SIZE DEPENDENT MORPHOLOGY OF ORGANIC AEROSOL

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by
Muhammad Bilal Altaf

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The dissertation of Muhammad Bilal Altaf was reviewed and approved* by the following

Miriam Arak Freedman  
Assistant Professor of Chemistry  
Dissertation Advisor  
Chair of Committee

David D. Boehr  
Associate Professor of Chemistry

Eugene E. Clothiaux  
Professor of Meteorology and Atmospheric Science

Raymond E. Schaak  
DuPont Professor of Materials Chemistry

Thomas E. Mallouk  
Evan Pugh Professor of Chemistry, Biochemistry and Molecular Biology, and Physics  
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
ABSTRACT

The Earth’s atmosphere is composed of a wide variety of gas phase species and particulate matter that have a large impact on our climate. Though our understanding of the climate system has improved significantly over the past few decades, the impact of aerosol particles remains uncertain. Aerosol particles can affect climate through the absorption and scattering of radiation (aerosol direct effect) and by serving as cloud condensation nuclei (aerosol indirect effect). It is known that aerosol particles cause a net cooling effect on the planet, but the magnitude of cooling is unclear and remains under investigation. A large part of this uncertainty is due to an incomplete understanding of the complex physical and chemical properties of aerosol particles such as composition, morphology, and phase state.

In this dissertation, we focus on investigating the role of particle size and composition in determining morphology. We have discovered that for some organic aerosol systems, particle morphology depends on size, where small particles are homogeneous and large particles are phase separated. To explore the origins of this size dependent behavior, we have worked with a model organic aerosol system, poly(ethylene glycol)-400 mixed with ammonium sulfate. We have used cryogenic-transmission electron microscopy to probe the effect of phase separation mechanism on particle morphology by varying the organic aerosol composition. Our results suggest that a size dependent morphology occurs due to an activated process, where the presence or absence of an activation barrier to phase separation controls the resulting morphology.
We have also explored the kinetics and thermodynamics of the phase separation process that results in a size dependent morphology by varying the experimental drying rates. Drying rates that span over four orders of magnitude were investigated. We have observed that at the fastest drying rates, the size of the transition region where both phase separated and homogeneous morphologies exist is on the order of ~100 nm. At the slowest drying rates, the transition region shifts to smaller diameters and the width narrows to ~3 nm. Our results suggest that a size dependent morphology persists to the slowest drying rates. Thus, we conclude that an underlying thermodynamic effect results in this size dependent behavior, rather than solely a kinetic phenomenon.

To determine the atmospheric implications of a size dependent morphology, we have used a cloud condensation nuclei counter to probe the effect of a homogeneous vs. a phase separated morphology on cloud condensation nuclei (CCN) activity. We have found that the activation diameters differ for particles which have the same composition, but varying morphology.

Since aerosol optical properties are a sensitive measure of particle structure, we have studied the morphology-resolved optical properties of organic aerosol using cavity ring-down spectroscopy. Our spectroscopy data indicate that the optical properties of core-shell and partially engulfed particles are approximately equal, but different than the prediction for homogeneous particles. By accurately parametrizing aerosol particle morphology, optical properties, and CCN activity we will be able to better predict heterogeneous chemistry in the atmosphere, in addition to the aerosol direct and aerosol indirect effects which play a critical role in constraining climate forcing.
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Chapter 1

Introduction

Aerosol Particles and the Earth’s Atmosphere

Aerosol particles have been a central focus of atmospheric chemistry research due to their chemical complexity and abundance in our atmosphere. Aerosol particles exist at the Earth’s surface up into the stratosphere and can range in size from a few nanometers to tens of micrometers. A large fraction of aerosol particles have natural origins and are emitted directly into the atmosphere from sources such as volcanoes, forest fires, sea salt, and dust. Biogenic emissions also contribute to aerosol, as gas species emitted by plants and trees become oxidized in the atmosphere. Anthropogenic emissions, on the other hand, are less abundant than natural aerosol emissions, but have a wide variety of sources ranging from automobile fuel combustion to industrial processes.\textsuperscript{1,2}

Depending on their size and chemical composition, aerosol particles can have a significant impact on human health and the Earth’s climate. Aerosol particles present a respiratory health hazard and also lead to poor visibility in urban areas, where particle concentrations are very high.\textsuperscript{3} Many environmental protection agencies have set air quality standards to limit the levels of air pollutants in order to improve air quality. Most agencies
regulate particulate matter less than 10 µm in diameter (PM$_{10}$) and/or 2.5 µm in diameter (PM$_{2.5}$). For instance, the United States Environmental Protection Agency (U.S. EPA) monitors particulate matter less than 2.5 µm in diameter (PM$_{2.5}$) which can travel deep into the lungs and cause chronic pulmonary illness. The U.S. EPA considers a daily average of PM$_{2.5}$ concentrations above 35 µg/cm$^3$ to be hazardous to human health, especially for sensitive groups with pre-existing respiratory illnesses.

