

ACID-SOAP COMPLEXES IN LEVITATED ATMOSPHERIC AEROSOL PROXIES: HUMIDITY AND OZONE RESPONSE

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Unsaturated fatty acids, such as oleic acid, are a major constituent in organic atmospheric aerosols. The main sources of oleic acid include marine and cooking emissions. The phase state of organic aerosols has been shown to be of importance to the reactivity of organic aerosols towards atmospheric oxidants such as ozone, implying a more significant effect on aerosol atmospheric lifetimes with implications for weather and pollution. Being surface active, fatty acids can self-assemble in water into a range of lyotropic liquid crystal (LLC) phases and we have previously shown this in levitated droplets of oleic acid/sodium oleate/water atmospheric aerosol proxies.¹

Here we present the observation of a crystalline oleic acid/sodium oleate acid-soap complex in our levitated aerosol proxy. Simultaneous Small-Angle/Wide-Angle X-ray Scattering (SAXS/WAXS) and Raman spectroscopy was used on our levitated particle to probe the structural (fig. 1) and chemical changes in the acid-soap complex during atmospherically-relevant humidity changes and exposure to ozone. The micro-focus capability on the I22 SAXS beamline at the Diamond light source (UK) made it possible to resolve structural differences within the particle on humidification. This has revealed an implied viscosity gradient within a humidifying acid-soap complex particle due to the formation of a micellar phase in the outer regions of the particle. Diffusion and viscosity gradients within atmospheric aerosol particles and particle proxies have been theorised and observed before. This is the first time this has been observed using SAXS.

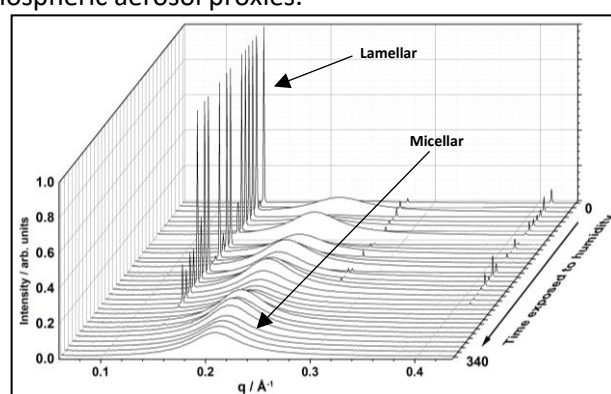
Ozonolysis of the levitated acid-soap complex revealed a significant decrease in reaction rate compared to pure oleic acid, it was also possible to see structural changes in the Raman spectrum as a result of ozonolysis; showing the degradation of the acid-soap complex with time exposed to ozone (fig. 2).

In summary, our lab-based observation of a crystalline acid-soap complex in a levitated particle and its response to ozone and an atmospherically-relevant humidity change has added to the dynamic nature of our atmospheric aerosol proxy. A humidity-dependent phase (and viscosity) change was observed and has implications for the atmospheric lifetime of unsaturated fatty acid aerosols and urban climate.

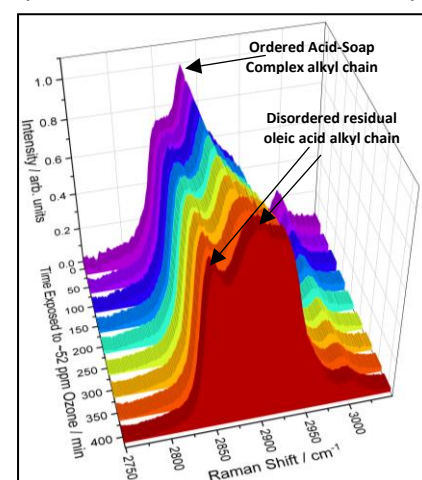
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REFERENCES:

1. Pfrang C., Rastogi K., Cabrera-Martinez E. R., Seddon A. M., Dicko C., Labrador A., Plivelic T. S., Cowieson N. and Squires A. M., 'Complex three-dimensional self-assembly in proxies for atmospheric aerosols' *Nat. Commun.*, **2017**, 8, 1724.



[Figure 1. The changing 1D SAXS pattern of the outer region a levitated acid-soap complex during exposure to >90% relative humidity]



[Figure 2. Evolution of the Raman spectrum of a levitated acid-soap complex during exposure to ~52 ppm O₃. Change in -CH₂ stretching region]