Cloud drop activation of insoluble aerosols aided by film forming surfactants

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Abstract. Cloud droplet activation of insoluble aerosols covered by insoluble surfactant films has been studied theoretically by combining the FHH activation theory and an equation of state suitable for surfactant films that are in an expanded state. The key parameters governing the surfactant's ability to suppress critical supersaturations are its partial molecular area at the water surface, and the size of the molecule. For a fixed size, molecules with larger molecular area are more efficient, whereas with a fixed area-to-volume ratio, smaller molecules are more efficient. Calculations made for stearic acid films on black carbon and illite aerosols indicate that the critical supersaturations are significantly lower than with pure particles, especially when the dry particle sizes are several hundred nanometers and larger. Furthermore, the reductions of the critical supersaturation are similar when stearic acid is replaced by water-soluble organics with hygroscopicity parameter (κ) values up to 0.1. However, mixtures of surfactant and water-soluble organics are relatively weaker in reducing critical supersaturations than either of these compounds alone.

1 Introduction

The activation of cloud condensation nuclei (CCN) into cloud droplets was first described theoretically by Köhler in the 1920's (Köhler, 1926). The CCN's considered by Köhler were composed of hygroscopic salts, and in the atmosphere salt particles are certainly the most important CCN class. However, other aerosol types such as organic aerosols and mineral dust can also act as CCN under suitable conditions. Furthermore, various physicochemical phenomena such as co-condensation of soluble gases and surface tension depression by different types of surfactants can modify the cloud drop activation process. The impact of water-soluble surfactants has been studied quite extensively both theoretically and experimentally (e.g., Xiong et al., 2022; Vepsäläinen et al., 2023; Schmedding and Zuend, 2023; Bain et al., 2023; Laaksonen and Malila, 2021, and references therein). Less attention has been given to film forming, water insoluble surfactants. Brief theoretical considerations about their effects on salt particle activation have been given by McFiggans et al. (2006) and Laaksonen and Malila (2021). Experimental studies have found quite minimal impact of insoluble surfactants on CCN activation of ammonium sulfate (Abbatt et al., 2005) and sea salt particles (Nguyen et al., 2017; Forestieri et al., 2018). Wang et al. (2018) studied experimentally the effect of oleic acid coatings on the activation of water insoluble $CaCO_3$ particles. They observed reduced CCN activity with thin coatings, apparently because water was not able to penetrate between the core particles and the coatings in which the hydrophobic ends

25   of oleic acid molecules were facing outward. With thick coatings, the CCN activity was enhanced relative to pure CaCO$_3$, but it remained unclear how much this was due to possible oleic acid bilayer formation (with hydrophilic ends of the molecules facing outward in the second layer) and how much due to a surface-active film formation on the activating droplets.

    Small amounts of film forming surfactants have a relatively insignificant effect on CCN activation of hygroscopic salt particles, for the simple reason that the activation diameters of cloud droplets are much larger than the dry CCN diameters.

30   For example, the surface area of a 400 nm ammonium sulfate particle grows by a factor of 500 by the time it activates. This means that if just a few monolayers of insoluble surfactant cover the dry particle, the surfactant film becomes so dilute at activation that it has almost no effect on the surface tension of the droplet. With water insoluble CCN the situation is different. The activation diameter of a droplet formed around a mineral particle is typically just a few tens of percents larger than the dry diameter, and therefore relatively small amounts of film-forming surfactants can have a much larger impact on CCN activation

35   than with hygroscopic salts.

    The purpose of this work is to examine theoretically the impact of water insoluble surfactants on the CCN activation of black carbon (BC) and illite particles. The FHH (Frenkel-Halsey-Hill) activation theory (Sorjamaa and Laaksonen, 2007) is used in describing the interaction between water vapor and the insoluble particles, and the surface tension reduction of water by surfactant films is treated using the equation of state (EoS) derived by Gaines Jr. (1978). Furthermore, the ability of film

40   forming surfactants to depress critical supersaturations of insoluble aerosols is compared to that of similar amounts of low hygroscopicity water soluble organics that cause no surface tension depression.

