

ABSTRACT

Title of Thesis: MIXED ORGANIC SURFACTANT EFFECTS
ON CLOUD CONDENSATION NUCLEI

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Atmospheric aerosols affect Earth's radiative budget through direct and indirect effects. The direct effects are well understood but the indirect effects have large uncertainty associated with them. Uncertainty is so great that even the sign of the radiative forcing associated with indirect effects is questioned. This work examines aerosol indirect behavior by assessing surfactant effects on the activation of aerosol particles into cloud droplets. Szyszkowski-Langmuir surface tension models are applied to Köhler theory to capture surfactant effects on aerosol activation behavior. Surfactant aerosols tested are succinic acid and sodium dodecyl sulfate (SDS). Results suggest that a small addition of surface active material (like SDS) to organic carboxylic acids (like succinic acid) can significantly change droplet activation behavior.

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NUCLEI

by

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Dedication

To my parents, John and Ngan Mitchell and my sister Alicia Mitchell. To all those that supported me on my path through life.

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I give sincere thanks to Dr. Akua Asa-Awuku for her guidance and support throughout my time at the University of Maryland. I truly believe she changed my life for the better when I was asked to participate in aerosol research. The opportunity I had been provided gave me purpose and restored my motivation to continue to pursue chemical engineering education.

Thanks to Dr. Qi Yao for training me in the operation of nearly all laboratory instruments I use. Thanks to Patricia Razafindrambinina and Kotiba Malek for help during CCN measurements. Thanks to the entire roster of Environmental Aerosol Research Lab members for the camaraderie and support. I have greatly enjoyed my time in the lab, and I cherish the memories made here.

Table of Contents

Dedication	ii
Acknowledgements.....	iii
Table of Contents.....	iv
List of Tables	v
List of Figures	vi
List of Abbreviations	vii
Chapter 1: Introduction	1
1.1 Aerosol Overview	1
1.2 Carbonaceous Aerosol Sources and Composition	2
1.2.1 Organic Carbon.....	2
1.2.3 Black Carbon	2
1.3 Direct Effects	5
1.4 Indirect Effects.....	7
1.5 Research Motivation	11
Chapter 2: Experimental Methods and Analysis	13
2.1 Tensiometer and Surface Tension Measurements	14
2.2 Aerosol Measurements.....	16
2.3 Differential Mobility Analyzer (DMA)	17
2.4 Condensation Particle Counter (CPC)	18
2.5 Cloud Condensation Nuclei Counter (CCNC).....	19
2.6 CCN Activity Data Analysis.....	19
Chapter 3: Results and Discussion.....	22
3.1 Surface Tension Measurements	22
3.2 Cloud Droplet Activation Measurement	26
Bibliography	37

List of Tables

Table 1. Szyszkowski-Langmuir	22
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List of Figures

Figure 1. Chemical Structure of Succinic Acid	13
Figure 2. Chemical Structure of Sodium Dodecyl Sulfate (SDS)	13
Figure 3. Tensiometer Pendant Drop Photo Example	16
Figure 4. Schematic for Cloud Condensation Activity Experiment.....	17
Figure 5. Succinic Acid Szyszkowski-Langmuir Curve	23
Figure 6. SDS Szyszkowski-Langmuir Curve	24
Figure 7. Mixed Solution Szyszkowski-Langmuir Curves	26
Figure 8. Ammonium Sulfate Activation Curves	27
Figure 9. 50nm SDS Köhler Curve Raoult and Kelvin Breakdown	29
Figure 10. Succinic Acid and SDS Köhler Curves	30
Figure 11. 0.6% Super Saturation Activation Curves	32
Figure 12. κ -Single Hygroscopicity Parameterization Without Surface Tension Correction	33
Figure 13. κ -Single Hygroscopicity parameterization With Surface Tension Correction	35

List of Abbreviations

CCN	Cloud Condensation Nuclei
CCNC	Cloud Condensation Nuclei Counter
CN	Condensation Nuclei
CMC	Critical Micelle Concentration
CPC	Condensation Particle Counter
DMA	Differential Mobility Analyzer
SDS	Sodium Dodecyl Sulfate
ZSR	Zdanovskii-Stokes-Robinson

Chapter 1: Introduction

1.1 Aerosol Overview

Aerosols are liquid or solid particles small enough to be suspended in gaseous mediums. Our atmosphere is one such gaseous medium in which aerosol particles are introduced through both natural and anthropogenic sources (Bond et al. 2013). A particular type of aerosols of interest are carbonaceous aerosols due to their association with anthropogenic emissions (Lohman et al. 2000). Typically, carbonaceous aerosol emissions are complex mixtures of chemical species and due to this complex nature, these aerosols are difficult to speciate and study. Included within carbonaceous aerosols is black carbon and this specific species is of interest due to its implications for cloud droplet activation discussed in greater detail in Section 1.4.

Black carbon is a very specific category of substance that is emitted alongside several other particles in combustion processes. Typical sources of black carbon emissions are engines, biomass burning, and industry (Goldberg, 1985). Diesel engines provide around 70% of black carbon emissions American continent and Europe (Bond et al. 2013). Fuels like coal and biomass provide 60 to 80% of the black carbon emissions throughout Asia and Africa (Bond et al. 2013). Black carbon total global emissions have been estimated to be about 7500 Gg per year using bottom-up accounting the caveat being that this estimate comes with a massive uncertainty range of 2,000 to 29,000 (Bond et al. 2013). The bottom-up inventory struggles with identifying the

exact amount of biomass burning and the types of technology utilized in the burning due to this type of fuel use being prevalent in developing countries without the means to catalogue and report these values (Lioussé et al. 1996). The major sources and regions of emission are widely agreed upon, but major uncertainty is still prevalent due to the previously discussed issues. This lack of data is thought to cause an underestimation of emissions from biomass sources (Lioussé et al. 1996).

1.2 Carbonaceous Aerosol Sources and Composition

Two major categories of carbonaceous aerosol are organic carbon and black carbon.

1.2.1 Organic Carbon

Organic carbon, also known as brown carbon, is usually emitted naturally through wild forest and savanna fires (Bond et al. 2013). Anthropogenic sources are majorly comprised of biofuel burning for heating, cooking, and energy production (Laskin et al. 2015). Composition of these aerosols include black carbon, brown carbon, and organic aerosol in varying mixture states (both internally and externally mixed) (Pratt et al. 2010). Both composition and mixture state depend on the emission source and burn conditions leading to the high level of variation and complexity when it comes to studying these aerosols.

1.2.3 Black Carbon

Black carbon is a specifically defined material that is formed during combustion of carbon-based fuels lack the oxygen required for a complete combustion (Bond et al. 2013). Mixing of reactants also affects the ability for complete combustion to take

place leading to incomplete combustion even in situations where appropriate amounts of oxygen are present. Black carbon is made distinctive by its physical properties which include: a mass absorption cross section of $5 \text{ m}^2 \text{ g}^{-1}$ at wavelengths of 550 nanometers, it is refractory keeping its form at high temperature until vaporizing at 4000 kelvin, insolubility in water and organic solvents, and its existence as an aggregate of small carbon spherules (Bond and Berstrom, 2006).

Spherules are formed in flames during combustion and form aggregates due to rapid coagulation (Grisdale, 1953). This sets apart black carbon aerosol from graphite which has a more ordered planar structure. Complex reactions of polycyclic aromatic hydrocarbon molecules form the precursors to black carbon, and it is the coagulation of these hydrocarbons that act as particle nuclei from which black carbon spherules begin to form (Bond and Berstrom, 2006). Individual black carbon spherules range in the size of tens of nanometers and quickly after their formation they form aggregates with other spherules to create large fractal structures (Liu et al. 2019).

After the newly produced black carbon particles are released into atmosphere; water vapor and species in the gas-phase condense onto the surface of the aggregate particles (Matsui et al. 2013). Particles that are newly emitted maintain an external mixing in which the different species are present in separate particles but over time the mixing changes to that of an internal mixing where the various chemical components are present together in individual particles (Hallberg et al. 1994). The internally mixed particles are obviously no longer pure black carbon and are referred

to as black carbon containing particles. The rate at which this mixing occurs warrants more study as time values given in past research varies greatly. In specific locations the internal mixing is found to occur a few hours after emission, but data is limited in order to make the conclusions on internal mixing throughout the atmosphere. Current aerosol models that simulate black carbon internal mixing estimate that the mixing occurs within one to five days (Bond et al. 2013).

Black carbon mixing has implications in terms of how direct and indirect effects are altered by interaction with other species. These mixing issues also speak to the complexity of modeling the cloud formation effects as the individual contribution of black carbon must be considered alongside the various black carbon containing particles that are formed due to internal mixing. The lack of understanding in these fields leads to the uncertainty associated with overall aerosol radiative forcing and specifically black carbon aerosol forcing.

Issues with the precise definition of black carbon are in the methods in which black carbon is emitted as aerosol (Bond et al. 2013). In combustion of carbon-based fuels there are always other materials that are emitted alongside black carbon. The aerosol produced by combustion is likely to be mixtures of substances along which black carbon resides. Past studies refer to combustion aerosol and soot as black carbon whereas the precise definition is not used correctly. The commonly accepted definition for black carbon is now carbonaceous material that: is strongly absorbs

visible light, is refractory, is insoluble in water, and exists as an aggregate of small carbon spherules (Bond et al. 2013).

This huge lack of uncertainty coupled with low time in atmosphere and the focus on local effects of black carbon emission leads to the development of global aerosol models that underestimate the atmospheric absorbing effects that black carbon has. Some of this underestimation can also be attributed to black carbon mixing effects and interactions with other atmospherically relevant substances that will alter its properties. Another contributing factor is the lack of emissions data outside of Europe and North America. Models have high confidence in the measurements in these regions but have high uncertainty in their estimates of black carbon emissions outside of these areas.

