COEXISTENCE OF THREE LIQUID PHASES IN INDIVIDUAL

ATMOSPHERIC AEROSOL PARTICLES

by

Yuanzhou Huang

B.A. Sc., University of Alberta, 2018

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

The Faculty of Graduate and Postdoctoral Studies

(Chemistry)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

December 2020

©Yuanzhou Huang, 2020

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the thesis entitled:

Coexistence of three liquid phases in individual atmospheric aerosol particles

submitted by	Yuanzhou Huang	in partial fulfillment of the requirements for
the degree of	Master of Science	
in	Chemistry	
Examining Com	mittee:	
Allan K. Bertra	m, Chemistry, UBC	
Supervisor		
Gren Patey, Ch	emistry, UBC	
Supervisory Co	ommittee Member	
Russ Algar. Ch	emistry. UBC	
Supervisory Co	ommittee Member	

Abstract

Aerosol particles are ubiquitous in the atmosphere and play an important role in air quality and the climate system. Atmospheric particles can contain mixtures of primary organic aerosol (POA), secondary organic aerosol (SOA), and secondary inorganic aerosol (SIA). To predict the role of such complex multicomponent particles in air quality and climate, information on the number and types of phases present in the particles is needed. However, the phase behavior of such particles has not been studied in the laboratory, and as a result, remains poorly constrained. Here we show that POA+SOA+SIA particles can often contain three distinct liquid phases: a low polarity organic-rich phase, a higher polarity organic-rich phase, and an aqueous inorganic-rich phase. Based on our results, when the elemental oxygen-to-carbon (O:C) ratio of the SOA is less than 0.8, which is common in the atmosphere, three liquid phases will often coexist within the same particle over a wide relative humidity range. In contrast, when the O:C ratio of the SOA is greater than 0.8, three phases will not form. We also demonstrate, using thermodynamic and kinetic modelling, that the presence of three liquid phases in such particles impacts their equilibration timescale with the surrounding gas phase and their ability to act as nuclei for liquid cloud droplets. A framework is also presented for predicting when and where three liquid phases will form in the atmosphere. Three phases will likely also impact the reactivity of these particles and the mechanism of SOA formation and growth in the atmosphere. These observations provide fundamental information necessary for improved predictions of air quality and aerosol indirect effects on climate.

Lay Summary

The research conducted in this thesis is to study the phase behavior of atmospheric aerosol particles to improve the predictions of air quality. Atmospheric particles can have both the heating and cooling effects on the climate by absorbing or scattering sunlight. To predict the impacts of aerosols on air quality and climate, information on the number and types of phases present in the particles is crucial since they can govern important aerosol processes and properties including aerosol growth and evaporation, optical properties, reactivity, and the ability of aerosols to act as nuclei for cloud droplets. In this thesis, we demonstrated the phase behavior, especially the coexistence of three liquid phases in the atmospheric particles by using a solvatochromic dye with fluorescence microscopy. Using thermodynamic and kinetic modelling, the impacts of the coexistence of three liquid phases on the atmosphere and climate were also discussed.

Preface

The details of my contribution to these three research chapters are as the following:

- Discussion with my supervisor Dr. Allan K. Bertram to identify research topics and designed the research with Dr. Allan K. Bertram and Dr. Fabian Mahrt
- Prepared all the samples for the experiments, including building up the environmental chamber to generate α-pinene SOA
- Performed the measurement on phase behavior of particles containing a mixture of POA, SOA, and SIA with trace amount of Nile red as a function of RH using the fluorescence microscope
- Collaborated with Dr. Manabu Shiraiwa (University of California, Irvine, CA, USA) and Dr. Andreas Zuend (McGill University, Montreal, QC, Canada) to set up and perform kinetic and thermodynamic simulations to study the impacts of particle phase behavior
- Conducted data analysis with the help of Shaun Xu
- Prepared all the figures and tables for the manuscript with the help of Dr. Fabian Mahrt
- Shared writing of the manuscript with Dr. Allan K. Bertram and Dr. Fabian Mahrt

Table of Contents

Abstractiii
Lay Summaryiv
Prefacev
Table of Contentsvi
List of tablesviii
List of Figuresix
List of Symbolsxi
List of Acronymsxiii
Acknowledgementsxiv
Dedicationxvi
Chapter 1: Introduction1
1.1. Atmospheric aerosols1
1.1.1. Types and internal mixing of atmospheric aerosols
1.1.1.1. Primary organic aerosols (POA)
1.1.1.2. Secondary aerosols
1.1.1.3. Internal mixing of POA+SOA+SIA
1.1.2. Importance of POA, SOA, and SIA particles
1.2. Phase behavior of atmospheric aerosols
1.3. Previous studies on the phase behavior of atmospheric aerosol particles containing POA,
SOA, and SIA5
1.4. Focus of this thesis
Chapter 2: Materials and Methods7
2.1. Overview
2.2. The generation of particles containing a mixture of squalane, 1 out of 21 different
oxygenated organic compounds, ammonium sulfate, and trace amounts of Nile red9
2.3. The generation of particles containing a mixture of squalane, secondary organic aerosol
generated in the laboratory, ammonium sulfate, and trace amounts of Nile red10
2.4. Fluorescence microscopy

Chapter 3: Results and Discussions: Phase Behavior of Atmospheric Aerosol Particles
Containing POA+SOA+SIA16
3.1. Phase behavior of atmospheric aerosol particles containing squalane, an SOA proxy,
ammonium sulfate, and trace amount of Nile red16
3.2. Phase behavior of particles containing mixtures of POA, SOA generated in the laboratory,
ammonium sulfate, and trace amount of Nile red26
Chapter 4: Atmospheric Implications of the Phase Behavior of POA+SOA+SIA Particles30
4.1. Implications for the mechanism of SOA formation and growth in the atmosphere30
4.2. Implications for the reactive uptake of N ₂ O ₅
4.3. Implications for the equilibration timescales for POA+SOA+SIA particles
4.4. Implications for the POA+SOA+SIA particles to activate into clouds
Chapter 5: Conclusion and Future Research Work
5.1. Phase behavior of POA+SOA+SIA particles and atmospheric implications
5.2. Consideration of future research work
5.2.1. Morphology of aerosol particles after liquid-liquid phase separation
5.2.2. POA with higher O:C values
Bibliography
Appendices
Appendix A: Generation of SOA using environmental chamber46
A.1. UBC environmental chamber overview
A.2. Injection system
A.3. Environmental chamber47
A.4. Aerosol characterization and collection
Appendix B52
Appendix C: Models for atmospheric implications of phase behavior of POA+SOA+SIA
particles55
C.1. Calculation of the equilibrium timescales between POA+SOA+SIA particles and
surrounding organic vapors and water vapor
C.2. Thermodynamic equilibrium predictions of POA+SOA+SIA particles activating into
cloud droplets
Bibliography for Appendices67

List of Tables

Table 2.1. Chemical structure, formula, excitation and emission wavelength for Nile red7
Table 2.2. Oxygenated organic compounds used in this experiment as proxies for atmospheric
SOA particles and their molecular formula, chemical structure (Obtained from Sigma-Aldrich),
O:C value and functional groups12
Table A1. Instrumentation used for gas phase analyzing and aerosol characterization for the UBC
environmental chamber
Table B1. Summary of results from studies with particles containing a mixture of squalane (proxy
for POA), 1 out of 21 different oxygenated organic compounds (proxy for SOA), and ammonium
sulfate (a major type of SIA in the atmosphere)
Table B2. Summary of results from studies with particles containing α -pinene SOA, ammonium
sulfate (a major type of SIA in the atmosphere), and either squalane or lubricating oil as a proxy
for POA54
Table C1. Fourteen different semi-volatile reaction products from the oxidation of α -pinene used
to represent SOA in this study

List of Figures

Figure 1.1. Mass percentage of POA, SOA, and SIA in urban and rural/remote areas based on
previous field measurements
Figure 1.2. Formation and internal mixing of atmospheric aerosol particles
Figure 1.3. Schematic diagram of the aerosol particle growth and their effects on climate5
Figure 2.1. Fluorescence microscopy images of organic particles containing the solvatochromic
dye Nile red and emission wavelengths
Figure 2.2. Experimental setup for the aerosol phase behavior measurement15
Figure 3.1. Fluorescence microscopy images of internally mixed particles containing squalane,
oxygenated organic compounds, and ammonium sulfate18
Figure 3.2. Illustration of the phase behavior of particles containing mixtures of primary organic
aerosol (POA), secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA) at
different RH values
Figure 3.3. Two liquids-three liquids separation relative humidity (2L-3L SRH) and crystallization
relative humidity (CRH) of particles containing squalane (POA proxy), a single oxygenated
organic compound (SOA proxy, 21 distinct cases) and ammonium sulfate (SIA proxy)21
Figure 3.4. Percentage of particles with a core-shell-shell morphology after the formation of three
liquid phases. In cases where a core-shell-shell morphology was not observed, a core-crescent-
shell morphology was observed
Figure 3.5. Comparison of the measured two liquids-three liquids separation relative humidity
(2L-3L SRH) values from the current study with the one liquid-two liquids separation relative
humidity (1L—2L SRH) reported by You et al

Figure 3.6. Fluorescence microscopy images of internally mixed particles containing squalane, α -
pinene SOA generated in the environmental chamber, and ammonium sulfate26
Figure 3.7. Fluorescence microscopy images of internally mixed particles containing lubricating
oil, α-pinene SOA generated in the environmental chamber, and ammonium sulfate28
Figure 4.1. The 2% equilibration timescale, $\tau_{2\%}$, for POA+SOA+SIA particles. The $\tau_{2\%}$ values
correspond to the characteristic time for a particle to reach a diameter within 2% of the new
equilibrium diameter after an initial perturbation of the gas phase concentrations
Figure 4.2. Thermodynamic equilibrium predictions for POA+SOA+SIA particles with a 50 nm
dry diameter during growth and activation into cloud droplets
Figure A1. Overview of the UBC environmental chamber setup, consisting of an injection system,
an environmental chamber, and the aerosol characterization and collection system as indicated by
the dashed boxes
Figure A2. Diagram of the injection systems of the environmental chamber
Figure A3. Ozone half-life within the UBC environmental chamber given by the change in ozone
concentration after stopping injection, while maintaining flows into and out of the environmental
chamber at constant values
Figure C1. Equilibrium phase compositions predicted by the AIOMFAC-based thermodynamic
gas-particle partitioning model for a dry mass fraction of 33.3% for each of squalane, α -pinene
SOA, and ammonium sulfate
Figure C2. Equilibrium phase compositions predicted by the thermodynamic gas-particle
partitioning model assuming ideal mixing in the liquid aerosol phase and a dry mass fraction of
33.3% for each of squalane, α-pinene SOA, and ammonium sulfate

List of Symbols

a_w	water activity
α	aqueous inorganic-rich phase
β	higher polarity organic-rich phase
γ	lower polarity organic-rich phase
С	concentration
<i>c^g</i>	mass concentration per unit volume of air for the gas phase ($\mu g/m^3$)
c^{α}	mass concentration per unit volume for the aqueous inorganic-rich phase ($\mu g/m^3$)
c^{β}	mass concentration per unit volume for the higher polarity organic-rich phase ($\mu g/m^3$)
C^{γ}	mass concentration per unit volume for the lower polarity organic-rich phase ($\mu g/m^3$)
CRH	crystallization relative humidity (%)
D	wet particle diameter (nm)
З	dielectric constant
σ	surface tension (nN/m)
λ_{ext}	excitation wavelength (nm)
λ_{em}	emission wavelength (nm)
MW	molecular weight (g/mol)
<i>0:</i> C	oxygen-to-carbon elemental ratio
P^0	pure compound vapor pressure (Pa)
ppb	parts per billion
ρ	density (g/ml)

R	universal gas constant
RH	relative humidity (%)
SRH	separation relative humidity (%)
$ au_2\%$	2% equilibration timescale (s)
Т	absolute temperature (K)
t	time (s)

wt% weight percent

List of Acronyms

AIOMFAC	Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients
CCN	cloud condensation nuclei
CPC	condensation particle counter
DMA	differential mobility analyzer
IN	ice nuclei
KM-GAP	kinetic multi-layer model of gas-particle interactions in aerosols and clouds
LV-OOA	low volatility oxygenated organic aerosol
MF	mass flow
OPC	optical particle counter
POA	primary organic aerosol
SOA	secondary organic aerosol
SIA	secondary inorganic aerosol
SV-OOA	semi-volatile oxygenated organic aerosol
SMPS	scanning mobility particle sizer
VOC	volatile organic compound
UV	ultraviolet light range

Acknowledgements

After finishing my Bachelor of Applied Science degree at the University of Alberta in April 2018, I made a very important decision to relocate from Edmonton to the beautiful coastal city of Vancouver to pursue a Master of Science degree at the University of British Columbia. Completing the master's thesis requires a lot of effort and this cannot be done successfully without the generous support from my supervisor, my family, and all the friends I made in Vancouver.