2   Theory

The FHH adsorption activation theory combines the FHH adsorption isotherm (Frenkel, 1946; Halsey, 1948; Hill, 1949) and the Kelvin equation to express the equilibrium saturation ratio of water vapor on the surface of a spherical insoluble particle

45   that has adsorbed N monolayers of water as

$$S = \exp\left(-AN^{-B}\right)\exp\left(\frac{2\gamma_w v_w}{kTR}\right) \tag{1}$$

Here, the FHH parameters describe the molecular interaction between the insoluble particle and water with A representing the strength of the interaction and B the rate of its decay as a function of distance. In the Kelvin term, γ_w is surface tension and v_w is molecular volume of water, k is the Boltzmann constant, T is temperature, and the droplet radius $R = R_d + d$ with R_d the

50   radius of the dry particle and $d = N d_m$ the thickness of the adsorption layer. The thickness of a water monolayer d_m is taken to be 2.84 Å.

    Amphiphilic organics that are completely immiscible in water, such as long-chain fatty acids, may form so called Langmuir films on the surface of water. The films are said to be in a compressed state when the film forming molecules are close packed. Upon dilution, the films enter so called expanded state, and highly diluted films are said to be in a gaseous state as they obey

55   the two-dimensional ideal gas law. Films in a gaseous state do not have much effect on the surface tension of water; in order to have a notable influence on cloud drop formation, the films should be in an expanded state at the point of activation. Gaines Jr.

(1978) derived, starting from the Gibbs adsorption equation, an EoS relating the surface area per surfactant molecule Ω_s and the surface pressure $\Pi = \gamma_w - \gamma$ that applies to expanded films. The surface tension of the film can be calculated from the EoS:

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$$\Pi = \frac{kT}{\omega_w}\left[\ln\left(1 + \frac{\omega_w}{\Omega_s - \omega_s}\right) - \ln f_w\right] \qquad (2)$$

Here ω_w and ω_s denote partial molecular surface areas of water and the surfactant, respectively. Partial molecular variables depend on concentration; however, in the calculations below, the molecular areas and volumes are taken to be constants. The volumes are assumed to be the same as their pure component values, and the molecular area for water, ω_w, is taken to be 9.7 Å^2. The film is assumed to be dilute enough so that the activity coefficient of water f_w in the surface layer can be approximated

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by unity. When calculating the effect of the surfactant film on cloud drop activation, γ_w in Eq.(1) is replaced by γ.

If the insoluble particle is coated, instead of film forming surfactants, by a small amount of water-soluble material that does not affect the surface tension, Eq. 1 is modified as follows (Kumar et al., 2011a):

$$S = \exp\left[-A\left(\frac{R - \epsilon_i^{1/3}R_d}{d_w}\right)^{-B}\right]\exp\left(\frac{2\gamma_w v_w}{kTR}\right)\exp\left(-\frac{\epsilon_s \kappa R_d^3}{R^3 - \epsilon_i R_d^3}\right) \qquad (3)$$

Here ϵ_i and ϵ_s denote the volume fractions of insoluble and soluble material, respectively, in the dry particle, and κ is the

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hygroscopicity parameter (Petters and Kreidenweis, 2007) of the soluble material.

3 Results and discussion

The two parameters that govern the ability of the film forming surfactants to impact cloud drop activation of insoluble particles are the partial molecular volume v_s and the partial molecular area ω_s. Figure 1 shows how they impact the CCN activation of BC particles with a 5% volume fraction of surfactant when the molecular mass is either 150 or 750 (density of the surfactant

75
is assumed to be 850 kgm^{-3} in all cases) and the molecular area is either 20 or 100 Å^2 (note that the combinations of these parameters used in the calculations do not refer to any specific surfactants and are not necessarily very realistic). As a base case, we have a model surfactant with low molecular mass and surface area (red line); critical supersaturations are shown as a function of dry particle diameter between 60 and 1000 nm. Increasing the partial molecular surface area while keeping the molecular volume constant results in increased CCN activity (cyan line). However, if the ratio of surfactant molecular volume

80
to surface area is kept constant, and both the volume and the surface area are increased, the result is decreased CCN activity (blue line).

