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Self-Assembly in Fatty Acid Aerosol Proxies: Phase Behaviour under Atmospherically-Relevant Conditions

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Fatty acids represent a significant portion of organic aerosol emissions, some of which act as cloud condensation nuclei (CCN). Unsaturated fatty acids in particular are reactive towards the atmospheric oxidant ozone; this chemical transformation may affect the CCN properties of the aerosol. Oleic acid is a major unsaturated fatty acid found in the atmosphere. Mixed with its sodium salt, oleic acid is known to self-assemble in water to form lyotropic liquid crystal (LLC) phases. These LLCs are viscous and in general have different physical properties compared to aqueous pure fatty acid mixtures. It has recently been shown that self-assembly may drastically reduce the ozonolysis reaction rate (Pfrang et al., Nat Commun, 2017, 8, 1724).

A combination of small-angle x-ray scattering (SAXS), Raman spectroscopy, IR spectroscopy and polarising light microscopy was used to study the LLC behaviour and reactivity of the atmospherically-relevant fatty acid/fatty acid soap/water mixtures of oleic acid (OA) and sodium oleate (SO). These atmospheric proxies have been studied as acoustically-levitated droplets, as thin films inside capillaries and as bulk mixtures with water and salt solutions.

A range of LLC phases have been observed when varying key parameters such as aqueous phase content, NaCl concentration and OA:SO ratio. Significantly, these bulk phases have been observed to change over a period of days. Furthermore, the addition of fructose to the mixture modifies the LLC phase, suggesting that other species found in the atmosphere may have an effect on self-assembly. This, combined with observations that composition affects reactivity with ozone, implies that OA may have a range of atmospheric lifetimes which are dependent on the local environment it is found in.

Additionally, preparation of OA:SO (1:1 wt) dry thin films affords acid-soap dimer crystals, which are structurally different to their OA and SO precursors and other mixtures of different ratios. Preliminary kinetic data suggest these structures also affect the reactivity of OA towards ozone. Humidification of these acid-soap dimers results in the formation of LLC phases, which add to the range of phases demonstrated by this system.

Synchrotron radiation has allowed for the simultaneous levitation, Raman and SAXS experiment to be realised and utilised probing both the chemistry (Raman) and structure (SAXS) of our levitated aerosol proxies during ozonolysis. Time-resolved structure change experiments with humidity on levitated droplets have shown that the phase within the droplet is humidity-dependent.

These combined laboratory investigations have demonstrated that these viscous systems can exist under atmospheric conditions and that they may provide an explanation for the discrepancy between laboratory-based and atmospheric lifetimes of unsaturated fatty acids.