In addition to the health impacts, aerosol particles also play an important role in influencing our climate. Aerosol climate interactions can be understood by the aerosol direct and aerosol indirect effects. The aerosol direct effect describes the interaction between aerosol particles and incoming solar radiation. The degree to which an aerosol particle absorbs or scatters sunlight depends on its physical properties. Particles containing pure sulfates and nitrates tend to scatter radiation and lead to a cooling effect on the atmosphere. Black carbon (soot particles), on the other hand, absorb radiation and warm the atmosphere. In addition to influencing climate by directly impacting the Earth’s radiation balance, aerosol particles can also alter climate indirectly by playing a critical role in cloud formation. Aerosol particles can serve as cloud condensation nuclei and have complex effects on cloud lifetime, reflectivity, and precipitation.

**Uncertainty in Aerosol-Climate Interactions**

We have an adequate understanding of the effect that greenhouse gases such as methane and carbon dioxide have on climate (i.e. they cause a net warming effect). In the case of aerosol particles, however, it is known that aerosol in the atmosphere causes a net cooling effect (radiative forcing <0), but the magnitude of cooling remains highly
uncertain.\textsuperscript{1} The aerosol direct effect has been estimated to be $-0.5 \pm 0.4 \text{ W m}^{-2}$, while the estimate for the indirect effect shows a contribution of $-0.70 \text{ W m}^{-2}$ with an uncertainty range of $-1.8$ to $-0.3 \text{ W m}^{-2}$.\textsuperscript{1} A large part of the uncertainty is due to the fact that we do not completely understand the physics and chemistry of the diverse population of aerosol particles in our atmosphere. Thus, in order to reduce this uncertainty, we need to better understand the reaction pathways of aerosol particles by determining and accurately modeling particle composition and morphology.\textsuperscript{5-7} Particle structure plays an important role in new particle formation and growth and can affect the heterogeneous chemistry and mass accommodation coefficients (a parameter which determines the transfer rate of gases into aqueous droplets) for aerosol loading in the atmosphere.\textsuperscript{8}

**Complex Structure of Organic Aerosol**

Organic aerosol particles have received great interest in the literature due to their chemical complexity and importance in reaction chemistry in the troposphere. Organic aerosol typically consists of several types of organic compounds mixed with inorganic salts.\textsuperscript{9-12} Previous studies have shown that within these complex mixtures of organic/inorganic particles, single particle morphology can vary.\textsuperscript{13,14} The chemical composition and particle morphology generally determine aerosol properties such as reactivity, optical properties, and cloud condensation nuclei activity. As the relative humidity (RH) is cycled within the atmosphere, these mixed organic aerosol particles can undergo phase transitions such as efflorescence, deliquescence, and liquid-liquid phase separation.\textsuperscript{15} Efflorescence is the loss of water resulting in crystallization, while deliquescence is the uptake of water resulting in dissolution. Liquid-liquid phase separation (LLPS) involves the separation of a system into an organic rich and an inorganic
rich liquid phase, whereas the mixing transition results in the two liquid phases combining into one phase.\textsuperscript{13-15} For some organic aerosol systems a hysteresis has been observed between separation and mixing, where the two phase transitions occur at distinct relative humidities.\textsuperscript{16} Figure 1-1 illustrates these phase transitions as a particle uptakes or loses water.

![Figure 1-1](image)

**Figure 1-1:** (a) Aerosol particle phase transitions and impact on growth factor as a particle uptakes or loses water due to a change in relative humidity. (b) Illustration of liquid-liquid phase separation, efflorescence, deliquescence, and mixing phase transitions resulting from a change in relative humidity.

The efflorescence and deliquescence phase transitions have been studied in great detail in the literature and previous work has shown the presence of confinement effects for these phase transitions for particles less than 40 nm.\textsuperscript{17} The presence of liquid-liquid phase separation in aerosol particles, however, was proposed in 2009 and much of the work
to understand the physics and chemistry of LLPS is currently being explored by research groups across multiple disciplines. Upon LLPS, aerosol particles can exhibit a large range of complex morphologies. The three common morphologies observed are homogeneous, core-shell, and partially engulfed. Particle composition and relative humidity are key factors in determining the resulting morphology.\textsuperscript{13-15,18}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{morphologies.png}
\caption{Possible morphologies of mixed inorganic/organic aqueous aerosol particles.}
\end{figure}

Although particle morphology of phase separated aerosol particles has been studied on the supermicrometer scale, when we began the studies described in this dissertation, complex aerosol structure had not been investigated under 1 $\mu$m. Our research group was the first to consider the structure of phase separated organic aerosol on the submicrometer scale, a size regime that is atmospherically relevant when considering the ability of aerosol particles to serve as cloud condensation nuclei.\textsuperscript{19} Unlike previous studies that determined supermicrometer aerosol particle morphology utilizing optical microscopy, we have used cryogenic-transmission electron microscopy to investigate submicron particle morphology.\textsuperscript{19-20} In our initial experiments, we have shown that for some systems aerosol particles exhibit a size dependence of morphology. As shown in Figure 1-3, we have observed that, for a given system of the same composition, upon the LLPS onset relative humidity, large particles undergo phase separation, while small particles remain homogeneous.\textsuperscript{19}
Figure 1-3: Illustration of the presence of a size dependent morphology upon liquid-liquid phase separation.

