Interfacial Photochemistry in Aerosol Droplets: The Impact of Surfactants

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UK Research and Innovation

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Background

The relationship between atmospheric aerosols and cloud formation are crucial for climate modelling, however, currently are not well understood[6].

Aerosols can serve as cloud condensation nuclei (CCN) after reaching a critical saturation point defined by the Köhler equation, which relates hygroscopicity and relative humidity (RH)[10]. This is very sensitive to surface tension, which is lowered by surfactants.

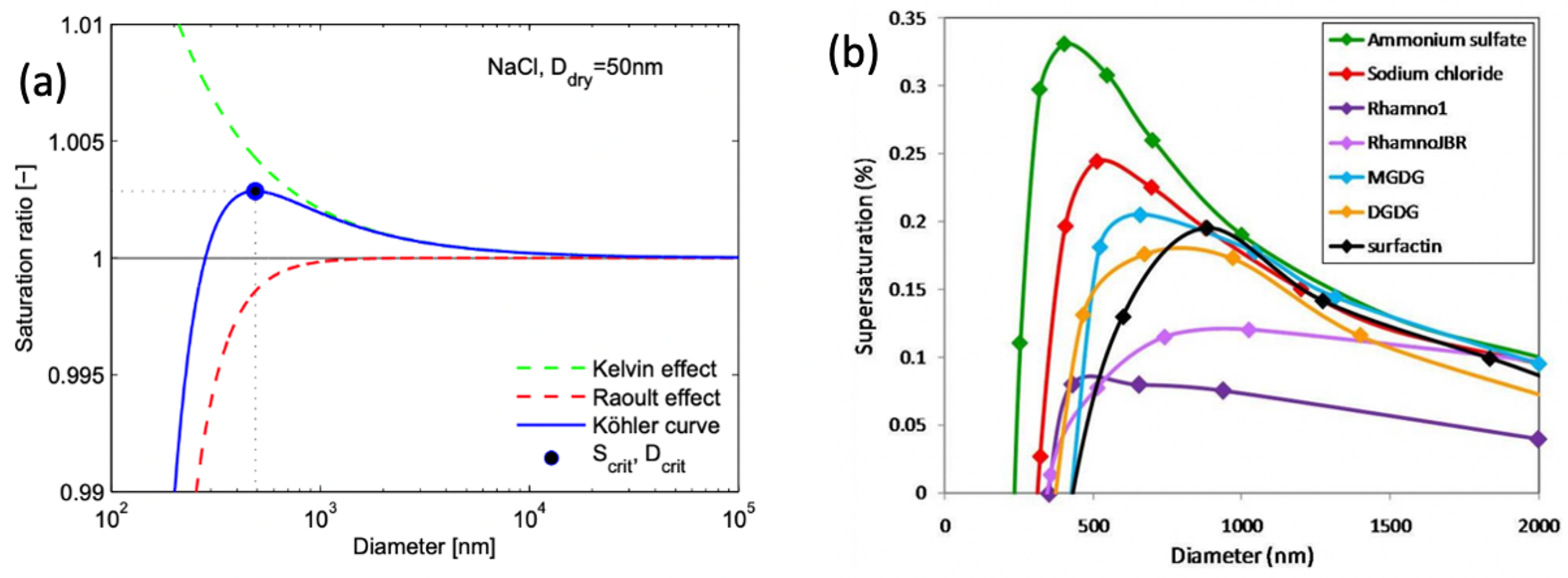
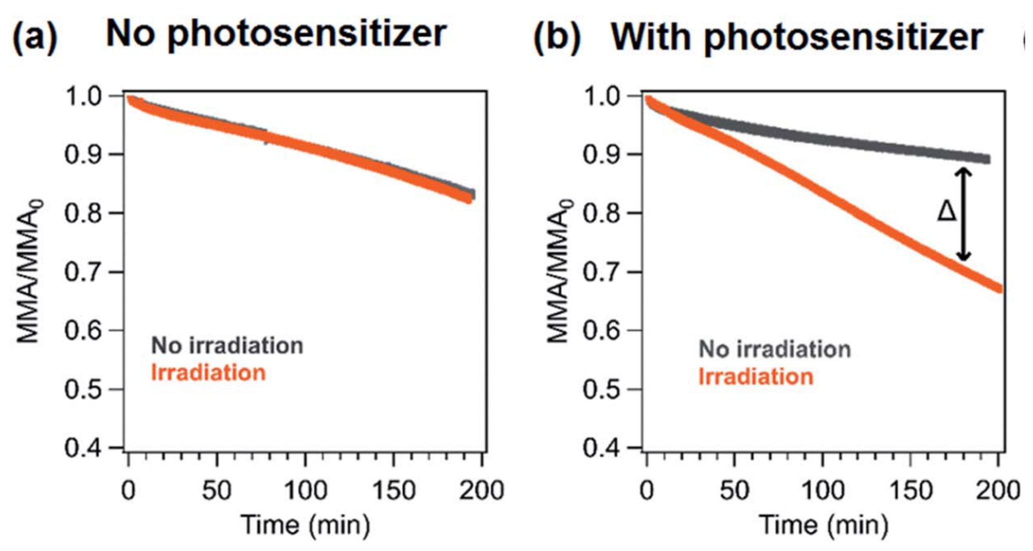


