

# Cloud Condensation Nuclei Activity of CaCO<sub>3</sub> Particles with Oleic Acid and Malonic Acid Coatings

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A figure for illustration of the responses is given in an extra file

*C1: Overall the paper is nicely illustrated but it contains some repetitive text blocs, especially in the result section, that could be avoided in order to ease the reading of this manuscript (and reinforcing also its content).*

## **Response:**

We thank the referee for the positive comment. We will optimize the text of our manuscript to avoid repetition and to make the text more efficient and easier to read.

*C2: While the argument of a bilayer of oleic acid does make sense, I'm still puzzled by the fact that the CCN properties are apparently higher for a coated particle compared to a pure oleic acid particle. I would have simply assumed that once thick enough, the water probing the surface does not see the core CaCO<sub>3</sub> particle (over the time scale of these experiments). In this situation, the pure oleic acid particle would exhibit a kind of upper limit for water adsorption and droplet activation. Maybe the authors could comment more on that, and maybe add the pure oleic acid data on their figures (this would ease the comparison with both systems).*

## **Response:**

Our CCN activity measurement showed that pure oleic acid particles up to 333 nm did not activate at 0.87% SS; this sets an upper limit for CCN activity of oleic acid particles ( $\kappa < 0.0005$ ), in agreement with Kumar et al. (2003) and Broekhuizen et al. (2004). In liquid state oleic acid (OA) forms micelle like structures, the hydrophilic

ends (the carboxyl groups) of oleic acid molecules tend to combine together by hydrogen bonds and the hydrophobic tails (the hydrocarbon chains) are exposed at the outside (Iwahashi et al., 2000; Garland et al., 2008). The arrangement of oleic acid molecules in pure oleic acid particles should be similar. Hydrophobic tails facing outwards can explain the hydrophobicity of the particle surface and the hindrance of the uptake of water, making the CCN activity of pure oleic acid particles very low. Dalirian et al. (2017) studied OA coatings on black carbon (BC). They also found *no* activation of pure OA, but droplet activation for OA coated BC particles at  $SS_{crit}$  lower than that of BC and pure OA. Their particles were larger than ours, though, but also more heavily coated, i.e. more OA like. So, better droplet activation than for pure OA seems to be possible in coated systems.

We assume that  $\text{Ca}(\text{OH})(\text{HCO}_3)$  structures act as hydrophilic sites on the surface of  $\text{CaCO}_3$  (Kuriyavar et al., 2000; Stipp, 1999; Stipp and Hochella, 1991; Neagle and Rochester, 1990). Garland et al. (2008) suggested that OA at sub-monolayer coverage form self-associated islands rather than uniformly covering the surfaces, and OA molecules were oriented vertically on both hydrophobic and hydrophilic surfaces with the hydrocarbon chains of oleic acid molecules facing away from the surface. This is in support of our working hypothesis: the formation of a hydrophobic surface film.

When  $\text{CaCO}_3$  particles are coated with only a small amount of oleic acid (less than one monolayer), the hydrophilic ends (the carboxyl groups) of oleic acid molecules will combine with the hydrophilic sites ( $-\text{OH}$  and  $-\text{HCO}_3$  groups) on  $\text{CaCO}_3$  surface by hydrogen bonds. We conclude that all hygroscopic sites on the  $\text{CaCO}_3$  surface are covered somewhere between  $50^\circ\text{C}$  and  $60^\circ\text{C}$  coating temperature, i.e. between  $14 \cdot 10^{-12}$  and  $23 \cdot 10^{-12}$   $\mu\text{g}$  OA mass per particle, as here the trend turns and droplet activation increase again. This would place the monolayer coverage above 3%, organic volume fraction. According to the measurements and calculations of the length of oleic acid molecule, the thickness of oleic acid sub-monolayer on solid surfaces, and the thickness of deuterated oleic acid monolayers at the air-water interface (Garland et al., 2008; King et al., 2009; Iwahashi et al., 2000), we determined 2.3 nm as the likely thickness of oleic acid monolayer on  $\text{CaCO}_3$  particles, accordingly a monolayer would be achieved at about 12-13% organic volume fraction. As a consequence the formation of the “hydrophilic bilayer” starts at sub-monolayer

coverage in accordance with island formation observed by Garland et al. (2008).

For  $\text{CaCO}_3$  particles coated with more OA (thicker than one monolayer, at 70 and 80 °C coating temperatures), OA in the first layer still combines with the  $\text{CaCO}_3$  surface by hydrogen bonds. We suppose that a portion of the carboxyl groups of oleic acid molecules, which are not in the first layer, will be exposed to the particle surface, in analogy to the formation of lipid bilayers, e.g. in cells, though the structure of this part of oleic acid is not known. The particle surface then becomes more hydrophilic. Activation of wettable, insoluble material can be described by the Kelvin term and a water absorption term, e.g. Frenkel Halsey Hill isotherm (Sorjamaa and Laaksonen, 2007, Kumar et al. 2009).