Dissertation Overview

The primary focus of the work described in this dissertation is understanding the origins of the size dependent morphology we have discovered. By investigating the fundamental physical chemistry behind the liquid-liquid phase separation process and the observed size dependence of model organic aerosol systems, we will be able to better predict aerosol morphology, composition, and optical properties in real systems. Chapter 2 discusses the instrumentation used to investigate particle morphology, cloud condensation nuclei activity, and aerosol optical properties.

In chapter 3, the experiments investigating the origins of the size dependence of morphology are described. We use a model organic aerosol system, poly(ethylene glycol)-400 mixed with ammonium sulfate at varying compositions to probe the effect of phase separation mechanism on particle morphology. Energy dispersive X-ray spectroscopy (EDS) is also used to obtain information about particle composition.

Chapter 4 explores the role of kinetics and thermodynamics on the observed size dependence. The goal of the work described in this chapter is to understand the large
transition region between phase separated and homogeneous structures and determine if an underlying thermodynamic effect impacts the presence of a size dependent morphology. Specifically, the role of particle drying rate is explored by using ammonium sulfate mixed with either pimelic acid or succinic acid, which are model systems for both anthropogenic and biogenic emissions.

Chapters 5 and 6 build upon the work discussed in chapters 3 and 4 by considering the atmospheric significance of a size dependent morphology. The effect of particle morphology on cloud condensation nuclei activity is determined in chapter 5 through the use of a cloud condensation nuclei counter (CCNC). In chapter 6, cavity ring-down spectroscopy is used to examine the morphology dependent optical properties and hygroscopicity of organic aerosol.

Finally, chapter 7 summarizes the main results of this dissertation and highlights our transition to apply our experiments to real atmospheric systems as we move forward. Preliminary data on two common biogenic aerosol systems, β-caryophyllene and α-pinene secondary organic aerosol particles, which were produced in the lab and characterized using transmission electron microscopy, is presented.

References


Chapter 2

Instrumentation

Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a versatile technique that allows imaging of a sample at a significantly higher resolution than light microscopes. TEM has been used for applications across a variety of disciplines ranging from the life and physical sciences to engineering. A TEM consists of four main components that include the electron optical column, vacuum system, electronics, and the control source.\(^1\)

The electron beam emerges from the electron gun at the top of the column and is condensed into a nearly parallel beam at the specimen by the condenser lens. In TEM, it is important that the specimen is thin enough to allow transmission of electrons through the sample. After passing through the specimen, transmitted electrons are collected and focused by the objective lens and a magnified real image of the specimen is projected onto a fluorescent screen at the bottom of the column. The electron path from the gun to the camera must be under vacuum to avoid collision of electrons with air molecules.\(^1\)
Upon interaction with the sample, electrons can be absorbed as a function of the thickness and composition of the specimen, resulting in amplitude and mass thickness contrast. Depending on the composition and structure of the specimen, electrons may also be scattered over small angles giving phase contrast in the image. It is also possible to obtain diffraction contrast in crystalline specimens, where electrons are scattered in very distinct directions that are a function of crystal structure.1

TEM can be coupled with spectroscopy techniques such as energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) to obtain elemental
information. In EDS, a high-energy beam of electrons is focused onto the sample to stimulate the emission of characteristic X-rays that offer information about the elemental composition of the sample. In EELS, the transmitted beam of electrons can be counted and sorted by an energy loss spectrometer according to the amount of energy lost in interactions with the specimen. The energy loss signal carries information about elemental, chemical, and electronic states of the sample atoms.

In the experiments described in this dissertation, we utilize cryogenic-transmission electron microscopy (cryo-TEM) to study the morphology of laboratory generated organic aerosol. Cryo-TEM is helpful in delaying the electron beam damage to the sample and allows for the imaging and characterization of organic aerosol particles.

**Aerosol Particle Generation and Collection**

Aerosol particles are generated from an aqueous solution that is drawn into a constant output atomizer. A nitrogen flow expands through an orifice on the atomizer to form a high-velocity jet that interacts with the aqueous flow, resulting in a fine spray that leaves the atomizer. The wet aerosol particles are passed through a series of driers to remove water from the sample and obtain a relative humidity below 2%. A cascade impactor (PIXE International Corp., Tallahassee, FL) is used to collect the dry aerosol particles onto 200 mesh copper TEM grids coated with continuous carbon (Electron Microscopy Science, Hatfield, PA).

**Condensation Particle Counter**

The number concentration of aerosol particles can be measured with a condensation particle counter (CPC). The CPC functions like an optical counter. Particles are first
enlarged by a condensing vapor to form easily detectable droplets. The CPC consists of three main components: the sensor, the signal-processing electronics, and the flow system. The sensor is made up of a saturator, condenser, and optical detector. Aerosol enters the saturator section and passes through a heated, liquid soaked wick which continually absorbs liquid from a reservoir. The CPC contains liquid butanol which evaporates and saturates the aerosol flow with butanol vapor. The vapor saturated aerosol passes into a vertical condenser tube that is thermoelectrically cooled. The cooled vapor becomes supersaturated and begins to condense onto particles to form larger droplets. These enlarged droplets pass from the condenser tube to the optical detector, where the light scattered by the droplets is collected at a $90^\circ$ angle and focused onto a low-noise photodiode.