Firstly, I would like to thank my supervisor, Dr. Allan K. Bertram. Before entering the graduate school, I always wish and hope to have a nice and supportive supervisor and choosing to join Allan's research group is one of the best decisions I have made throughout my academic career! Thank you Allan for the valuable advice, suggestions and technical support you provided whenever I met challenges in my research and experiments. Moreover, the care, kindness and understandings you showed me when I met troubles warmed my heart and helped me overcome the difficulties and hard times living abroad in a new city.

Secondly, I would like to thank Dr. Fabian Mahrt, the new postdoc joining the Bertram's group in January 2020. Working with you is both pleasant and fun! Your knowledge in atmospheric aerosols, skills in writing manuscript and suggestions on improving figures and diagrams helped me to be successful as a future chemist. Thank you Fabian for your constant support editing and proofreading my manuscript for publication and of course the fun time we had visiting local breweries, dining out, hiking, and road trips. I would also like to thank Dr. Elena Polishchuk, coordinator of the UBC bioservice laboratory. Elena is such a nice lady who is always wearing a smile on her face and willing to help students. Without her support on fluorescence microscopy, it will be impossible for me to finish my thesis and submit my paper for publication.

Thirdly, I would like to thank the Bertram group members who provided a friendly, welcoming and supportive atmosphere. Jesse, Kris, Adrian, Soleil, Julia, Elli, Erin, Jingwei, Yu, Shaun, Yi, Fabian and Anand, it is really fun and happy to work with you. I would also like to thank Des Lovrity from the mechanical shop and Benny Ng from the electric shop who are always efficient in finishing the work requests I constantly submitted.

Finally, my biggest thank to my family and friends who support me wholeheartedly during my graduate study and research at UBC. Thank you Shaun, Jingwei, Fabian, Elli and Anand for the various extracurricular activities we had together---it is really a great fun to explore different restaurants in the city, tasting flights of beer and cider, cooking delicious cuisines, and playing Uno and Monopoly with you guys! I would like to thank Tingting Zhao, Siyu Miao and Xianzhe Yin from our department. You are really awesome friends who are always willing to chatting and sharing stories during our spare time. I would also like to say thank you to Shujing Zhao, my best friend in China who constantly has an open ear to me and encourages me when I meet difficulties. Last but not least, I would like to say thank you to my cousins, parents and grandparents. Your care and love are the biggest support for me to live a happy and enjoyable life in Canada!

To my parents, Weifan Zhou and Lin Huang, and to my grandparents, Jingxi Zhou, Lingyu Cui, and Shufu Lin, and to my grandpa Zheng Huang, a World War II veteran who passed away peacefully in April 2019.

Chapter 1. Introduction

1.1 Atmospheric aerosols

Atmospheric aerosols are airborne suspensions of liquid or solid particles in the Earth's atmosphere, with particle diameters in the range of 10^{-5} to 1 µm (1) and are among the central topics in current environmental research because of their importance for atmospheric chemistry and physics, the biosphere, climate and public health (2). Based on the sources of these atmospheric aerosols, they can be classified as natural or anthropogenic. Natural sources include volcanoes, forest fires and ocean spray while the anthropogenic sources include fuel combustion, transportation, industrial processes and solid waste disposal (1).

1.1.1 Types and internal mixing of atmospheric aerosols

A large fraction of atmospheric aerosols can be classified as primary organic aerosol (POA), secondary organic aerosol (SOA), and secondary inorganic aerosol (SIA), especially for sizes less than 1 μ m, which are of interest in this study. In Fig. 1.1, the mass percentage of POA, SOA, and SIA in the urban and rural/remote areas are illustrated based on several field studies. For both urban and rural areas, the SIA accounts for more than 50% of the total aerosol mass, while in urban environments, there are more POA and less SOA compared with rural areas.





Rural/Remote Areas

Figure 1.1. Mass percentage of POA, SOA, and SIA in urban and rural/remote areas based on previous field measurements. The values are obtained from Zhang et al (3). The split in each of the box represents the mean value of the mass percentage based on measurements from multiple locations in the world. The error bar represents twice the standard deviation according to those measurements.

1.1.1.1 Primary organic aerosols (POA)

Primary atmospheric aerosols are directly emitted as liquids or solids from sources such as biomass burning and incomplete combustion of fossil fuels. The source of the POA can be further split up into coal combustion-related organic aerosols, biomass burning organic aerosols, cooking-related organic aerosols, and traffic-related hydrocarbon-like organic aerosols (4). According to a field measurement in UK, for the POA, 40% were related to the traffic sources, 34% were related to the cooking source, while 26% correspond to solid fuel aerosols (5).

1.1.1.2 Secondary aerosols

Secondary aerosols are formed by the oxidation of gas phase vapors followed by nucleation and condensation. Alternatively, secondary aerosols can be formed by heterogeneous and multiphase chemical reactions (6). There are two types of secondary aerosols: secondary organic aerosols (SOA) and secondary inorganic aerosols (SIA). Natural sources such as vegetation and

anthropogenic sources such as transport emit volatile organic compounds into the atmosphere, which can be oxidized into SOA. Examples of volatile organic compounds from natural sources including α -pinene and sesquiterpenes such as β -caryophyllene, while toluene is an example of a volatile organic compound from anthropogenic sources that lead to SOA. Components of SIA include sulfate, nitrate, and ammonium. Secondary aerosols account for a significant fraction of ambient tropospheric aerosols (6).



Figure 1.2. Formation and internal mixing of atmospheric aerosol particles. POA corresponds to primary organic aerosols, SOA corresponds to secondary organic aerosols, and SIA corresponds to secondary inorganic aerosols. The POA particles are shown in green, the SOA particles are shown in red, while the SIA particles are shown in grey. Both anthropogenic sources such as fuel combustion and natural sources such as tree emissions are included. The formation of secondary aerosols involve the oxidation of gas phase vapors and multiphase chemical reactions.

1.1.1.3 Internal mixing of POA+SOA+SIA

As shown in Fig. 1.2, in the atmosphere, POA, SOA, and SIA can become internally mixed within the same particle by coagulation, gas-particle partitioning, cloud processing, and multiphase chemical reactions (7–9). Previous studies have shown that these processes typically occur on the order of hours, and as a result, individual particles containing mixtures of POA, SOA, and SIA are expected to be important in the atmosphere (9–13). We refer to these internally mixed aerosols as POA+SOA+SIA particles in this research.

1.1.2 Importance of POA, SOA, and SIA particles

Atmospheric aerosols can affect public health. For example, numerous studies have shown that the concentrations of aerosols are correlated with severe negative health effects such as cardiovascular, respiratory diseases and cancer (2, 14). Recent research showed that the atmospheric aerosols result in over 3 million premature deaths globally per year (15).

In addition, aerosol particles can also have significant effects on climate, which will further affect the atmospheric and oceanic circulation and biogeochemical cycles (2). The effects of aerosols on climate can be classified as either direct or indirect (Fig. 1.3). Atmospheric particles can have direct effects on climate by the scattering and absorption of solar radiation. They can also have indirect effects by acting as cloud condensation nuclei (CCN) or ice nuclei (IN), which leads to a change in cloud properties and precipitation, and scatter solar radiation (Fig. 1.3).



Figure 1.3. Schematic diagram of the aerosol particle growth and their effects on the climate. The figure is based on Pöschl (2005) and Renbaum-Wolff et al. (2013).

1.2 Phase behavior of atmospheric aerosols

To predict the impacts of aerosols on air quality and climate, information on the number and types of phases present in atmospheric aerosol particles is crucial. This is because the number and types of phases govern important aerosol processes and properties including aerosol growth and evaporation, optical properties, reactivity, and the ability of aerosols to act as nuclei for cloud droplets (16–22).

1.3 Previous studies on the phase behavior of atmospheric aerosol particles containing POA, SOA, and SIA

Previous studies on the phase behavior of atmospheric particles have focused on pure SIA (23), pure SOA (19, 24), mixtures of POA and SOA (25–30), and mixtures of SOA and SIA (17, 18, 20). Studies with mixtures of POA and SOA have shown that one or two liquid phases can form

in individual particles, depending on the properties of the POA and SOA and the ambient relative humidity (RH) (25–28, 30). Similarly, studies with mixtures of SOA and SIA revealed that one or two liquid phases can form depending on the SOA and SIA properties and the RH (17, 18, 20). Surprisingly, in a recent study, three liquid phases were observed in some mixtures of SOA and SIA proxies (31). However, two liquid phases were reported in the majority of these experiments, and conditions favoring three liquid phases were unclear and not elucidated.

The phase behavior of particles containing POA, SOA, and SIA have so far only been investigated using molecular dynamics simulations of nanoparticles less than 10 nm in diameter (32). Three separate chemically distinct domains were observed in these simulations, but laboratory studies are needed in order to confirm these predictions, especially for particles with larger diameters, which make up the vast majority of the mass of atmospheric particulate matter.

1.4 Focus of this thesis

This thesis focuses on laboratory studies of the phase behavior of POA+SOA+SIA particles and the implications of this phase behavior. In chapter 2, the materials and methods for the laboratory studies are discussed. In chapter 3, the results and discussions are presented from the laboratory studies. In this chapter we show that these particles can often contain three distinct liquid phases: a low polarity organic-rich phase, a higher polarity organic-rich phase, and an aqueous inorganic-rich phase. In chapter 4, the atmospheric implications of phase behavior of POA+SOA+SIA particles are discussed. In chapter 5, some possible future research topics are introduced and discussed.

Chapter 2. Materials and methods

2.1 Overview

In the current study, a solvatochromic dye and fluorescence microscopy are used to determine the phase behavior of POA+SOA+SIA particles as a function of RH. Although solvatochromic dyes have been used widely in biology and chemistry (e.g. ref 33), they have, so far, not been used to characterize the phase behavior of atmospheric aerosols. The solvatochromic dye used in the current study was Nile red (9-diethylamino-5H-benzo[α]phenoxazine-5-one)(Table 2.1).

Table 2.1. Chemical structure, formula, excitation and emission wavelength for Nile red. λ_{ext} and λ_{em} represent the excitation and emission wavelength.

Chemical name	Nile red		
IUPAC name	9-diethylamino-5H-benzo[α]phenoxazine-5-one		
Empirical formula	$C_{20}H_{18}N_2O_2$		
Chemical structure	H ₃ C N O O H ₃ C		
Fluorescence properties	$\begin{array}{l} 487 \text{ nm} \leq \lambda_{ext} \leq 489 \text{ nm} \\ 530 \text{ nm} \leq \lambda_{em} \leq 550 \text{ nm} \text{ (Non-polar)} \\ \lambda_{em} \geq 590 \text{ nm} \text{ (Polar)} \end{array}$		

Nile red is a solvatochromic dye that fluoresces at different wavelengths depending on the polarity of the surrounding chemical environment (34). For our experimental conditions, Nile red fluoresced green to yellow in a low polarity organic-rich phase and orange to red in a higher polarity organic-rich phase (Fig. 2.1). On the other hand, Nile red was non-fluorescent in an aqueous phase due to its low solubility and quantum yield in water (34).



Figure 2.1. Fluorescence microscopy images of organic particles containing the solvatochromic dye Nile red and emission wavelengths. The chemical composition, oxygen-to-carbon (O:C) ratio, and dielectric constant (ε) of the particles are indicated above each column. The O:C and ε are included as indicators of the polarity of the particles. Values for ε correspond to values at a temperature of 298 K and are taken from the literature: Sedrez et al. (35) (squalane); Circular et al. (36) (diethyl sebacate); Sarode et al. (37) (poly (propylene glycol) 425); Kalakkunnath et al. (38) (poly (ethylene glycol) diacrylate); Sengwa et al. (39) (poly (ethylene glycol) 300). The images were recorded at relative humidities of 70% (top row) and 30% (bottom row), respectively. The dashed boxes roughly indicate the emission wavelength of the Nile red when embedded within the organic particles. For the low polarity organic phase, Nile red fluoresces green to yellow, and for the higher polarity organic phase, Nile red fluoresces orange to red.

In the first series of experiments, we studied particles containing a mixture of squalane (proxy for POA), 1 out of 21 different oxygenated organic compounds (proxy for SOA), ammonium sulfate (a major type of SIA in the atmosphere), and trace maount of Nile red. In Section 2.2 the generation of these particles are discussed. In the second series of experiments, we studied particles containing mixtures of POA, secondary organic aerosol generated in the laboratory, ammonium sulfate, and trace amounts of Nile red. In section 2.3. the generation of these particles are discussed. In section 2.4. the fluorescence microscopy measurements are discussed.