Figure 2 shows the impact of stearic acid films on the critical supersaturations of BC particles (FHH parameters $A = 12$, $B = 1.93$; Laaksonen et al., 2020). Stearic acid was assumed to have a partial molecular surface area of 32 Å^2 on the surface of water (Stewart et al., 2023). The black line indicates pure BC, and the blue and red solid lines correspond to mixed particles

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with 1% and 5% volume fractions of stearic acid, respectively. Similarly as in Figure 1, the impact of the surfactant increases with increasing dry diameter. The reason for this is that the surface-to-volume ratio decreases with particle size. Thus, the 1%
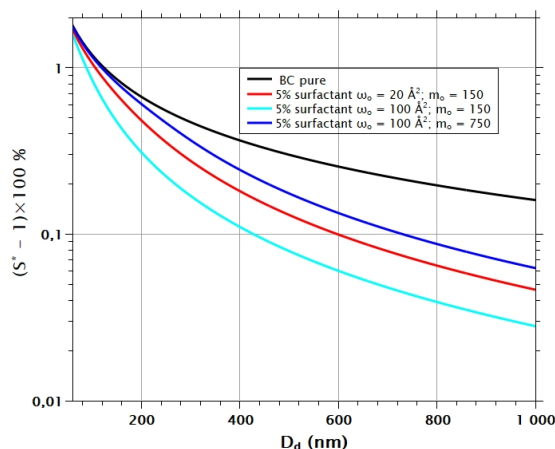
Figure 1. Critical supersaturations as a function of dry particle diameter for pure BC particles, and BC particles with 5% volume fraction of insoluble surfactant with molecular surface areas and molecular masses as indicated in the legend. Density of the surfactant was assumed to be 850 kg m^{-3} in each case. Note that the combination of molecular surface area and mass may not be realistic especially in the most CCN active case shown here.
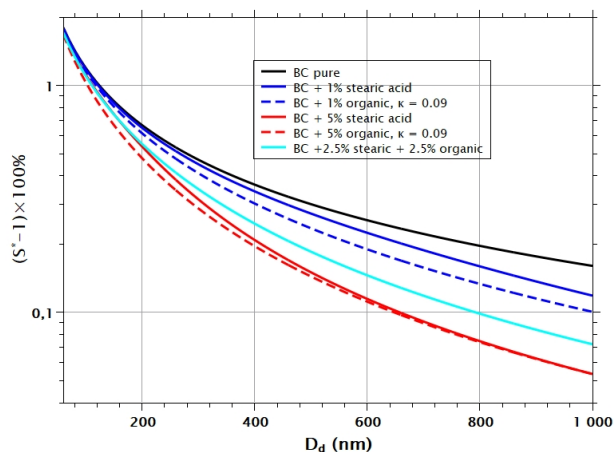
Figure 2. Critical supersaturations as a function of dry particle diameter for (1) pure BC particles, (2) BC particles with 1% and 5% volume fractions of insoluble surfactant (stearic acid), (3) BC particles with 1% and 5% volume fractions of soluble organic with $\kappa = 0.09$, and (4) BC particles with 2.5% volume fraction of stearic acid and 2.5% volume fraction of organic with $\kappa = 0.09$.