1.3 Direct Effects

Aerosol climate effects are categorized as direct and indirect effects (Rap et al. 2013). Black carbon direct effects are the absorption of sunlight. The dark coloration of black carbon leads to heating of the atmosphere due to black carbon aerosol in atmosphere collecting heat (Zhuang et al. 2019). This stops radiation from reaching the surface and from being reflected back to space. This direct effect is the most widely understood climate effect black carbon has and has the least amount of uncertainty associated with it. Black carbon having a strong absorption of visible light is a distinguishing characteristic of the substance as an atmospherically present

aerosol. No other atmospherically relevant substance has such a powerful direct effect (Hong et al. 2020).

Although understanding of the direct effects maintains the highest confidence relative to the indirect and semi-direct effects there are still issues with constraining certain factors affecting black carbon direct radiative forcing (Chung et al. 2011).

Atmospheric absorption measurements require an estimation of absorption caused by either dust or black carbon (Chin et al. 2009). Dust stands as the largest obstacle to precise measurement of black carbon absorption throughout the globe (Liao et al. 1998). Measurements easily give false positives on black carbon absorption when it is signal from general mineral dust being picked up (Yang et al. 2009). Alongside black carbon's low time in atmosphere and highly variable concentration from region to region is dust aerosol with the same properties. This property associated with black carbon already makes quantification difficult, but the interference of dust makes matters worse. Measurements near regions where biomass burning is prevalent see almost double the amount of black carbon optical depth than is being used in models (Ruiguang et al. 2018). Measurements are preferably taken in regions that produce the largest fractions of black carbon aerosol as resources are limited but this places a bias on information generated. Models based on this information are limited by the lacking long-term observations and scope of measurements causing uncertainty in black carbon direct effects.

1.4 Indirect Effects

What constitutes the largest uncertainty when attempting to understand aerosol climate response are the indirect and semi-direct effects of substances like black carbon (Menon et al. 2002). Indirect effects refer to phenomena atmospheric aerosols are involved in such as manipulation of cloud formation by acting as cloud condensation nuclei or altering ice particle formation and conditions for precipitation (Lohmann et al. 2007). Climate effects associated with these cloud phenomena are the aerosol indirect effects. Semi-direct effects refer to the local temperature changes aerosol cause that consequently affect cloud formation leading to clouds having their associated climate effects altered (Johnson et al. 2004). These cloud effects are complex and numerous causing even the sign of these effects to be uncertain at this point (IPCC, 2013). Most studies indicate a net cooling caused by indirect and semi-direct effects, but the complex mixture of warming and cooling effects associated with cloud forcing calls estimates into question.

Black carbon's effects on clouds are categorized in four ways. The first effect is the change in temperature caused by absorption of energy by black carbon aerosol. This change in temperature modifies cloud distributions by simply altering the environmental temperature in which clouds reside (Xu et al. 2019). The second effect is alteration of cloud droplet density and the lifetime of clouds in atmosphere (Kuwata et al. 2009). Presence of aerosol can serve typically as a force increasing the number of cloud droplets as water vapor now has greater opportunity to condense onto the surface of a particle. Third effect is altering the phase partitioning in ice-

liquid clouds and changing the conditions for precipitation to occur (Schill et al. 2020). Fourth is a change in number of ice droplets in solid phase clouds (Heintzenberg and Charlson 2009).

Methods for analyzing the contributions an aerosol has towards cloud formation involves quantifying its tendency to act as cloud condensation nuclei. This is when a particle acts as the seed for the formation of a cloud droplet. The particle serves as a surface for which water vapor can begin to condensate and subsequently form one of the many droplets found in a cloud (Hudson, 1993). This initial condensation is referred to as activation. Different particles will have different tendencies to serve as cloud condensation nuclei and quantifying these properties gives insight into how aerosols affect cloud formation (Novakov et al. 1993).

The properties of a particle that affect its ability to act as a cloud condensation nucleus are its size, chemical composition, and the water vapor concentration around the particle (Heintzenberg and Charlson 2009). The amount of water vapor in the vicinity of the water particle is quantified using supersaturation and, in regard to cloud condensation activity, the supersaturation point at which the particle first activates is referred to as the critical supersaturation (Seinfeld and Pandis, 2006). The lower the supersaturation required to activate a particle the more active that particle is in the formation of clouds. Particle size also affects activity in that smaller particles require greater supersaturation meaning larger particles are easier to activate. A characteristic of more active particles is a relatively high solubility (Kumar et al.

2003). Black carbon is insoluble and, when freshly emitted, the black carbon particles are small (Wu et al. 2018). This would indicate that black carbon has a poor contribution to cloud formation however these characteristics are altered the longer black carbon remains in atmosphere (Riemer et al. 2010). Further research is needed on this subject matter to develop a better model of how black carbon affects cloud formation with regard to its dynamic properties over its time in atmosphere.

The complex tangle of effects black carbon aerosol has on clouds includes conflicting influence on the heating and cooling associated with indirect effect radiative forcing. Liquid clouds have increased number of droplets with higher black carbon aerosol concentration which causes a negative radiative forcing (Ramanathan et al. 1989). Interacting with this is the effectiveness of black carbon to serve as cloud droplet nuclei which is found to be low for pure carbon. Consideration is given to black carbon particles serving as sites that collect soluble material (Liu et al. 2017). This would decrease the amount of cloud droplet nucleus sites therefore increasing positive radiative forcing with the reduction of clouds. Black carbon itself has light absorbing properties and within cloud droplets will decrease cloud albedo (Martins et al. 1998). This heats clouds and aids in their dispersion leading to a positive radiative forcing. Ice nucleus effects vary depending on conditions leading to both increase and decrease of ice particles in cirrus clouds (Hendricks et al. 2005). The net effect of black carbon on these clouds is uncertain as the cirrus cloud stability is dependent on a large amount of variables.

Current understanding of black carbon activation utilizes closure concepts which compare experimentally measured activation of black carbon to predictions utilizing size of particle and particle composition (Bond et al. 2013). Predictions have traditionally overestimated activation when compared to experimental results. The properties of freshly emitted black carbon speaks to this discrepancy. Externally mixed black carbon does not activate as much as predicted and when the externally mixed black carbon is treated as a pure, non-active black carbon particle the predictions match more closely to measurement (Samset et al. 2015). There is doubt associated with these methods as the consideration of internally mixed particles and black carbon particles with coatings of other chemical species are not considered. These varied states of black carbon particles can represent the more atmospherically aged black carbon that has a higher chance of serving as cloud condensation nuclei.

Climate models do consider aerosols in the formation of clouds, but some ignore the effects of black carbon likely due to the assumption that freshly emitted black carbon does not serve as effective cloud condensation nuclei (Bond et al. 2013). Even further simplification beyond the consideration of activation properties is basing the cloud formation model on the mass of particles. Empirical relations are used to relate numbers of cloud droplets to the mass of aerosol present in atmosphere (Lamarque et al. 2013). With this methodology only the most hydrophilic particles are considered and differences in activation properties are not accounted for. More sophisticated models do take into account the size distributions of particles and their hygroscopicity (Tegen et al. 1996). There are also methods that model competition between particles

in which more easily activated particles reduce supersaturation making it even harder for less active particles to serve as nuclei. This may attribute to the black carbon assumption as competition with other aerosols will decrease freshly emitted black carbon's chances to activate even further (Bond et al. 2013).

1.5 Research Motivation

Pure graphitic black carbon must atmospherically oxidize or age before it is wettable and able to form droplets. Due to the need for black carbon to age in order to act as viable cloud condensation nuclei there is scientific interest in the alterations that occur and facilitate CCN activation. One such area of study is the presence of surfactant both in atmosphere and/or in co-emission alongside black carbon, leading to a circling back to an interest in organic carbon/brown carbon emissions.

The chemical composition of atmospheric black carbon and commercially bought black carbon can vary with source. Thus, for this study, specific organic compounds are used to simulate the atmospheric organic aerosol composition of an aged carbonaceous species. Upon further study of surfactants in the aerosol cloud condensation nuclei space a gap was noticed. The Faccini et al. 1999 paper discusses fog droplets collected in Po Valley, Italy that display large decreases in surface tension due to the presence of organic solutes within the fog droplets. Discussion within the paper describes theory on how lowered cloud droplet surface tension causes increased number of cloud droplets thereby enhancing the aerosol indirect effect. The aerosol in the study was a mixture of water-soluble organic compounds.

Cloud condensation activation measurements for surfactant aerosol mixtures had not been taken from the perspective of applying surface tension corrections for individual species. The direction for research is then established to further understanding of surfactant effects.

The focus of the study now centers on the cloud activation properties of surfactant aerosols specifically to establish a baseline understanding of how they behave on their own before attempting to apply this to complex mixtures and coatings. Two surfactants are chosen to study: a strong surfactant, sodium dodecyl sulfate (SDS) and a weak surfactant, succinic acid. Both compounds are organic, wettable, with low hygroscopicity. Succinic acid was of interest due to its atmospheric relevance (Blower et al. 2013). SDS was chosen for study due to its widespread presence in literature as a standard strong surfactant throughout the scientific community.

Chapter 2: Experimental Methods and Analysis

This work explores the droplet forming properties of two organics: succinic acid and sodium dodecyl sulfate (SDS). Succinic acid (Sigma Aldrich 99+) is a carboxylic acid with the molecular formula $C_4H_6O_4$.

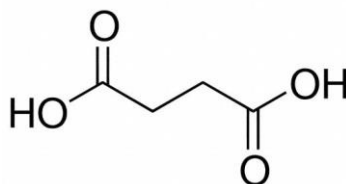


Figure 1. Chemical structure of succinic acid.

Succinic acid is partially soluble in water: 1g in 13mL of cold water (O'Neil 2001).

SDS is not as atmospherically relevant as succinic acid but serves as a good representative for strong surfactants. SDS (Fischer Scientific 99+) is a synthetic organic compound with the formula $NaC_{12}H_{25}SO_4$.