![Figure 2-2: Simplified schematic of a condensation particle counter.](image)
Differential Mobility Analyzer

A differential mobility analyzer (DMA) can be used to size select aerosol particles of a known size fraction from a polydisperse aerosol flow. Aerosol particles first enter an impactor that removes large particles by inertial impaction. Before entering the DMA, the aerosol flow enters a $^{85}$Kr neutralizer, which exposes the aerosol to high concentrations of bipolar ions. The particles undergo collisions with the neutralizer and reach a state of charge equilibrium, where the fraction of particles carrying a charge $N$ is given by

$$f(N) = 10 \left[ \sum_{i=0}^{5} a_i(N) \left( \frac{D_p}{nm} \right)^i \right]$$

(1)

where $D_p$ is the particle diameter, and $a_i$ is the coefficient based on the Fuchs charge distribution model (1963).\textsuperscript{3-4} Equation 1 is used to calculate the fraction of $\pm 1$ and $\pm 2$ charged particles. For the fraction of particles carrying higher order charges, an extended equation based on the derivation by Gunn (1956) can be used.\textsuperscript{5}

The charged aerosol passes from the neutralizer into the DMA that consists of two concentric metal cylinders. The inner cylinder is maintained at a controlled negative voltage, while the outer cylinder is electrically grounded. This setup creates an electrical field between the two cylinders and allows only particles with a narrow range of electrical mobility to be extracted and classified by the DMA. The particle diameter, $D_p$, of the size selected aerosol can be related to the center rod voltage by

$$\frac{D_p}{C} = \frac{2neVL}{3\mu q_{sh} \ln \frac{r_2}{r_1}}$$

(2)
where $C$ is the Cunningham slip correction, $n$ is the number of elementary charges on the particle, $e$ is the elementary charge, $V$ is the average voltage on the inner center rod, $L$ is the length between the exit slit and polydisperse aerosol inlet, $\mu$ is the gas viscosity, $q_{sh}$ is the sheath air flow rate, $r_2$ is the outer radius of annular space, $r_1$ is the inner radius of annular space.\(^6\)

\[ \text{Figure 2-3: Schematic of a differential mobility analyzer attached to an aerosol neutralizer.} \]
Cloud Condensation Nuclei Counter

Aerosol particles play an important role in cloud droplet formation. Determining the physical and chemical properties of aerosol particles that serve as cloud condensation nuclei (CCN) is critical in understanding and accurately modeling the aerosol indirect effect. A cloud condensation nuclei counter (CCNC) can be used to measure the concentration of CCN and determine the role of particle composition in cloud droplet formation. Furthermore, a CCNC can be used in the field to investigate the effect of pollution on clouds and precipitation in urban environments. In this work, we use a commercially available CCNC developed by Droplet Measurement Technologies (DMT, Boulder, Colorado) to study the CCN properties of laboratory generated organic aerosol. The DMT CCNC consists of a cylindrical vertical column in which the aerosol and sheath air flow from top to bottom. The instrument takes advantage of the difference in diffusion rates between water vapor and heat. Water vapor diffuses from the warm and humidified column walls toward the centerline at a faster rate than heat. This results in a thermodynamically unstable supersaturated water vapor state. Thus, to achieve equilibrium, the supersaturated water vapor condenses on the aerosol particles in the sample air and results in the formation of droplets. The centerline supersaturation value can be controlled by the user by modifying the temperature gradient and flow rate in the column. An optical particle counter is used to count and size the particles. This information can be used in combination with a differential mobility analyzer and condensation particle counter to determine the fraction of particles that are CCN activated as a function of water vapor supersaturation and particle size.
Figure 2-4: Simplified schematic of a cloud condensation nuclei counter showing the temperature gradient within the CCN column that allows control of the centerline water vapor supersaturation.

Cavity Ring-Down Spectroscopy

Cavity ring-down spectroscopy (CRDS) is a highly sensitive technique due to its long effective pathlength. CRDS has been used to determine the optical properties of size-selected aerosol particles. \(^8\)\(^-\)\(^10\) The CRDS instrument has a cavity that is capped with two highly reflective mirrors at each end. As light propagates through the cavity, the light transmitted through the back-mirror decays in intensity. When a sample enters the cavity, it either absorbs or scatters the light and increases the rate of decay, which is termed the ring-down time. Essentially, the extinction coefficient (which is the sum of the scattering and absorption of light by the sample) is measured. The extinction coefficient and particle
concentration (measured with a condensation particle counter) can be used to determine
the extinction cross section of the species of interest. A detailed description of CRDS
and its application to organic aerosol are presented in chapter 6.

References


Chapter 3

Role of Nucleation Mechanism on the Size Dependent Morphology of Organic Aerosol

This chapter has been adapted from: Muhammad Bilal Altaf, Andreas Zuend, Miriam Arak Freedman, “Role of Nucleation Mechanism on the Size Dependent Morphology of Organic Aerosol”, Chemical Communications, 2016, 52, 9220-9223.

Abstract

The origins of the size dependent morphology of organic aerosol are explored by probing the morphology of poly(ethylene glycol)-400/ammonium sulfate mixtures using cryogenic-transmission electron microscopy. Surprisingly, we observe a size dependence at some compositions, but not at others. Our results suggest that size dependence occurs due to an activated process.

