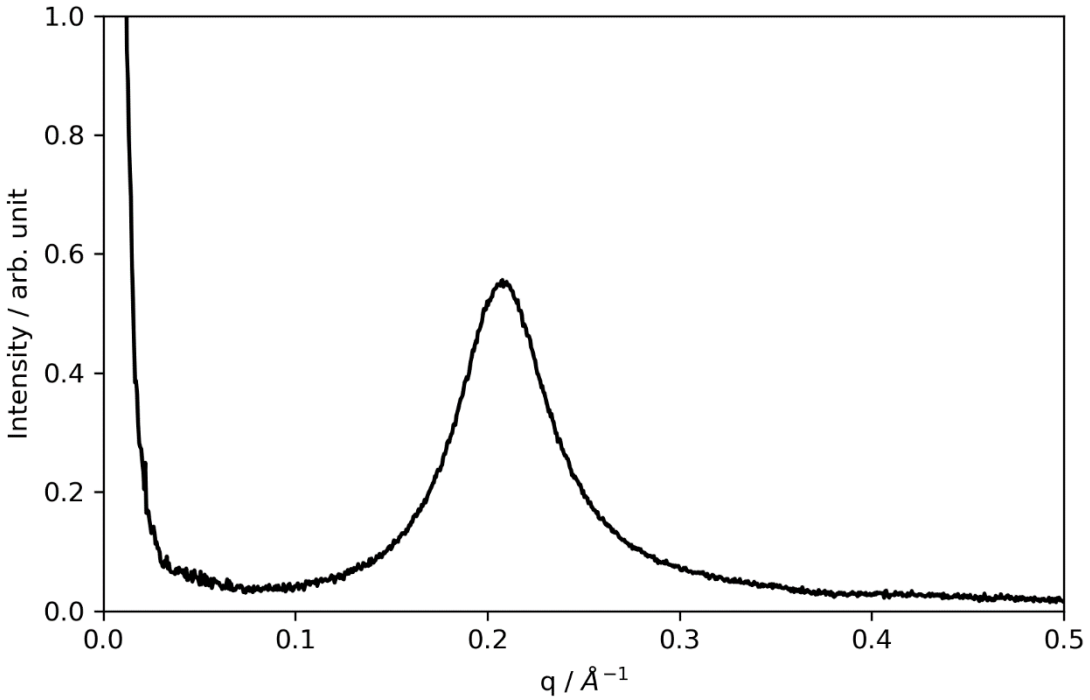

Figure S1. 1D SAXS pattern of a levitated particle of oleic acid:sodium oleate in a 1:1 wt held at 90 % RH for ~ 300 min. This peak corresponds to the inverse micellar phase with a d-spacing of 30.1 Å.

A sample of oleic acid-sodium oleate mixture (1:1 wt) was levitated and humidified to 90 % for ~ 300 min to obtain the inverse micellar phase. The *d*-spacing observed for this system was 30.1 Å. There is a significant difference in *d*-spacing when compared with the *d*-spacings observed in our fructose-containing mixtures in the main text. The levitation-SAXS experiment is described in detail elsewhere (Pfrang et al., 2017; Seddon et al., 2016).

S3 Identifying the ordered inverse micellar phases observed

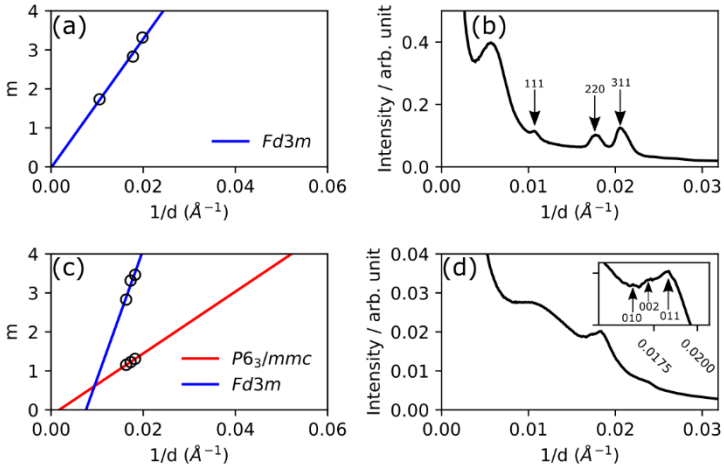

Figure S2. Indexing the inverse micellar cubic phases observed in this study. (a) - The m vs 1/d plot with linear fit for the Fd3m cubic phase symmetry observed at high RH and (b) - the corresponding SAXS pattern with the miller indices (hkl) of each scattered peak. (c) & (d) are the same plots for the P6₃/mmc symmetry observed during ozonolysis with an additional linear fit to the Fd3m symmetry, showing that the P6₃/mmc space group corresponds the best to the fitted peak positions.