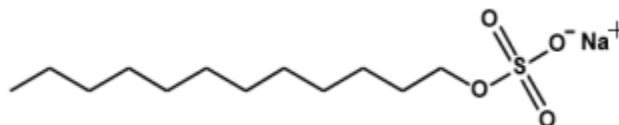


Figure 2. Chemical structure of sodium dodecyl sulfate (SDS).

SDS is similarly soluble to succinic acid with 1g dissolving in 10mL of water (O'Neil 2013). Binary mixtures of SDS and succinic acid were created for tensiometer and aerosol measurements.

2.1 Tensiometer and Surface Tension Measurements

Solutions for pendant drop testing were created using initial stock solutions of both succinic acid and SDS. These stock solutions were diluted with DI water to achieve the concentrations desired prior to measurement. The original pure stock solutions were mixed to create the 25% SDS and 50% SDS molar percent mixtures. Similar to the pure solutions; these mixed stock solutions were diluted to concentrations desired for measurement. The One Attension Theta Flex tensiometer captures images at 33 frames per second. Each image constitutes one measurement of surface tension of the droplet solution. Each concentration was given 5-10 seconds to capture images leading to 165-330 individual surface tension reports for each sample. An average of these measurements was taken as the final surface tension measurement for the specific sample concentration along with the variance in the measurements to serve as a measure of error. Lab DI water was also tested as a baseline for calibration. Also, to supply the value for the pure water surface tension (σ_0) for equation (1).

A One Attension Theta Flex ® tensiometer measured the surface tension measurements of solutions of varying concentration to establish a Szyszkowski-Langmuir model curves of the data.

$$\sigma = \sigma_0 - \Gamma_{max}RT * \ln \left(1 + \frac{c}{\beta} \right) \quad (1)$$

Equation (1) is the Szyszkowski-Langmuir equation that can be used to predict surface tension of solutions of varying concentrations (c). Surface tension measurements of solutions of varying concentrations are measured using the tensiometer and the Szyszkowski-Langmuir curve is fitted to the data. The two fitted empirical constants are the maximum surface excess (Γ_{max}) and the inverse Langmuir adsorption coefficient (β). The remaining equation symbols are pure water surface tension (σ_0), universal gas constant (R), and temperature (T).

The pendant drop method determined the surface tension of organic mixture droplet solutions. In this method, small amounts of droplet solution (5-10 μ l, similar to droplet sizes found in the ambient) are used. The shapes of droplets hanging from the tips of needles can be modeled using the following equation:

$$\gamma = \frac{\Delta\rho g R_0^2}{X} \quad (2)$$

where γ is surface tension, $\Delta\rho$ is density difference between fluids, g is gravitational constant, R_0 is radius of drop curvature at apex, and X is shape factor. Shape factor is defined by the Young-Laplace equation expressed as three dimensionless first order equations which are numerically solved using iterative approximations based on images taken by the computer of the hanging droplet (Figure 3).

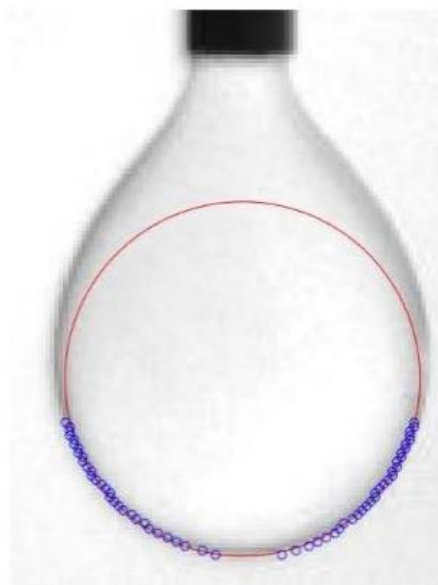


Figure 3. Example of one of the pendant droplet solution pictures taken by the instrument. Droplets hang from the tip of the needle and deformation from spherical shape is captured by the software as seen in the construction of the red circle within the hanging droplet (Image from Bolden et al. 2015).

2.2 Aerosol Measurements

The solutions of pure succinic acid and SDS as well as the 25% and 50% SDS mixtures were atomized to create aerosol particles. Pressurized air is run over the solution to create a low-pressure area that carries the solution into the atomizer's nozzle. This nozzle sprays the solution into the stream of air where it exists as aerosol droplets. These droplets are dried using a desiccant dryer; particles are dried such that the dry particle is considered the nucleus for water-vapor condensation. After the dry aerosol is created it can then be analyzed for cloud condensation activity using the final three instruments indicated in Figure 4. The subsequent instrumentation measure: particle size, particle number, and the ability to form droplets at a constant

supersaturation. Further explanation of these instruments is given in the following sections.

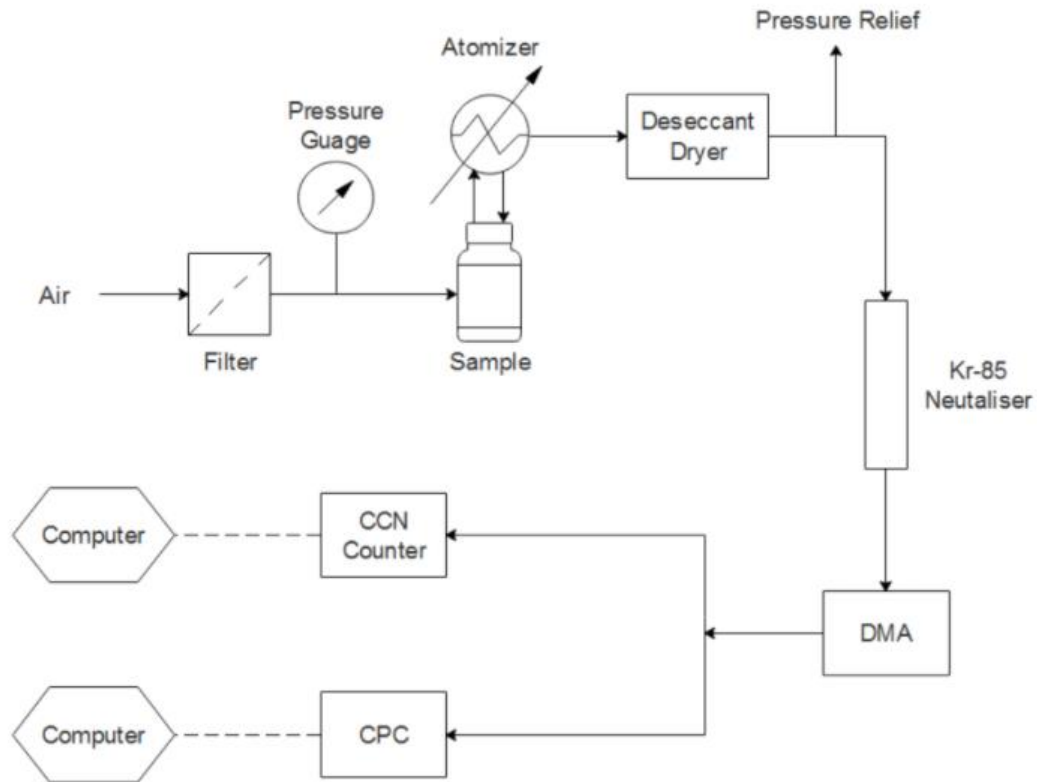


Figure 4. Schematic for experimental setup testing cloud condensation activity of generated aerosol particles.

2.3 Differential Mobility Analyzer (DMA)

Aerosol size is determined using an electrical field and uniform charge given to aerosol particles. A krypton-85 neutralizer treats entering aerosol to bring these particles to a well-defined charge. The charged particles are then passed through an electrical field to determine the particles' electrical mobility. The distance the charged particles move in the electrical field is reliant on the particles' electrical mobility and

this characteristic is dependent on the particle size which in this case is particle diameter. For the purposes of the experiment, the differential mobility analyzer (DMA) sorts particles in a scanning mode where particles small to large diameter are output over time to give a controlled stream of particles of increasing size. Particles from the DMA are then split between a condensation particle counter (CPC) for total counting and determination of total aerosol concentration and a cloud condensation nuclei counter (CCNC) where the viability of the aerosol to form clouds is determined.

2.4 Condensation Particle Counter (CPC)

The total number of aerosol particles is determined using the Condensation Particle Counter (CPC). The CPC uses butanol to grow the dry particles to optical detectable sizes. The CPC can detect aerosol particles as small as 2.5 nanometers. Aerosol particles initially too small to reflect light are increased in size using butanol vapor to condense onto the particles causing droplets to form and grow to sizes that can be detecting using light. These newly formed butanol droplets are counted using an optical counting laser. By specifying the volumetric flow rate into the CPC a concentration of aerosol particles is then calculated. Through interface with the DMA a number concentration of particles of different diameters can be found and a distribution of the particles' sizes can be constructed.

2.5 Cloud Condensation Nuclei Counter (CCNC)

Similar to the CPC the CCNC counts aerosol particles but instead of determining the total number of aerosol particles the CCNC counts only aerosol particles that have successfully activated as cloud condensation nuclei. Atmospheric conditions for the formation of clouds are simulated using a humidification chamber where particles are exposed to air supersaturated with water vapor. Supersaturation conditions are obtained using temperature gradients and the principle that water vapor diffuses from the walls to the center of the chamber faster than heat causing the water to condense onto the aerosol particles traveling through the center of the chamber.

Particles that have successfully been activated, or in other words have had water condense upon them and rapidly grow to micron droplet sizes, are counted using an optical particle counting laser. Supersaturation within the chamber can be specified by the user from a range of 0.2% to 2.0% supersaturation (Robert Nenes, 2005). The experiments run utilized supersaturations of 0.4, 0.6, 0.8, and 1.0%. Each supersaturation was run for approximately 15 minutes to create sets of three to six acceptable scans corresponding to each supersaturation.