2.2 The generation of particles containing a mixture of squalane, 1 out of 21 different oxygenated organic compounds, ammonium sulfate, and trace amounts of Nile red

Two solutions were first generated gravimetrically: 1) a solution of squalane (2 wt %) and Nile red (9-diethylamino-5H-benzo[α]phenoxazine-5-one, 10 mg L⁻¹) dissolved in hexane, and 2) a solution containing 1 out of 21 different oxygenated organic compounds (1 wt %) and ammonium sulfate (1 wt %) dissolved in purified water (Millipore, resistivity \geq 18.2 M Ω cm). Next, the solutions were nebulized (Meinhard, TR-30-C0.5) consecutively onto a siliconized hydrophobic glass slide (12 mm diameter, Hampton Research, HR3-277). After nebulization, the solvents (hexane and water) evaporated, leaving behind particles with diameters between 50 to 70 µm, containing a mixture of squalane, the specific SOA proxy compound, ammonium sulfate, and trace amounts of Nile red. The 21 different types of oxygenated organic compounds that have been used as proxies for atmospheric SOA to study the phase behavior of aerosol particles are shown in Table 2.2, including their formula, chemical structures, functional groups and O:C ratio. These compounds cover the range of average O:C values of most atmospheric SOA particles, which is approximately from 0.1 to 1.0 (40–42).

2.3. the generation of particles containing mixtures of POA, secondary organic aerosol generated in the laboratory, ammonium sulfate, and trace amounts of Nile red

Ozonolysis of α -pinene was carried out to produce SOA particles at mass loadings between 60 and 80 µg m⁻³ in an environmental chamber (see Appendix A). SOA particles were continuously collected from the environmental chamber onto hydrophobic glass slides coated with FluoroPel 800 (Cytonix) for ~24 h by inertial impaction, using a multi-orifice single-stage impactor (MSP Corporation) operated at a constant flow rate of 15 L min⁻¹ and a cut-size below 0.18 µm (aerodynamic particle diameter). A solution of squalane (2 wt %) or 5W30 lubricating oil (2 wt %) and Nile red dissolved in hexane was also generated. After collecting the SOA, solutions of ammonium sulfate and squalane (POA proxy) or lubricating oil (POA proxy) were nebulized consecutively onto the same glass slides, similar to the method discussed above.

2.4. fluorescence microscopy

The phase behavior of the particles was investigated using an inverted fluorescence microscope (Olympus, Model IX70), equipped with a mercury arc lamp (USH-103D, Ushio) as the light source, and coupled to an RH-controlled flow cell (Fig. 2.2). Images were captured with a color-CCD camera (Olympus, Model DP80) using a U-MNIB fluorescence filter cube (Olympus), resulting in excitation at $470 \le \lambda \le 490$ nm and emission at $\lambda > 515$ nm, where λ is the wavelength of the photons. Nile red has an excitation wavelength between 487 nm and 489 nm, and an emission maxima wavelength between approximately 530 nm and 550 nm in most nonpolar solvents, and an emission maxima wavelength ≥ 590 nm for polar substances (34). For all our experiments the exposure time (excitation time) was approximately 500-800 ms.

For the measurement of the phase behavior of aerosol particles, the slide containing the particles was located within the RH-controlled flow cell (Fig. 2.2). The temperature of the flow cell was

maintained constant at 295 \pm 1 K in all the experiments and continuously monitored by a thermocouple (T-type, OMEGA, Model FF-T-20-100). The RH was controlled by continuously passing a mixture of humid and dry nitrogen gas through the flow cell (total flow of 1.2 L min⁻¹). The dew point of the gas stream was measured downstream of the flow cell using a dew point hygrometer (General Eastern, Model M4/E4). The RH of the gas was calculated from the dew point and the temperature of the flow cell. Calibration of the RH was achieved by measuring the deliquescence RH of pure ammonium sulfate particles and comparison to values reported in the literature (80.0±1.4% at 295 K,ref 23).

At the beginning of each phase separation experiment, the particles were equilibrated at around 95% RH for a period of approximately 10 minutes. Next, the RH was decreased at a ramp rate of approximately 0.5% RH min⁻¹ until one of the following conditions occurred: phase separation within the particle was observed, the particle effloresced, or the RH of the flow cell was less than 0.5%. During the experiments movies were captured at 9 frames per second, using the colored CCD-camera controlled through the CellSens software (OLYMPUS, Dimension Version 1.18) and the focus of the microscope was manually adjusted so the focal plane corresponded to the interior of the particles on the glass slide. From the fluorescence images, the number and types of phases in the particles were determined. When the RH of the flow cell decreased, the size of the particles on the hydrophobic glass slide also decreased and shrank due to the loss of water, and as a result, some particles that were in focus at higher RH values became out of focus at lower RH values.

Table 2.2. Oxygenated organic compounds used in this experiment as proxies for atmospheric

 SOA particles and their molecular formula, chemical structure, O:C value and functional groups.

 The structures are obtained from Sigma-Aldrich website.

Compounds	Chemical Formula	Chemical Structure	0:C	Functional Groups
2,5-hexanediol	C ₆ H ₁₄ O ₂	H ₃ C H ₃ C OH CH ₃	0.33	alcohol
Poly (Propylene) glycol 425 (PPG-425)	$C_{3n}H_{6n+2}O_{n+1} \\$	CH ₃ H↓O↓↓OH	0.38	alcohol, ether
Suberic acid monomethyl ester	C9H16O4	HO	0.44	carboxylic acid, ester
Poly (Ethylene) glycol diacrylate (PEG Diacrylate)	$C_{2n+6}H_{4n+6}O_{n+3}$	H_2C H_2C H_2C H_2C H_2	0.50	ester, ether, C-C double bond
1,2,6-trihydroxyhexane	C ₆ H ₁₄ O ₃	он но ОН	0.50	alcohol
Poly (Ethylene) glycol 600 (PEG-600)	$C_{2n}H_{4n+2}O_{n+1}$	H O H	0.54	alcohol, ether
Vanillymandelic acid	C ₉ H ₁₀ O ₅	НО ОН ОН	0.56	alcohol, aromatic, carboxylic acid, ether
2,5-hydroxybenzoic acid	C7H6O4	НО ОН	0.57	alcohol, aromatic, carboxylic acid

Compounds	Chemical Formula	Chemical Structure	0:C	Functional Groups
Diethylmalonic acid	C7H12O4	О НО Н ₃ С — СН ₃	0.57	carboxylic acid
3,3-dimethylglutaric acid	C7H12O4	O HO H ₃ C CH ₃ OH	0.57	carboxylic acid
Poly (Ethylene) glycol 300 (PEG-300)	$C_{2n}H_{4n+2}O_{n+1} \\$	н↓о∽} _п он	0.58	alcohol, ether
Poly (Ethylene) glycol 200 (PEG-200)	$C_{2n}H_{4n+2}O_{n+1}$	н ↓о пон	0.63	alcohol, ether
Poly (ethylene glycol) bis (carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$		0.63	ester, ether, carboxylic acid
2-methylglutaric acid	$C_{6}H_{10}O_{4}$	но О СН ₃ ОН	0.67	carboxylic acid
2,2-dimethylsuccinic acid	C ₆ H ₁₀ O ₄	HO O H3C CH ₃	0.67	carboxylic acid
Diethyl-L-tartrate	$C_8H_{14}O_6$	H ₃ C O O CH ₃	0.75	alcohol, ester
Glutaric acid	$C_5H_8O_4$	но	0.80	carboxylic acid

Compounds	Chemical Formula	Chemical Structure	0:C	Functional Groups
Levoglucosan	$C_{6}H_{10}O_{5}$	OH OH OH OH OH	0.83	alcohol, ether
Glycerol	C ₃ H ₈ O ₃	но он	1.0	alcohol
Maleic acid	C4H4O4	но Он	1.0	carboxylic acid, C-C double bond
Citric acid	C ₆ H ₈ O ₇		1.17	alcohol, carboxylic acid



Figure 2.2. (a). Experimental setup for the aerosol phase behavior measurement. MF represents mass flow. Figure courtesy from Natalie R. Smith. (b). The fluorescence microscopy setup and schematic diagram illustrating the operating principle. Figure courtesy from Olympus website.

Chapter 3. Results and discussions: phase behavior of atmospheric aerosol particles containing POA+SOA+SIA

3.1 Phase behavior of atmospheric aerosol particles containing squalane, an SOA proxy, ammonium sulfate, and trace amounts of Nile red

As mentioned above, in the first series of experiments, we studied particles containing a mixture of squalane (proxy for POA), 1 out of 21 different oxygenated organic compounds (proxy for SOA), and ammonium sulfate (a major type of SIA in the atmosphere). Squalane has an elemental oxygen-to-carbon (O:C) ratio of 0, similar to POA from diesel and gasoline engines (22, 32). The 21 oxygenated organic molecules chosen for this study have O:C ratios ranging from 0.33 to 1.17 (Table 2.2), covering the range of average O:C values of most atmospheric SOA particles (33).

One of the striking results from our study is that when the O:C value of the SOA proxy was less than 0.8, in almost all cases (14 out of 16 cases), we observed three phases coexisting within the same particle over a wide RH range. Shown in Fig. 3.1a-b are images for two of these cases as the RH was decreased from ~95% to 0%. At 90% RH, the particles contained two liquid phases, namely a low polarity organic-rich phase (indicated by the green to yellow color) and an aqueous phase (indicated by the dark color or absence of fluorescence). We refer to the aqueous phase as an aqueous inorganic-rich phase since ammonium sulfate, which has a high solubility in water, will most likely partition predominantly into this phase. At 70% and 50% RH, the particles contained three liquid phases, namely a low polarity organic-rich phase (indicated by the orange to red color). At 30% and 0% RH, ammonium sulfate was predominately present in crystallized form inside the particle, as

indicated by the irregular structure of the particle cores, resulting in particles containing two liquid phases and one crystalline phase.

In contrast to the cases for O:C less than 0.8, when the O:C of the SOA proxy was greater than or equal to 0.8, three liquid phases were never observed. Shown in Fig. 3.1c are images for one of these cases, as the RH was decreased from ~95% to 0%. For this case, the particles contained two liquid phases for the full RH range investigated. At 90% to 30% RH the particles contained a low polarity organic-rich phase and an aqueous inorganic-rich phase. At 0% RH the particles contained a low polarity organic-rich phase and a higher polarity organic-rich phase. As the RH was decreased from 30% to 0%, the inner phase changed gradually from an aqueous inorganic-rich phase to a higher polarity organic-rich phase, based on the gradual color change, caused by a continuous loss of water from the inner phase.

(a) Squalane/2,5-hexanediol (O:C=0.33)/Ammonium sulfate



Figure 3.1. Fluorescence microscopy images of internally mixed particles containing squalane, oxygenated organic compounds, and ammonium sulfate. Fluorescence was due to trace amounts of Nile red embedded within the particles. Images were recorded for decreasing RH. Indicated above each row is the composition of the particles and the elemental oxygen-to-carbon (O:C) ratio of the SOA proxy. For these experiments, squalane was used as the POA proxy, 1 of 21 oxygenated organic compounds was used as the SOA proxy and ammonium sulfate was used as the SIA proxy. The scale bar applies to all images shown.

As illustrated in Fig. 3.2, two types of phase transitions were observed in our experiments as the RH was decreased: liquid–liquid phase separation and crystallization of ammonium sulfate. We refer to the RH at which we first observed these phase transitions as the separation relative humidity (SRH) and crystallization relative humidity (CRH), respectively. To make it clear that the liquid–liquid phase separation involved a transition from two liquid phases (2L) to three liquid phases (3L) we use the notation 2L–3L SRH.



Figure 3.2. Illustration of the phase behavior of particles containing mixtures of primary organic aerosol (POA), secondary organic aerosol (SOA) and secondary inorganic aerosol (SIA) at different RH values. For O:C less than 0.8, liquid-liquid phase separation and crystallization can both occur. However, for higher O:C values, only crystallization of ammonium sulfate occurs. 2L-3L SRH represents the two liquids-three liquids separation relative humidity, and CRH represents the crystallization relative humidity.