Introduction

One of the most uncertain aspects in our understanding of the climate system is the impact of aerosol particles.\(^1\) Aerosol particles affect climate through the absorption and scattering of radiation, heterogeneous chemistry, and interactions with clouds.\(^2\) These effects stem in part from the composition, morphology, and phase state of the particles.
Recently, these physical and chemical properties have been of particular interest for aerosol particles composed of organic compounds and salts.\textsuperscript{3-5} The morphology of aerosol particles has especially been the focus of current research as it is a complex property and can vary depending on particle composition and size.\textsuperscript{5-7} As the relative humidity (RH) is cycled within the atmosphere, these mixed particles can undergo liquid-liquid phase separation (LLPS) to form coexisting liquid phases.\textsuperscript{8,9,11-13} Liquid-liquid phase separation may occur through nucleation-and-growth or spinodal decomposition mechanisms (Figure 3-1a).\textsuperscript{9} Nucleation-and-growth occurs when a system reaches the metastable region in a phase diagram, where an energy barrier must be overcome to form a critical nucleus (i.e. a molecular cluster of distinct composition), the growth of which will lead to an additional liquid phase. In spinodal decomposition, however, phase separation occurs throughout the entire solution volume as a concerted process without an energy barrier impeding this phase separation mechanism.\textsuperscript{10} Among some systems that undergo LLPS and are prepared under the same environmental conditions (i.e. the same temperature, pressure, and initial RH), a size dependent morphology has been observed, where small particles are homogeneous and large particles are phase separated.\textsuperscript{7} In this Communication, we explore the role of the phase separation mechanism on the morphology of particles.

To determine whether the phase separation mechanism affects the size dependent morphology of organic aerosol, we have characterized the morphology of aqueous poly(ethylene glycol) 400 (PEG-400)/ammonium sulfate mixtures. Figure 3-1b shows the phase diagram for the bulk water + PEG-400 + ammonium sulfate system, predicted based on a PEG-specific parameterization of the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) thermodynamic model\textsuperscript{11,12} using the method of
Zuend et al. Additional information about the model and the computed phase diagram is given in the Supplementary Information (see Figure 3-5, ESI†). The point where the binodal and spinodal curves meet is known as the critical point (also known as plait point). In the immediate vicinity of the critical point, conditions may be favorable for LLPS to take place via spinodal decomposition. At all other dry compositions, however, a metastable one-liquid-phase area needs to be crossed, where the nucleation-and-growth mechanism dominates.

![Figure 3-1](image)

**Figure 3-1:** (a) Sketch of distinct liquid-liquid phase separation mechanisms. (b) Predicted bulk phase diagram of the aqueous PEG-400 + ammonium sulfate system at 298.15 K by an AIOMFAC-based model, shown for the RH range between 75 % and 95 %. The shaded areas indicate metastable (light blue) and unstable (dark blue) single-phase mixture compositions. In the white area outside of the binodal curve, a single homogeneous liquid phase is the stable thermodynamic state. Dashed grey lines with labels are isolines of water activity, representing tie-lines for coexisting phase compositions within the LLPS region. The pink dash-dotted curve indicates the solubility limit of ammonium sulfate with respect to its crystalline state.

Previous optical microscopy studies (using droplets of several tens of micrometers in diameter) by Ciobanu et al. have observed a visual signature which suggests that the aqueous PEG-400/ammonium sulfate system phase separates via spinodal decomposition in the range from 60/40 to 40/60 organic/inorganic dry mass ratio. We have studied
several organic to inorganic ratios (indicated in Figure 3-1b) both within and outside the spinodal decomposition range observed by Ciobanu et al., to determine the impact of the phase separation mechanism on particle morphology. The morphologies of particles that are atomized at high RH (RH ≥ 96%) and dried in the gas phase to less than 2% RH (with a drying rate of 87.2% RH/s and at a temperature of 295 K) are determined using cryogenic-transmission electron microscopy (cryo-TEM). We have also used energy dispersive X-ray spectroscopy (EDS) to obtain particle composition information and have shown that regardless of particle size and morphology, the overall composition is uniform (see Figure 3-6 and S3, ESI†).