2.6 CCN Activity Data Analysis

Hygroscopicity of the aerosol is determined by the comparison of total aerosol count to number of activated particles. When the ratio between the activated particles and total number of particles is 50% the critical properties of the aerosol can be determined which are important values in the discussion of how hygroscopic a particle is. The two critical parameters typically sought after in experiments are critical diameter or critical

supersaturation. With one term the other can be determined and with the experimental setup described here the critical diameter is more easily found. For a given particle diameter, D_d , the critical saturation, S_c , is calculated from the Köhler theory as follows:

$$\ln S_c = \left(\frac{4\alpha^3 \rho_w M_s}{27\nu \rho_s M_w D_d^3} \right)^{1/2}, \text{ where } \alpha = \frac{4\sigma_s M_w}{RT \rho_w} \quad (3)$$

σ_s is the surface tension, M_w is the molecular weight of water, R the universal gas constant, T is the sample temperature, ρ_w is the density of water, D_d is the dry activation diameter, and S_c is the critical saturation, ρ_s is the density of solute, and ν is the disassociation factor of solute. It is important to note that the critical saturation is typically higher than 1, such that the critical supersaturation is defined by $s_c = S_c - 1$.

Due to the scanning style of the DMA releasing particles of specific sizes to the CCNC operated at a set supersaturation; the particle diameter at which the critical 50% ratio between activated particles and total number of particles becomes trivial to find. With the critical dry activation diameter found the associated critical saturation is found using equation 3. The critical diameter of the aerosol can be converted to a single hygroscopicity parameter. To quantify the activation behavior of the aerosol using a single parameter the hygroscopicity parameter κ is introduced (Petters and Kreidenweis, 2007).

$$\kappa = \frac{4\alpha^3}{27D_d^3 \ln^2 S_c}, \text{ where } \alpha = \frac{4\sigma_s M_w}{RT \rho_w} \quad (4)$$

Smaller κ values below 0.3 indicates lower CCN activity and larger κ , greater than 0.5, indicate higher CCN activity. κ is assumed to be volume additive. That is, the volume fraction of a binary mixture can be written as follows:

$$\phi_i = \frac{V_i}{V} \quad (5)$$

where ϕ_i is the volume fraction in the aerosol. It should be noted that the kappa derived from equation 4 assumes that the surface tension of the droplet is that of water (as commonly accepted in literature). In this work, the surface tension in equation 4 is replaced with the Szyszkowski-Langmuir model (Equation 1) to correct for the surfactants dissolved in the droplet solution. Concentration at the point of activation is estimated by dry diameter size. The dry particle is assumed to completely dissolve into a droplet of the same volume. The droplet solution is assumed to be well mixed. This theoretical droplet represents the surface tension conditions used to find κ and thereby quantify surface tension corrected hygroscopicity.

Chapter 3: Results and Discussion

3.1 Surface Tension Measurements

The surface tension of succinic acid was measured with the pendant drop technique (Figure 5). Succinic acid is weakly surface active. Only at concentrations above 0.1 mol L⁻¹ will succinic acid depress surface tension more than 5% of pure water. The data points do not plateau at high concentrations and no critical micelle concentration (CMC) is observed. The measured values can be fit to the Szyszkowski-Langmuir equation. Fitted constants for experimental data are 21.1×10^{-6} mol m⁻² for maximum surface excess (Γ_{max}) and 3.68×10^{-3} mol L⁻¹ for Langmuir adsorption coefficient (β) and are reported in Table 1. The Szyszkowski-Langmuir fit derived from measurements in this study is like that of the Lee et al. 2014 article.

Table 1. Collection of Szyszkowski-Langmuir fitted constants for pure SDS, pure succinic acid, 25% SDS, and 50% SDS.

	Γ_{max} (10^{-6} mol/m ²)	β (10^{-3} mol/l)
Succinic Acid Experiment	21.1	3.68
Succinic Acid Literature [#]	2.13 ± 0.15	319 ± 32
SDS Experiment	19.6	7.10
SDS Literature ^{\$}	3783	1997
25% SDS	6.89	6.60
50% SDS	9638	7647.3

[#] Values obtained from Lee et al 2014.

^{\$} Values obtained from Mysel 1986.

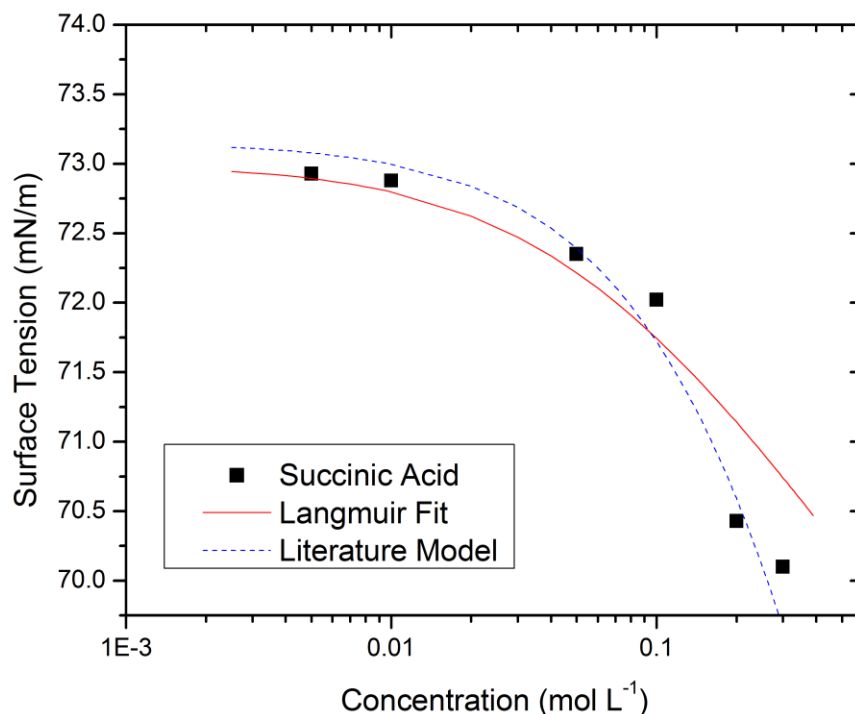


Figure 5. The surface tension pendant drop measurements of succinic acid with experimental data marked by the solid black squares. Error bars are included but are small enough to be obfuscated by the data points. Szyszkowski-Langmuir fit to data points is provided (solid red line). Published surface tension model (dashed blue line) from Lee et al. (2014).

The surface tension of SDS was measured with the pendant drop technique (Figure 6). SDS is a strong surfactant (Singer and Tjeerdema, 1993) and can depress the surface tension to 40 mN m⁻¹ at concentrations then than 0.01 mol L⁻¹. Notably, the surface tension value plateaus and SDS approaches a critical micelle concentration at 0.008 (Fig. 6). This data is consistent with CMC values as reported by Zhang et al. in their 2014 paper. A Szyszkowski-Langmuir fit is applied to the data collected before the CMC point (Table 1). Fitted constants for experimental data are: 19.6 x 10⁻⁶ mol

m^{-2} for maximum surface excess (Γ_{max}) and $7.10 \times 10^{-3} \text{ mol L}^{-1}$ for Langmuir adsorption coefficient (β). A higher maximum surface excess energy and Langmuir adsorption is indicative of a compound with strong surface active properties. The Szyszkowski-Langmuir fit agrees well with the literature model reported in Mysels' 1986 paper on the surface tension of pure SDS.

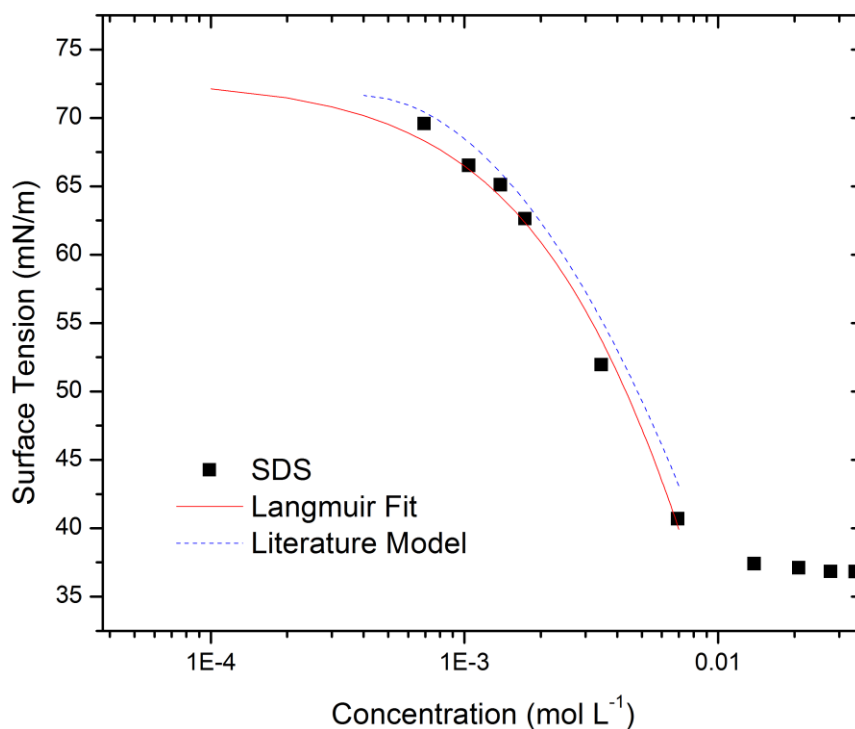


Figure 6. The surface tension pendant drop measurements at 25°C for Sodium Dodecyl Sulfate (closed squares). Error bars are included. Szyszkowski-Langmuir fit to data points is provided (solid red line). Published surface tension model from Zhang (2014) represented by the dashed blue line.

