

Investigating parameters governing liquid-phase cloud activation of atmospheric particles

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Academic dissertation for the Degree of Doctor of Philosophy in Applied Environmental Science at Stockholm University to be publicly defended on Thursday 15 March 2018 at 10.00 in De Geersalen, Geovetenskapens hus, Svante Arrhenius väg 14.

Abstract

Aerosol-cloud interactions are one of the main sources of uncertainties in modeling and predicting the Earth's climate. To overcome this uncertainty, we need to improve the understanding about the processes and parameters defining how aerosol particles turn into cloud condensation nuclei (CCN) or ice nuclei (IN) to produce cloud droplets or ice crystals. The focus of this dissertation is on liquid phase cloud droplets. The thesis investigates the effect of water solubility and surface tension on the CCN activity of atmospheric aerosol particles. These parameters are among the key properties defining how an aerosol particle can turn into a cloud droplet. The main goals of this thesis are to investigate 1) the CCN activity of aerosol particles containing both water soluble and insoluble substances and 2) the contribution of molecular-scale surface structure to the surface tension and CCN activity of atmospherically relevant aqueous mixtures.

In the first part of this thesis, the CCN activity of water-insoluble aerosol constituents coated by water-soluble or sparingly soluble species was investigated. The results showed that the CCN activity of the insoluble silica and black carbon particles, with sizes between 100 and 300 nm, increased with the amount of the coating on the insoluble cores and at thick enough coating approached the CCN activity of the soluble species. Moreover, controlled dry coating of the insoluble BC cores yielded a size-independent distribution of the coating material on the insoluble cores, which was not achieved by wet coating of the silica particles. The results also confirmed that by knowing the fraction of soluble material (coating thicknesses), the existing theories gave a reasonable estimate of the CCN activity for the mixed soluble-insoluble particles. Finally, the results highlight the need for including the impacts of co-emitted or later condensed compounds in estimates of the climate impacts of atmospheric insoluble aerosol species.

In the second part of the thesis, surface propensity of succinic acid, pure or mixed with soluble inorganic salts in the aqueous droplets, were quantified via molecular-level surface composition measurement by X-ray Photoelectron Spectroscopy (XPS). The XPS and molecular dynamic (MD) simulations of succinic acid aqueous solutions showed strong enrichment of the succinic acid at the surface of the liquid droplets compared to the bulk solution. This effect was more pronounced in the presence of the highly soluble inorganic salts like NaCl and $(\text{NH}_4)_2\text{SO}_4$ in the system. The modeled surface tension of the pure organic or mixture of organic and inorganic substances, using surface enrichment factors derived from the XPS experiments were in good agreement with the experimental surface tension data. This demonstrates the high potential of XPS for direct measurements of the surface composition of atmospherically relevant aqueous mixtures. The results suggest that for modeling the phase-state and water content of the atmospheric particles, the contribution by the surface layer needs to be considered, because aqueous droplet can contain larger amounts of organic compounds than the bulk solubility limit of the solutions. However, the effect of the aqueous surface composition on the CCN activation of particles consisting of the studied mixtures was estimated to be very small.

The results presented in this thesis provide new insights into the relationship between aerosol particle composition and cloud condensation nuclei activity. However, the effect of more realistic complex mixtures will require more research. The results showed that for modeling semi-volatile species, the partitioning between the gas and condensed phase needs to be considered. In addition, along with the liquid-phase cloud activation, the ice nucleation ability of the particles made of soluble and insoluble species requires to be further investigated.

Keywords: *CCN activation, surface tension, coated aerosols, black carbon.*

Stockholm 2018

<http://urn.kb.se/resolve?urn=urn:nbn:se:su:diva-152128>

ISBN 978-91-7797-105-4

ISBN 978-91-7797-106-1

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INVESTIGATING PARAMETERS GOVERNING LIQUID-PHASE
CLOUD ACTIVATION OF ATMOSPHERIC PARTICLES

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ISBN print 978-91-7797-105-4

ISBN PDF 978-91-7797-106-1

Printed in Sweden by Universitetservice US-AB, Stockholm 2018

Distributor: Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University

To Rayan

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In the first part of this thesis, the CCN activity of water-insoluble aerosol constituents coated by water-soluble or sparingly soluble species was investigated. The results showed that the CCN activity of the insoluble silica and black carbon particles, with sizes between 100 and 300 nm, increased with the amount of the coating on the insoluble cores and at thick enough coating approached the CCN activity of the soluble species. Moreover, controlled dry coating of the insoluble BC cores yielded a size-independent distribution of the coating material on the insoluble cores, which was not achieved by wet coating of the silica particles. The results also confirmed that by knowing the fraction of soluble material (coating thicknesses), the existing theories gave a reasonable estimate of the CCN activity for the mixed soluble-insoluble particles. Finally, the results highlight the need for including the impacts of co-emitted or later condensed compounds in estimates of the climate impacts of atmospheric insoluble aerosol species.

In the second part of the thesis, surface propensity of succinic acid, pure or mixed with soluble inorganic salts in the aqueous droplets, were quantified via molecular-level surface composition measurement by X-ray Photoelectron Spectroscopy (XPS). The XPS and molecular dynamic (MD) simulations of succinic acid aqueous solutions showed strong enrichment of the succinic acid at the surface of the liquid droplets compared to the bulk solution. This effect was more pronounced in the presence of the highly soluble inorganic salts like NaCl and $(\text{NH}_4)_2\text{SO}_4$ in the system. The modeled surface tension of the pure organic or mixture of organic and inorganic substances, using surface enrichment factors

derived from the XPS experiments were in good agreement with the experimental surface tension data. This demonstrates the high potential of XPS for direct measurements of the surface composition of atmospherically relevant aqueous mixtures. The results suggest that for modeling the phase-state and water content of the atmospheric particles, the contribution by the surface layer needs to be considered, because aqueous droplet can contain larger amounts of organic compounds than the bulk solubility limit of the solutions. However, the effect of the aqueous surface composition on the CCN activation of particles consisting of the studied mixtures was estimated to be very small.

The results presented in this thesis provide new insights into the relationship between aerosol particle composition and cloud condensation nuclei activity. However, the effect of more realistic complex mixtures will require more research. The results showed that for modeling semi-volatile species, the partitioning between the gas and condensed phase needs to be considered. In addition, along with the liquid-phase cloud activation, the ice nucleation ability of the particles made of soluble and insoluble species requires to be further investigated.

Keywords: CCN activation, surface tension, coated aerosols, black carbon

Sammanfattning

Interaktioner mellan aerosoler och moln är en av de största källorna till osäkerhet vid modellering och förväntad utveckling av jordens klimat. För att övervinna denna osäkerhet måste vi förbättra förståelsen för processer och parametrar som definierar hur aerosolpartiklar blir till molnkondensationskärnor (CCN) eller iskärnor (IN) vilka producerar molndroppar eller iskristaller. Denna avhandling fokuserar på molndroppar i vätskefas. Avhandlingen undersöker effekten av vattenlöslighet och ytspänning på CCN-aktiviteten hos atmosfäriska aerosolpartiklar. Dessa parametrar är bland de viktigaste egenskaperna som definierar hur en aerosolpartikel kan omvandlas till en molndroppe. Huvudmålen med denna avhandling är att undersöka 1) CCN-aktiviteten hos aerosolpartiklar innehållande både vattenlösliga och olösliga substanser och 2) hur molekylär ytstruktur bidrar till ytspänningen och CCN-aktivitet hos atmosfäriskt relevanta vattenlösningar.

I den första delen av denna avhandling undersöktes CCN-aktiviteten hos icke-vattenlösliga aerosolbeståndsdelar belagda med vattenlösliga eller svagt lösliga ämnen. Resultaten visade att CCN-aktiviteten hos de olösliga kiseldioxid- och svarta kolpartiklarna, med storlekar mellan 100 och 300 nm, ökade med mängden beläggning på de olösliga kärnorna och vid tillräckligt tjock beläggning nåddes nästan CCN-aktiviteten för helt lösliga ämnen. Vidare gav kontrollerad torr beläggning av de olösliga BC-kärnorna en storleksoberoende fördelning av beläggningsmaterialet på de olösliga kärnorna, vilket inte uppnåddes genom våt beläggning av kiseldioxidpartiklarna. Resultaten bekräftade också att genom att känna till fraktionen av lösligt material (beläggningstjocklekar) gav de befintliga teorierna en rimlig uppskattning av CCN-aktiviteten för de blandade lösliga/olösliga partiklarna. Slutligen lyfter resultaten fram behovet av att inkludera effekterna av samutsläppta eller senare kondenserade lösliga föreningar i beräkningar avseende klimatpåverkan från olösliga aerosoltyper.

I den andra delen av avhandlingen kvantifierades ytbenägenhet för bärnstenssyra, ren eller blandad med lösliga oorganiska salter i vattendropparna via mätning av molekylskalig ytkomposition genom röntgenfotoelektron-spektroskopi (XPS). Mätningarna visade stark anrikning av bärnstenssyra vid ytan av vätskedropparna jämfört med bulklösningen. Denna effekt var mer tydlig vid förekomsten av höglösliga oorganiska salter som NaCl och $(\text{NH}_4)_2\text{SO}_4$. Den beräknade ytspänningen för de rent organiska lösningarna och de blandade med oorganiska ämnen där ytberikningsfaktorer härrör från XPS-experimenten, var i god överensstämmelse med de experimentella ytspänningsdata. Detta viasar på

storpotential för användning av XPS för direkta mätningar av ytkompositionen av atmosfäriskt relevanta vätskeblandningar innehållande vatten. Resultaten visar att för att simulera fas- och vattenhalten i de atmosfäriska partiklarna måste ytfastillskottet beaktas, eftersom vattenhaltig droppe kan innehålla större mängder organiska föreningar än lösningsgränsens löslighetsgräns. Eftersom, effekten av den vattenhaltiga ytkompositionen på CCN-aktiveringen av partiklar som bestod av de studerade blandningarna uppskattades som liten.

Resultaten som presenteras i denna avhandling ger nya insikter i förhållandet mellan aerosolpartikelkompositionen och molnkondensationskärnaktivitet. Effekten av mer realistiska komplexa blandningar kommer dock att kräva ytterligare forskning. Vidare så måste partitioneringen mellan gas och kondenserad fas beaktas för modellering av delvis flyktiga substanser. Dessutom behövs mer analys av iskärnbildningsförmågan hos partiklarna bestående av både lösliga och olösliga ämnen.