Shown in Fig. 3.3 and listed in Table B1 (See Appendix B) are the 2L–3L SRH and CRH values measured in our experiments as a function of the O:C ratio of the SOA proxy. When the O:C ratio of the SOA proxy was less than 0.8, the average 2L–3L SRH was most often between 100% and 70%. On the other hand, 2L–3L SRH was not observed when the O:C ratio of the SOA proxy was greater than 0.8 (Fig. 3.3). The average CRH was most often between 35% and 45% when the O:C ratio of the SOA proxy was less than 0.8. This range overlaps with the CRH reported for aqueous ammonium sulfate particles (23). The good agreement between the CRH in the POA+SOA+SIA particles when the O:C value is less than 0.8 for the SOA proxy and the CRH for aqueous ammonium sulfate is consistent with ammonium sulfate and the SOA proxy, the average CRH was always less than 40% or, in some cases, crystallization was completely suppressed. This is consistent with ammonium sulfate being in the same phase as the SOA proxy, with the latter lowering the supersaturation of crystalline ammonium sulfate in the particles (43).


Figure 3.3. Two liquids-three liquids separation relative humidity (2L–3L SRH, blue squares) and crystallization relative humidity (CRH, black triangles) of particles containing squalane (POA proxy), a single oxygenated organic compound (SOA proxy; 21 distinct cases studied) and ammonium sulfate (SIA proxy). 2L–3L SRH correspond to the RH at which a two liquids (2L) to three liquids (3L) phase separation event was first observed with decreasing RH. CRH corresponds to the RH at which crystallization of ammonium sulfate was first observed with decreasing RH. The grey squares indicate the cases where 2L–3L SRH was not observed over the full range of RH values studied. The dashed curves indicate the fit of the data in order to guide the eyes.

In our experiments, liquid-liquid phase separation resulted in either a core-crescent-shell morphology (Fig. 3.1a) or core-shell-shell morphology (Fig. 3.1b), with the majority of the particles that underwent liquid-liquid phase separation (78%) revealing a core-shell-shell morphology. The fraction of the particles that had core-shell-shell morphology after the phase separation was shown in Fig. 3.4 and Table B1.No trend was observed between the morphology type and the O:C ratio of the SOA proxy. In all cases, the low polarity organic-rich phase was on the exterior of the particle and the aqueous inorganic-rich phase was in the interior of the particle. This is consistent with the expected thermodynamic driving forces favoring an enhancement of low-polarity, low-surface tension compounds at the air-particle interface. This is also consistent with the molecular dynamics simulations of Karadima et al. (32), who reported that the oxygenated organic molecule cis-pinonic acid (O:C = 0.3) was mainly located between alkanes (O:C = 0) and aqueous ammonium sulfate domains in their nanoparticles. While the particles in our experiments were suspended on hydrophobic glass substrates, which could influence the resulting morphology, previous results have shown good agreement between the morphology of particles deposited on hydrophobic glass substrates and particles levitated in the gas phase (44). However, different metastable morphologies may form depending on the formation mechanism of the particles (30, 45). As a result, care should be taken when extrapolating morphologies observed here to atmospheric particles.



Figure 3.4. Percentage of particles with a core–shell–shell morphology after the formation of three liquid phases. In cases where a core-shell-shell morphology was not observed, a core–crescent–shell morphology was observed. Data shown are listed in Table B1.

Several previous studies have investigated the phase behavior of particles containing mixtures of SOA and SIA proxies. In these studies, two liquid phases were often observed when the O:C value of the SOA proxy was less than 0.8, while one liquid phase was observed when the O:C value was greater or equal to 0.8, similar to the O:C trend observed here (20, 46). Furthermore, the 2L–3L SRH values measured here are in good agreement with the one liquid (1L) to two liquids (2L) separation relative humidity values (i.e. 1L–2L SRH values) reported by You et al. (47) in particles

containing ammonium sulfate and the same oxygenated organic molecules as used here, but without squalane (Fig. 3.5). This agreement provides compelling evidence that the POA proxy, at least the one used in our experiments does not significantly influence the mixing thermodynamics (e.g. chemical potentials) of the SOA and SIA proxies. Several previous studies have also investigated the phase behavior of particles containing proxies of POA and SOA. In these studies, two liquid phases were often observed or inferred when the O:C value of the POA was low (25–30, 48). Our results unify the previous studies that investigated the phase behavior of mixtures of POA and SOA on the one hand, and mixtures of SOA and SIA on the other hand.



Figure 3.5. Comparison of the measured two liquids-three liquids separation relative humidity (2L–3L SRH) values from the current study with the one liquid-two liquids separation relative humidity (1L—2L SRH) reported by You et al. (47). SRH corresponds to the RH at which liquid-liquid phase separation was first observed when decreasing the RH from ~95% to 0%. The color of the symbol indicates the elemental oxygen-to-carbon (O:C) ratio of the oxygenated organic material used as a SOA proxy. The error bars represent two standard deviations from the mean plus the uncertainty of the RH measurement. The data from You et al. (47) correspond to SRH in ternary mixtures of a SOA proxy, ammonium sulfate, and water, while the data from this study correspond to SRH in quaternary mixtures of squalane, a SOA proxy, ammonium sulfate, and water (see Table B1). The dashed black line corresponds to the 1:1 identity line.

3.2 Phase behavior of particles containing mixtures of POA, SOA generated in the laboratory, ammonium sulfate, and trace amounts of Nile red

The experiments described above, each with a single oxygenated organic compound as a proxy for SOA, provide a framework for predicting when three liquid phases may form in atmospheric aerosol particles containing mixtures of POA, SOA, and SIA. As a next step, we carried out similar experiments to those described above, but replaced the oxygenated organic compounds with SOA generated in an environmental chamber by ozonolysis of α -pinene (See Appendix A). SOA generated in an environmental chamber contains tens to hundreds of oxygenated organic species, similar to atmospheric SOA (49). Furthermore, ozonolysis of α -pinene is a major source of SOA in the atmosphere (50). For particles containing squalane, α -pinene SOA, and ammonium sulfate, three phases coexisted over the full range of RH values studied (Fig. 3.6). From 90% to 50% RH, three liquid phases were observed: a low polarity organic-rich phase, a higher polarity organic-rich phase. At 30% to 0% RH, the particles contained two liquid phases and crystalline ammonium sulfate.



Figure 3.6. Fluorescence microscopy images of internally mixed particles containing squalane, α pinene SOA generated in the environmental chamber, and ammonium sulfate. Fluorescence was due to trace amounts of Nile red embedded within the particles. Images were recorded for decreasing RH. The O:C ratio of α -pinene SOA is based on previous studies (51, 52). Squalane was used as the POA proxy and ammonium sulfate was used as the SIA proxy. The scalar bar applied to all images.

At low relative humidities ($\leq 50\%$), a higher polarity organic-rich phase consisting of mostly α pinene SOA can become highly viscous and can even approach the glassy state (53). A highly viscous phase has implications for the time needed to reach equilibrium between POA+SOA+SIA particles and the surrounding gas phase. This aspect will be addressed below, but for convenience, we will continue to refer to the higher polarity organic-rich phase as a liquid. For the particles containing squalane, α -pinene SOA, and ammonium sulfate, the 2L–3L SRH was greater than 88.0% (Table B2). Since the O:C value of SOA from the ozonolysis of α -pinene is 0.29 to 0.43 for our experimental conditions (51, 52), this 2L–3L SRH is consistent with the results obtained using 1 out of 21 oxygenated organic compounds individually as a SOA proxy (compare pink star with blue squares in Fig. 3.3).

As another step toward real atmospheric POA+SOA+SIA particles, we also investigated the phase behavior of particles containing mixtures of lubricating oil, α -pinene SOA, and ammonium sulfate. Unburnt lubricating oil has an O:C value of approximately 0.02 (26), and makes up a large fraction of POA from motor vehicles (54). In these studies, three phases were also observed for the full RH range studied (Fig. 3.7). For this particle type, the 2L–3L SRH was greater than 88.7% (Table B2), consistent with the results obtained when using squalane as a POA proxy.



Lubricating oil /a-pinene SOA (0:C=0.29-0.43)/Ammonium sulfate

Figure 3.7. Fluorescence microscopy images of internally mixed particles containing lubricating oil, α -pinene SOA generated in the environmental chamber, and ammonium sulfate. Fluorescence was due to trace amounts of Nile red embedded within the particles. Images were recorded for decreasing RH. Lubricating oil was used as a proxy for POA, and the O:C ratio is 0.02 based on previous research (26). The scalar bar applied to all images.

The overall picture that clearly emerges is the likely coexistence of three liquid phases at intermediate RH values in particles containing POA, SOA, and SIA, if the O:C value of the SOA is less than 0.8 and the O:C value of the POA is approximately 0.02 or less. These results are directly relevant for POA from motor vehicles, which are a major contributor to POA in urban environments (55, 56).

Measurements during field studies have detected two main types of oxygenated organic aerosol in the atmosphere, referred to as semi-volatile oxygenated organic aerosol (SV-OOA) and lowvolatility oxygenated organic aerosol (LV-OOA, ref 42). SV-OOA has average O:C values ranging from approximately 0.21 to 0.49 and corresponds to freshly formed SOA, while LV-OOA has average O:C values ranging from 0.59 to 0.87 and corresponds to more oxidized SOA resulting from atmospheric aging processes. Based on the O:C values of SV-OOA and LV-OOA, and the range for which liquid–liquid phase separation was observed in our experiments (O:C < 0.8), we expect particles consisting of POA, SIA, and newly formed SOA to often contain three liquid phases. On the other hand, particles consisting of POA, SIA, and aged SOA may consist of two or three liquid phases, depending on the average O:C ratio of the aged SOA. These combined results provide further evidence that the coexistence of three liquid phases is most likely a common occurrence in atmospheric particles containing POA, SOA, and SIA.

Chapter 4. Atmospheric implications of the phase behavior of POA+SOA+SIA particles

4.1 Implications for the mechanism of SOA formation and growth in the atmosphere

The coexistence of three liquid phases in POA+SOA+SIA particles has important implications for the mechanism of SOA formation and growth in the atmosphere. For descriptions of SOA formation in large-scale atmospheric models, it is often assumed that SOA can form by absorptive partitioning of semi-volatile organic compounds into existing POA (57). Our results suggest that this SOA–POA mixing mechanism may be less important than often assumed since our results show that POA and newly formed SOA can exist in separate phases in the same particle. This conclusion is consistent with previous studies using just POA and SOA (25–30, 48) and has important implications for policies being considered to reduce SOA concentrations in urban environments (58).

4.2 Implications for the reactive uptake of N₂O₅

The presence of three liquid phases has implications for the rate of uptake of reactive gases into POA+SOA+SIA particles, for example, considering the reactive uptake of N_2O_5 . N_2O_5 reacts efficiently on aqueous inorganic-rich particles, which leads to a reduction of the gas phase pollutants NO_2 and O_3 and an increase in particle phase nitrate in the atmosphere (21, 59). Having both a low polarity organic-rich phase of extremely low water content and a higher polarity organic-rich phase on the outside of an aqueous inorganic-rich core could substantially limit the reactive uptake of N_2O_5 by acting as sequential barriers through which N_2O_5 must diffuse through (60). A reduction of the reactive uptake of N_2O_5 would lead to an increase in NO_2 and O_3 but a decrease in particle-phase nitrate (21, 59). Therefore, the coexistence of three liquid phases should be taken into consideration when evaluating the rate of reactive uptake of gases into the particles.

4.3. Implications for the equilibration timescales for POA+SOA+SIA particles

A low polarity organic-rich phase and a higher polarity organic-rich phase on the outside of an aqueous inorganic-rich core could also reduce the rate of uptake of organic vapors and water vapor into these particles and, hence, increase the time needed to reach equilibrium between the particles and the surrounding gas phase. To quantify this effect, we used the kinetic multilayer model of gas–particle interactions in aerosols and clouds KM-GAP (22, 61) coupled with the aerosol inorganic–organic mixtures functional groups activity coefficients (AIOMFAC) thermodynamic model (62, 63) to calculate the equilibration timescales between POA+SOA+SIA particles and surrounding organic and water vapors. A description of the KM-GAP and AIOMFAC models are included in Appendix C. In the simulations, we used particles of a dry diameter of 200 nm and dry mass percentages of 33.3% POA, 33.3% SOA and 33.3% SIA, based on the ambient measurements in Vancouver, Canada (3). For POA we used squalane, for SOA we used 14 representative organic compounds of α -pinene SOA (See Table C1), and for SIA we used ammonium sulfate.