Results/Discussion

As shown in the cryo-TEM images for the 80/20 PEG-400/ammonium sulfate mass ratio (1.32/1 PEG-400/ammonium sulfate molar ratio), we observe a size dependence of morphology, where large particles have phase separated (core-shell) structures and small particles have a homogeneous (single-phase) morphology (Figure 3-2a). This organic/inorganic ratio falls outside the range for spinodal decomposition observed by Ciobanu et al. and also as indicated by the phase diagram in Figure 3-1b. Thus, we expect this system to phase separate by nucleation-and-growth. The smallest phase separated particles observed for the 80/20 PEG-400/ammonium sulfate mass ratio are 86 nm in diameter and the largest homogeneous particles are 182 nm in diameter (Figure 3-2b). Particles larger than these size regimes are phase separated, and those that are smaller are homogeneous.
Surprisingly, at a 50/50 PEG-400/ammonium sulfate mass ratio (0.330/1 PEG-400/ammonium sulfate molar ratio), we observe no size dependence of morphology, as all particles down to diameters of approximately 20 nm are phase separated (Figure 3-3). Note that in our cryo-TEM experiments we study particles down to ~20 nm because particles smaller than this size become difficult to distinguish from the background at higher magnifications in addition to undergoing immediate electron beam damage. The behavior of the 50/50 PEG-400/ammonium sulfate system suggests that phase separation may be taking place at or near the critical point. If the energy barrier to phase separation is absent, the system may undergo spinodal decomposition, which could lead to phase separation occurring rapidly throughout the entire solution volume as a concerted process, resulting in phase separated structures at all particle sizes.
To further explore the result we obtained for the 50/50 PEG-400/ammonium sulfate system, we have worked with intermediate organic/inorganic ratios near the 50/50 mass ratio. We have investigated the 60/40, 52/48, and 45/55 PEG-400/ammonium sulfate systems. The 60/40 and 45/55 PEG-400/ammonium sulfate systems exhibit a size dependence of morphology similar to that shown earlier for the 80/20 PEG-400/ammonium sulfate system (see Figure 3-8 and S5 in ESI† for discussion). However, at an organic to inorganic ratio close to 50/50, such as the 52/48 PEG-400/ammonium sulfate system, we observe a size dependence of morphology, but there is a shift in the transition region between homogeneous and phase separated particles (i.e. phase separated particles are now observed down to smaller diameters). The smallest phase separated particles are 39 nm in diameter, and the largest homogeneous particles are 97 nm in diameter (Figure 3-4). Particles larger than these size regimes are phase separated, and those that are smaller are homogeneous.

Figure 3-3: (a) Cryo-TEM image of 50/50 PEG-400/ammonium sulfate mixture. (b) Histogram for the 50/50 PEG-400/ammonium sulfate system showing that particles at all sizes undergo phase separation.
Figure 3-4: Histogram showing the size dependent behavior of the morphology of 52/48 PEG-400/ammonium sulfate mixture. Large particles are phase separated (blue), while smaller particles have a homogeneous morphology (red).

The results observed for the 52/48 PEG-400/ammonium sulfate system suggest that at this composition we are approaching the critical point where the binodal and spinodal curves touch (Figure 3-1b). As the composition of a system is shifted towards the critical point region, the activation barrier for phase separation decreases because the surface tension of the formation of a new interface approaches zero.\textsuperscript{10,12} The shift of phase separated particles to smaller diameters, as observed for the 52/48 mass ratio, is consistent with theory which expects the activation barrier for phase separation to decrease near the critical point region.\textsuperscript{10,12} We note that the phase diagram in Figure 3-1b indicates the critical point occurs at a PEG-400/ammonium sulfate mass ratio of approximately 43/57 instead of the experimental signature we observe for the critical point region at a 50:50 mass ratio. Since the phase diagram presented in Figure 3-1b is for a bulk system, the position of the critical point may shift at small particle sizes. In addition, the activation energy barrier may vary at the smaller sizes and if too high, the system may skip over the
binodal and cross the metastable region (i.e. avoid nucleation and growth) and instead phase separate via spinodal decomposition.

The inhibition of the formation of a new phase due to the presence of a nucleation barrier can be explained for the nucleation-and-growth process. As a system reaches the metastable region in a phase diagram, concentration fluctuations reach a critical amplitude to form a critical nucleus. The total Gibbs energy required for the formation of a nucleus can be written as

$$\Delta G_{\text{nucleation}} = 4\pi r^2 \gamma - (4\pi/3)r^3 \Delta G_v$$

(1)

where $r$ is the radius of the nucleating phase, $\gamma$ is the interfacial surface tension between the nucleus and the local composition in its surroundings, and $\Delta G_v$ is the change of Gibbs free energy per unit volume. The decrease in the molar Gibbs free energy ($\Delta G$) of the system is the driving force for the creation of a new phase, which is critical in providing the additional energy required to overcome the interfacial energy between the two new phases. At small particle sizes, the interfacial energy component dominates and prevents nucleation. At larger sizes, the volumetric driving force dominates and the energy barrier to nucleation is reduced, allowing the formation of a new phase. We also note that the viscosity of particles can inhibit phase separation. The stochastic nature of the phase separation process and viscosity of the particles at the point of phase separation during fast drying likely causes the width of the transition region where both phase separated and homogeneous morphologies are observed in our experiments. For instance, in a high viscosity scenario, particles at smaller sizes may not have enough time to undergo a sufficiently large compositional fluctuation event that would lead to particle-wide phase separation during the drying stage of the experiments. We note that the drying rates in
the ambient atmosphere are orders of magnitude smaller than those used in our experiments and thus will be explored further in future work. We also note that the transition region between homogeneous and phase separated particles for the PEG-400/ammonium sulfate systems is greater than that of the systems we have previously explored. This may result in part from the total number of particles analyzed. Since we study single particles using the cryo-TEM technique and use area equivalent diameters, a significantly greater number of total particles analyzed (as done in this work) can give us a more accurate representation of the transition region between the two morphologies observed.