Nyckelord: CCN-aktivitet, ytspänning, belagda aerosoler, svart kol

List of papers and author's contribution

I CCN activation of fumed silica aerosols mixed with soluble pollutants

M. Dalirian, H. Keskinen, L. Ahlm, A. Ylisirniö, S. Romakkaniemi, A. Laaksonen,
A. Virtanen and I. Riipinen

Published in Atmospheric Chemistry and Physics (ACP), 15, 3815-3829, 2015, doi: 10.5194/acp-15-3815-2015

- I had the main responsibility for conducting and analyzing the laboratory experiments, compared the experimental results to the existing theories and wrote most of the paper with help from the co-authors.

II Succinic acid in aqueous solution: Connecting microscopic surface composition and macroscopic surface tension

J. Werner, J. Julin, M. Dalirian, N. L. Prisle, G. Öhrwall, I. Persson, O. Björneholm and I. Riipinen

Published in Physical Chemistry Chemical Physics (PCCP), 16, 21486-21495, 2014, doi: 10.1039/c4cp02776k

- I conducted the macroscopic surface tension model calculations using input from the experimental data and molecular dynamic simulations. Furthermore, I compared these results to experimental data on surface tensions and wrote the sections of the paper describing these calculations and their results.

III Surface partitioning in organic–inorganic mixtures contributes to the size-dependence of the phase-state of atmospheric nanoparticles

J. Werner, M. Dalirian, M. Walz, V. Ekholm, U. Wideqvist, S. J. Lowe, G. Öhrwall, I. Persson, I. Riipinen and O. Björneholm

Published in Environmental Science and Technology (EST), 50 (14), 7434–7442, 2016, doi: 10.1021/acs.est.6b0078

- In this study, I conducted the surface tension measurements and calculations. I also compared the calculated surface tensions to the experimental values. In addition, I contributed by writing the sections of the paper related to my work.

IV Cloud droplet activation of black carbon particles coated with organic compounds of varying solubility

M. Dalirian, A. Buchholz, D. Schlesinger, J. Ström, A. Virtanen and I. Riipinen

Published as a discussion paper in Atmospheric Chemistry and Physics Discussions (ACPD), 2017, doi: 10.5194/acp-2017-1084

Under review for Atmospheric Chemistry and Physics (ACP)

- I contributed to the planning of the laboratory experiments, conducted the measurements, analyzed the results by comparing them to the theoretical values and finally wrote the paper with help from the co-authors.

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Abbreviations

a_w	water activity
APM	Aerosol Particle Mass analyzer
BC	Black Carbon
BSA	Bovine Serum Albumin
DMA	Differential Mobility Analyzer
CCN	Cloud Condensation Nuclei
CCNc	Cloud Condensation Nuclei counter
CN	Condensation Nuclei
CPC	Condensation Particle Counter
CRAICC	CRyosphere-Atmosphere Interactions in a Changing Arctic Climate
d_c	critical droplet diameter
d_{core}	core diameter
d_{dry}	particle dry diameter
D_f	fractal dimension
d_p	droplet diameter
d_{va}	vacuum aerodynamic diameter
ERC	European Research Council
FHH	Frenkel-Halsey-Hill
g	surface enrichment factor
GF	Growth factor
GHG	GreenHouse Gas
IN	Ice Nuclei
IPCC	Intergovernmental Panel on Climate Change
m	molality

MD	Molecular Dynamics
M_w	molar mass of water
N_A	Avogadro's constant
NaCl	sodium chloride
$(\text{NH}_4)_2\text{SO}_4$	ammonium sulfate
OC	Organic Carbon
OPC	Optical Particle Counter
PE	PhotoEmission
P_w	partial pressure of water vapor
P_w°	saturation pressure of water vapor
R	universal gas constant
RH	Relative Humidity
s	supersaturation
S	saturation ratio
SMPS	Scanning Mobility Particle Sizer
SP-AMS	Soot Particle Aerosol Mass Spectrometer
T	temperature
V	volume
x	mole fraction
XPS	X-ray Photoelectron Spectroscopy
γ	activity coefficient
κ	hygroscopicity parameter
ε	volume fraction
ρ	density
σ	surface tension
ω	mass fraction

1 Introduction

Atmospheric aerosols are microscopic solid or liquid particles suspended in the air. Examples of such particles are salt particles from ocean spray, windborne dust particles, photochemically produced particles, smoke from vehicles, wildfires and power plants as well as cloud droplets or ice crystals. Atmospheric aerosols can travel over distances of several thousands of kilometers and their size spans from a few nanometers for freshly produced particles from gas-to-particle conversion up to almost 1 mm for large dust particles (Hinds 1999; Petzold and Kärcher 2012). After entering the atmosphere, these particles undergo physical and chemical aging processes like condensation, coagulation and chemical reactions.

Atmospheric aerosols influence the global climate via scattering and absorbing solar radiation, modifying cloud properties and thus influencing the hydrological cycle and the Earth's radiative budget (Myhre et al. 2013; Colbeck and Lazaridis 2014). A balanced radiative budget refers to a balance between outgoing (infrared), and incoming (solar) radiative energy. In a radiative balance, the Earth's climate system is in an equilibrium state (Myhre et al. 2013; Boucher 2015). In reality, however, the climate system is never at equilibrium because of perturbations caused by natural (e.g. volcanic eruptions) and anthropogenic (e.g. emissions from the combustion of fossil fuels and biofuels) activities (Haywood and Boucher 2000; Boucher 2015). Due to human activities since the start of the industrial era, the anthropogenic perturbations are now more intensive than the natural perturbations (Myhre et al. 2013; Boucher 2015). The perturbations of the climate system are characterized by a quantity called radiative forcing, which corresponds to the net change (in Wm^{-2}) in the radiative balance of the Earth system due to the climate perturbation (Jacob 1999; Myhre et al. 2013; Boucher 2015).

Figure 1 illustrates how different compounds affect the radiative balance of the Earth's climate. Greenhouse gases (GHGs) like CO_2 and CH_4 , emitted from the anthropogenic sources, have the largest contributions to the increased radiative forcing and warming the Earth system. Along with the GHGs, atmospheric aerosols are affecting the radiative forcing of the climate system directly by aerosol-radiation interactions and indirectly by aerosol-cloud interactions. In other words, the direct climate effect of the aerosols refers to the absorption and scattering of solar and thermal radiation, while the indirect aerosol effect refers to changes in cloud characteristics, microphysical properties and lifetime of clouds (Twomey 1974; McCormick and Ludwig 1976; Haywood and Boucher

2000; Lohmann and Feichter 2005; Boucher et al. 2013; Myhre et al. 2013; Colbeck and Lazaridis 2014). Most of the aerosols like dust and sulfate primarily scatter the solar radiation and cool the climate by their negative forcing, but black carbon particles (BC) have been estimated to have an overall positive net impact on the forcing, thus warming the climate (Fig. 1). This positive forcing can, on the other hand, be counteracted by species like organic carbon (OC), which can be co-emitted with BC from e.g. biomass burning.

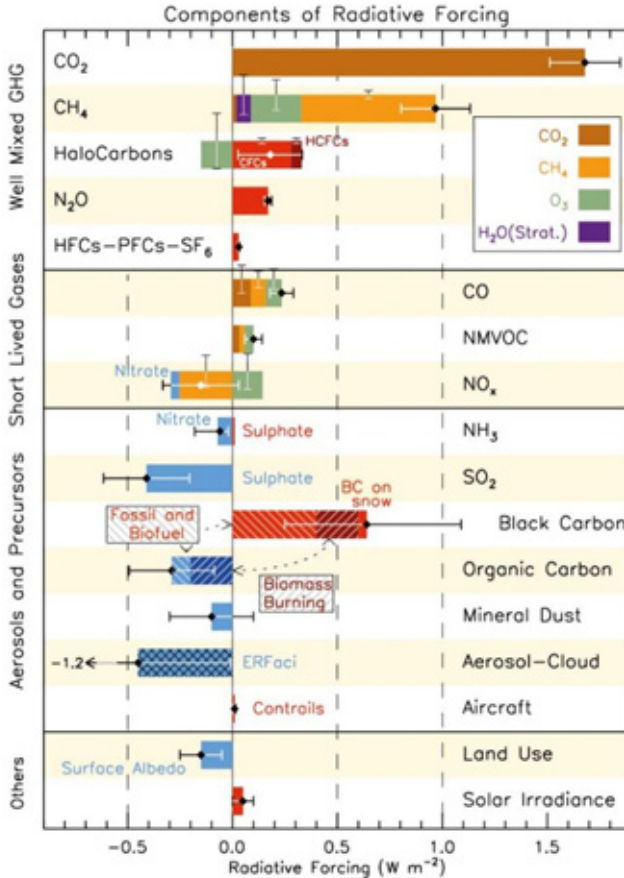


Figure 1: Radiative forcing bar chart for the period 1750–2011 based on emitted gases, aerosols or aerosol precursors as well as some other key processes reported by IPCC 2013 (Myhre et al. 2013).

Aerosol particles influence the microphysical properties of liquid clouds through their role as cloud condensation nuclei (CCN), which control the concentration and size of cloud water droplets. Aerosol particles also alter the microphysical properties of ice and mixed-phase clouds by acting as ice nuclei to form the ice phase (Boucher 2015). Clouds influence aerosol populations by removing

aerosols from the atmosphere. Aerosol-cloud interactions, have a negative net radiative forcing and cool the Earth's climate (Fig. 1, Boucher et al. 2013; Myhre et al. 2013). However, despite a large amount of research in recent decades, there are still challenges and uncertainties in understanding aerosol-cloud interactions (Boucher et al. 2013; Lee et al. 2013; Boucher 2015). In the atmosphere, positive forcer compounds like BC can be mixed by other existing or co-emitted hygroscopic compounds, that can enhance the ability of these particles to act as CCN to form cloud droplets, which can turn them into a net negative climate forcer. However, because of the large variation in mixing of components in the atmosphere, improved understanding of aerosol-cloud interactions is necessary to overcome uncertainties in this field and make better estimates of the impact by the emitted compounds (Myhre et al. 2013). In this regard, studying the processes and parameters determining how an aerosol particle turn into a CCN and furthermore cloud droplet or ice crystals is of particular importance.

Generally, CCN are aerosol particles capable of forming cloud droplets (activate) under atmospheric water supersaturations. CCN activation takes place via uptake of water vapor primarily by the hydrophilic part of atmospheric particles. This hygroscopic growth of aerosols leads to the activation of aerosol particles into CCN, initiating cloud formation (Seinfeld and Pandis 2006; Petzold and Kärcher 2012). The ability of an aerosol particle to become a cloud droplet depends on chemical composition and physical properties of the particle (Henning et al. 2005). Water solubility and surface tension are among the physical properties affecting the CCN activity of atmospheric aerosol particles.