To determine equilibration timescales, first, an AIOMFAC-based equilibrium model (16) was used to predict the bulk equilibrium composition of the gas phase and the particle phases as a function of RH, including component activities and liquid phase viscosities. Next, in the kinetic multilayer model simulations, at selected RH levels, the individual gas phase concentrations of organic vapors and water vapor were enhanced by 40% and 1%, respectively, and the time required for the particles to reach within 2% of the new equilibrium diameter (defined as the 2% equilibration timescale, $\tau_{2\%}$.) was calculated with KM-GAP coupled to AIOMFAC. For additional details see Appendix C. Our simulations confirm that 200 nm dry diameter particles with three separate phases have relatively long equilibration timescales, with values ranging from 85 s to 5000 s for RH values ranging from 95% to 10% (Fig. 4.1). The long equilibration timescales are due to the relatively slow gas–particle partitioning of semi-volatile organics alongside a faster partitioning of water. In contrast, simulations with POA+SOA+SIA particles assuming a single, homogeneously mixed phase and ideal mixing, though less realistic, resulted in shorter equilibration timescales, with values ranging from 45 s to 65 s for the same RH range (Fig. 4.1). Long equilibration timescales between the particles and surrounding gas phase have implications for interpreting measurements of hygroscopic growth of atmospheric aerosols, since these measurements often assume equilibration timescales of less than 10 s (64, 65).



Figure 4.1. The 2% equilibration timescale, $\tau_{2\%}$, for POA+SOA+SIA particles. The $\tau_{2\%}$ values correspond to the characteristic time for a particle to reach a diameter within 2% of the new equilibrium diameter after an initial perturbation of the gas phase concentrations; here the surrounding organic vapors and water vapor were initially enhanced by 40% and 1%, respectively. A dry diameter of 200 nm and dry mass fractions of 33.3% POA, 33.3% SOA, and 33.3% SIA

were used in these simulations. Blue markers: timescale for the three-phase particles, accounting for non-ideal mixing and assuming a core–shell–shell morphology with POA in the outer shell and SOA predominantly in the middle shell. Red markers: timescale for forced single-phase particles, assuming ideal mixing among all constituents.

4.4 Implications for the POA+SOA+SIA particles to activate into clouds

The presence of multiple phases in POA+SOA+SIA particles can also influence the ability of such particles to activate into liquid cloud droplets (66). To quantify this effect, we calculated the equilibrium wet diameter, surface composition, and surface tension of a 50 nm dry diameter particle containing 33.3% POA, 33.3% SOA, and 33.3% SIA as it grows with increasing RH and is activated into a liquid cloud droplet (Fig. 4.2). The calculations are based on Köhler theory and the output from the AIOMFAC model, which is discussed in more details in Appendix C.

The calculations show that the minimum environmental water vapor supersaturation required to activate such POA+SOA+SIA particles into a cloud droplet is about 0.42% (the maximum of the solid blue curve in Fig. 4.2a). Prior to and at the point of activation, the particles are predicted to be completely or partially covered with a low polarity organic-rich phase (Fig. 4.2c and 4.2d), which results in a reduction and size-dependent evolution of the surface tension of the particles compared to the surface tension of pure water (Fig. 4.2b). This reduction in surface tension prior to and at activation causes a decrease in the supersaturation needed to activate the particles into cloud droplets compared to a particle with the same composition but assuming no surface tension reduction (Fig. 4.2a). A decrease in the supersaturation needed to activate particles in the ultrafine size range (less than 100 nm diameter) leads to a higher potential for more particles to become activated into cloud droplets under typical conditions at cloud base and, hence, a possible indirect

aerosol composition and morphology effect on climate. Ignoring this effect will lead to underpredictions of the cloud condensation nucleation ability of POA+SOA+SIA particles.



Figure 4.2. Thermodynamic equilibrium predictions for POA+SOA+SIA particles with a 50 nm dry diameter during growth and activation into cloud droplets. (**a**) Supersaturation with respect to water as a function of the wet diameter of the particle. (**b**) Surface tension, σ , as a function of the wet diameter of the particle. In (a) and (b), the blue curve represents the case with the low polarity organic-rich phase on the exterior of the particle, causing a reduction in the surface tension of the particle. For full surface coverage of the organic-rich phase, a minimum layer thickness of 0.3 nm was assumed. The kink in the blue curve at ~0.2 µm diameter indicates the limit of full surface coverage by the low polarity organic-rich phase, γ , with only partial coverage for larger diameters; at this point most compounds from the higher polarity organic-rich phase, β , have already

dissolved into the aqueous inorganic-rich phase, α . In (a) and (b) the dashed green curve represents the comparison case with assumed constant surface tension, σ , of 72 mN m⁻¹, corresponding to the surface tension of water. (c) Predicted radial phase thicknesses (see schematic in d) for the three phases when assuming a core–shell–shell morphology as function of RH. (d) Sketch of anticipated particle morphology changes prior to and beyond the size at the cloud droplet activation point (not to scale). The images in the middle and to the right illustrate the states for RH > 99% and into the supersaturated regime.

Chapter 5. Conclusion and future research work

5.1 Phase behavior of POA+SOA+SIA particles and atmospheric implications

Using a solvatochromic dye (Nile red) and fluorescence microscopy, we showed that POA+SOA+SIA particles can often contain three distinct liquid phases: a low polarity organic-rich phase, a higher polarity organic-rich phase, and an aqueous inorganic-rich phase. Based on our results, when the elemental oxygen-to-carbon (O:C) ratio of the SOA is less than 0.8, which is common in the atmosphere, three liquid phases will often coexist within the same particle over a wide relative humidity range. In contrast, when the O:C ratio of the SOA is greater than 0.8, three phases will not form.

We also demonstrated, using thermodynamic and kinetic modelling, that the presence of three liquid phases in such particles impacts their equilibration timescale with the surrounding gas phase and their ability to act as nuclei for liquid cloud droplets. Three phases will likely also impact the reactivity of these particles and the mechanism of SOA formation and growth in the atmosphere. These observations provide fundamental information necessary for improved predictions of air quality and aerosol indirect effects on climate.

5.2 Consideration of future research work

5.2.1 Morphology of aerosol particles after liquid-liquid phase separation

In our experiments, liquid–liquid phase separation resulted in either a core–crescent–shell morphology (Fig. 3.1a) or core–shell–shell morphology (Fig. 3.1b), with the majority of the particles that underwent liquid–liquid phase separation (78%) revealing a core–shell–shell morphology. The particles in our experiments were suspended on hydrophobic glass substrates. Additional studies are needed to confirm that similar morphologies are observed if the same types of particles are suspended in the gas-phase. Moreover, the reason why core-shell-shell morphology

dominates and the relationship between the preferred morphology and the corresponding surface energy should also be studied (30).

5.2.2 POA with higher O:C values

In this study, squalane and lubricating oil were used as proxies for the POA, which both have a low O:C values. Additional studies are also needed to extend our results to POA with higher O:C values, such as POA from cooking and biomass burning sources.

Since proxies were used to represent POA, SOA, and SIA in our experiments, studies on real aerosol particles collected from the atmosphere are also needed. Aerosol particles are ubiquitous in the atmosphere and play an important role in air quality and the climate system, and these studies will lead to improved representations of aerosols in models for air quality and climate predictions.

Bibliography

- J. I. Steinfeld, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. *Environ. Sci. Policy Sustain. Dev.* (1998) https://doi.org/10.1080/00139157.1999.10544295.
- U. Pöschl, Atmospheric aerosols: Composition, transformation, climate and health effects.
 Angew. Chemie Int. Ed., 44, 7520–7540 (2005).
- Q. Zhang, *et al.*, Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys. Res. Lett.* (2007) https://doi.org/10.1029/2007GL029979.
- 4. Y. Wang, *et al.*, A review of aerosol chemical composition and sources in representative regions of China during wintertime. *Atmosphere (Basel)*. **10**, 1–15 (2019).
- 5. D. Allan, *et al.*, Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities. *Atmos. Chem. Phys.* **10**, 647–668 (2010).
- M. Hallquist, *et al.*, The formation, properties and impact of secondary organic aerosol: Current and emerging issues. *Atmos. Chem. Phys.* (2009) https://doi.org/10.5194/acp-9-5155-2009.
- 7. C. Marcolli, B. Luo, T. Peter, Mixing of the Organic Aerosol Fractions: Liquids as the Thermodynamically Stable Phases. *J. Phys. Chem. A* **108**, 2216–2224 (2004).
- B. Ervens, B. J. Turpin, R. J. Weber, Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): A review of laboratory, field and model studies. *Atmos. Chem. Phys.*, 11, 11069–11102 (2011).
- 9. N. Riemer, A. P. Ault, M. West, R. L. Craig, J. H. Curtis, Aerosol Mixing State: Measurements, Modeling, and Impacts. *Rev. Geophys.*, 2, 187–249 (2019).
- 10. D. M. Murphy, et al., Single-particle mass spectrometry of tropospheric aerosol particles.

J. Geophys. Res. Atmos. 111, D23S32 (2006).

- K. A. Pratt, K. A. Prather, Aircraft measurements of vertical profiles of aerosol mixing states. J. Geophys. Res. Atmos. 115, D11305 (2010).
- B. P. Vester, *et al.*, Composition and mixing state of the urban background aerosol in the Rhein-Main area (Germany). *Atmos. Environ.* 41, 6102–6115 (2007).
- Q. Ye, *et al.*, Spatial Variability of Sources and Mixing State of Atmospheric Particles in a Metropolitan Area. *Environ. Sci. Technol.* 52, 6807–6815 (2018).
- K. Katsouyanni, *et al.*, Confounding and effect modification in the short-term effects of ambient particles on total mortality: Results from 29 European cities within the APHEA2 project. *Epidemiology* 12, 521–531 (2001).
- 15. J. Lelieveld, J. S. Evans, M. Fnais, D. Giannadaki, A. Pozzer, The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* **525**, 361–371 (2015).
- A. Zuend, J. H. Seinfeld, Modeling the gas-particle partitioning of secondary organic aerosol: The importance of liquid-liquid phase separation. *Atmos. Chem. Phys.* 12, 3857– 3882 (2012).
- U. K. Krieger, C. Marcolli, J. P. Reid, Exploring the complexity of aerosol particle properties and processes using single particle techniques. *Chem. Soc. Rev.*, 41, 6631–6662 (2012).
- Y. You, M. L. Smith, M. Song, S. T. Martin, A. K. Bertram, Liquid-liquid phase separation in atmospherically relevant particles consisting of organic species and inorganic salts. *Int. Rev. Phys. Chem.*, 33, 43–77 (2014).
- 19. L. Renbaum-Wolff, *et al.*, Observations and implications of liquid-liquid phase separation at high relative humidities in secondary organic material produced by α -pinene ozonolysis

without inorganic salts. Atmos. Chem. Phys. 16, 7969–7979 (2016).

- M. A. Freedman, Phase separation in organic aerosol. *Chem. Soc. Rev.*, 46, 7694–7705 (2017).
- 21. N. Riemer, *et al.*, Relative importance of organic coatings for the heterogeneous hydrolysis of N2O5 during summer in Europe. *J. Geophys. Res. Atmos.* **114**, D17307 (2009).
- M. Shiraiwa, A. Zuend, A. K. Bertram, J. H. Seinfeld, Gas-particle partitioning of atmospheric aerosols: Interplay of physical state, non-ideal mixing and morphology. *Phys. Chem. Chem. Phys.* 15, 11441–11453 (2013).
- S. T. Martin, Phase transitions of aqueous atmospheric particles. *Chem. Rev.* 100, 3403–3454 (2000).
- 24. N. Rastak, *et al.*, Microphysical explanation of the RH-dependent water affinity of biogenic organic aerosol and its importance for climate. *Geophys. Res. Lett.* **44**, 5167–5177 (2017).
- 25. C. Song, *et al.*, Effect of hydrophobic primary organic aerosols on secondary organic aerosol formation from ozonolysis of α-pinene. *Geophys. Res. Lett.* **34**, L20803 (2007).
- A. Asa-Awuku, M. A. Miracolo, J. H. Kroll, A. L. Robinson, N. M. Donahue, Mixing and phase partitioning of primary and secondary organic aerosols. *Geophys. Res. Lett.* 36, L15827 (2009).
- T. D. Vaden, C. Song, R. A. Zaveri, D. Imre, A. Zelenyuk, Morphology of mixed primary and secondary organic particles and the adsorption of spectator organic gases during aerosol formation. *Proc. Natl. Acad. Sci. U. S. A.* 17, 6658–6663 (2010).
- E. S. Robinson, R. Saleh, N. M. Donahue, Probing the Evaporation Dynamics of Mixed SOA/Squalane Particles Using Size-Resolved Composition and Single-Particle Measurements. *Environ. Sci. Technol.* 49, 9724–9732 (2015).