In order to identify the cubic close-packed inverse micellar phases observed in this study, a relationship between the Miller indices (*hkl*) of each scattering plane and 1/*d* for each observed reflection is defined. We define a parameter (*m*) which is unique to each cubic symmetry group observed here:

$$m = \sqrt{(h^2 + k^2 + l^2)} \quad \text{(Fd3m symmetry)(Seddon et al., 1990)} \qquad \text{(S1)}$$

$$m = \sqrt{\frac{4}{3}(h^2 + k^2 + hk) + \frac{l^2}{R^2}} \quad \text{(P6₃/mmc symmetry)(Clerc, 1996)} \qquad \text{(S2)}$$

R is the ratio of the cubic unit cell dimensions (*c*/*a*) for the hexagonal close-packing of spheres for the P6₃/mmc space group, with a theoretical value of 1.663 (Clerc, 1996). A linear relationship between *m* and experimentally observed peak positions 1/*d* with an intercept at 0 would mean that the phase assignment is correct. This is the case for the Fd3m

phase observed at high RH and with an organic composition of 50 wt % fructose (Fig. S2(a)). The cubic phase observed during ozonolysis of a 33 wt % fructose film is assigned to the $P6_3/mmc$ arrangement, although the intercept was not quite 0. This may be due to the difficulty in fitting peaks which clearly have an overlapping scattering peak, affecting peak position determination (Fig. S2(c) & (d)). What is certain is that this set of peaks did not correspond to the Fd3m phase.

The slopes of these plots give the unit cell dimension (a) for each phase. These were 165 Å for the Fd3m phase and 79 Å for the $P6_3/mmc$ phase. This corresponds to a micellar diameter of 117 Å for the Fd3m phase (where $a = \sqrt{2}$ x diameter) and 79 Å for the $P6_3/mmc$ phase (where a = diameter). These values are higher than the 80 Å (Fd3m) and 76 Å ($P6_3/mmc$) indexed in a previous study on levitated particles of this system without fructose (Pfrang et al., 2017). This further corroborates what was discussed in the main text: the addition of fructose increases the size of inverse micelles formed.

S4 Explanation of the calculation of the hygroscopicity parameter (κ)

Calculation of κ for the inverse micellar (close-packed and disordered) is based on using the *d*-spacing as the distance between the centres of two adjacent inverse micelles. The "core" of each micelle is fructose (for the dry sample) and fructose + water (on humidification). The diameter of the core (d_{core}) is therefore determined by knowledge of the lipid monolayer thickness (l_m) and *d*-spacing (d):

$$d_{core} = d - 2l_m \quad \text{(S3)}$$

The volume fraction of the core (ϕ_{core}), which under dry conditions is the volume fraction of fructose, is therefore easily calculated:

$$\emptyset_{core} = \left(\frac{V_{core}}{V_{total}}\right) = \left(\frac{d_{core}}{d}\right)^3 \quad \text{(S4)}$$

Taking a dry 20 wt % fructose mixture with a *d*-spacing of 41 Å, the weight percentage of fructose in the mixture can be calculated – this should be close to 20 wt % if the assumption of l_m = 10 Å is valid. For 1 cm^3 of lipid:

$$m_{fruc} = \emptyset_{core} \times \rho_{fruc} \quad \text{(S5)}$$

$$\frac{m_{fruc}}{m_{total}} = \frac{m_{fruc}}{\rho_{lip} + m_{fruc}} \quad \text{(S6)}$$

Where ρ_{lip} and ρ_{fruc} are the densities of the lipid and fructose, respectively. m_{fruc} and m_{total} are the masses of fructose per cm^3 of lipid and total mass, respectively. With ρ_{lip} = 1 g cm^{-3}, the predicted weight percentage of fructose in the mixture is ~ 22 wt %, this is similar to the amount weighed into the mixture.