Early studies on aerosol–cloud interactions assumed that CCN are formed from aerosols that contain significant amounts of soluble material such as pure sea salt, sulfate particles and some organics (Giebl et al. 2002; Abbatt et al. 2005; Mcfiggans et al. 2006; Huff Hartz et al. 2006; Rosenorn et al. 2006; Padró et al. 2007; Petters and Kreidenweis 2007; Rissman et al. 2007; King et al. 2009; Henning et al. 2010; Kristensson et al. 2010). Recent studies suggest that water-insoluble particles, which come from different natural (e.g. dust) and anthropogenic (e.g. BC and fumed silica) sources can also act as CCN, since they can grow via adsorbing water on to their surfaces (Sorjamaa and Laaksonen 2007; Kumar et al. 2009, 2011a, b; Sullivan et al. 2010; Dalirian et al. 2015). In ambient air, atmospheric aerosol particles often contain both water-soluble and water-insoluble substances. These particles can be formed, for instance, when insoluble particles are coated by condensing soluble species during their aging in the atmosphere. The soluble material may be co-emitted or introduced during the aging of the aerosol. Studies have recently suggested that the absorption of water onto the slightly soluble part of the coated particles increases the water uptake by the particles and facilitates the process of activation (CCN activity) (Saathoff et al. 2003; Levin et al. 2005; Dusek et al. 2006; Zhang et al. 2008; Hings et al. 2008; Henning et al. 2010, 2012; Stratmann et al. 2010; Tritscher et al. 2011; Dalirian et al. 2015; Maskey et al. 2017). Despite these recent studies, because of the complex chemical composition of the real atmospheric aerosols, accurate

measurements and calculations of the CCN activation of mixed particles are still relatively scarce.

CCN activity studies have traditionally assumed that the surface tension of atmospheric droplets is equal to that of pure water and neglect the dependence of surface tension to the droplet composition (Giebl et al. 2002; Kreidenweis et al. 2005; Mcfiggans et al. 2006; Petters and Kreidenweis 2007; Kristensson et al. 2010). Since atmospheric aerosols usually contain components composed of organic and inorganic molecules with different water solubilities, improved knowledge of the effect of these substances on the surface tension and cloud droplets activation of atmospheric aerosols is of particular importance. Surface tension is a macroscopic property quantifying microscopic molecular interactions (Prisle et al. 2010; Ottosson et al. 2011; Werner et al. 2014). Although significant progress has recently been made in understanding the thermodynamics of atmospheric inorganic and organic aerosol constituents; little is known about their direct interactions with each other (Clegg et al. 2003; Clegg and Seinfeld 2006a, b). However, some studies suggest that inorganic salts could be capable of modifying the surface propensity of organic molecules in atmospheric droplets (Prisle et al. 2010, 2012; Ruehl and Wilson 2014), quantifying the molecular mechanisms affecting surface partitioning in terms of surface vs. bulk concentration allows more detailed surface tension considerations in aerosol-cloud interaction studies (Werner et al. 2016).

1.1 Scientific goals of the thesis

The main goal of this thesis was to study the parameters affecting the CCN probability of the aerosol particles. To take into account the effect of complex chemical composition of the aerosol particles, the CCN activity of particles containing water-soluble species (e.g. ammonium sulfate sucrose and levoglucosan) and water-insoluble species (e.g. fumed silica and BC) were investigated. To study the surface partitioning of the water-soluble components and its effect on the surface tension of the aqueous droplets, molecular surface structure of the aqueous solutions containing only organic (succinic acid) or mixed organic (succinic acid)-inorganic (ammonium sulfate/sodium chloride) species were investigated and connected to the surface tension of the mixtures.

Specifically, the aim of this thesis was to respond to the following scientific questions:

1) What is the effect of water solubility on the CCN activity of the atmospheric aerosols?

More specifically, the following questions were investigated:

- a. What is the effect of soluble coating on the CCN activation of insoluble particles?
- b. How does the coating technique used in the laboratory experiments influence the results?
- c. Is it possible to describe the CCN activity results by existing theories?
- d. What are the implications of the results in describing the characteristics, behavior and effects of atmospheric aerosol particles?

2) What is the contribution of molecular-scale surface structure to the surface tension and CCN activity of atmospherically relevant aqueous mixtures of organic and inorganic species?

More specifically, the following questions were investigated:

- a. How is the surface of the aqueous droplet affected by the presence of organic and inorganic species?
- b. How does the microscopic surface structure of the aqueous droplets connect to the macroscopic surface tensions?
- c. What are the implications of the results for atmospheric aerosol particles?

2 Theoretical background

In the atmosphere, aerosol particles serve as condensation nuclei (CN); which means that they act as surfaces for water vapor and other semi-volatile gases to condense on (Colbeck and Lazaridis, 2014). The growth of aerosol particles by taking up water vapor from surrounding atmosphere is referred to hygroscopic growth and it takes place by water vapor condensing at a given relative humidity (RH). RH (expressed in %) is defined as follows:

$$RH = \frac{P_W}{P_W^{\circ}} \times 100\% \quad (1)$$

where, P_W [Pa] is the partial (usually equilibrium) pressure of water vapor at a given ambient temperature and P_W° is the saturation pressure of water vapor at the same temperature. The hygroscopic growth of aerosol particles is described by the parameter called growth factor (GF) (McFiggans et al. 2005; Lohmann et al. 2016), which is defined as the ratio of the diameter of a particle at a specific RH to its dry diameter, $GF = d(RH)/d_{dry}$ (McFiggans et al. 2005). The term hygroscopic growth refers to subsaturated conditions, where the RH is below 100% (Fig. 2). Whenever the ambient RH exceeds 100%, the air becomes supersaturated and the humidity is high enough for the particles to reach a critical size threshold and act as CCN to grow (activate) and form cloud droplets (Lohmann et al. 2016).

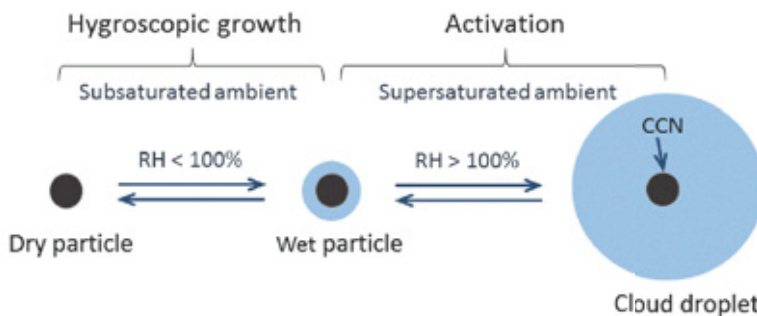


Figure 2: Schematic representation of aerosol particle growth and activation by condensation of water vapor.

For a given particle composition and size, the ambient water concentration above which the particle starts to grow without a limit and activates to make a cloud droplet (Fig. 2), is described by Köhler theory. This theory was introduced by

Swedish meteorologist Hilding Köhler (1936) and is based on equilibrium thermodynamics (Köhler 1936; Seinfeld and Pandis 2006). Formulation of the Köhler theory demonstrates that along with physical dimensions of the aerosol particles, water-solubility and surface tension are the key properties needed to describe their CCN activity potential.

In this section, first the Köhler theory and some of its derivatives for describing the CCN activation of water-soluble and water-insoluble species and their mixtures are briefly introduced. Second, some commonly used methods and theories are addressed to describe the surface tensions of aqueous solutions containing soluble impurities. The parts of sections 2.1 and 2.2 in quotation marks build directly upon the theories presented in my licentiate thesis (Dalirian 2014).

2.1 Köhler theory and its derivatives

Köhler theory is based on the assumption that the water in the aerosol is in thermodynamic equilibrium with its surrounding atmosphere. According to Köhler theory, the water vapor equilibrium pressure over saturation vapor pressure (known as the saturation ratio) needed to form a droplet is a function of size and chemical composition of the aerosol (Seinfeld and Pandis 2006; Colbeck and Lazaridis 2014). This theory combines two counteracting effects: Kelvin and Raoult effects. According to the Kelvin effect, higher ambient water pressure is required to maintain equilibrium over a curved droplet surface compared to a planar surface. Based on the Raoult law, lower ambient vapor pressure is required to maintain equilibrium over water solution compared to pure water (Pruppacher and Klett 1997; Seinfeld and Pandis 2006; Boucher 2015).

By combining the Kelvin effect and Raoult law, the Köhler equation provides the saturation ratio (S) at a given radius of water droplet formulated as follows (Seinfeld and Pandis 2006):

$$S = \frac{P_W}{P_W^*} = a_W \exp\left(\frac{4\sigma_{sol}M_w}{RT\rho_{sol}d_p}\right) \quad (2)$$

where d_p [m] is the droplet diameter, σ_{sol} [N m⁻¹] is the surface tension and ρ_{sol} [kg m⁻³] is the density of the solution, M_w [kg mol⁻¹] is the molar mass of water, R [m³ Pa mol⁻¹ K⁻¹] is the universal gas constant and T [K] is the temperature. a_W is water activity in the solution and is equal to $x_W\gamma_W$, where x_W is the mole fraction of water and γ_W is the activity coefficient of water in the solution.

The first term of the Köhler equation (a_W) expresses the Raoult law (chemical composition or solubility effect) and the second term within the exponential describes the Kelvin (curvature) effect (Seinfeld and Pandis 2006; Boucher 2015). Figure 3 illustrates the combined effect from these two terms on the equilibrium supersaturation of water over solution droplets.

"Supersaturation s is defined as $S-1$ and is usually expressed as a percentage. The maximum point of the Köhler curve represents the critical supersaturation (s_c) point, which is located at the critical droplet diameter (d_c):

$$\left. \frac{ds}{dp} \right|_{d_p=d_c} = 0 \quad (3)$$

Following the Köhler curve (Fig. 3), for any atmospheric supersaturation less than s_c and droplet diameters less than d_c , the droplets will be in equilibrium with the environment and thus grow or shrink driven only by changes in the atmospheric supersaturation." However, if the environment supersaturation is equal or larger than the s_c , the equilibrium droplet size increases to reach d_c value. As long as the ambient is supersaturated (RH is above 100%), growth beyond d_c will rapidly transform the particle into a cloud droplet (Pruppacher and Klett 1997; Seinfeld and Pandis 2006). This process is called cloud droplet activation.