Figure 1. (a) Example Köhler curve in the blue, with the dot at the critical supersaturation point, the Raoult (red dotted line) and Kelvin effect (green dotted line)[12]. (b) Resulting Köhler curves for two salt solutions (ammonium sulfate and sodium chloride) and five biosurfactants[4].

Because of the complexities of studying the relationship of aerosol composition and surface tension, **most climate models assume aqueous aerosols have the surface tension of water**[11]. This potentially underestimates CCN formation, having climactic and radiative forcing implications.



It is also necessary to examine how different aerosol components are affected by photochemistry, as this has been shown to affect the physical properties of surfactants in the presence of photosensitizers[9] (Fig. 2).

Figure 2. Decay of palmitic acid monolayer (a) with and (b) without the presence of a photosensitizer[9].

Objectives

There are three main stages to this project, each aiming at studying different properties of aerosol chemistry:

- **Structural Properties:** Using small-angle X-ray scattering
- **Physiochemical Properties:** Using optical tweezers
- **Chemical Properties:** Using single droplet mass spectrometry

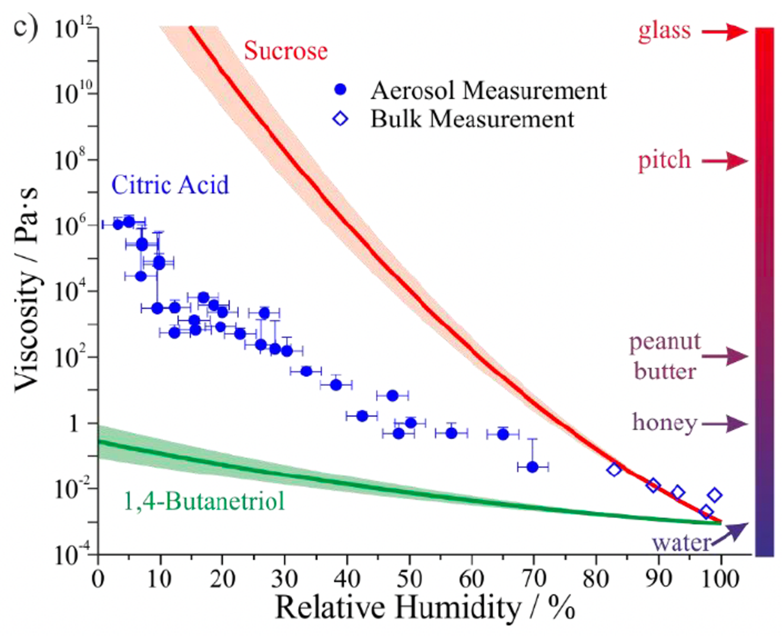


Figure 3. Viscosity vs RH plot for sucrose, citric acid and 1,4-Butanetriol. Note that for citric acid, aerosol measurements can be performed in a range inaccessible to bulk measurements.[1]

Overarching themes:

- **Increasing complexity of droplets studied.** Solutions will be studied by increasing their complexity from salts → surfactants → salts + surfactants → salts + surfactants + photosensitizers.
- **Prioritizing analysis of droplets in levitated/suspended state.** Solutions display different properties when comparing bulk to micron-sized droplets (example in Fig. 3).
- **Exposing droplets/solutions to photochemistry.**

Responsible Innovation

The work from this project will be freely accessible to the public when published. There are no potential harmful ethical, political, or social consequences to this work.