The molar addition of SDS results in non-linear surface tension behavior (Figure 7). A 25% molar additional of SDS to succinic acid decreases overall surface tension significantly. A critical micelle concentration is observed near $\sim 0.01 \text{ mol L}^{-1}$. When

the molar concentration is 50% SDS and 50% succinic acid, the CMC is observed at a similar concentration of pure SDS at $\sim 0.08 \text{ mol L}^{-1}$. The surface tension and height of the plateau decreases with increasing SDS. Error bars associated with each of the tensiometer measurements are present and are notably larger in the mixture data. This higher margin of error may stem from complex mixing interactions between SDS and succinic acid that may disrupt surface tension forces. Noticeably, Figure 7 displays a viable 30% decrease in surface tension (from 72 mN m^{-1} to about 50.4 mN m^{-1}) caused by solutions including SDS. If these depressed surface tensions are achieved in atmosphere the Faccini et al.1999 paper indicates there will be a 20% increase in number of cloud droplets. This has large implications in the estimation of aerosol indirect effects on climate as the 20% increase in cloud droplets is predicted to have a 1 W m^{-2} decrease in radiative forcing. This decrease in radiative forcing is comparable in magnitude to the green house gas heating radiative effects of carbon dioxide (IPCC, 2013).

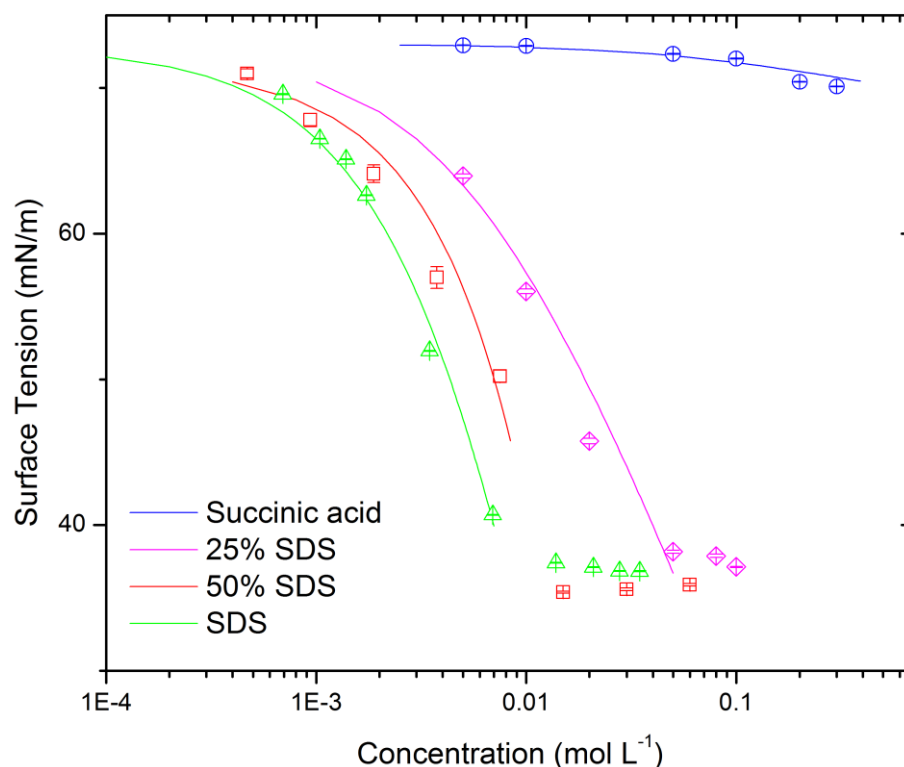


Figure 7. The surface tension pendant drop measurements at 25°C for Sodium Dodecyl Sulfate (closed squares). Error bars are included. Szyszkowski-Langmuir fit to data points is provided (solid red line). Published surface tension model from Zhang (2014) represented by the dashed blue line.

3.2 Cloud Droplet Activation Measurement

Figure 8 displays the activated fraction of ammonium sulfate calibration aerosol versus particle diameter. The activation curves represent the relationship between aerosol size and the atmospheric water content necessary to activate these particles into cloud droplets. For a constant supersaturation, there requires a critical size for particles to form droplets. Hence at small particle sizes no particles form droplets and the activated fraction is zero. As particle sizes increase, the activated fractions increase to one and all particles (condensation nuclei, CN) form droplets (Cloud Condensation Nuclei). The critical diameter, dp_{50} is defined at 50% efficiency. At

high instrument supersaturations, particles at smaller sizes readily activate. In Figure 8, the activation curves from left to right decrease in instrument supersaturation. Higher supersaturation allows smaller particles to activate more readily. The critical diameter for $(\text{NH}_4)_2\text{SO}_4$ at 1.0% supersaturation is $22.4 \pm 0.2\text{nm}$. Lower supersaturation requires larger particles to activate. The critical diameter for $(\text{NH}_4)_2\text{SO}_4$ at 0.4% supersaturation is $35 \pm 2\text{nm}$. The critical diameter can be converted to the single parameter hygroscopicity, κ . The single parameter hygroscopicity is 0.601 for an ammonium sulfate particle.

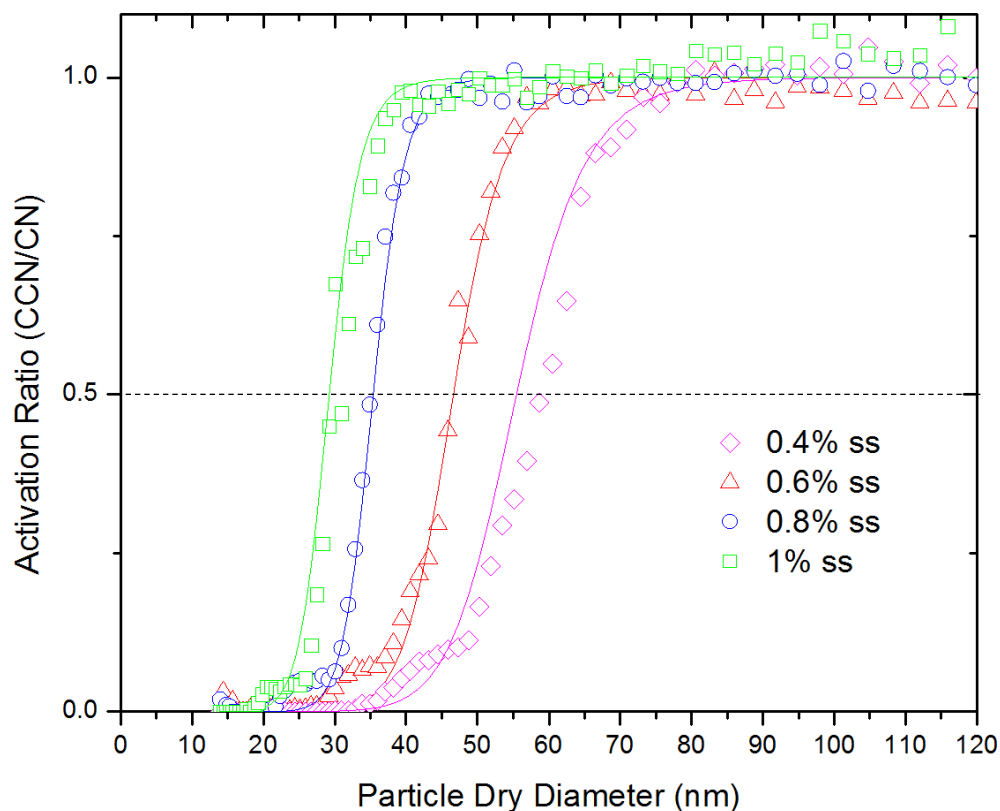


Figure 8. Cloud condensation nuclei counter data for ammonium sulfate typically used to calibrate the CCNC instrument. Each color represents percent supersaturation the aerosol particles are exposed to. Shapes are experimental data with sigmoidal fits to the data represented by the solid lines.

A particle of constant size exposed to supersaturation will grow and form a droplet.

Figure 9 displays the theoretical growth of a 50nm SDS particle based on the

following equation:

$$S = \frac{2\sigma M_w}{RT\rho_w\left(\frac{D}{2}\right)} - \frac{3nM_w}{4\pi\rho_w\left(\frac{D}{2}\right)^3} \quad (5)$$

where σ refers to droplet surface tension, M_w is molecular weight of water, ρ_w is density of water, R is universal gas constant, T is temperature, n is number of solute molecules, and D refers to wet particle diameter. Equation 5 is referred to as the Köhler model with the left and right terms representing Kelvin and Raoult effects respectively. When the Köhler model was used in the past the surface tension term was assumed to equal surface tension of pure water. In this project the surface tension term is substituted for the Szyszkowski-Langmuir equations to represent surface tension of the actual droplet solutions.

A particle exposed to an increasing subsaturated (< 100% RH) condition will grow. As the particle increases wet droplet size, the curvature decreases, and water vapor readily condenses on the surface (Kelvin effect). As the droplet grows, the droplet solution becomes more dilute, and the water activity of the droplet approaches that of the molar fraction of water (Raoult effect). The combination of competing effects creates a maximum, that defines a critical supersaturation required for the dry particle to undergo uncontrollable growth. At larger wet diameters (greater than 1 μm), the effects of curvature and dissolution are negligible and converge.