When carboxylic groups of OA are exposed at the surface, the interaction of water with the OA layer becomes stronger. In terms of the Kelvin/FHH approach, the surface water interaction becomes stronger and  $A_{\text{FHH}}$  increases and likely also the interaction between the higher water layers ( $B_{\text{FHH}}$  decreases). From this point of view water adsorption by the “OA bilayer” should become similar to thin malonic acid layers. In addition, when droplets form, oleic acid will transfer to the surface of the droplets and lower the surface tension of the solution (the surface tension of oleic acid is  $0.033 \text{ J m}^{-2}$ , which is much lower than that of pure water of  $0.072 \text{ J m}^{-2}$ ). Thus, the activation of OA coated particles is probably a complex interaction between formation of specific hydrophobic layers and more hydrophilic multilayers, surface tension effects and for the largest coating amounts, simple size effects. As shown in Figure S1,  $SS_{\text{crit}}$  for OA is lower than for thin malonic acid coatings, probably because of the surface tension effect, but higher than for thick MA coatings, because of the missing solute effect.

We will implement parts of this discussion in the manuscript, highlighted in yellow.

*C3: If my reading is correct, the  $\text{CaCO}_3$  particles with a thick coating do exhibit better CCN properties than the pure oleic acid particles (if my reading is incorrect, this would highlight that an in-depth editing would be beneficial for the reader). How can you explain such a fact? Is the  $\text{CaCO}_3$  surface leading to some kind of ordering of*

*the adsorbed organic acid (which might not be observed in the pure homogeneous organic particle) leading effectively to the above mentioned bilayer structure?*

**Response:**

Your reading is correct. Note, the oleic acid coatings achieved at 70° or 80°C coating temperature are still thin. The largest coating thickness is about 10 nm at an organic volume fraction of 44%, which corresponds to about 4 monolayers of oleic acid (assuming the thickness of oleic acid monolayer on CaCO<sub>3</sub> particles is about 2.3 nm). To our knowledge, no previous study has investigated the structure of oleic acid coating on particle or solid surface thicker than one monolayer.

In our understanding the arrangement of oleic acid molecules in the thin coatings will be influenced by the CaCO<sub>3</sub> core (the polar, hydrophilic sides) and can thus be different from the arrangement of oleic acid molecules in pure oleic acid particles. Water can probably adsorb at the carboxylic groups facing outward (“bilayer” type structure) and diffuse through the thin oleic acid coatings. It may form an adsorbed water phase near the CaCO<sub>3</sub> surface. This could push the oleic acid out to act as surfactant which lowers the Kelvin term. Such a process should also happen in pure oleic acid particles. Because of the presence of CaCO<sub>3</sub> core the SS to achieve is lower than for pure OA.

We will explicitly refer to the lower  $\kappa$  of pure oleic acid in relation to higher  $\kappa$  observed for the oleic acid coated CaCO<sub>3</sub>.

*C4: Is the temperature in the coating device leading to some kind of ordering (for instance, by increase surface mobility before an ordering when cooling down)? Also, oleic acid has only a moderate thermal stability as it decomposes at higher temperature (typically at temperature at a factor 2 higher than those used here), potentially via an epoxide pathway in presence of air (and enhanced by light or metallic traces). Could traces of oxidized products nevertheless affect the composition of the coating at 80 °C already? If so, then this effect should increase with time. Did the authors observed any variation with time of kappa at 80 °C? Did the authors tried*

*to have thicker coatings at lower temperature by changing the gas flow conditions in their coating device?*

**Response:**

We agree with the referee that the temperature in the coating device can increase the surface mobility of OA molecules, which would help to optimize the layering arrangement (ordering) of adsorbed oleic acid molecules on CaCO<sub>3</sub> surface.

We can exclude oxidation of OA since we used high-purity N<sub>2</sub> (Linde LiPur 6.0, purity 99.9999%, Linde AG, Munich, Germany) and we did not have much light in our system because both the coating device and the flow tube were covered with light tight materials (black polyurethane foam). Metallic traces might exist in our system, though, as we used some stainless steel tubes in our system.

The only way in which we modified the time between coating process and particle detection was provided by a flow tube to increase the average residence time from 5.8 to 23.7 s. Longer residence time (by 23.7 s) had no significant impact on CCN activity for both oleic acid coated particles and malonic acid coated particles at both dry and 47% RH conditions, probably because the coating process was already completed in the coating device and no further reactions occurred in the flow tube.

At the beginning of our experimental study, we modified the gas flow condition in the coating device in order to choose an appropriate gas flow condition. But we only measured the particle size when we changed the gas flow condition. After finding the appropriate gas flow conditions, we fixed the gas flow condition and did not change it anymore.

*C5: Line 238. This sentence is unclear.*

**Response:**

This sentence should be: In the discussion we also use the coating mass per particle to give a rationale, which is easier to imagine, to the finding and classification.

*C6: Line 249: where a polydisperse*

**Response:**

This sentence should be: In cases where a polydisperse aerosol was coated ...

*C7: Line 296: remained at*

**Response:**

This sentence should be: The  $\kappa$  value remained at  $0.0028 \pm 0.0001$  at 60 °C and increased to  $0.0036 \pm 0.0001$  at 80 °C.

And we also made the revision in our manuscript according to your comments.

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