The goal of the study is to better understand how aerosol composition affects their ability to act as CCN, and therefore an outcome of this work would be to improve current climate models.

Policy and Scientific Innovation

From a policy perspective, improving climate models can help better inform policy that aims at tackling climate change. The work done in this study will use a range of innovative tools to perform single droplet analysis. The work from this study could set a new standard to examine aerosol properties and their changes with photochemistry.

Methodology

Small-angle X-Ray Scattering (SAXS)

SAXS allows for the analysis of structural 3-D rearrangements of surfactant films and droplets. By changing the surrounding RH, structural changes of surfactant rearrangement can be analysed. Chemical changes can also be monitored with acoustically levitated droplets where Raman spectroscopy is added to the set-up[7] (Fig. 4)

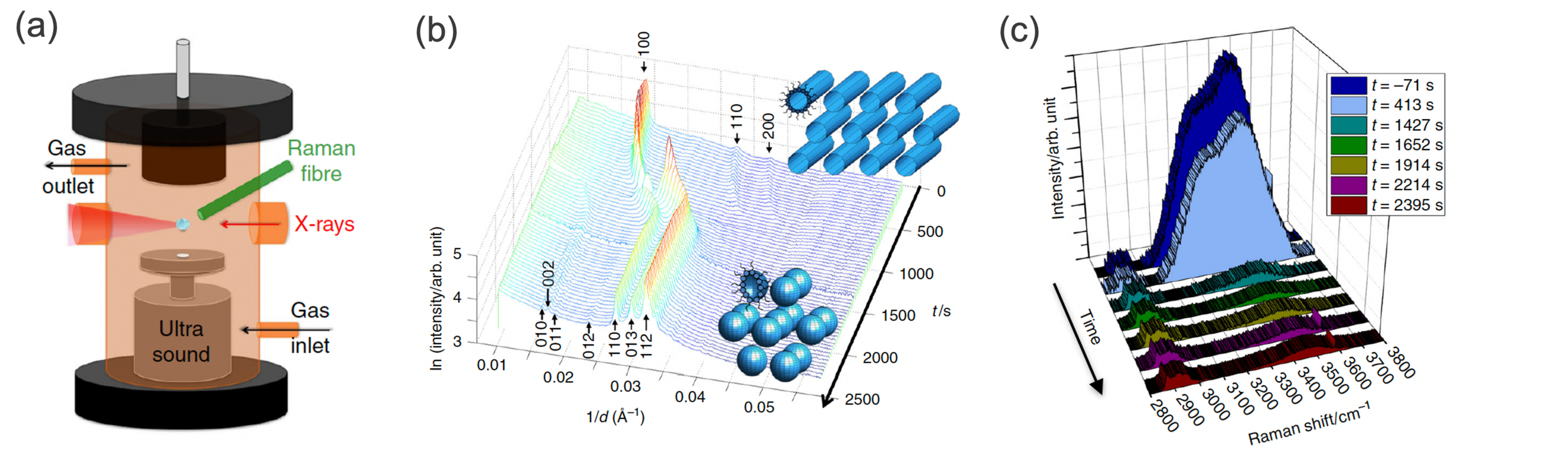


Figure 4. (a) Experimental set up combining SAXS and Raman spectroscopy analysis of an acoustically levitated droplet. Examples of (a) structural data and (c) chemical data from this set-up over time.[7]