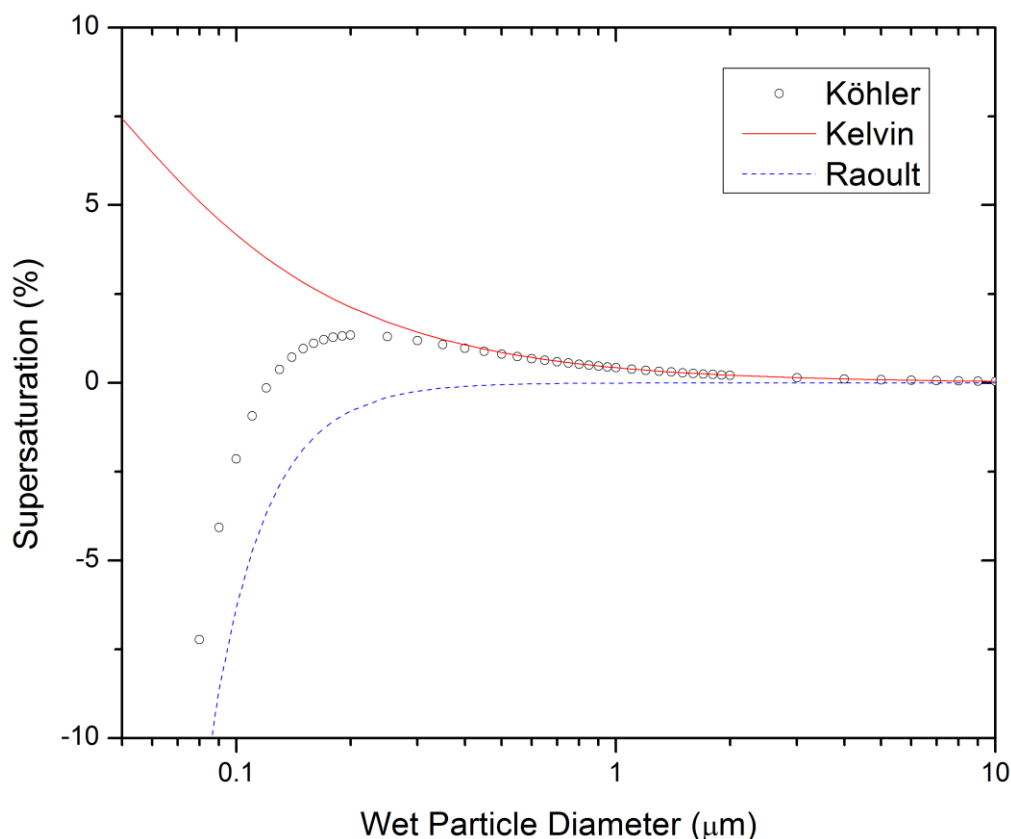


Figure 9. Example Köhler curve for a 50nm SDS particle with surface tension corrections applied. The figure shows the dependence of the Kelvin and Raoult effects. Köhler theory droplet stability (open circles) is the balance between surface forces and curvature (Kelvin, red solid line) and solute (Raoult blue dashed line) effects.

Figure 10 curves show droplet growth and stability through the balancing of Kelvin and solute effects. The maxima of these curves represent theoretical prediction of critical supersaturation associated with the specific aerosol dry diameter. The maxima of the succinic acid Köhler curves are smaller than the maxima of the SDS curves. This implies that succinic acid more readily activates into cloud droplets relative to SDS. Lower critical supersaturations indicate less atmospheric water needed to activate aerosols of specific dry diameters. These theoretical curves imply pure

succinic acid is more hygroscopic than pure SDS and therefore requires less water to activate for small particle sizes ($< 0.5 \mu\text{m}$). The difference in Köhler curves can be attributed to two main ideas. Firstly, SDS is a higher molecular weight compound with greater molar volume. Thus, the dissolved molar volume is less than that of succinic acid and has a smaller Raoult effect. The surface tension in this diagram is assumed to be that of pure water as is commonly applied to atmospheric organics. Thus, the Kelvin effect is not modified by surface tension depression as measured in Figure 7. If the surface tension correction is applied the curves are shifted slightly downward indicating the increased activation behavior.

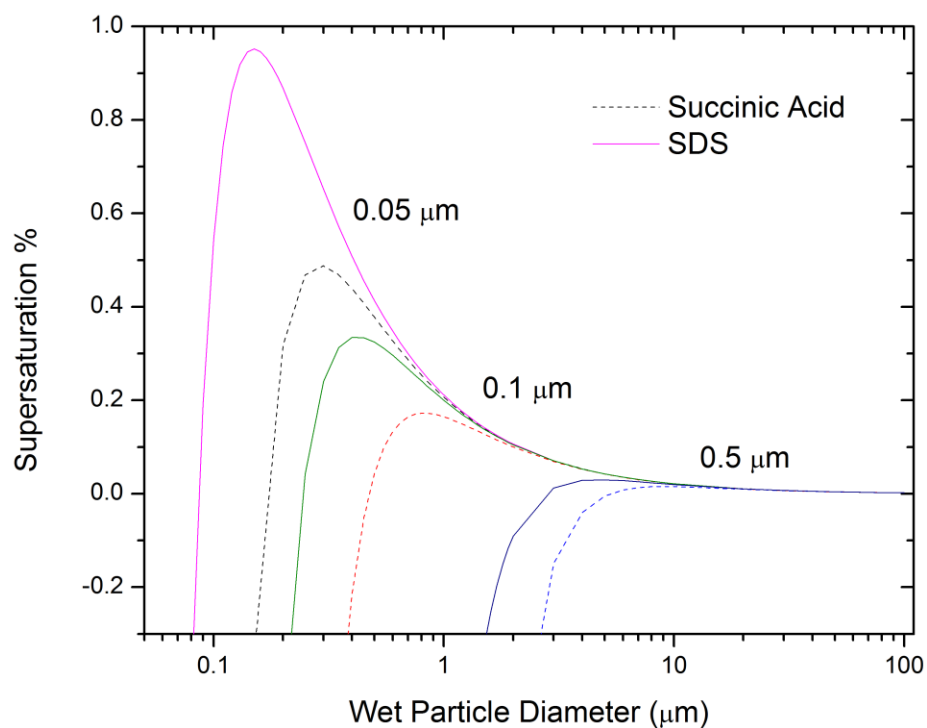


Figure 10. Köhler curves for pure succinic acid and SDS with three different curves representing three different dry diameters of aerosol particles: 0.05, 0.1, and 0.5 micrometers. Surface tension correction is applied here.

Figure 11 agrees with the Köhler theoretical prediction for pure succinic acid activating more readily than pure SDS. Simple Köhler theory assumes the addition of binary mixtures is volume additive and that the water activity of the solution can be estimated with Zdanovskii-Stokes-Robinson (ZSR) models (Petters and Kreidenweiss 2007; Clegg et al. 2004). In the case of mixtures of the two species there are non-ideal interactions that complicate the activation behavior. The 100% SDS mixtures activate most readily among the SDS solutions. Mixtures of 25% and 50% SDS have similar activation behavior with 25% and 50% SDS as the least active solutions. SDS has a larger molecular weight and molar volume. Thus, the contribution to the Raoult effect is less than that of succinic acid. It requires a greater amount of water vapor to activate. However, SDS is a strong surfactant thus the Kelvin term decreases and thus makes the overall critical supersaturation smaller.

The 25% and 50% SDS compositions are associated with the largest critical diameters indicating that they are the least active even compared to pure SDS. The assumption that the solutes are well mixed within the activating droplets may be the cause for this discrepancy. Both succinic acid and SDS are surfactants and may encounter complex interactions as they compete for space on the interfacial boundary. Solute species present in droplets may prefer the bulk which alters the Raoult effects. Alternatively, solutes may partition to the surface of the droplet to then alter Kelvin effects on the droplet (Lin et al. 2020). Succinic acid and SDS have different dissolution properties. Succinic acid is a small carboxylic acid that readily dissolves in bulk solution. SDS is a long carbon chained molecule with a polar head group. It dissolves but is more

likely to partition to the surface of the droplet and act as a strong surfactant. Along with this effect there may be complex partitioning of the solutes taking place within the mixed solutions as one species may dominate the surface layer forcing the other into the bulk thereby altering the cloud droplet activation properties of the aerosol (McGraw et al. 2021).

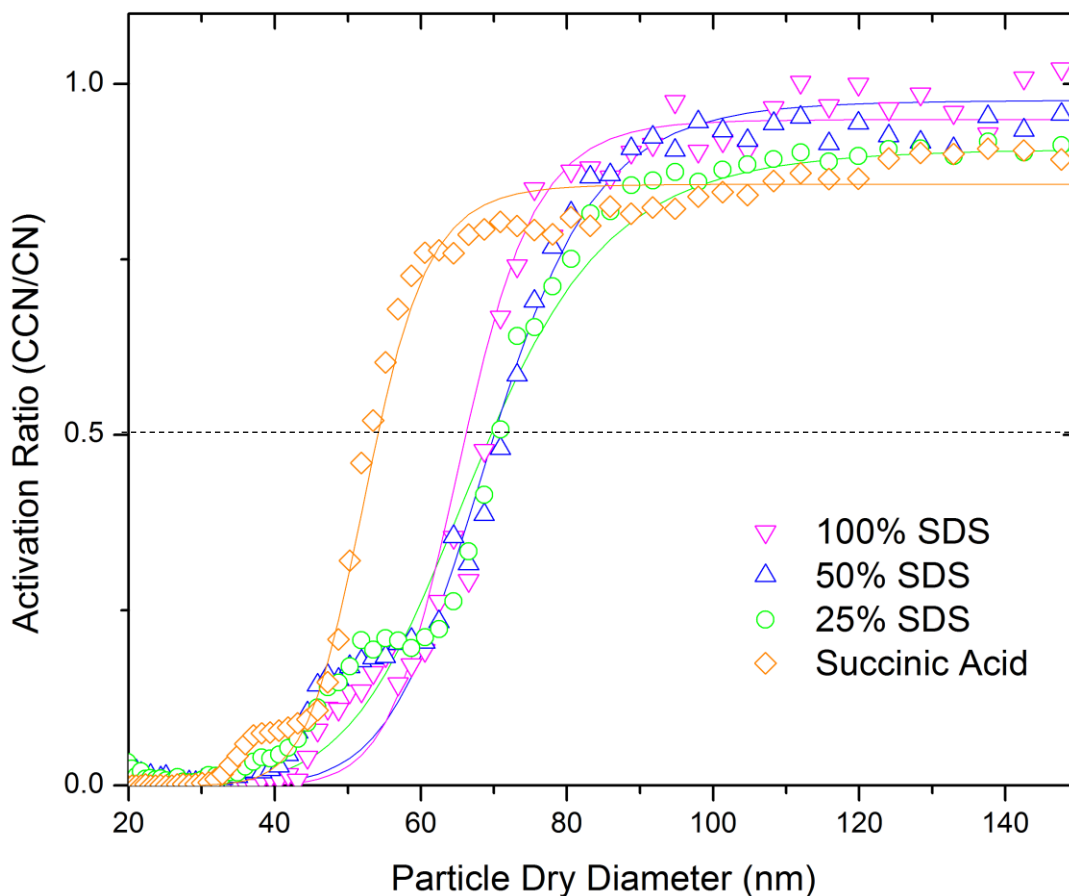


Figure 11. Cloud condensation data for mixtures of SDS and succinic acid at 0.6% super saturation. As the different mixtures are exposed to the same super saturation, the indication for the most active composition is the smallest critical diameter (the point at which the sigmoids intersect with the horizontal line at 50% activation).