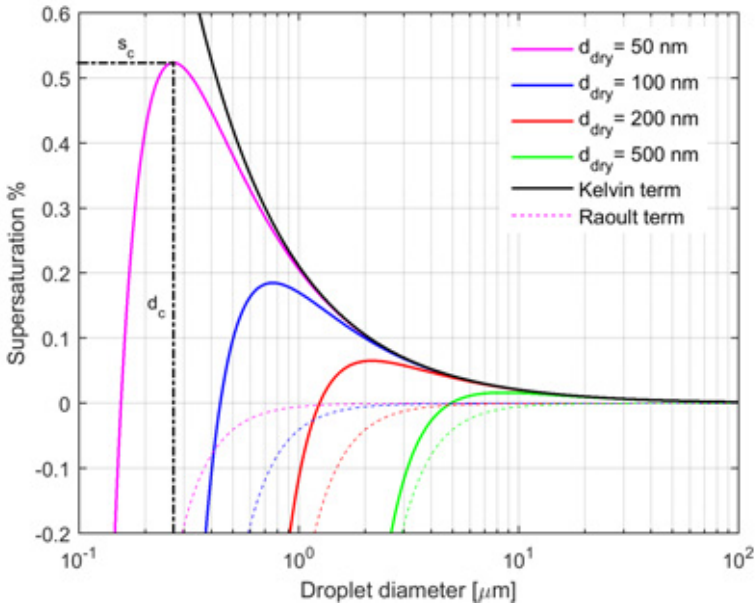


Figure 3: Köhler curves for various dry diameters of ammonium sulfate particles, representing the competition between Kelvin (black curve) and Raoult (dashed curves) terms. s_c and d_c are critical supersaturation and droplet diameter at critical point for the particle with the dry diameter of 50 nm.

2.1.1 κ -Köhler theory

" κ -Köhler theory was introduced by Petters and Kreidenweis (2007). They used a single hygroscopicity parameter κ to describe the relationship between particle dry diameter and cloud condensation nuclei (CCN) activity. This theory is applicable for hygroscopic compounds (Petters and Kreidenweis 2007).

In their parameterization, the hygroscopicity parameter κ is defined through its effect on the water activity of the solution (Petters and Kreidenweis 2007):

$$\frac{1}{a_w} = 1 + \kappa \frac{V_S}{V_W} \quad (4)$$

where, V_S [m³] is the volume of the dry particulate matter and V_W [m³] is the volume of the water.

Combining Eq. 4 with classical Köhler theory (Eq. 2), and assuming that the surface tension and density effects of the solute in the Kelvin term are negligible, yields the κ -Köhler theory for estimating the equilibrium saturation ratio of water over the solution droplets (Petters and Kreidenweis 2007):

$$S = \frac{d_p^3 - d_{dry}^3}{d_p^3 - d_{dry}^3(1-\kappa)} \exp\left(\frac{4\sigma_{sol}M_w}{RT\rho_w d_p}\right) \quad (5)$$

where d_{dry} is particle dry diameter. κ value can alternatively be calculated from the paired (S_c, d_{dry}) values from experimental data using the following expression (Petters and Kreidenweis 2007):

$$\kappa = \frac{4A^3}{27d_{dry}^3 \ln^2 S_c} \quad (6)$$

in which, S_c is the saturation ratio at the critical point and $A = \frac{4\sigma_{sol}M_w}{RT\rho_w}$.

2.1.2 Adsorption activation theory

Adsorption activation theory was first applied by Sorjamaa and Laaksonen (2007) for cloud droplet activation of wettable insoluble compounds. "They assumed that the droplet growth happens through multilayer adsorption. This theory includes the FHH (Frenkel-Halsey-Hill) adsorption isotherm (e.g. Lowell et al. 2004) in Köhler theory instead of the solute term. Assuming a uniform distribution of adsorbed water molecules over the particle surface the activity of the water will be in the form (Sorjamaa and Laaksonen 2007; Kumar et al. 2009):

$$a_w = \exp(-A_{FHH}\theta^{-B_{FHH}}) \quad (7)$$

where A_{FHH} and B_{FHH} are empirical constants. The parameter A_{FHH} characterizes the interactions between adsorbed molecules (in this case water) as well as the surface and adjacent adsorbate molecules. The parameter B_{FHH} characterizes the attraction between the solid surface and the adsorbate in the following layers (Sorjamaa and Laaksonen 2007). θ is the surface coverage (i.e. the number of adsorbed layers of water) and can be obtained using the following expression:

$$\theta = \frac{d_p - d_{dry}}{2d_w} \quad (8)$$

in which, $d_w=2.75 \text{ \AA}$ ($2.75 \times 10^{-10} \text{ m}$) is the diameter of a water molecule adsorbed on the particle surface (Kumar et al. 2009).

By substituting a_w from the FHH adsorption theory to Eq. 2, the equilibrium saturation ratio for the droplet is thus as follow:

$$S = \exp(-A_{FHH}\theta^{-B_{FHH}})\exp\left(\frac{4\sigma_w M_w}{RT\rho_w d_p}\right) \quad (9)$$

Sorjamaa and Laaksonen (2007) suggested the range $0.5 < B_{FHH} < 3$ and $0.1 < A_{FHH} < 3$ for adsorption isotherm parameters based on previous literature. Later, Kumar et al. (2011a) studied in more detail the CCN activity of dry-generated regional dust and clay/mineral aerosols and introduced values for A_{FHH} and B_{FHH} within the range introduced by Sorjamaa and Laaksonen (2007)."

2.1.3 Shell and core model

"The shell and core model introduced by Kumar et al. (2011b) describes the CCN activation of particles containing both water-insoluble and soluble components. The model combines the κ -Köhler and adsorption activation theories assuming that the particles are spheres made of an insoluble core and a layer of soluble material as a shell. The soluble material is assumed to coat the insoluble part, resulting in the following relation between water supersaturation, particle size and composition:

$$S = \frac{4\sigma_w M_w}{RT\rho_w d_p} - \frac{\varepsilon_s d_{dry}^3 \kappa}{(d_p^3 - \varepsilon_i d_{dry}^3)} - A_{FHH} \left(\frac{d_p - \varepsilon_i^{1/3} d_{dry}}{2d_w} \right)^{-B_{FHH}} \quad (10)$$

where ε_i and ε_s are the insoluble and soluble volume fractions in the dry particles. To estimate the coating thicknesses and insoluble and soluble volume fractions in the particles, the following equations can be used:

$$d_{dry} = d_{core}/\varepsilon_i^{1/3} \quad (11)$$

$$\varepsilon_s = 1 - \varepsilon_i \quad (12)$$

where d_{core} (m) is the insoluble core diameter. The following assumptions have been made in the derivation of Eq. 10 from Eqs. 2 and 9: first, the effects of the solute on the Kelvin term have been assumed to be small, second, the supersaturations have been assumed to be small enough to justify approximating the exponential term with its series expansion."

2.2 Surface tension modeling

"According to the Köhler theory (Eq. 2), the surface tension of the solution droplet is among the important parameters describing the CCN activity of water-soluble particles – although it is often approximated with pure water surface

tension for simplicity. Accumulation of surface active species (surfactants) on the surface of aqueous droplets can reduce the surface tension (Shulman et al. 1996), which lowers the critical supersaturation needed to activate a given aerosol particle and enables activation of smaller particles. As a result, larger fractions of the atmospheric aerosol size distribution become CCN and a larger number of cloud droplets will be produced (Twomey 1974; Tuckermann 2007).

The surface tension of solutions reveals information on the structure and energetics of the surface region between the gas and liquid phases. The boundary between a liquid phase and a gas phase can be considered a third (surface) phase with properties distinct from those of the liquid and gas. In a liquid mixture, the composition of the surface layer is generally not the same as that of the bulk. The surface tension of a mixture is thus usually not a simple function of the surface tensions of the pure components.

Several techniques are available to estimate the surface tension of aqueous solutions (σ_{sol}). They can be divided into two categories: those based on empirical relations like the Szyszkowski equation (Szyszkowski 1908) and the Szyszkowski-Langmuir relation (Langmuir 1917) and those describing surface-containing systems based on thermodynamic principles. The empirical relations can be used when the pure component surface tensions do not differ greatly and when the deviations from ideal solution behavior are not large (Poling et al. 2000). In practice, these relations have been used most often to describe experimental data. Thermodynamic-based methods require more complex calculations, but lead to more reliable results (Poling et al. 2000)."

2.2.1 Simple mixture model

"In the simplest possible mixture model σ_{sol} is expressed as a linear combination of the pure compound surface tensions. σ_{sol} is calculated from a mole fraction average of the surface tensions of pure components (Poling et al. 2000):

$$\sigma_{sol} = \sum_i^n x_i \sigma_i \quad (13)$$

where x_i is mole fraction and σ_i (N m^{-1}) is surface tension of component i . This equation gives an approximate estimate of σ_{sol} and predicts a linear relationship between the mixture surface tension and the surface tension of pure components."

2.2.2 Sprow and Prausnitz model

"This model is a thermodynamic model introduced by Sprow and Prausnitz (Sprow and Prausnitz 1966a, b) and later used by e.g. Li et al. (1999) for aqueous electrolyte solutions. Since the surface layer usually differs in composition from that of the bulk phases, the surface compositions are needed for predictions of the surface tension. Sprow and Prausnitz (1966a, b) assume thermodynamic

equilibrium between the surface and bulk layers and the partial molar surface area of water at the surface layer is considered equal to that of the bulk phase. With these assumptions, the surface tension of the aqueous solution σ_{sol} can be approximated with:

$$\sigma_{sol} = \sigma_w + \frac{RT}{A_w} \ln \frac{a_w^S}{a_w^B} \quad (14)$$

where σ_w is the surface tension of pure water, R is the universal gas constant, T is the absolute temperature of the system and A_w ($\text{m}^2 \text{mol}^{-1}$) is the molar surface area of water in aqueous solutions as (Li et al. 1999):

$$A_w = (V_w)^{2/3} (N_A)^{1/3} \quad (15)$$

where N_A (mol^{-1}) is Avogadro's constant and V_w ($\text{m}^3 \text{mol}^{-1}$) the molar volume of pure water which is equal to the quotient of the molar mass of water and its density M_w/ρ_w . a_w^S and a_w^B are the activities of water in the surface and bulk layers, respectively. The water activity is calculated separately for the bulk solution using x_w^B , γ_w^B and for the surface layer using x_w^S , γ_w^S .

Li et al. (1999) assumed for aqueous solution containing electrolytes that the molality (mol kg^{-1}) of electrolyte i in the surface layer is proportional to that in bulk liquid:

$$m_i^S = g \cdot m_i^B \quad (16)$$

where g is a proportionality constant called the surface enrichment factor."

3 Materials and methods

This section contains a brief description of the materials and techniques to produce water-insoluble particles coated by species with varying solubilities, as well as the instruments used for measuring the size distribution, mass and CCN activation of these particles. Second, the experimental techniques and simulations used to quantify the surface composition of the aqueous solution as well as the instrument used to directly measure the surface tension of the solutions are briefly introduced.