Optical Tweezers

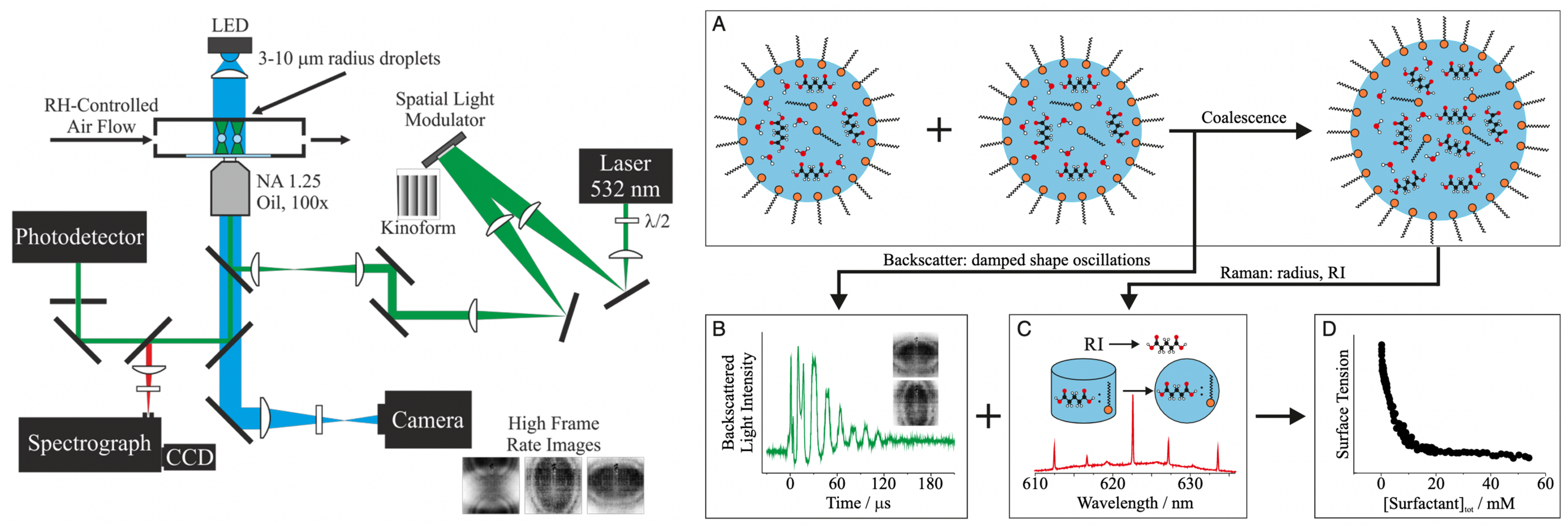


Figure 5. (Left) Optical tweezer experimental set up[1]. (Right) Graphic depicting how data is collected using the optical tweezer by (A) having two droplets coalesce, collecting (B) elastic backscattering and (C) Raman backscattered light, and lastly (D) getting surface tension data[3].

Optical tweezers allow the determination of droplet size, refractive index and surface tension, as well as monitoring droplet chemistry. This is done by steering droplets held by two optical traps (continuous wave 532nm laser), driving their coalescence.[1,2,3,8]

Raman backscattered light is used to determine droplet size, refractive index, and information on the droplet's chemistry.

Elastic backscattering light (paired with size information from Raman data) are used to determine the droplets surface tension.

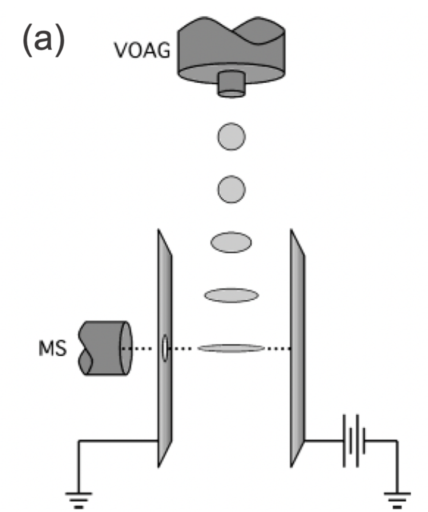
Single Droplet Mass Spectrometry

Mass spectrometry performed on a single levitated droplet would allow examination of its chemistry under different environment (e.g., changing RH, exposure to light to induce photochemistry, exposure to different gaseous environments).

Field-induced droplet ionization mass spectrometry (FIDI-MS), suspends a droplet between two charged plate electrodes. When a critical field is applied, the droplet is forced into a prolate shape with two symmetrical jets of progeny droplets (Fig. 6). The charged progeny droplets are then analyzed with MS[5].

Pending work in the Bzdek group, a quadrupole will suspend and apply the necessary electric field to micron sized droplets. Comparing the MS results with the presence and absence of photochemistry will provide insight into chemical changes that occur with different solutions of suspended droplets.

(a)



(b)

Figure 6. (a) Example of a FIDI-MS set-up using a vibrating orifice aerosol generator as the aerosol source, and (b) an image of a prolate 170 μm methanol droplet and two jets emitting progeny droplets. [5]

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