Figure 12 displays the single parameter hygroscopicity without surface tension corrections applied. Agreeing with Figures 10 and 11 is succinic acid having the highest κ hygroscopicity parameter. Pure SDS maintains a higher hygroscopicity than the mixed surfactant solutions. The 25% SDS mixture is indicated to be slightly more hygroscopic than 50% SDS.

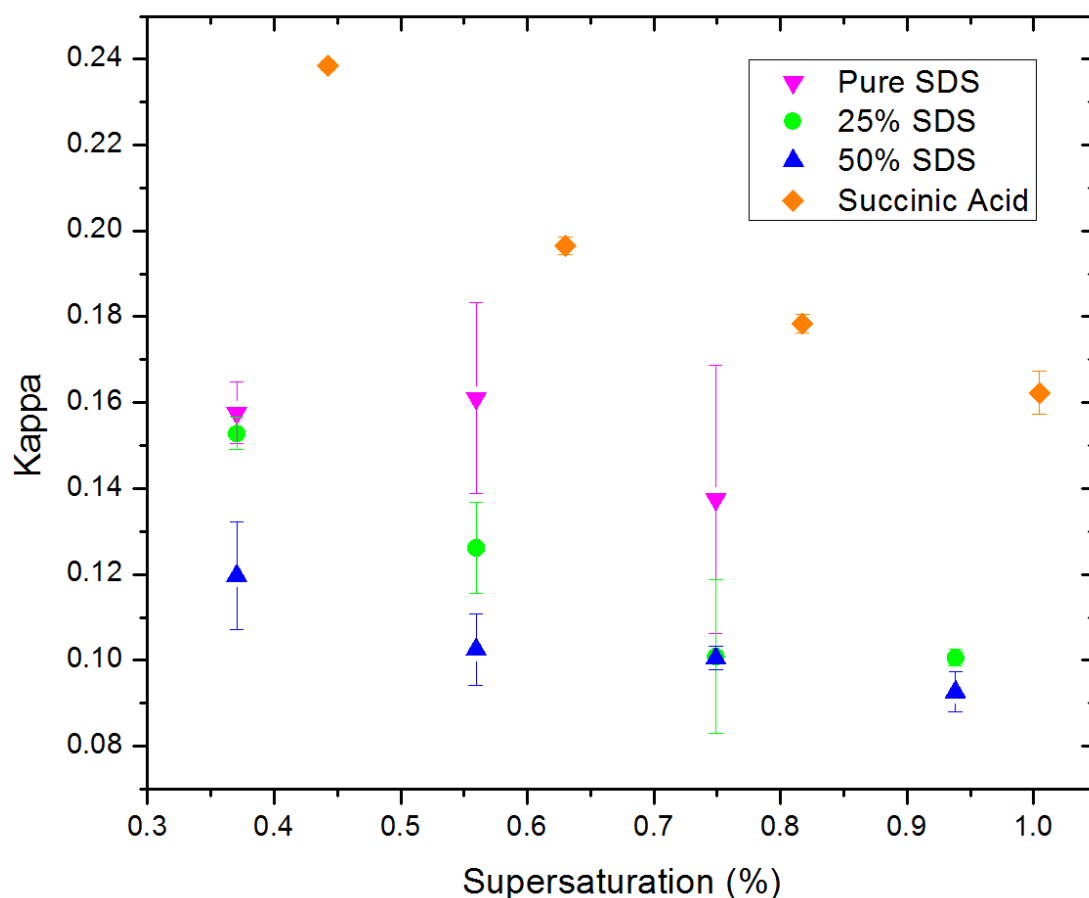


Figure 12. κ -single hygroscopicity parameterization of SDS, SDS mixtures, and pure succinic acid with no surface tension corrections. Kappa representation constructed from multitudes of activation curve data (example of one set of curves for supersaturation near 0.6% given in the previous figure) for four different supersaturations. Each mixture is tested multiple times per supersaturation and activation curves are generated through which critical parameters can be extracted from. Variance between these runs is represented in the error bars as critical parameters will vary from experiment to experiment thereby propagating error in the estimation of kappa.

Figure 13 shows the single parameter hygroscopicity of measured SDS and SDS aerosol mixtures with the correction for surface tension applied. Compared to Figure 12 the κ parameter is shifted upwards for succinic acid and 25% SDS solutions. Pure SDS and 50% SDS solutions have κ parameters shifting downwards. The surface tension correction indicates that the 25% SDS solution is nearly as hygroscopic if not more hygroscopic than pure SDS.

Figures 12 and 13 display decreases in kappa as super saturation increases. As discussed previously, this study relies on the assumption of droplets having well mixed solutions. In the case of kappa decreasing with higher supersaturations there may be complex mechanisms occurring during the activation of the dry aerosol particle. This non-linear behavior likely relates to partitioning and the non-linear behavior observed in the surface tension measurements associated with the surfactant mixtures. As activation begins and water condenses onto the dry particle the assumption is that the solute dissolves and is well mixed in the volume of water based on the original size of the dry particle (assumed to be spherical).

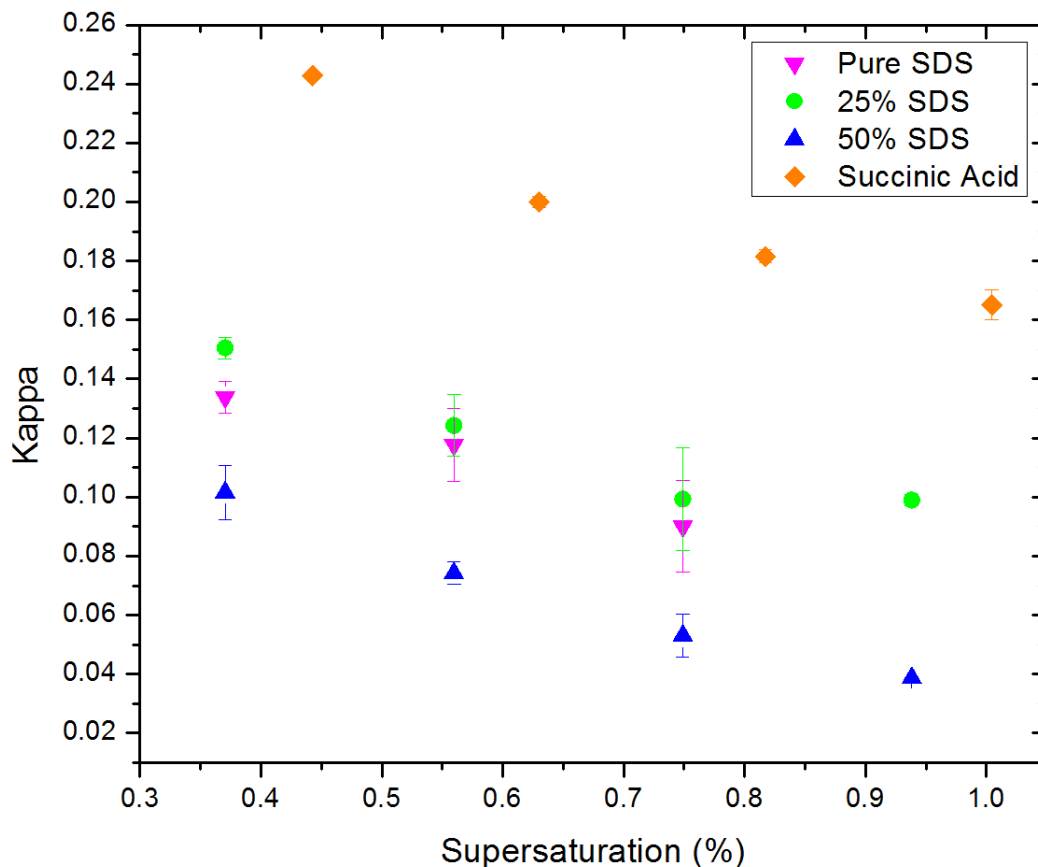


Figure 13. κ -single hygroscopicity parameterization of SDS, SDS mixtures, and pure succinic acid with surface tension corrections. Variance between these runs is represented in the error bars as critical parameters will vary from experiment to experiment thereby propagating error in the estimation of kappa.