- J. Ye, C. A. Gordon, A. W. H. Chan, Enhancement in Secondary Organic Aerosol Formation in the Presence of Preexisting Organic Particle. *Environ. Sci. Technol.* 50, 3572– 3579 (2016).
- K. Gorkowski, N. M. Donahue, R. C. Sullivan, Aerosol Optical Tweezers Constrain the Morphology Evolution of Liquid-Liquid Phase-Separated Atmospheric Particles. *Chem* 6, 204–220 (2020).
- T. M. Kucinski, J. N. Dawson, M. A. Freedman, Size-Dependent Liquid-Liquid Phase Separation in Atmospherically Relevant Complex Systems. *J. Phys. Chem. Lett.* 10, 6915– 6920 (2019).
- K. S. Karadima, V. G. Mavrantzas, S. N. Pandis, Insights into the morphology of multicomponent organic and inorganic aerosols from molecular dynamics simulations. *Atmos. Chem. Phys.* 19, 5571–5587 (2019).
- C. Reichardt, Solvatochromic dyes as solvent polarity indicators. *Chem. Rev.* 94, 2319–2358 (1994).
- P. Greenspan, E. P. Mayer, S. D. Fowler, Nile red: A selective fluorescent stain for intracellular lipid droplets. *J. Cell Biol.* 100, 965–973 (1985).
- 35. P. C. Sedrez, C. J. Noriega Sanchez, M. J. da Silva, J. R. Barbosa, Addendum to "Dielectric Constant of Mixtures of Carbon dioxide and n-Dodecane Between 283 K and 343 K, Int. J. Thermophysics 41, 26, 2020": Complementary Results for Mixtures of Carbon dioxide and Squalane Between 283 K and 343 K. *Int. J. Thermophys.* **41** (2020).
- 36. E. R. S. Circular, N B S, Arthur A. Maryott, *Table of Dielectric Constants of Pure Liquids* (1951).
- 37. A. V. Sarode, A. C. Kumbharkhane, Study of dielectric relaxation and thermodynamic

behaviour in poly(propylene glycol) using Time Domain Reflectometry. J. Mol. Liq. 160, 109–113 (2011).

- S. Kalakkunnath, D. S. Kalika, H. Lin, R. D. Raharjo, B. D. Freeman, Molecular relaxation in cross-linked poly(ethylene glycol) and poly(propylene glycol) diacrylate networks by dielectric spectroscopy. *Polymer (Guildf)*. 48, 579–589 (2007).
- R. J. Sengwa, K. Kaur, R. Chaudhary, Dielectric properties of low molecular weight poly(ethylene glycol)s. *Polym. Int.* 49, 599–608 (2000).
- A. C. Aiken, *et al.*, O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environ. Sci. Technol.* 42, 4478–4485 (2008).
- J. L. Jimenez, *et al.*, Evolution of organic aerosols in the atmosphere. *Science (80-.).* 326, 1525–1529 (2009).
- 42. N. L. Ng, *et al.*, Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmos. Chem. Phys.* **10**, 4625–4641 (2010).
- 43. A. K. Bertram, *et al.*, Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon ele. *Atmos. Chem. Phys.* **11**, 10995–11006 (2011).
- 44. M. Song, C. Marcolli, U. K. Krieger, D. M. Lienhard, T. Peter, Morphologies of mixed organic/inorganic/aqueous aerosol droplets. *Faraday Discuss.* **165**, 289–316 (2013).
- K. Gorkowski, N. M. Donahue, R. C. Sullivan, Emulsified and Liquid-Liquid Phase-Separated States of α-Pinene Secondary Organic Aerosol Determined Using Aerosol Optical Tweezers. *Environ. Sci. Technol.* **51**, 12154–12163 (2017).

- L. Nandy, C. S. Dutcher, Phase Behavior of Ammonium Sulfate with Organic Acid Solutions in Aqueous Aerosol Mimics Using Microfluidic Traps. J. Phys. Chem. B 122, 3480–3490 (2018).
- Y. You, L. Renbaum-Wolff, A. K. Bertram, Liquid-liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride. *Atmos. Chem. Phys.* 13, 11723–11734 (2013).
- 48. J. Ye, *et al.*, Predicting Secondary Organic Aerosol Enhancement in the Presence of Atmospherically Relevant Organic Particles. *ACS Earth Sp. Chem.* **2**, 1035–1046 (2018).
- I. Kourtchev, *et al.*, Molecular composition of biogenic secondary organic aerosols using ultrahigh-resolution mass spectrometry: Comparing laboratory and field studies. *Atmos. Chem. Phys.* 14, 2155–2167 (2014).
- M. Kanakidou, *et al.*, Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.*, 5, 1053–1123 (2005).
- J. E. Shilling, *et al.*, Loading-dependent elemental composition of α-pinene SOA particles.
 Atmos. Chem. Phys. 9, 771–782 (2009).
- P. S. Chhabra, *et al.*, Elemental composition and oxidation of chamber organic aerosol.
 Atmos. Chem. Phys. 11, 8827–8845 (2011).
- 53. J. P. Reid, *et al.*, The viscosity of atmospherically relevant organic particles. *Nat. Commun.*,
 9, 956 (2018).
- D. R. Worton, *et al.*, Lubricating oil dominates primary organic aerosol emissions from motor vehicles. *Environ. Sci. Technol.* 48, 3698–3706 (2014).
- 55. R. Subramanian, N. M. Donahue, A. Bernardo-Bricker, W. F. Rogge, A. L. Robinson, Contribution of motor vehicle emissions to organic carbon and fine particle mass in

Pittsburgh, Pennsylvania: Effects of varying source profiles and seasonal trends in ambient marker concentrations. *Atmos. Environ.* **40**, 8002–8019 (2006).

- 56. J. R. Brook, *et al.*, Investigation of the motor vehicle exhaust contribution to primary fine particle organic carbon in urban air. *Atmos. Environ.* **41**, 119–135 (2007).
- 57. S. H. Chung, J. H. Seinfeld, Global distribution and climate forcing of carbonaceous aerosols. *J. Geophys. Res. Atmos.* **107(D19)**, 4407 (2002).
- A. G. Carlton, H. O. T. Pye, K. R. Baker, C. J. Hennigan, Additional Benefits of Federal Air-Quality Rules: Model Estimates of Controllable Biogenic Secondary Organic Aerosol. *Environ. Sci. Technol.* 52, 9254–9265 (2018).
- 59. F. J. Dentener, P. J. Crutzen, Reaction of N2O5 on tropospheric aerosols: impact on the global distributions of NOx, O3, and OH. *J. Geophys. Res.* **98**, 7149–7163 (1993).
- M. Folkers, T. F. Mentel, A. Wahner, Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N2O5. *Geophys. Res. Lett.* 30, 1644 (2003).
- M. Shiraiwa, C. Pfrang, T. Koop, U. Pöschl, Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): Linking condensation, evaporation and chemical reactions of organics, oxidants and water. *Atmos. Chem. Phys.* 12, 2777–2794 (2012).
- 62. A. Zuend, C. Marcolli, B. P. Luo, T. Peter, A thermodynamic model of mixed organicinorganic aerosols to predict activity coefficients. *Atmos. Chem. Phys.* **8**, 4559–4593 (2008).
- 63. A. Zuend, *et al.*, New and extended parameterization of the thermodynamic model AIOMFAC: Calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups.

Atmos. Chem. Phys. 11, 9155–9206 (2011).

- 64. S. P. Hersey, *et al.*, Composition and hygroscopicity of the Los Angeles Aerosol: CalNex.*J. Geophys. Res. Atmos.* 118, 3016–3036 (2013).
- 65. T. Shingler, *et al.*, Airborne characterization of subsaturated aerosol hygroscopicity and dry refractive index from the surface to 6.5km during the SEAC4RS campaign. *J. Geophys. Res.* 121, 4188–4210 (2016).
- 66. J. Ovadnevaite, *et al.*, Surface tension prevails over solute effect in organic-influenced cloud droplet activation. *Nature* **546**, 637–641 (2017).

Appendices

Appendix A. Generation of SOA using environmental chamber

A.1 UBC environmental chamber overview

Secondary organic aerosol (SOA) is produced within a continuous flow environmental chamber by the dark ozonolysis of α -pinene (1). In continuous-flow mode the inflow is balanced by the outflow monitored by a differential pressure feedback system. This allows the environmental chamber to reach and maintain a steady state SOA mass loading and in turn facilitates SOA sample collection over an extended time period. Here, the volatile organic compounds (VOC) injection rate was chosen to reach steady-state mass loadings of SOA between 60 and 80 µg/m³, as determined from the Optical Particle Counter (OPC) number size distribution. After steady state conditions were established, the particles were collected over a period of 24 hours using a multiorifice single-stage impactor. A schematic diagram of the chamber setup is shown in Fig. A1 and the main components, namely the injection system, the chamber, and the aerosol characterization and collection system are briefly described below.

A.2 Injection system

A schematic of the injection system is shown in Fig A2. Dry, clean, and hydrocarbon-free air is produced by a pure air generator (Aadco, model 737). The pure air generator takes in room air and removes hydrocarbons such as water and NOx to provide a clean dry input flow for the environmental chamber, but having ambient concentration of O_2 and CO_2 , as well as a RH of less than 1% (2). The RH of the air from the pure air generator is constantly monitored using a RH-sensor (Vaisala, model HMT 330). Ozone is generated by passing the clean air over an ultraviolet lamp (Jelight, model 600 Ozone Generator). A syringe pump (Cole-Parmer, single syringe infusion pump model 74900-00) is used to inject the VOC-solution, consisting of a mixture (2 wt %) of α -

pinene dissolved in cyclohexane into a heated glass bulb (120°C). In the heated bulb the mixture was evaporated and subsequently carried into the environmental chamber using the filtered air at a flow rate of 17.8 L min⁻¹. Cyclohexane was added to the environmental chamber as a scavenger for hydroxyl radicals, which can be produced in some reaction pathways from the ozonolysis of α -pinene (3).

A.3 Environmental chamber

The environmental chamber consisted of a flexible 1.8 m³ Teflon bag (Ingeniven), suspended in an aluminium enclosure. UV-lights (Sylvania Blacklight, 40 W λ mode \approx 360 nm) that surrounded the chamber, were mounted on the inside of the enclosure for photochemical studies but were not used in the current experiments. The theoretically expected residence time of aerosols in the chamber, based on the flow rates and volume of the chamber, was 1.6 h. In addition to this theoretical estimation, we also measured the half-life of ozone in the chamber (Fig. A3). Ozone was continuously injected into the chamber using flow rates identical to our experiments (see above) but without injecting the α -pinene/cyclohexane mixture. After ozone concentrations reached a steady state value (horizontal line at times -0.5 to 0 h in Fig. A3), ozone generation was stopped but total flow rates were kept constant. The time measured for ozone to decrease to half of its original concentration after stopping ozone production was around 1.5 h (dashed lines in Fig. A3), consistent with the calculated residence time.

A.4 Aerosol characterization and collection

The environmental chamber is continuously being monitored by a set of gas phase analyzers and a suite of aerosol characterization instrumentation that are regularly switched on to monitor the aerosol (Table A1). This includes an ozone analyzer (Thermo Scientific, model 49i), a scanning mobility particle sizer (TSI SMPS 3969) consisting of a differential mobility analyzer (TSI DMA 3080) and a water-based condensation particle counter (TSI CPC 3782), and an optical particle counter (OPC, Grimm, model 11-S). The SMPS was operated at an aerosol-to-sheath flow ratio of 0.3:3, allowing to measure the aerosol particle size distribution within the size range of 14.9 nm to 673 nm. An optical particle counter (OPC, Grimm, model 11-S) was used to measure the concentration of particles with size between 250 nm to 32 μ m. At the exit of the environmental chamber, SOA was collected by inertial impaction.



Figure A1. Overview of the UBC environmental chamber setup, consisting of an injection system, an environmental chamber, and the aerosol characterization and collection system as indicated by the dashed boxes. RH=relative humidity, VOC=volatile organic compound, OPC=optical particle counter, SMPS=scanning mobility particle sizer.



Figure A2. Diagram of the injection systems of the environmental chamber. The arrows show the flow direction for pure clean dry air, 2 wt% α -pinene solution as the precursor VOC (with cyclohexane as the OH scavenger), and ozone. Mass flow controllers (MFCs) are used to regulate flow rates in the injection systems.



Figure A3. Ozone half-life within the UBC environmental chamber given by the change in ozone concentration after stopping injection, while maintaining flows into and out of the environmental chamber at constant values. At time zero, the ozone production was shut off. The dashed lines indicate the half-life, defined as the time required for the ozone concentration to drop to half of its initial value. Typical initial concentrations of ozone were approximately at 340 ppb_v.

Table A1. Instrumentation used for gas phase analysing and aerosol characterization for the UBC
 environmental chamber.