3.1 Investigating the effect of water solubility on CCN activity

To address the first research question and study the CCN activity of the mixed water soluble and water-insoluble particles, insoluble particles were coated with various soluble species using two different coating techniques. We began by studying particles containing fumed silica, which is one of the products produced commercially using flame reactors, coated by some partly soluble species (Paper I). The soluble species used in Paper I were ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) (a water-soluble inorganic salt), sucrose (a water-soluble organic sugar) and bovine serum albumin (BSA) (a large water-soluble protein). In Paper IV, we used BC (regal black, 400R) particles and coated them with some atmospherically relevant organic species. BC-containing particles are emitted into the atmosphere through e.g. incomplete combustion of fossil fuels, biomass and biofuels (Bond et al. 2004). The organic compounds we used in this part of the study were glutaric acid, levoglucosan (both water-soluble organics) and oleic acid (a sparingly soluble organic compound). The components used in the measurements along with their physical properties are listed in Table 1.

Two different methods were applied to produce mixed/coated particles: wet coating and dry coating. The coated particles in Paper I were produced by first dissolving the insoluble fumed silica and soluble species in water and then atomizing and drying the particles. The coated particles used in Paper IV were generated by first producing pure BC particles (by atomizing-drying method) and then coating them with organics via evaporating the organic species in a furnace and condensing the organic vapor on the BC particles by cooling the particles.

After particle generation, laboratory measurements were performed to study their CCN activity. The experimental CCN activity results were compared to theoretical calculations using the existing frameworks described in Sect. 2.1.

Furthermore, size distribution, mass analysis and shape characterization of the agglomerated fumed silica and BC particles provided more information about the size and morphology of the produced particles.

Table 1: Thermodynamic properties of components used in the CCN measurements.

	Molar mass (g/mol)	Density (g/cm ³)	Solubility in water (mol/kg)	κ
SiO ₂	60.08 ^a	2.16 ^d	-	-
Regal black	-	1.7-1.9 ^e	Insoluble ^e	-
(NH ₄) ₂ SO ₄	132.14 ^a	1.77 ^a	5.78 ^a	0.61 ^k
Sucrose	342.3 ^a	1.58 ^a	5.96 ^a	0.084 ^l
BSA	66500 ^b	1.362 ^b	0.022 ^g	0.013 ^m
Glutaric acid	132.16 ^a	1.429 ^a	10.8 ^h (at 25°C)	0.113-0.176 ^k
Levoglucosan	162.14 ^c	1.7±0.1 ^f	8.23 ⁱ (at 20°C)	0.193-0.223 ^k
Oleic acid	282.46 ^a	0.894 ^a	Very low, 3.76×10 ⁻⁹ ^j	-

^a Haynes et al. (2017)

^b Mikhailov et al. (2004)

^c Sigma-Aldrich, Chemie GmbH

^d Grayson (1985)

^e Regal black 400R safety datasheet, Cabot Corp.

^f Predicted, ACD/Labs Percepta Platform - PhysChem Module

^g Shiraiwa et al. (2011)

^h Soonsin et al. (2010)

ⁱ Zamora et al. (2011)

^j Demond and Lindner (1993)

^k Petters and Kreidenweis (2007)

^l Ruehl et al. (2010)

^m This work

3.1.1 Measuring the size distribution of the aerosol particles

A Scanning Mobility Particle Sizer (SMPS; Wang and Flagan 1990; Kulkarni et al. 2011) was used in Papers I and IV to measure the size distribution of the studied particles. It is a combination of a Differential Mobility Analyzer (DMA) and a Condensation Particle Counter (CPC).

DMA was first introduced by Knutson and Whitby (1975) and later became a standard technique for size classification of aerosol particles according to their electrical mobility. With the DMA, particles are selected within a narrow interval of mobilities from a polydisperse aerosol. Before the aerosol particles enter the DMA, they are brought to a charge equilibrium using a bipolar diffusion charger (Kulkarni et al. 2011; Wiedensohler et al. 2012). A DMA can be used separately to select the size of the aerosols (as in our experimental setups in Papers I and IV)

or in combination with a CPC in devices such as the SMPS to determine the size distribution of particles.

CPC is an instrument capable of counting aerosol particles by first enlarging them via using the particles as nucleation centers to create droplets in a supersaturated working fluid vapor (e.g. n-butanol) (Kulkarni et al. 2011). Once condensation begins, particles larger than a threshold diameter grow quickly into larger droplets and pass through an optical detector where they are counted (Agarwal and Sem 1980; Stolzenburg and McMurry 1991; Kulkarni et al. 2011). CPCs can be used separately to count the number density of particles or in combination with other devices such as a DMA.

3.1.2 Aerosol Particle Mass analyzer (APM)

The Aerosol Particle Mass Analyzer (APM) was used to investigate the morphology of the pure fumed silica particles (Paper I). A combination of a DMA and an APM is often used to determine mass of the mobility size-selected agglomerated particles (McMurry et al. 2002; Park et al. 2003). The APM classifies aerosol particles according to their mass-to-charge ratio by balancing the electrostatic and centrifugal forces on the particles (Fig. 4). Since the centrifugal force is proportional to the particle mass and the electrostatic force is proportional to the amount of electric charge of the particle, only particles of a specific mass-to-charge ratio will be taken out of the APM (Ehara et al. 1996; Kulkarni et al. 2011).

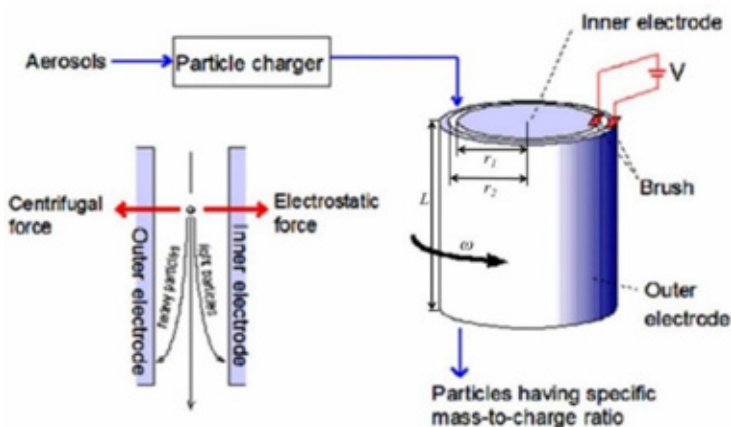


Figure 4: Operating principle of the APM (KANOMAX Inc.). Aerosol particles are first passed through a bipolar charger and then introduced into the annular space between two rotating coaxial cylindrical electrodes. Only the particles with the balanced centrifugal and electrostatic forces exit the annular space (Kulkarni et al. 2011).

3.1.3 Soot particle aerosol mass spectrometer (SP-AMS)

A Soot Particle Aerosol Mass Spectrometer (SP-AMS) was used to investigate the chemical composition and aerodynamic size of particles containing BC and the organic coatings in Paper IV. The SP-AMS is a combination of the high-resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne Research Inc.) and the Single Particle Soot Photometer (SP2, Droplet Measurement Technologies Inc.) (Onasch et al. 2012; Corbin et al. 2014; Willis et al. 2014; Ahern et al. 2016). To describe briefly, in SP-AMS the particles are separated by vacuum aerodynamic diameter in a particle time-of-flight region before they are vaporized, ionized and analyzed by a time-of-flight mass spectrometer (Onasch et al. 2012). The SP-AMS contains a tungsten vaporizer to evaporate non-refractory organic particulate matters, which operates at 600°C and an intracavity infrared (IR) laser which heats and vaporizes refractory BC particles (Onasch et al. 2012; Corbin et al. 2014; Willis et al. 2014; Canagaratna et al. 2015).

3.1.4 CCN activity measurements by a CCN counter (CCNc)

The CCNc used in Papers I and IV is a continuous-flow thermal-gradient diffusion chamber manufactured by Droplet measurements techniques (DMT) (Fig. 5). The principal of the CCNc operation relies on the difference between heat and mass diffusivity. By maintaining a constant temperature gradient along the flow direction through the chamber, differences in thermal and water vapor diffusivity establish supersaturation (s) in the chamber (Roberts and Nenes 2005). Then the particles with a critical supersaturation s_c smaller than the chamber's supersaturation will grow by the condensation of water vapor and activate as CCN (Roberts and Nenes 2005).

The CCNc operates at supersaturations between 0.1% and 1.5% and the particles that activate to cloud droplets at the set supersaturation will grow large enough to be detected by the optical particle counter (OPC) at the outlet of the CCNc. The ratio of the number concentration of activated particles (measured by OPC) to the total particle concentration (measured with a CPC) yields the activation ratio of the particle at each supersaturation of the CCNc instrument.

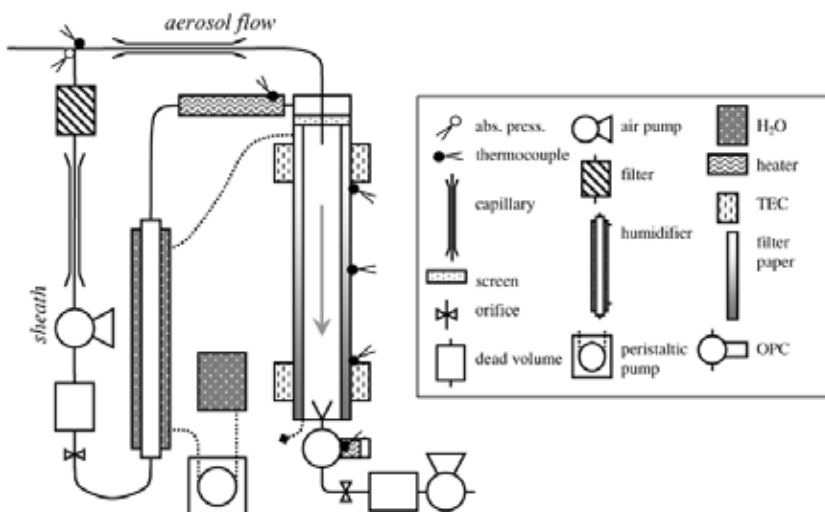


Figure 5: Schematic of the CCN Counter (Roberts and Nenes 2005). The inner surface of the CCN column is maintained wet. The inlet flow is first split into aerosol and sheath flow. The volumetric ratio of the sheath and aerosol flowrates are set to be 10 to 1. The sheath flow is passed through a filter, flowmeter, pump, humidifier and heater before entering the wetted column. After rejoining the sheath and aerosol flows at the top of the CCN column, it flows vertically downward through the column, where the temperature gradient has been provided. Then the particles with a critical supersaturation less than the column's supersaturation activate and grow into droplets, which are then large enough to be detected by an Optical Particle Counter (OPC).