For a hydrated inverse micelle, the volume of core per volume of lipid (V_{core} / V_{lip}) can be measured under dry and wet conditions, where the core is respectively fructose, and fructose + water, with knowledge of the volume of fructose per volume of lipid (V_{fruct} / V_{lip}) calculated

from the dry *d*-spacing. The volume of water (V_w) in cm^3 for a lipid volume of V_{lip} = 1cm^3 can then be calculated by subtraction of $\frac{V_{\mathrm{fruct}}}{V_{\mathrm{lip}}}$ from $\frac{V_{\mathrm{core}}}{V_{\mathrm{lip}}}$, substituting in V_{lip} = 1, so :

$$\frac{V_{\mathrm{fruct}}}{V_{\mathrm{lip}}} = \frac{\emptyset_{core,dry}}{(1-\emptyset_{core,dry})} \quad \text{(S7)}$$

$$\frac{V_{\mathrm{core}}}{V_{\mathrm{lip}}} = \frac{\emptyset_{core,wet}}{(1-\emptyset_{core,wet})} \quad \text{(S8)}$$

$$V_w = \emptyset_{core,wet} - \emptyset_{core,dry} \quad \text{(S9)}$$

Again, for V_{lip} = 1cm^3, calculation of the dry volume (V_d) is then simply a case of adding the volume of lipid (1 cm^3) to V_{fruct}. This, along with water activity (a_w) is then plugged into equation (2) in the main text to calculate κ. In this example case, a value of 0.034 is returned at 90 % RH and a wet *d*-spacing of 66 Å.

Calculations are similar for the lamellar phase, which consists of a bilayer separated by a layer of water + fructose (hydrated) or fructose (dry), which in the latter case has thickness d_{fruc}. The overall repeat spacing for the dry phase is d_{dry} which is the thickness of the fructose + the thickness of the bilayer. The monolayer thickness l_m is calculated as follows from the dry *d*-spacing and volume fraction of fructose (ϕ_{fruc}):

$$d_{fruc} = \emptyset_{fruc} \times d_{dry} \quad \text{(S10)}$$

$$\emptyset_{lip,dry} = 1 - \left(\frac{d_{fruc}}{d_{dry}}\right) \quad \text{(S11)}$$

$$\emptyset_{fruc,dry} = 1 - \emptyset_{lip,dry} \quad \text{(S12)}$$

$$l_m = \frac{(\emptyset_{lip,dry} \times d_{dry})}{2} \quad \text{(S13)}$$

From this V_w and V_d ("dry" volume = volume of lipid + volume of fructose) per 1 cm^3 lipid can be calculated at each humidity and κ calculated. Note that $\phi_{\mathrm{core,dry}}$ for the inverse micellar

phase is equivalent to $\phi_{fruc,dry}$ in these lamellar phase calculations – there is technically no "core" to the lamellar phase.

For the inverse hexagonal phase the area of a neutral surface (A_n), defined at a place along the length of the cylinder formed by the lipid molecule, can be derived (Asghar et al., 2015). This area is constant for any nanostructure formed by that lipid, hence "neutral". Knowing this and the molecular volume of the lipid (V_m), A_n can be derived from the dry lamellar phase formed by this system (Asghar et al., 2015):

$$A_n = \frac{2V_m}{d_{lam}\emptyset_{lip}} \quad \text{(S14)}$$

The volume of the molecule based on the location of the neutral surface (V_n) for the inverse hexagonal phase is defined via the following relationship and substituting in V_m and A_n from the lamellar phase:

$$\emptyset_{lip} = \frac{8\pi}{\sqrt{3}}\frac{V_n V_m}{(A_n d)^2} \quad \text{(S15)}$$

ϕ_{lip} can now be calculated from the *d*-spacings derived from the hexagonal phase SAXS data. Calculations then proceed by assuming 1 cm^3 of lipid and deriving the mass of fructose per mass of liquid from the mixture composition. From that, volume fractions can be calculated as per the inverse micellar calculations and V_w is calculated (V_d = volume of lipid + volume of fructose). The hygroscopicity data for each phase is summarised in Table S2 below.

Nanostructure	***wt % fructose***	***κ***	***κ (uncert.)***	***Thickness / μm***
Inv. Mic.	20	0.342	0.02	39
Inv. Mic.	33	0.48	0.03	293
Inv. Mic.	50	0.35	0.05	34
Lam.	20	0.023	0.001	39
Hex.	33	0.048	0.002	293

Table S2. Hygroscopicity data for each phase measured from changes in nano-structural *d*-spacing with changes in humidity.

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