Complexity arises as consideration of the shape of the dry particle is taken into account along with concepts of internal and external mixing within the mixed SDS and succinic acid aerosol particle. Beyond the dry particle considerations are the issues of mixing within solution of an activated wet particle. The partitioning of the various solute species may alter the Köhler theory droplet stability model (McGraw et al. 2021) causing further discrepancies when attempting to characterize activation behavior with the kappa parameter. Overall, the results suggest that a small addition

of surface active material (like SDS) to organics like carboxylic acid can significantly change activation behavior

Bibliography

- Bolden, J. Determining Surface Tension Using The Pendant Drop Method. Department of Chemistry and Physics Georgia Regents University, Augusta, GA, 2015.
- Bond, T. C.; Bergstrom, R. W.; Light absorption by carbonaceous particles: An investigative review, *Aerosol Sci. Technol.* **2006**, 40(1), 27–67.
- Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Bernsten, T.; Deangelo, B. J.; Flanner, M. G.; Ghan, S.; Kärcher, B.; Koch, D.; et al. (2013) Bounding the role of black carbon in the climate system: A scientific assessment. *Journal of Geophysical Research: Atmospheres* **2013**, 118 (11), 5380–5552
- Chin, M.; Diehl T.; Dubovik O.; Eck T. F.; Holben B.N.; Sinyuk A.; Light absorption by pollution, dust, and biomass burning aerosols: A global model study and evaluation with AERONET measurements. *Ann. Geophys.* **2009**, 27(9), 3439–3464,
- Chao Liu; Ji Li; Yan Yin; Bin Zhu; Qian Feng; Optical properties of black carbon aggregates with non-absorptive coating. *Journal of Quantitative Spectroscopy and Radiative Transfer* **2017**, Volume 187, Pages 443-452
- Chul E. Chung; Kyunghwa Lee; Detlef Müller; Effect of internal mixture on black carbon radiative forcing, *Tellus B: Chemical and Physical Meteorology* **2012**, 64:1.
- Clegg, Simon L.; John H. Seinfeld; Improvement of the Zdanovskii–Stokes–Robinson Model for Mixtures Containing Solutes of Different Charge Types. *The Journal of Physical Chemistry A* **2004**, vol. 108, no. 6, pp. 1008–1017.
- Eleanor J. Highwood; Robert P. Kinnersley; When smoke gets in our eyes: The multiple impacts of atmospheric black carbon on climate, air quality and health. *Environment International* **2006**, Volume 32, Issue 4, Pages 560-566.
- Facchini, M., Mircea, M., Fuzzi, S. *et al.* Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **1999**, 401, 257–259.
- Goldberg, E D.; Black carbon in the environment: properties and distribution. United States: N. p., **1985**.
- Grisdale, R. O.; The Formation of Black Carbon. *Journal of Applied Physics* **1953**, vol. 24, no. 9, pp. 1082–1091.
- Hallberg, A.; J. A. Ogren; K. J. Noone; K. Okada; J. Heintzenberg; I. B. Svenningsson; The influence of aerosol particle composition on cloud droplet formation, *J. Atmos. Chem.* **1994**, 19, 153–171

- Heintzenberg, J.; R. J. Charlson; Clouds in the perturbed climate system: Their Relationship to energy balance, atmospheric dynamics, and precipitation, *Strüngmann Forum Report* **2009**, Volume 2, ISBN-10: 0-262-01287-1, The MIT Press, Cambridge, MA.
- Hendricks, J., et al; Do Aircraft Black Carbon Emissions Affect Cirrus Clouds on the Global Scale? *Geophysical Research Letters* **2005**, vol. 32, no. 12.
- Hong, C.; Zhang, Q.; Zhang, Y. *et al*; Weakening aerosol direct radiative effects mitigate climate penalty on Chinese air quality. *Nat. Clim. Chang* **2020**. 10, 845–850.
- Hudson, J. G., Cloud condensation nuclei, *J. Applied Meteor.* **1993**, 32, 596–607.
- IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. *Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA*, **2013**, 1535 pp.
- John H. Seinfeld; Spyros N. Pandis. ATMOSPHERIC CHEMISTRY AND PHYSICS From Air Pollution to Climate Change. *John Wiley & Sons, Inc* **2006**.
- Johnson, B. T. et al; The Semi-Direct Aerosol Effect: Impact of Absorbing Aerosols on Marine Stratocumulus. *Quarterly Journal of the Royal Meteorological Society* **2004**, vol. 130, no. 599, 2004, pp. 1407–1422.
- Kuwata; Mikinori et al.; Critical Condensed Mass for Activation of Black Carbon as Cloud Condensation Nuclei in Tokyo. *Journal of Geophysical Research* **2009**, vol. 114, no. D20.
- Lee, Y. H. et al.; Evaluation of preindustrial to present day black carbon and its albedo forcing from Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.* **2013**, 13, 2607–2634.
- Liao, H.; J. H. Seinfeld; Radiative Forcing by Mineral Dust Aerosols: Sensitivity to Key Variables. *Journal of Geophysical Research: Atmospheres* **1998**, vol. 103, no. D24, pp. 31637–31645.
- Lin et al.; Effects of Surface Tension Time-Evolution for CCN Activation of a Complex Organic Surfactant. *Environmental Science: Processes & Impacts* **2020**, vol. 22, no. 2, 2020, pp. 271–284.
- Liousse C.; J. E. Penner; C. Chuang; J. J. Walton; H. Eddleman; H. Cachier; A global three-dimensional model study of carbonaceous aerosols, *J. Geophys. Res.* **1996**, 101(D14), 19411–19432

Liu Chao et al.; Black Carbon Aggregates: A Database for Optical Properties. *Journal of Quantitative Spectroscopy and Radiative Transfer* **2019**, vol. 222-223, pp. 170–179.

Lohmann Ulrike et al.; Indirect Effect of Sulfate and Carbonaceous Aerosols: A Mechanistic Treatment. *Journal of Geophysical Research: Atmospheres* **2000**, vol. 105, no. D10, pp. 12193–12206.

Lohmann U.; Stier P.; Hoose C.; Ferrachat S.; Kloster S.; Roeckner E.; and Zhang J.; Cloud microphysics and aerosol indirect effects in the global climate model ECHAM5-HAM, *Atmos. Chem. Phys.* **2007**, 7, 3425–3446.

Martins; J. Vanderlei et al; Effects of Black Carbon Content, Particle Size, and Mixing on Light Absorption by Aerosols from Biomass Burning in Brazil. *Journal of Geophysical Research: Atmospheres* **1998**, vol. 103, no. D24, pp. 32041–32050.

Matsui H. et al.; Development and Validation of a Black Carbon Mixing State Resolved Three-Dimensional Model: Aging Processes and Radiative Impact. *Journal of Geophysical Research: Atmospheres* **2013**, vol. 118, no. 5, pp. 2304–2326.

McGraw; Robert; Jian Wang; Surfactants and Cloud Droplet Activation: A Systematic Extension of Köhler Theory Based on Analysis of Droplet Stability. *The Journal of Chemical Physics* **2021**, vol. 154, no. 2, p. 024707.

Menon, S; Climate Effects of Black Carbon Aerosols in China and India. *Science* **2002**, vol. 297, no. 5590, pp. 2250–2253.

Novakov, T.; Penner, J.; Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. *Nature* **1993**, 823–826.

N. Riemer; M. West; R. Zaveri; R. Easter; Estimating black carbon aging time-scales with a particle-resolved aerosol model. *Aerosol Sci.* **2010**, 41, pp. 143-158

Petters, M. D.; Kreidenweis, S. M.; A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.* **2007**, 7, 1961–1971.

Pradeep Kumar; Broekhuizen, K.; Abbatt, J. P. D.; Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.* **2003**, 3, 509–520.

Pratt, Kerri A.; Kimberly A. Prather; Aircraft Measurements of Vertical Profiles of Aerosol Mixing States. *Journal of Geophysical Research* **2010**, vol. 115, no. D11.

Ramanathan, V. et al.; Cloud-Radiative Forcing and Climate: Results from the Earth Radiation Budget Experiment. *Science* **1989**, vol. 243, no. 4887, pp. 57–63.

- Rap Alexandru et al.; Natural Aerosol Direct and Indirect Radiative Effects. *Geophysical Research Letters* **2013**, vol. 40, no. 12, pp. 3297–3301.
- Rap, A.; Scott, C. E.; Spracklen, D. V.; Bellouin, N.; Forster, P. M.; Carslaw, K. S.; Mann, G.; Natural aerosol direct and indirect radiative effects. *Geophysical Research Letters* **2013**, 40(12), 3297-3301.
- Samset, B. H.; G. Myhre; Climate Response to Externally Mixed Black Carbon as a Function of Altitude. *Journal of Geophysical Research: Atmospheres* **2015**, vol. 120, no. 7, pp. 2913–2927.
- Schill; Gregory P. et al.; The Contribution of Black Carbon to Global Ice Nucleating Particle Concentrations Relevant to Mixed-Phase Clouds. *Proceedings of the National Academy of Sciences* **2020**, vol. 117, no. 37, pp. 22705–22711.
- Tegen Ina; Andrew A. Lacis; Modeling of Particle Size Distribution and Its Influence on the Radiative Properties of Mineral Dust Aerosol. *Journal of Geophysical Research: Atmospheres* **1996**, vol. 101, no. D14, pp. 19237–19244.
- Wu, Y.; Cheng, T. H.; Liu, D. T.; Allan, J. D.; Zheng, L. J.; Chen, H. Light Absorption Enhancement of Black Carbon Aerosol Constrained by Particle Morphology. *Environ. Sci. Technol.* **2018**, 52, 6912– 6919.
- Xu, Ruiguang et al.; Effect of Biomass Burning on Black Carbon (BC) in South Asia and Tibetan Plateau: The Analysis of WRF-Chem Modeling. *Science of The Total Environment* **2018**, vol. 645, 2018, pp. 901–912.
- Xu, J.; Zhang, J.; Liu, J.; Yi, K.; Xiang, S.; Hu, X.; Wang, Y.; Tao, S.; Ban-Weiss, G.; Influence of cloud microphysical processes on black carbon wet removal, global distributions, and radiative forcing, *Atmos. Chem. Phys.* **2019**, 19, 1587–1603.
- Yang, M.; Howell, S. G.; Zhuang, J.; Huebert, B. J.; Attribution of aerosol light absorption to black carbon, brown carbon, and dust in China – interpretations of atmospheric measurements during EAST-AIRE, *Atmos. Chem. Phys.* **2009**, 9, 2035–2050.
- Yasunari, T. J.; Bonasoni, P.; Laj, P.; Fujita, K.; Vuillermoz, E.; Marinoni, A.; Cristofanelli, P.; Duchi, R.; Tartari, G.; Lau, K.-M.; Estimated impact of black carbon deposition during pre-monsoon season from Nepal Climate Observatory – Pyramid data and snow albedo changes over Himalayan glaciers, *Atmos. Chem. Phys.* **2010**, 10, 6603–6615.
- Zhuang, B.L.; Chen, H.M.; Li, S. *et al.*; The direct effects of black carbon aerosols from different source sectors in East Asia in summer. *Clim Dyn* **2019**, 53, 5293–5310.