3.2 Surface phenomena affecting CCN activity

To address the second research question, we quantified surface concentrations of aqueous solutions containing pure succinic acid species (Paper II) or in the presence of highly soluble inorganic salts (Paper III), in particular ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and sodium chloride (NaCl). Succinic acid is a dicarboxylic acid, which is one of the common oxidation products of biogenic volatile organic compounds. Ammonium sulfate and sodium chloride are two of the most abundant salts in atmospheric aerosol particles, originating from e.g. industrial emissions and sea spray.

In Paper II, we presented direct measurements of the surface structure of aqueous solutions containing succinic acid and linking these observations to the macroscopic surface tension of this system. The water-vapor interface of aqueous solutions of succinic acid, where pH value and bulk concentration was varied, was studied using the surface sensitive X-ray photoelectron spectroscopy (XPS). The XPS experiments were supplemented by analyzing the density profiles of the solution with molecular dynamics (MD) simulations, which enabled the quantification of surface concentration of succinic acid as a multiple of the bulk concentration (known as surface enrichment factor g). These derived surface

compositions were used to determine the surface tension of the studied solutions and the results were compared to the existing surface tension data.

In Paper III, a novel approach was introduced to determine the surface composition of aqueous solutions containing succinic acid and sodium chloride or ammonium sulfate. It combined XPS experiments with measurements of macroscopic surface tension and the interpretation of the data with thermodynamic modeling of the surface vs. bulk. Specifically, the Langmuir adsorption model was used together with surface tension measurements to quantify the maximum surface contribution of the photoemission (PE) signals for the pure succinic acid solutions. This maximum contribution was assumed to be the same in the presence of the inorganic salts, which yielded the surface composition of the succinic acid in the presence of inorganic salts. These surface compositions were used to determine the surface tension of the mixed organic-inorganic aqueous solutions and the results were compared to the existing or measured surface tension data.

3.2.1 XPS experiments

XPS is a surface and composition sensitive technique, which is well established and has recently been combined with a vacuum liquid micro-jet to characterize the surface of the highly volatile aqueous solutions (Bergersen et al. 2007; Winter 2009 and references therein). This combination is capable of probing the chemical composition and molecular level distribution of the aqueous solutions. To describe briefly, liquid sample is injected into a vacuum chamber through a glass nozzle, whereas it forms a liquid micro-jet and interacts with X-ray radiation (Winter 2009; Ottosson et al. 2011; Werner et al. 2014). At a given kinetic energy, the observed photoemission (PE) intensity of the emitted electrons is proportional to the concentration of a compound in the surface layer (Werner et al. 2014).

As it is described in Papers II and III, the surface propensities of succinic acid in aqueous solution for various concentrations and pH values were measured in the absence (Paper II and III) or the presence (Paper III) of the inorganic salts. The succinic acid abundance in the interface region was monitored via its carbon 1s (C1s) photoemission (PE) lines.

3.2.2 Classical molecular dynamics (MD)

Classical MD simulations (Allen and Tildelsey 1987; Frenkel and Smit 2002) were used in Paper II to estimate the surface layer thicknesses, which allowed quantifying the surface sensitivity of XPS experiments. MD is a computer simulation method based on Newtonian mechanics, which is used to study the particle structure and dynamics in a molecular level. MD simulation provides density profiles, in form of density vs. distance from the interface, which yields the thickness of the surface region (Werner et al. 2014). The surface thickness

from MD simulations was used to quantify the PE intensities from the XPS experiments in the form of surface enrichment factors (g) of succinic acid at the aqueous interface.

3.2.3 Surface tension measurements

Pendant drop method was used in Paper III for the direct surface tension measurements. In this method analyzing the shape of a pendant drop leads to the surface tension of the droplet, since the shape of a drop is determined by a combination of surface tension and gravity effects (Holmberg et al. 2002). The advantage of this method is that only a very small amount of the liquid is required for the measurements. In this method, a drop is formed and expelled from the tip of a vertical tube by slowly pumping the liquid through the tube (see Fig. 6). When the drop's weight (volume) reaches the magnitude balancing the surface tension of the liquid, it starts to detach from the tube and the surface tension is calculated by drop shape analyzing software using the shadow image of a pendant drop (Holmberg et al. 2002).



Figure 6: Pendant drop method. The volume (or the weight) of a pendant drop is proportional to the liquid surface tension (Holmberg et al. 2002).

4 Results and discussion

4.1 Effect of the water-soluble species on the CCN activity of water-insoluble particles

4.1.1 Mass analysis of the particles

Since fumed silica and BC particles are agglomerates, mass analysis of the size classified particles (by a DMA) could provide a better understanding of their shape. Analyzing the data from APM measurements for pure fumed silica particles in Paper I and SP-AMS measurements for pure BC particles in Paper IV yielded the effective density and furthermore, the fractal dimension (D_f) of these particles. The effective density (ρ_{eff}) is the particle density of a sphere with the same mobility diameter and mass as the actual particle (DeCarlo et al. 2004). The fractal dimension (D_f) is a parameter used to describe the geometry of agglomerated particles and can be defined by the scaling of the particle mass or effective density (Rogak and Flagan 1990; Ström et al. 1992; Virtanen et al. 2004).

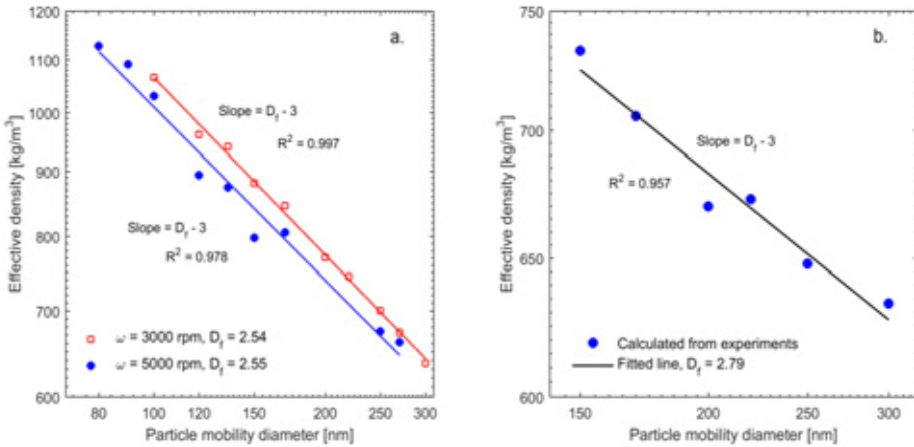


Figure 7: Effective density vs. particle mobility diameter for: a) pure fumed silica particles at two different rotation speeds (3000 and 5000 rpm) of the APM ($D_f = 2.54$ & 2.55 , Paper I), b) pure BC particles ($D_f = 2.79$, Paper IV).

The fractal dimension of the silica particles was estimated to be around 2.55 (Fig. 7a), which was in good agreement with the previous studies (Ibaseta and Biscans

2010; Keskinen et al. 2011). The D_f value of 2.79 (Fig. 7b) was determined for pure BC particles, which was close to the value ($D_f \approx 3$) reported by Onasch et al. (2012). The derived D_f values for silica and BC particles suggested that the structure of these particles were closer to spherical or compact aggregates ($D_f = 3$) rather than line-like structures ($D_f = 1$). We therefore concluded that the insoluble particles studied in this thesis were “compact agglomerates”; thus, the electrical mobility diameters of these particles (measured by DMA) could be used in all the CCN activity calculations.

4.1.2 CCN activity of the pure and coated particles

For analyzing the CCN activity of the generated particles, the activation ratio vs. supersaturation curves were prepared for each set of experiments. Then, a sigmoid curve was fitted to each set of activation ratio data. The supersaturation at which 50% of the particles are CCN activated was assumed to represent the critical supersaturation (s_c) point (e.g. Fig. 4 in Paper I).

Investigating the CCN activity of the pure insoluble silica and BC particles showed that increasing the particle diameter for pure insoluble silica and BC particles resulted in decreased critical supersaturation and that the particles became more CCN active (Figs. 5-6 in Paper I and Fig. 4 in Paper IV), which is in line with adsorption activation theory (see Eq. 9). Fitting the experimental s_c values with the adsorption activation theory (Eqs. 3 and 9) resulted in the A_{FHH} and B_{FHH} values listed in Table 2. However, because of lack of data about the wet diameters of the particles at critical supersaturation, it was difficult to uniquely constrain these parameters. To overcome this problem, the A_{FHH} and B_{FHH} parameters were fitted by setting the constraints $0.1 < A_{FHH} < 3.0$ and $0.5 < B_{FHH} < 3.0$ (Sorjamaa and Laaksonen 2007).

Table 2: FHH adsorption parameters.

	A_{FHH}	B_{FHH}
Fumed silica	2.5	1.62
BC	0.5	1.2

For the pure water-soluble ammonium sulfate and sucrose particles investigated in Paper I, the experimentally determined s_c values were in good agreement with those calculated using κ -Köhler theory (Eqs. 3 and 5) and κ values from previous studies (see Table 1 of Paper I). The κ value of 0.013 was fitted for the pure BSA particle. No CCN activity measurements were performed for the pure soluble species used in Paper IV, with the exception for oleic acid that is sparingly soluble in water. As expected, no evidence of activation was observed for the pure oleic

acid particles at the measured supersaturations up to 1%, which was in good agreement with the previous studies (e.g. Broekhuizen et al. 2004).

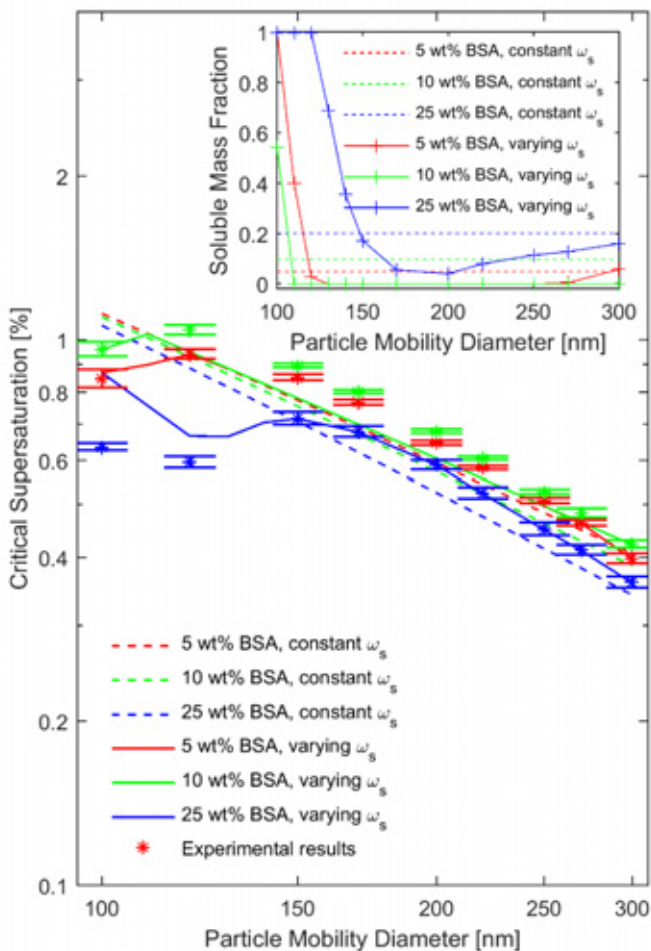


Figure 8: Experimental and theoretical critical supersaturations for silica particles coated by BSA for different particle mobility diameters. Error bars represent the minimum vs. maximum values of supersaturation corresponding to the minimum vs. maximum values of supersaturation corresponding to the error bars on activation ratio curves (e.g. Fig. 8b in Paper I) at the critical supersaturation point (CCN/CN = 50%). The inset displays the assumed soluble mass fractions corresponding to the dashed and solid lines in the main figure. The size-dependent values have been determined by fitting the soluble mass fraction to the critical supersaturations obtained from experimental data corresponding to each mobility diameter (Paper I).