Nanoscale effects have been previously observed for the deliquescence and efflorescence phase transitions of sodium chloride aerosol particles. The deliquescence (DRH) and efflorescence (ERH) relative humidities increase for sodium chloride particles with diameters < 40 nm due to the Kelvin effect, which states that the vapor pressure over a curved surface is greater than that over a flat surface. A similar trend was not observed for ammonium sulfate, as the DRH and ERH values for 6 nm and 60 nm particles showed only a weak size dependence. The difference between the size dependent behavior of phase transitions of these salts has been explained using an extension of Köhler theory. Though the dry chemical composition of our particles is the same at a given mass ratio due to the low volatility of PEG-400 and ammonium sulfate, the water content will be affected by the Kelvin effect for a given RH. As a result, the Kelvin effect likely affects the concentration of solute in the particles at the smallest sizes, which may increase the RH at which the separation into two liquid phases occurs. We note that this effect competes with the interfacial energy contribution of the system, which tends to decrease the RH at which LLPS occurs. Thus, the combination of the two opposing effects likely leads to a smaller
deviation from the bulk system LLPS onset RH than when each effect is considered individually (see Tables S1 and S2 in ESI† for detailed discussion).

Our results indicate that a size dependence of morphology is observed where phase separation takes place predominantly by nucleation-and-growth; in other words, in the presence of an activation barrier. The size dependence of morphology should be a widespread phenomenon in the atmosphere among systems that undergo phase separation, particularly for rather viscous particles experiencing rapid drying. This result has consequences for new particle growth as differences in morphology (i.e. homogeneous vs. phase separated) will have implications for the mass accommodation coefficient, a parameter which determines the transfer rate of gases into aqueous droplets for organic aerosol loading. Since low volatility organics may prefer to be in an organic-rich phase, the presence of a size dependent morphology where small particles are homogeneous may lead to lower growth rates than expected and impact the formation of cloud condensation nuclei (CCN). CCN activation is sensitive to the size, composition, surface tension, and morphology of aerosol particles < 200 nm. The presence of a size dependent morphology may lead to phenomena where small particles are homogeneous at low RH, but as the particles grow with increasing RH, they may reach a size and composition that leads to phase separation prior to becoming an effective CCN. Thus, a size dependent morphology may impact the hygroscopic properties of these particles, which could affect CCN concentrations and further influence cloud formation, albedo, and precipitation.18
Conclusions

In summary, we have reported on the origins of the size dependence of morphology of organic/inorganic aerosol particles through the study of the PEG-400/ammonium sulfate system. Our results suggest that a size dependence of morphology requires an activation barrier. For an 80/20 PEG-400/ammonium sulfate mass ratio, which phase separates through nucleation-and-growth, we observe a size dependent morphology where small particles are homogeneous and large particles are phase separated. At a 52/48 organic/inorganic mass ratio, we observe a shift in size dependent behavior where particles remain phase separated down to smaller diameters. This result suggests that we are approaching the critical point at this composition and the activation barrier to phase separation is decreasing. At a 50/50 PEG-400/ammonium sulfate mass ratio, we observe only phase separated structures down to approximately 20 nm, indicating that the activation barrier is low enough (or possibly absent) to allow phase separation to proceed rapidly at all particle sizes studied. Since phase separation by nucleation-and-growth should be a common occurrence in the atmosphere, we expect the majority of phase separating atmospheric particles to have a size dependent morphology (especially fine and ultrafine aerosol particles), which may have important implications for the growth of freshly nucleated, nanometer-sized particles and the formation and activation of cloud condensation nuclei. Our results on the morphology of particles as a function of their nucleation mechanism may also have application to biophysical chemistry, where aqueous two-phase systems are widely studied, and materials chemistry, where nanoscale effects on nanoparticle properties have been observed for a wide variety of systems.
References

(1) Stocker, T.F. et al., IPCC, 2013. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.


Supplementary Information

Summary

This supplementary information contains detailed experimental methods for the cryo-transmission electron microscopy (cryo-TEM) experiments. We also provide information regarding particle composition, the resolution of the cryo-TEM technique, and the ability to distinguish between liquid-liquid phase-separated and homogeneous particles for the PEG-400/ammonium sulfate system based on electron beam damaging behavior. The histograms for the 60/40 and 45/55 PEG-400/ammonium sulfate systems are also included. In addition, a description of the computed bulk phase diagram and a discussion of the interfacial energy contribution of the aqueous PEG-400/ammonium sulfate system are provided.

Computed Bulk Phase Diagram

In the following, a brief discussion of the computed phase diagram is provided. Figure 3-1b of the main text shows a phase diagram of the pseudo-ternary system water + PEG-400 + ammonium sulfate at 298.15 K. Figure 3-5 shows the same phase diagram yet provides additional information on the Gibbs energy difference (color axis) between the (initial) single-phase state (of known composition) and the two-phase, liquid-liquid phase-separated state (if it is the stable equilibrium state). The pink curves in Figs. 1b and S1 mark the solubility limit of ammonium sulfate. At relative humidities below the pink curve (here below ~80 %), a crystalline phase of ammonium sulfate would be in equilibrium with the liquid phases – or as done in the shown computation, the liquid phases would actually be supersaturated with respect to dissolved ammonium sulfate. The two points where the
pink curve intersects with the binodal represent the predicted (dry) compositions of the two coexisting liquid phases in liquid-liquid equilibrium. Similarly, in Figure 3-1b, the intersections of isolines of water activity with the binodal indicate the compositions of coexisting phases (this is why they can be considered as tie-lines). The water contents of the coexisting phases are obtained from a related plot (not shown) where the ordinate is mass fraction of water rather than mole-fraction-based water activity.