Instrument	Measured parameter		
Thermo Scientific Model 49i	Ozone concentration in the chamber		
Thermocouple type K (OMEGA)	Temperature of the glass bulb		
Vaisala (HMT 330)	RH of the flow from pure air generator		
Avantes AvaSpec-ULS 3648 spectrometer	UV light spectrum		
Scanning mobility particle sizer (TSI 3080	Partiala size distribution (14.0, 673 nm)		
DMA and 3782 CPC)	raticle size distribution (14.9-073 mil)		
Optical Particle Counter (OPC, Grimm,	Particle size distribution (250 nm 32 um)		
model 11-S)	r article size distribution (250 mil-52 μm)		

Appendix B

Table B1. Summary of results from studies with particles containing a mixture of squalane (proxy for POA), 1 out of 21 different oxygenated organic compounds (proxy for SOA), and ammonium sulfate (a major type of SIA in the atmosphere). 2L-3L SRH correspond to the two liquids-to-three liquids separation relative humidity. CRH corresponds to the crystallization relative humidity of ammonium sulfate. O:C represents the elemental oxygen-to-carbon ratio of the SOA proxy. Results are based on observations of 3 to 8 individual particles for each particle type. All values were determined for a decreasing relative humidity (RH). Relative errors in SRH and CRH represent 2σ plus the uncertainty of the hydrometer (±2.5%). "Not observed" indicates that three liquid phases or three amorphous phases were not observed in the experiments over the full RH range.

Compound	O:C	2L—3LSRH (%)	CRH (%) [#]	Morphology after 2L—3L SRH (% core–shell–shell) [§]
2,5-hexanediol	0.33	84.7±5.0	40.1±5.7	20
Poly (Propylene) glycol 425 (PPG-425)	0.38	90.9±9.2	37.9±8.0	100
Suberic acid monomethyl ester	0.44	≥89.6*	36.5±5.1	100
Poly(Ethylene) glycol diacrylate (PEG Diacrylate)	0.50	≥89.8*	37.3±5.2	100
1,2,6-trihydroxyhexane	0.50	72.3±4.3	43.9±9.6	100
Poly (Ethylene) glycol 600 (PEG-600)	0.54	88.6±2.9	41.7±7.5	50
Vanillymandelic acid	0.56	72.3±5.4	41.3±9.3	100
2,5-hydroxybenzoic acid	0.57	Not observed	42.2±10.3	Not observed

Compound	O:C	2L—3LSRH (%)	CRH (%) [#]	Morphology after 2L—3L SRH (% core–shell–shell) [§]
Diethylmalonic acid	0.57	83.1±5.7	42.8±8.6	83
3,3-dimethylglutaric acid	0.57	80.9±4.3	45.5±4.3	100
Poly (Ethylene) glycol 300 (PEG-300)	0.58	83.7±3.3	42.7±9.4	86
Poly (Ethylene) glycol 200 (PEG-200)	0.63	79.5±5.7	40.1±9.1	50
Poly(ethylene glycol) bis (carboxymethyl) ether	0.63	86.3±3.7	41.8±13.9	50
2-methylglutaric acid	0.67	73.1±6.1	43.1±7.5	100
2,2-dimethylsuccinic acid	0.67	Not observed	42.9±4.4	Not observed
Diethyl-L-tartrate	0.75	89.2±3.1	48.4±6.3	100
Glutaric acid	0.80	Not observed	28.8±15.6	Not observed
Levoglucosan	0.83	Not observed	10.0±18.8	Not observed
Glycerol	1.0	Not observed	3.2±13.3	Not observed
Maleic acid	1.0	Not observed	18.1±18.8	Not observed
Citric acid	1.17	Not observed	0±2.5	Not observed

* If three liquids were observed within a particle at the beginning of an experiment when the flow cell was equilibrated at the highest RH in the experiment, we reported a lower limit to 2L–3L SRH, taking into account the uncertainty in the hygrometer.

If ammonium sulfate did not crystallize throughout the full RH range explored, a value of 0%RH was used to calculate the average CRH.

[§] The percentage of particles with core-shell-shell morphology for cases where liquid-liquid phase separation was observed.

Table B2. Summary of results from studies with particles containing α -pinene SOA, ammonium sulfate (a major type of SIA in the atmosphere), and squalane or lubricating oil as a proxy for POA. 2L–3L SRH correspond to the two liquids–three liquids separation relative humidity. CRH corresponds to the crystallization relative humidity of ammonium sulfate. Results are based on observations of at least four individual particles for each particle type. All values were determined for a decreasing relative humidity. O:C corresponds to the elemental oxygen-to-carbon ratio of the POA proxy or the SOA. The O:C of the α -pinene SOA is estimated based on data from previous studies (4, 5).

РОА	O:C (POA)	SOA	O:C (SOA)	2L—3L SRH (%)	CRH (%)	Morphology after 2L—3L SRH (% core–shell–shell) [§]
Squalane	0	α-pinene	0.3 –	\geq 88.0 [*]	32.5 ± 4.5	100
		SOA	0.43			
Lubricating	0.06-0.1	α-pinene	0.3 –	\geq 88.7 [*]	35.1 ± 3.8	15
oil	(6)	SOA	0.43			

* Since three liquid phases were observed within the particle at the beginning of all measurements when the flow cell was equilibrated at the highest possible RH during the experiments, the values reported here denotes a lower limit to the 2L–3L SRH, which includes the uncertainty in the hygrometer.

[§] The percentage of particles with core—shell—shell morphology after liquid–liquid phase separation (the remainder exhibiting a core-crescent-shell morphology).

Appendix C. Models for atmospheric implications of phase behavior of POA+SOA+SIA particles

C.1 Calculation of the equilibration timescale between POA+SOA+SIA particles and surrounding organic vapors and water vapor

The equilibration timescales shown in Fig. 4.1 (main text) were computed by coupling the aerosol inorganic–organic mixtures functional groups activity coefficients (AIOMFAC) model (7–9) to the kinetic multi-layer model of gas–particle interactions in aerosols and clouds (KM-GAP, refs 10, 11). Squalane was used to represent primary organic aerosol (POA); 14 different semi-volatile reaction products from the oxidation of α -pinene were used to represent SOA (Table C1) similar to Shiraiwa et al. (11); ammonium sulfate was used to represent secondary inorganic aerosol (SIA). Dry mass percentages of 33.3% POA, 33.3% SOA, and 33.3% SIA were assumed, based on ambient measurements from Vancouver, Canada (12). In addition, we assumed that squalane formed a separate low polarity phase and ammonium sulfate did not crystallize in this system at low RH values for simplicity.

To calculate equilibration times, first the equilibrium chemical composition of the gas phase and the condensed phases for this POA+SOA+SIA system were computed at 298 K as a function of water activity (a_w) using an AIOMFAC-based thermodynamic gas–particle and liquid–liquid equilibrium model similar to Zuend and Seinfeld (13) and Shiraiwa et al. (11). AIOMFAC is a thermodynamic mixing model using functional group information for chemical structures and explicitly accounts for non-ideal mixing effects within organic–inorganic phases by means of activity coefficient predictions. Here, non-ideality refers to the mixing behavior of the species within liquid particle phases, whereas the gas phase is assumed to be an ideal gas mixture. The AIOMFAC-based partitioning model was used to predict the amounts of water and semi-volatile

organic material in the condensed phases and the gas phase at bulk system equilibrium. This equilibrium is a nonlinear function of all components interacting with each other in the different phases, which also depends on the pure component, liquid-state vapor pressures of all volatile compounds; these were estimated using the EVAPORATION model (14). The results from these simulations are shown in Fig. C1. Three liquid phases (or two liquid phases and one solid phase) were simulated with a total particulate mass concentration of approximately 45 μ g m⁻³ for all *a*_w values below 0.95. Fig. C1 shows the calculations for decreasing RH conditions starting from high water activity, with ammonium sulfate remaining dissolved down to the crystallization RH; hence showing the water activity range between ~33% and ~100%.

After the equilibrium composition was predicted by AIOMFAC (Fig. C1), we used this information as input for the KM-GAP model to determine equilibration timescales between the POA+SOA+SIA particles and the surrounding gas phase. Equilibration timescales were determined by perturbing the system from its equilibrium state. This was achieved by initializing the KM-GAP simulations with the RH enhanced by 1% from a given equilibrium input value and by increasing the organic vapor concentrations by 40% at a selection of RH levels in the range from 10% to 95%. The 2% equilibration timescale, $\tau_{2\%}$, was then calculated as the time required for the particles to grow and reach a diameter within 2% of their simulated new equilibrium diameter given these initial perturbations. For these simulations, populations of particles of 200 nm dry diameter were used consistently at each RH level, but with the initial wet diameter adjusted to the expected equilibrium size at that RH. This was done to ensure that approximately the same amount of water-free mass was present in each particle at the beginning of a simulation. The wet diameter at each RH level, used to initialize the calculations, was determined via predicted growth factors from the AIOMFAC calculations from the dry diameter and the additional uptake of matter
due to hygroscopic growth and concomitant partitioning of semi-volatile organics. The size distribution was assumed to be monodisperse, with the total number concentration of particles adjusted for each RH level considered in order to reach a consistent dry mass loading of roughly $45 \ \mu g \ m^{-3}$. This protocol was followed to ensure that the KM-GAP simulations were initialized with consistent overall gas–particle equilibrium conditions, as predicted by the AIOMFAC-based model. We note, however, that accounting for the Kelvin effect in the KM-GAP simulations, but not in the bulk equilibrium output from AIOMFAC, leads to a slight deviation from equilibrium at time zero. This can be considered as another perturbation of the system at initialization, with the effect being small for 200 nm dry diameter particles.

Within KM-GAP, the gas-particle system is treated as a number of stacked compartments and layers, between which mass transport can take place. Mass transport is treated as a kinetic flux from one layer to the next adjacent layer, considering gas-phase diffusion and bulk diffusion. For organic molecules, particle phase diffusivities were calculated from viscosities of the respective phase and using the Stokes-Einstein relation as outlined in Shiraiwa et al (11). Viscosities of the higher polarity organic-rich and water-rich phases were estimated for each RH value using the chemical composition (Fig. C1) and the AIOMFAC-VISC method described by Gervasi et al. (15) to convert chemical composition to viscosity. For the low polarity organic-rich phase, experimentally determined viscosities of squalane at 298 K were used. For water molecules, particle phase diffusivities were calculated using percolation theory as described in Shiraiwa et al. (11). In the simulations, after some material had diffused into the low polarity organic-rich phase, activity coefficients in that phase were calculated with AIOMFAC and used to determine the solubilities of the diffusing species in the low polarity organic-rich phase, which is needed for the equilibration time predictions of KM-GAP.

The calculated equilibration timescales are shown in Fig. 4.1 (main text). Water re-equilibrates on sub-second timescales for this POA+SOA+SIA system, and hence, the rate limiting step for equilibration shown in Fig. 4.1 was the re-equilibration of semi-volatile organic species within the particles. As mentioned above, crystallization of ammonium sulfate was not allowed for these simulations. Therefore, the data points below 40% RH are an extrapolation in terms of thermodynamic ammonium sulfate metastability. However, if crystallization of ammonium sulfate was included, it would predominantly deplete the dissolved ammonium sulfate content in the core phase, but would very likely not change the viscosities of the low polarity or higher polarity organic-rich phases, since, according to the predictions shown in Fig. C1, ammonium sulfate is only sparingly soluble in those phases. Hence, the determined equilibration time scales for 40% to 10% RH should be relevant for POA+SOA+SIA particles with crystalline cores as well.

For comparison of the equilibration timescale calculations described above with those for a simpler particle representation, additional simulations were run for a single-phase particle system, in which POA, SOA, and SIA are assumed to exhibit ideal mixing. For this case, POA, SOA, ammonium sulfate ions, and water were all assumed to mix ideally in a single phase, and partitioning of water and semi-volatile organic molecules into the condensed phase was predicted using Raoult's law. Shown in Fig. C2 is the predicted equilibrium bulk composition of the gas phase and the condensed phase as a function of water activity based on these assumptions. The total particulate mass concentration computed for these assumptions yielded ~ 50 μ g m⁻³ at 40% RH. The equilibrium compositions shown in Fig. C2 were then used to predict the liquid phase viscosity, the related diffusivities of the components, and the equilibration timescales at each RH level using KM-GAP, as described above. A total mass concentration of 50 μ g m⁻³ was used to determine the total number concentration of the monodisperse, ideally mixed particles at each RH. The results for these

simulations are also shown in Fig. 4.1. They illustrate that assuming/enforcing ideal mixing, and therefore a single particle phase, results in shorter equilibration timescales between the particles and the surrounding gas phase.