For the silica particle coated/mixed with soluble species (ammonium sulfate, sucrose or BSA) in paper I, the results showed that for the particles with the same

mobility diameters, the critical supersaturation was higher for pure silica particles than for the particles containing soluble material. By increasing the amount of the soluble species, the s_c values decreased and the pure soluble particles had the lowest critical s_c values (see Fig. 8 in paper I). The theoretical values for the critical supersaturation of the coated particle were calculated using the shell-and-core model (Eqs. 3 and 10). Two assumptions were made in the s_c calculations: a) soluble mass fractions (ω_s) are constant at different diameters and b) soluble mass fractions are size-dependent. The results showed that the small particles contain considerably higher fractions of soluble material compared to the larger ones (see Figs. 9-11 in paper I), which indicates uneven distribution of the soluble material as a function of particle size. As is evident from Fig. 8 for the silica particle coated by BSA, particles smaller than 150 nm in diameter were dominated by pure BSA particles. Therefore, the mixed particles generated in this part of the study could not be compared satisfied to theoretical calculations, since soluble mass fractions (ω_s) has not been accurately estimated and had to be fitted instead.

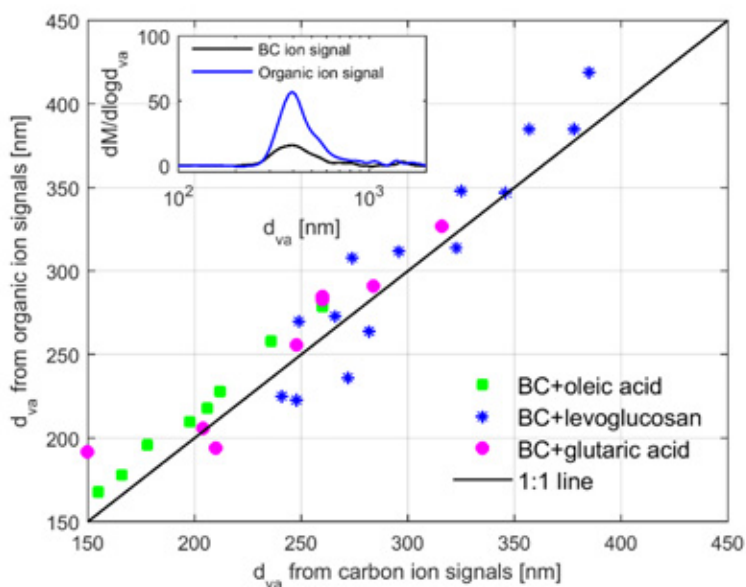


Figure 9: Vacuum aerodynamic diameters (d_{va}) from organic and carbon ions signals from SP-AMS for particles containing BC coated with various organic compounds (Paper IV). The inset represents mass size distribution vs. d_{va} extracted from BC and organic ion signals for monodispersed 200 nm BC particles coated by 27 nm levoglucosan. The coating thickness was estimated from the mobility size measurements by SMPS.

Contrary to the coated silica particles, the BC particles in Paper IV were coated relatively evenly via controlled condensation of glutaric acid, levoglucosan or

oleic acid. As shown in Fig. 9, the vacuum aerodynamic diameters (d_{va}) derived for the total organic and BC ion signals in the particle time-of-flight region of the SP-AMS were almost the same, which indicates a relatively even coating of the BC particles; i.e. there was almost no trace of pure BC or organic particles in the system.

As expected, the uncoated BC particles showed higher critical supersaturation at different mobility diameters than BC particles with organic coating of the same size (see Figs. 5-7 in Paper IV). Moreover, the s_c values decreased by increasing the amount of organic coating in the particles. As an example, Fig. 10 illustrates the critical supersaturations as a function of the particle mobility diameter for BC cores covered by levoglucosan.

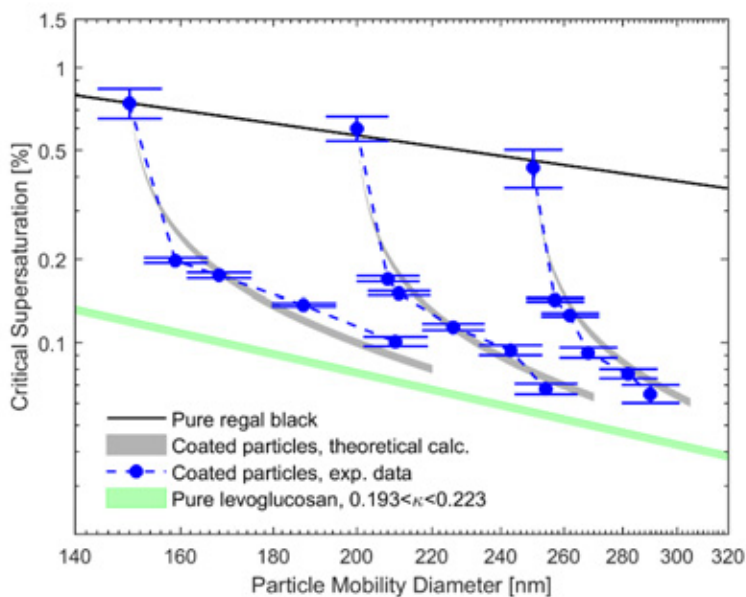


Figure 10: Experimental and theoretical critical supersaturations for BC particles coated by levoglucosan for different particle mobility diameters. The black line represents the calculated critical supersaturations of the pure BC particles using the FHH adsorption activation theory. The gray shaded areas define the critical supersaturations calculated using shell-and-core model and variety of the κ values reported in the literature for levoglucosan (see Table 1). The green shaded area represents the critical supersaturations from the κ -Köhler theory for the pure levoglucosan particles with the range of κ values from literature. Error bars represent the experimental uncertainty in the critical supersaturation s_c corresponding to each mobility diameter (Paper IV).

Comparing the experimental results to the theoretical calculations using the shell-and-core model (Sect. 2.1.3) showed good agreement between the measurements and modeled values for BC cores coated by glutaric acid/levoglucosan. The

amount of organics coated on the BC cores dominated the CCN activity of these particles and at the larger coating thicknesses, these particles behaved like pure organic particles, because the s_c values approached the values for pure organics. For the critical supersaturations of the BC particles coated by oleic acid, no theoretical values were presented (see Fig. 7 in paper IV) as no hygroscopicity data is available for pure oleic acid particles. According to our measurements and previous studies (e.g. Broekhuizen et al. 2004), these particles are CCN inactive. However, the s_c measurements showed that in spite of the anticipated CCN inactivity of the pure oleic acid it enhanced the CCN activity of the BC. An explanation for this enhancement might be e.g. the arrangement of the oleic acid molecules on the surface of the BC cores as compared with pure oleic acid particles (Garland et al. 2008). Finally, it is concluded that theoretical calculations using the shell-and-core model by Kumar et al. (2011) could give a reasonable estimate of the CCN activity of insoluble cores coated by soluble species via controlled coating techniques.

4.2 Surface phenomena affecting the CCN activity

The XPS measurements and MD simulations for different concentrations of pure succinic acid in aqueous solutions in Paper II showed the tendency of the succinic acid molecules to accumulate on the surface of the aqueous solutions until the surface region became saturated with succinic acid. Therefore, the concentration of succinic acid in the surface region was higher, compared to the bulk concentration.

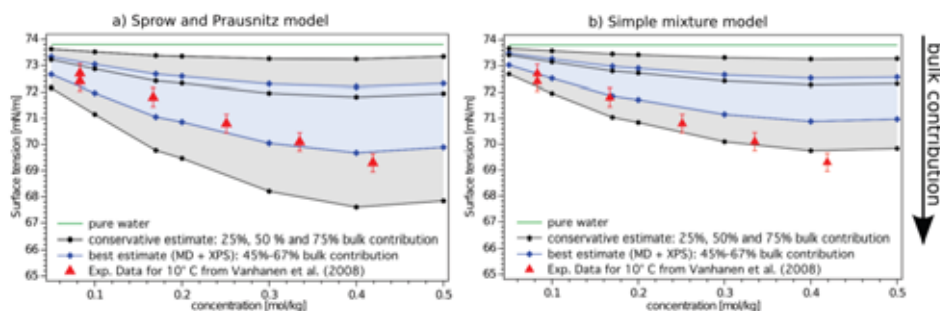


Figure 11: The surface tension values vs. bulk concentration calculated by a) the Sprow and Prausnitz model and b) the simple mixture model, using surface enrichment factors from XPS experiments and MD simulations and their comparison to experimental data at 10°C (Paper II). Red symbols: Experimental data from Vanhanen et al. (2008). Black lines: surface tension of aqueous solutions of succinic acid calculated using the conservative estimate of enrichment factors from XPS experiments. Blue lines: surface tension of aqueous solutions of succinic acid calculated by combination of XPS experiments and MD simulations. The green curve corresponds to the surface tension of pure water at 10°C.

The combination of the results obtained from the MD simulation and XPS experiments in Paper II yielded the concentration of succinic acid in the surface layer as a multiple of the known bulk concentrations (or surface enrichment factors, g) of 2-53 over the concentration range studied. These surface enrichment values were used as input for two thermodynamic models: simple mixture model and Sprow and Prausnitz model (for more information see Paper II and Sect. 2.2) to determine surface tension of the aqueous succinic acid solutions. As shown in Fig. 11, the modeled surface tension values reproduced the measured surface tension values of Vanhanen et al. (2008) with only minor deviations at higher concentrations. However, there were larger deviations between the measured surface tensions and the values derived from the simple mixture model, compared to the Sprow and Prausnitz model.