volume fraction in a 60 nm dry particle translates into a sparse surface coverage of stearic acid molecules on BC, with a single molecule occupying on average a surface area of 505 Å^2. A full monolayer coverage on the BC particle (with stearic acid
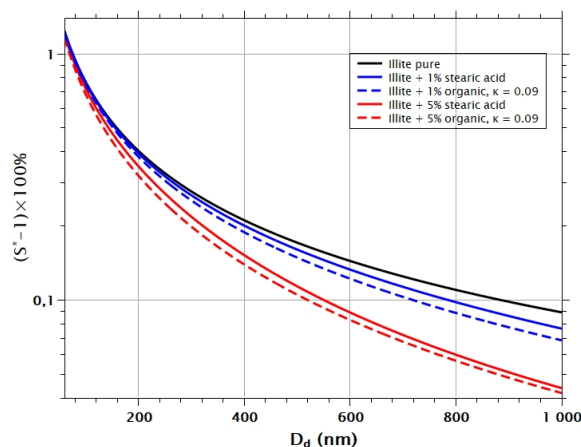
Figure 3. Critical supersaturations as a function of dry particle diameter for pure illite particles, illite particles with 1% and 5% volume fractions of stearic acid, and illite particles with1% and 5% volume fractions of soluble organic with $\kappa = 0.09$.

surface area of 32 Å^2) occurs only close to D$_d$ = 950 nm. With a 5% volume fraction, stearic acid covers the BC particle fully

90   just below D$_d$= 190 nm.

The dashed lines in Figure 2 show critical supersaturations for BC particles mixed with 1 and 5% volume fractions of water soluble organic with $\kappa = 0.09$. In the calculations, it was assumed that the organic species has no effect on water surface tension. With 5% volume fractions, the water soluble organic and stearic acid suppress the critical supersaturations of BC particles by almost the same amount. However, with the 1% volume fractions, the water-soluble organic is somewhat more

95   efficient.

The solid cyan line in Figure 2 shows critical supersaturations for BC particles mixed with 2.5% volume fraction of stearic acid and a similar volume fraction of the organic with $\kappa = 0.09$. Interestingly, this mixture shows markedly reduced CCN activity compared with either of the 5% volume fraction mixtures. This is especially important to notice, as it may be difficult to produce particles coated with pure insoluble surfactant via vapor deposition mechanism such that the water can penetrate

100   through the coating during a CCN activation experiment (Schwier et al., 2012; Wang et al., 2018). More practical methods to ensure film formation on the activating cloud droplet might involve introducing some water-soluble species together with the insoluble surfactant. It would then be important to be able to account for the joint effects of all species on the CCN activation.

Figure 3 is similar to Figure 2 otherwise, but the insoluble particle is illite (FHH parameters $A = 1.02$, $B = 1.12$; Kumar et al., 2011b). Illite is somewhat more CCN active than BC. On the other hand, stearic acid does not suppress the critical

105   supersaturations quite as effectively with illite as with BC; with 1-micron particles, $(S^* - 1)$ of illite drops by 51% due to 5% volume fraction of stearic acid, whereas with BC the drop is 67%. Also, with illite, the water soluble organic with $\kappa = 0.09$ causes a slightly bigger reduction of critical supersaturation relative to stearic acid, than with BC.
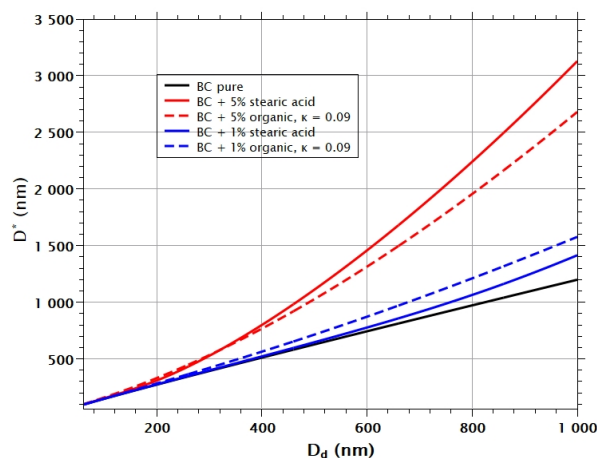
Figure 4. Critical radii as a function of dry particle diameter for pure BC particles, and BC particles with 5% and 1% volume fractions of insoluble surfactant (stearic acid) and BC particles with 5% and 1% volume fractions of soluble organic with $\kappa = 0.09$.