C.2 Thermodynamic equilibrium predictions of POA+SOA+SIA particles activating into cloud droplets

The thermodynamic equilibrium predictions of POA+SOA+SIA particles during growth and activation into cloud droplets was performed using the AIOMFAC-based equilibrium composition and the Köhler equation (16). The approach used here is the same as the one used by Ovadnevaite et al. (17) except for considering three liquid phases in this study (a low polarity organic-rich phase, a higher polarity organic-rich phase, and an aqueous inorganic-rich phase) compared to two phases (a higher polarity SOA phase and an aqueous inorganic-rich phase) considered by Ovadnevaite et al. For these predictions, the AIOMFAC-derived bulk equilibrium composition predictions of the POA+SOA+SIA system described above (see also Fig. C1) were processed as a function of coupled a_w , bulk composition, and predicted diameter (growth factor) data for a selected dry diameter. Next, the Köhler equation was used to calculate a droplet's equilibrium water vapor saturation ratio, S_w , as a function of the wet diameter of the particles,

$$S_w = a_w \exp\left[\frac{4\sigma M_w}{RT\rho_w D}\right].$$
(C1)

Here, a_w is the mole-fraction-based water activity, R is the universal gas constant, T is the absolute temperature, M_w is the molar mass of water, ρ_w is the density of liquid water, σ is the surface tension of the droplet, and, D is the wet particle diameter. The wet particle diameter D was calculated by assuming a 50 nm dry diameter and by summation of the partial volume contributions

of the chemical species, including water, at the specified a_w . At any particle composition, hence related diameter, the surface tension (σ) of the droplet was determined based on an assumed morphology, the phase-behavior of the particles, and the composition of the individual phases. Where three liquid phases coexist, a core–shell–shell morphology was assumed with the low polarity organic-rich phase forming the outer shell of the particle. The surface tension of a pure organic phase was set to 30 mN m⁻¹ (17) while for the water-rich phase the value for pure water, ~72 mN m⁻¹ at 298 K was assumed. For the organic-rich phases containing both organics, inorganic ions and water, the surface tension was calculated using a volume-fraction-weighted mean of the pure-component surface tension values. If the thickness of the low polarity organicrich phase was < 0.3 nm (approximately an average monolayer thickness), a partial coverage of the droplet by the low polarity phase was assumed (Fig. 4.2d). In this case, the effective surface tension of the droplet was determined as the surface-area-weighted mean of surface tensions from all liquid phases contributing to the surface of the droplet. For additional details on the surface tension calculations see Ovadnevaite et al. (17).

Key results from these calculations are shown in Fig. 4.2 in the main text. For wet diameters of $D \le 200$ nm, the low-polarity phase completely covers the growing droplet, which leads to a significant reduction in the surface tension of the particle compared to the surface tension of a pure water droplet (Fig. 4.2b). For 200 nm $\le D \le 500$ nm, the particle is partially covered by the low-polarity phase, possibly in the form of a partially covered structure as indicated in Fig. 4.2d (right-most image). A fractional surface coverage by the low-polarity organic-rich phase causes a substantial reduction in the effective particle surface tension and an enhanced ability of the particle to act as a cloud condensation nucleus compared to the assumption of a constant surface tension of equivalent magnitude to that of pure water (Fig. 4.2a). The critical supersaturation for the

lowered, evolving surface tension case was ~0.42% compared to ~0.77% for an assumed constant surface tension of 72 mN m⁻¹. This is consistent with previous calculations that showed that accounting for the evolving surface tension due to the presence of organic material at the surface of droplets can lead to a considerable reduction in the critical supersaturation needed for cloud droplet activation (17–21).



Figure C1. Equilibrium phase compositions predicted by the AIOMFAC-based thermodynamic gas–particle partitioning model for a dry mass fraction of 33.3% for each of squalane, α -pinene SOA, and ammonium sulfate. Each panel shows stacked bar graphs. The predicted mass concentrations of water are omitted for clarity. (**a** – **d**) Mass concentrations per unit volume of air for the gas phase (C^g), the aqueous inorganic-rich phase (C^{α}), the higher polarity organic-rich phase (C^{β}), and the low polarity organic-rich phase (C^{γ}). Calculations were performed for a temperature of 298 K and variable water activities (*a*_w from 0.34 to 0.9999), which is equivalent

to relative humidity in thermodynamic equilibrium, for a decreasing relative humidity scenario (no solid ammonium sulfate), and constant total concentrations (gas + liquid) of all other components.



Water activity a_w

Figure C2. Equilibrium phase compositions predicted by the thermodynamic gas-particle partitioning model assuming ideal mixing in the liquid aerosol phase and a dry mass fraction of 33.3% for each of squalane, α -pinene SOA, and ammonium sulfate. Each panel shows stacked bar graphs. The predicted mass concentrations of water are omitted for clarity. (**a**, **b**) Mass concentrations per unit volume of air for the gas phase (C^g) and the single, ideally mixed (here by enforced assumption) liquid phase (C^{α}). Calculations are performed at a temperature of 298 K and variable water activities with suppressed crystallization of ammonium sulfate and constant total concentrations (gas + liquid) of all other components.

Table C1. Fourteen different semi-volatile reaction products from the oxidation of α -pinene used to represent SOA in this study. The table is adapted from Shiraiwa et al. (11). List of species and corresponding stoichiometric yields are derived from the MCM chamber simulation reported by Shilling et al. (4) for the reaction of 0.9 ppbv α -pinene. Simulation conditions: T = 298.15 K, 40 % RH, 300 ppbv ozone, 0.94 ppmv 1-butanol, dry ammonium sulfate seed particles, and 3.4 h residence time.

Name (MCM) ^a	Structure	Molar Mass (g mol ⁻¹)	P ⁰ (298.15K) (Pa) ^b	Mass Yield ^c	Molar Yield
С107ООН		200.231	7.8328×10^{-3}	0.35051	0.23849
PINONIC	H ₃ C OH OH	184.232	1.5345×10^{-2}	0.18951	0.14013
С97ООН	он	188.221	$5.4035 imes 10^{-4}$	0.15883	0.11496
С108ООН	° ~ ~ ° ° °.	216.231	1.8447 × 10 ⁻³	0.11597	0.07307
С89СО2Н		170.206	4.6884×10^{-2}	0.07496	0.06000
PINIC	о он	186.205	4.7358×10^{-5}	0.04554	0.03332

Name (MCM) ^a	Structure	Molar Mass (g mol ⁻¹)	P ⁰ (298.15K) (Pa) ^b	Mass Yield ^c	Molar Yield
С921ООН	но Сон	204.220	4.4946 × 10 ⁻⁶	0.03662	0.02443
С109ООН		200.231	1.5128 × 10 ⁻²	0.02834	0.01928
С812ООН	но	190.194	1.2132 × 10 ⁻⁶	0.02977	0.02132
HOPIONIC	HOLICH	200.232	7.6498 × 10 ⁻⁵	0.02205	0.01500
C811OH	он он	158.094	3.1129 × 10 ⁻³	0.01591	0.01371
С813ОН		206.193	2.0391 × 10 ⁻⁷	0.01249	0.00825
ALDOL_dimer ^d		368.421	1.1579 × 10 ⁻¹¹	N/A	0.00600
ESTER_dimer ^d		368.421	$2.5\overline{279} \times 10^{-11}$	N/A	0.00150

- a. Unique compound names as assigned by the MCM model (exceptions: the dimer compounds)
- b. Pure compound (subcooled) vapor pressure as predicted by the EVAPORATION model from Compernolle at al. (14) without diacid correction.
- c. Predicted stoichiometric mass yield (μg of compound formed per μg of α -pinene reacted). The stoichiometric mass and molar yields are calculated with the assumption of

conservation of total carbon mass from the parent hydrocarbon, based on the predicted product distribution given in Table 1 of Shilling et al. (4) for 0.9 ppbv α -pinene reacted under the stated conditions.

d. The "ALDOL dimer" compound (formed by aldol condensation of C108OOH + C89CO2H) and the "ESTER dimer" compound (formed by ester formation of HOPINONIC + PINIC) are not predicted by the MCM model, rather they are assumed to form in the particle phase and related concentrations are calculated with the partitioning model. Two dimer compounds as surrogates for several dimers assumed to exist in the condensed phase. The ALDOL_dimer is formed by aldol condensation of C108OOH + C89CO2H; the ESTER_dimer is formed by ester formation from HOPINONIC + PINIC. A stoichiometric yield of 10% with respect to the maximum possible amounts (from the involved monomers) are here assumed for both dimers.

Bibliography for appendices

- S. M. King, T. Rosenoern, J. E. Shilling, Q. Chen, S. T. Martin, Increased cloud activation potential of secondary organic aerosol for atmospheric mass loadings. *Atmos. Chem. Phys.* (2009) https://doi.org/10.5194/acp-9-2959-2009.
- S. M. King, T. Rosenoern, J. E. Shilling, Q. Chen, S. T. Martin, Cloud condensation nucleus activity of secondary organic aerosol particles mixed with sulfate. *Geophys. Res. Lett.* 34, L24806 (2007).
- J. H. Kroll, N. M. Donahue, V. J. Cee, K. L. Demerjian, J. G. Anderson, Gas-phase ozonolysis of alkenes: Formation of OH from anti carbonyl oxides. *J. Am. Chem. Soc.* 124, 8518–8519 (2002).
- J. E. Shilling, *et al.*, Loading-dependent elemental composition of α-pinene SOA particles.
 Atmos. Chem. Phys. 9, 771–782 (2009).
- P. S. Chhabra, *et al.*, Elemental composition and oxidation of chamber organic aerosol. *Atmos. Chem. Phys.* 11, 8827–8845 (2011).
- A. Asa-Awuku, M. A. Miracolo, J. H. Kroll, A. L. Robinson, N. M. Donahue, Mixing and phase partitioning of primary and secondary organic aerosols. *Geophys. Res. Lett.* 36, L15827 (2009).
- 7. A. Zuend, C. Marcolli, B. P. Luo, T. Peter, A thermodynamic model of mixed organicinorganic aerosols to predict activity coefficients. *Atmos. Chem. Phys.* **8**, 4559–4593 (2008).
- A. Zuend, C. Marcolli, T. Peter, J. H. Seinfeld, Computation of liquid-liquid equilibria and phase stabilities: Implications for RH-dependent gas/particle partitioning of organicinorganic aerosols. *Atmos. Chem. Phys.* 10, 7795–7820 (2010).
- 9. A. Zuend, et al., New and extended parameterization of the thermodynamic model

AIOMFAC: Calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups. *Atmos. Chem. Phys.* **11**, 9155–9206 (2011).

- M. Shiraiwa, C. Pfrang, T. Koop, U. Pöschl, Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): Linking condensation, evaporation and chemical reactions of organics, oxidants and water. *Atmos. Chem. Phys.* 12, 2777–2794 (2012).
- M. Shiraiwa, A. Zuend, A. K. Bertram, J. H. Seinfeld, Gas-particle partitioning of atmospheric aerosols: Interplay of physical state, non-ideal mixing and morphology. *Phys. Chem. Chem. Phys.* 15, 11441–11453 (2013).
- 12. N. L. Ng, *et al.*, Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmos. Chem. Phys.* **10**, 4625–4641 (2010).
- A. Zuend, J. H. Seinfeld, Modeling the gas-particle partitioning of secondary organic aerosol: The importance of liquid-liquid phase separation. *Atmos. Chem. Phys.* 12, 3857– 3882 (2012).
- S. Compernolle, K. Ceulemans, J. F. Müller, Evaporation: A new vapour pressure estimation methodfor organic molecules including non-additivity and intramolecular interactions. *Atmos. Chem. Phys.* 11, 9431–9450 (2011).
- 15. N. R. Gervasi, D. O. Topping, A. Zuend, A predictive group-contribution model for the viscosity of aqueous organic aerosol. *Atmos. Chem. Phys.* **20**, 2987–3008 (2020).
- 16. H. Köhler, The nucleus in and the growth of hygroscopic droplets. *Trans. Faraday Soc.* 32, 1152–1161 (1936).
- 17. J. Ovadnevaite, et al., Surface tension prevails over solute effect in organic-influenced cloud

droplet activation. Nature 546, 637–641 (2017).

- N. L. Prisle, T. Raatikainen, A. Laaksonen, M. Bilde, Surfactants in cloud droplet activation: Mixed organic-inorganic particles. *Atmos. Chem. Phys.* 10, 5663–5683 (2010).
- 19. C. R. Ruehl, J. F. Davies, K. R. Wilson, An interfacial mechanism for cloud droplet formation on organic aerosols. *Science* (80-.). **351**, 1447–1450 (2016).
- 20. P. Liu, *et al.*, Resolving the mechanisms of hygroscopic growth and cloud condensation nuclei activity for organic particulate matter. *Nat. Commun.* **9**, 4076 (2018).
- 21. J. F. Davies, A. Zuend, K. R. Wilson, Technical note: The role of evolving surface tension in the formation of cloud droplets. *Atmos. Chem. Phys.* **19**, 2933–2946 (2019).