The results of Paper II showed the direct relation between surface concentration of succinic acid on the molecular level and macroscopic surface tension of aqueous solutions. Indeed, the potential of the XPS technique for further determining the surface tension of atmospherically relevant solutions was established in this section of the thesis.

Investigating the surface properties of the aqueous solutions containing succinic acid and inorganic salts ($(\text{NH}_4)_2\text{SO}_4$ or NaCl) in Paper III showed that the inorganic ions were depleted from the aqueous surface and remained in the bulk of the solution, while succinic acid molecules resided closer to the interface and dominated the solute population in the surface region. The results also indicated that the presence of strongly hydrated inorganic salt ions in the system increased the population of weakly hydrated succinic acid molecules at the surface region, where it was less favorable for the hydrated ions to reside.

Parameterization of the XPS measurements by Langmuir adsorption isotherm at any concentration of the succinic acid and $(\text{NH}_4)_2\text{SO}_4$ or NaCl yielded the surface compositions (see Table 1 of Paper III) and consequently, the surface enrichment factors (g) of the mixed solutions. The corresponding surface tension predictions as well as the measured values (see table S2 in Supporting Information of Paper III) for mixed solutions containing succinic acid and $(\text{NH}_4)_2\text{SO}_4$ are shown in Fig. 12. The modeled values are in good agreement with those obtained from direct measurements of the surface tension. As illustrated in Fig. 12, the presence of the inorganic salt increased the surface tension of the solution, compared to when only succinic acid is present as solute.

The results of Paper III suggest that common inorganic salts are capable of enhancing the surface propensity of less soluble organic species in the atmospheric droplets, thus affecting the surface tensions of aqueous droplets containing these components. Although only one atmospherically relevant organic acid was studied, the results can likely be generalized to other organic compounds with similar moderate surface activities existing in the atmosphere. Due to the enhanced concentration of the organic species on the surface of the droplets compared to the bulk phase, specifically small atmospheric droplets with

high surface-to-bulk ratio can contain significantly larger amount of the organic compound than the bulk solubility limit. Although there is a small impact of the surface composition on the CCN activation, the interphase contribution needs to be considered in the modelling of the phase-state and water content of the hygroscopic particles. This is due to the effect of the surface layer on the solubility limit.

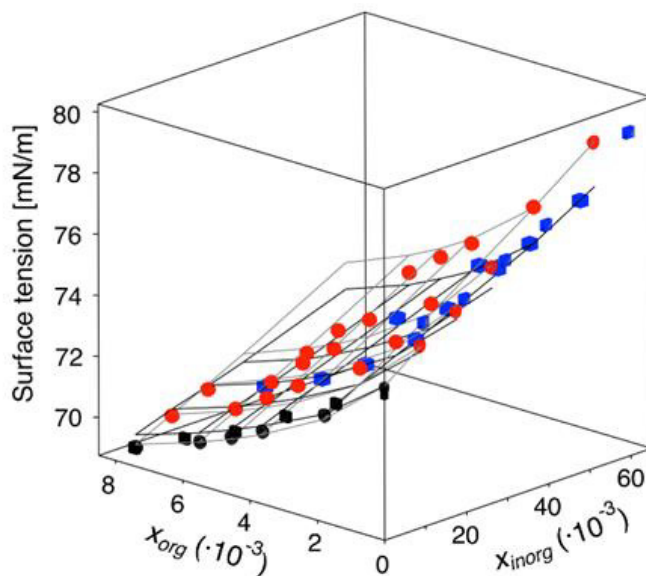


Figure 12: Surface tension as a function of solution composition (Paper III). Experimental values are shown for pure succinic acid (black spheres) and mixed with $(NH_4)_2SO_4$ (red spheres) (listed in Table S2 of the SI of paper III) or NaCl (blue boxes) (taken from Vanhanen et al. (2008)). Modeled surface tension values are presented for the mixed solutions of succinic acid and $(NH_4)_2SO_4$, where activity coefficients were calculated via the E-AIM model (black lines) and the E-UNIFAC model (grey lines).

5 Conclusions

In this dissertation, I have presented the results obtained from measurements and modeling of the CCN activation, where insoluble particles were coated with soluble species. The surface structure and surface tension of droplets containing organic or mixed organic-inorganic species with different water-solubilities have also been investigated. In the following, I outline the key conclusions addressing the scientific questions stated in chapter 1 of the thesis.

1) CCN activity of insoluble particles depends strongly on the amount of the water-soluble species that these particles acquired by e.g. condensation processes during atmospheric aging.

The results of Papers I and IV indicated that:

- a. The CCN activity of silica and BC particles increased after coating with water-soluble or sparingly soluble species. The amount of the coating on the insoluble cores governs the CCN activity of these particles, and with increasing the coating thicknesses, the CCN activity approaches that of the pure soluble component.
 - Even though the coating material is CCN inactive (e.g. oleic acid in Paper IV), it could enhance the activity of the insoluble particles via e.g. its arrangement on the surface of the insoluble cores.
- b. Controlled coating of the insoluble core by first producing the insoluble core and then coating them via condensation process (e.g. BC particles coated by organic species in Paper IV) yielded an even distribution of the coating material on the insoluble cores. Such size-independent coating was not possible for the wet-generated mixed particles (e.g. silica particles coated by soluble species in Paper I).
- c. By knowing the fraction of soluble material (coating thicknesses), which was achieved by controlled coating of insoluble particles, the shell-and-core model by Kumar et al. (2011) gave a reasonable estimate of the CCN activity for the mixed soluble-insoluble particles.
- d. The results demonstrate the importance of the insoluble particles like BC as atmospheric CCN, as in ambient conditions insoluble particles usually

form internal mixtures with other aerosol species. This highlights the need for including the impacts of co-emitted or later condensed compounds in estimates of the climate impacts of insoluble particles such as BC.

2) Molecular-level surface composition measurements can be used to yield the surface tension of the atmospheric solutions, which is required for accurate modeling of atmospheric aerosols.

The results of Papers II and III revealed that:

- a. The XPS experiments and the MD simulations showed strong enhancement of the water-soluble surfactant organics (e.g. succinic acid) at the surface of the liquid droplets compared to the bulk solution. The enhancement effect was more pronounced in the presence of highly soluble inorganic salts like NaCl and $(\text{NH}_4)_2\text{SO}_4$.
- b. The modeled surface tension of the pure organic and mixed organic inorganic mixtures, using surface enrichment factors derived from the XPS experiments were in good agreement with the experimental surface tension data. These results confirm the link between microscopic surface structure and macroscopic surface tensions of atmospheric droplets.
- c. Since liquid aerosol particles can contain larger amounts of organic compounds than the bulk solubility limit, for modeling the atmospheric aerosol, the surface layer contribution to the phase-state and water content of the particles needs to be considered. However, it did have significant impact on the CCN activation of particles consisting of the mixtures studied in this thesis.

6 Outlook

The research described in this dissertation has helped to gain more information about the relationship between aerosol particle composition and its effect on cloud condensation nuclei activity. However, there is still much to learn about cloud activation of realistic atmospheric aerosol and the processes influencing the distribution of soluble and insoluble material in the particles. Therefore, further research in this field should aim to strengthen the understanding of the interactions between aerosols physical and chemical properties, cloud activation, and climate change.

The results concerning the CCN activation of particles made of both soluble and insoluble species confirmed the impact of the soluble species that might be co-emitted with or later condensed on the insoluble particles during atmospheric aging. Therefore, considering the effect of the soluble component on the cloud activation of insoluble particles like soot and dust in modeling the aerosol-cloud interactions is of particular importance. Furthermore, it would be worth examining more complex mixtures of soluble and insoluble species and their effect on the CCN activity. The CCN activity measurements for particle made of BC and oleic acid interestingly showed that, although oleic acid is CCN inactive it could enhance the CCN activity of the BC particles. The reason could be e.g. the arrangement of the oleic acid on the surface of the BC particles. This hypothesis could be investigated by studying the molecular structure of the BC and oleic acid via e.g. molecular dynamic simulations.

The surface structure study of the aqueous nanoparticles demonstrated that the contribution of particle surface is an important parameter and needs to be considered in modeling the phase and water content of these particles, because the properties of these particles can deviate from predictions based on only bulk properties (Paper III). It should be mentioned that in addition to the thermodynamic of the condensed phase, the partitioning between the gas and condensed phase need to be considered when modeling the semi volatile species.

The focus of this thesis was on liquid-phase cloud activation of aerosol particles. In the atmosphere, ice formation in clouds is also an important process affecting the properties of clouds and precipitation formation. As is shown in the Fig. 1, by the presence of BC in the snow, it acts as a positive radiative forcer. Therefore, it is worth to examine if coating of BC by other substances can change its radiative

properties. On the other hand, coating of originally insoluble particles such as BC with soluble material has been hypothesized to reduce the Ice Nuclei (IN) activity of these particles (Möhler et al. 2005). Although, for example Friedman et al. (2011) showed that coating by water soluble substances cannot significantly alter the ice nucleation behavior of soot particles, the effect of soluble species on the IN ability of the other insoluble particle (e.g. dust) needs to be further investigated.

7 Acknowledgements

I would first like to thank Ilona Riipinen, HC Hansson and Ari Laaksonen to have provided me this opportunity to start my research in atmospheric sciences as a PhD student.

I am specifically grateful for my main supervisor, Ilona Riipinen for always being available to guide me, for her great and helpful ideas and advices. Ilona, you have supported me academically and emotionally through the rough road during my PhD studies. Your enthusiasm about the research encouraged me during my studies.

I would also like to thank my other supervisors, Ari Laaksonen and Annele Virtanen to provide me this opportunity to do my experiments in the Aerosol Physics lab in Kuopio campus of the University of Eastern Finland. Annele, I am grateful for your great ideas and supports during my experiments in the lab. Many thanks to the other people in the Aerosol Physics lab in Kuopio, especially Pasi Miettinen, Arttu Ylisirniö, Angela Buchholz and Helmi Keskinen for their great help during my measurements.

I also express my great gratitude to the PhD students, postdocs and other personnel in the ACES department, especially “Atmospheric Science Unit (Luftlab)” for being a good company, influencing and enhancing my research and helping me enjoying my time during my studies. I thank Ulla Wideqvist to help me doing my experiments in the lab. I would also like to thank the advisors of my PhD committee, Johan Ström and Margareta Hansson for all their help during my studies. Special thanks to Johan Ström for being available to help me with his valuable ideas and comments to improve the quality of my papers and thesis. Special thanks to Asa, Narges and Zahra to be involved in my happiness and sadness moments at the ACES.

Last but not least, I would like to thank my dear family, my mother, father, brother and sisters to always support and encourage me, my husband, Pouria, to be a part of my life and making me believe in myself and finally my son, Rayan, to come to my life and fill it with more love, joy and happiness.

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