Figure 4 show critical radii of BC particles and their mixtures with stearic acid and the organic with $\kappa = 0.09$. With the 5% mixtures (red lines), the difference between stearic acid and the water-soluble organic substance is larger than with the
110   critical supersaturation. Similarly as with water soluble surfactants, reduced surface tension leads to increased critical radii compared with water soluble species that reduce critical supersaturation without affecting surface tension (Ruehl et al., 2016). However, with the 1% mixtures (blue lines), the water soluble organics produce larger critical radii than stearic acid. This flip-over compared to the 5% mixtures is obviously due to much smaller surface tension reduction, as depicted in Figure 5. With 5% volume fraction of stearic acid, the surface tension drops rapidly until a dry diameter of about 250 nm, and thereafter
115   the decrease is more gradual. With the 1% volume fraction mixtures, the drop of surface tension is almost linear throughout the dry diameter range.

4   Conclusions

The impact of water insoluble film-forming surfactants on the cloud drop activation of insoluble particles was studied theoretically by combining the FHH activation theory and an EoS for expanded surfactant films. The surfactant properties that
120   influence critical supersaturations are the partial molecular area and the partial molecular volume. Increasing the area while keeping the size of the molecule constant leads to decreased critical supersaturations; however, if the ratio of the molecular area and volume is kept constant, smaller molecules are more efficient in promoting CCN activation.

Model calculations were made for systems consisting of either BC or illite particles, and stearic acid as the film forming surfactant. In addition, the surfactant impacts on critical supersaturations were compared to those of an unspecified organic
125   compound with a hygroscopicity parameter $\kappa = 0.09$. A 5% volume fraction of stearic acid suppressed the critical supersat-
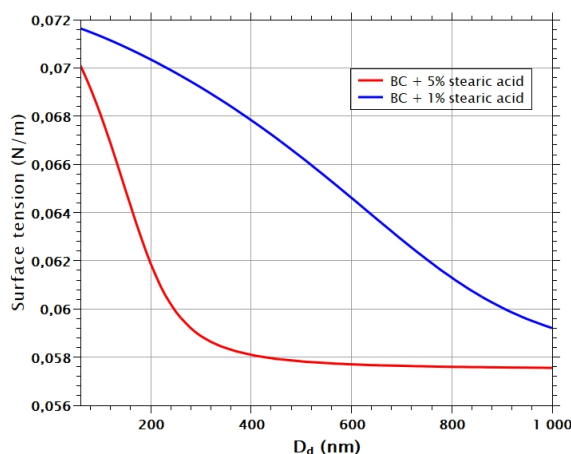
Figure 5. Surface tension of critical droplet as a function of dry particle diameter for pure BC particles with 5% and 1% volume fractions of stearic acid.

urations of both BC and illite particles with quite considerable effects at dry particle diameters of about 200 nm and larger. The percentual impact on the critical supersaturation was slightly larger with BC particles than with illite. With 1% volume fractions, the suppression of critical supersaturations was smaller, but not completely insignificant at large particle diameters close to a micrometer.

130   Compared to the water-soluble organic, the impacts of stearic acid on critical supersaturations were quite similar when BC particles and 5% volume fractions of either stearic acid or the organic were considered. With all other mixtures, the water-soluble organic was somewhat more CCN efficient. With critical radii, a flip-over was seen between the 1% and 5% mixtures with BC; the water-soluble organic produced larger critical radii than stearic acid in the 1% case, but with the 5% case, the surface tension depression by stearic acid was sufficiently strong to make the critical radii larger than those produced by the
135 water-soluble organic.

    Interestingly, it was seen that the impacts of stearic acid and the water-soluble organic on CCN activity of insoluble particles are not additive, as a mixture with 2.5% volume fractions of both substances reduced the critical supersaturations of BC particles less than in either of the 5% volume fraction cases.

Code availability. The FORTRAN codes used for the calculations are available upon request to Ari Laaksonen (ari.laaksonen@fmi.fi).

140   *Competing interests.* The author declares no competing interests.

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