We note that the computed phase diagram pertains to a bulk system of the three mixture components, i.e., to a system where the surface/volume ratio is tiny and interfacial energies between the liquid phases and of the gas-liquid interface are negligible compared to the energy content of the bulk volume of phases. In other words, the shown phase diagram describes the situation of large droplets (typically for diameters > 200 nm) for which a size effect on phase separation is negligible. Such phase diagrams can be computed based on thermodynamic theory and a model that allows for the computation of the Gibbs energies of different phase compositions. While droplet size effects will slightly alter the exact positions of the binodal and spinodal curves, the bulk phase diagram offers insight into the approximate locations of metastable and unstable single-phase compositions and the expected onset RH of liquid-liquid phase separation (LLPS).

Here we use the thermodynamic group-contribution model called Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC), developed by Zuend et al., for the calculation of activity coefficients of the different mixture species at given compositions. In contrast to other organic-inorganic systems where the organic molecules do not contain large numbers of repetitive units, an accurate description of oligomers and polymers like PEG in aqueous solutions is rather difficult.
For example, it is known that phase equilibria of PEG oligomers are poorly represented by the set of standard functional groups and associated model parameters of the widely-used UNIFAC model\textsuperscript{4,5}, as discussed by Ninni et al.\textsuperscript{6} This limitation also affects the AIOMFAC model, which contains a modified UNIFAC model. Recently, a PEG-specific oxyethylene group (-CH\textsubscript{2}-O-CH\textsubscript{2}- ; the monomer unit in PEG oligomers) was introduced in order to develop a PEG-specific AIOMFAC model parameterization of aqueous PEG solutions and to account for interaction effects of PEG oligomers of various molar masses with ammonium and sulfate ions in solution. A detailed description of this specific AIOMFAC parameterization will be discussed in a separate manuscript. The phase diagram itself was computed based on the liquid-liquid phase equilibrium prediction method by Zuend and Seinfeld\textsuperscript{7} within the modeling framework of Zuend et al.\textsuperscript{1}

The dashed contour lines of Gibbs energy difference between a single-phase state and the stable equilibrium state shown in Figure 3-5 allow for an estimation of the effect of an activation energy penalty on the onset water activity (or RH) of LLPS due to the energy requirement of the formation of a new interface between two liquid phases. For example, in the case where the additional interfacial energy for a mixture of overall 50/50 PEG-400/ammonium sulfate mass ratio (\(w_d(\text{salt}) = 0.5\)) would amount to 2 J/mol, the binodal curve would shift to lower water activities and would be represented by the dashed contour line of 2.0 J/mol. That is, this interpretation of the additional information given by the computed phase diagram would mean that the onset RH of LLPS would shift from \(~90.3\%\) to \(~87.8\%\) RH for \(w_d(\text{salt}) = 0.5\). However, not included in this estimation is the Kelvin effect accounting for the effect of droplet curvature, which tends to increase the RH of phase separation (due to its effect on droplet water content) and would lead to a smaller
effective change in LLPS onset RH, as discussed in the main text. Generally, for solution droplets of small size (diameters less than ~200 nm) a size-dependent phase diagram would be necessary to include both the Kelvin effect and interfacial energy (surface tension) effects accurately.\(^8\) This also means that the mixture composition of the critical point is essentially both a size- and temperature-dependent quantity.

**Figure 3-5:** Computed phase diagram of the water + PEG-400 + ammonium sulfate bulk system at 298.15 K. Shown is the phase diagram in terms of water activity (equivalent to RH at equilibrium with the liquid mixture) versus mass fraction of ammonium sulfate, wd(salt), in terms of the dry (water-free) mixture composition. The solid white curve is the predicted binodal and the dotted white curve the spinodal. The dashed white curves are contour lines of constant Gibbs energy difference between a (forced) single phase state and the stable (two-phase) state at thermodynamic equilibrium (color axis). The dash-dotted pink curve marks the solubility limit of ammonium sulfate.

**Size dependence and effect of the liquid-liquid interfacial energy contribution**

The formation of a new liquid phase in an eventually liquid-liquid phase-separated system, here considered for a concentric core-shell morphology of a spherical droplet,
introduces a thermodynamic energy barrier associated with the formation and expansion of the interfacial area between the two liquid phases. Based on the computed phase diagram for the bulk system, we discuss here the approximate impact and droplet size dependence of the interfacial Gibbs energy contribution on the phase separation onset RH. The interfacial Gibbs energy contribution is one of the size dependent energy contributions that will affect the locations of the binodal and spinodal curves in a composition-based phase diagram of a small droplet at constant temperature. Thus, an estimate of the interfacial energy contribution allows for an estimate of the shift in onset RH of LLPS (to lower RH). We note that there are other size-dependent effects that will influence the thermodynamic phase behavior for a given droplet size and morphology. These other effects include (i) the Kelvin (curvature) effect on the equilibrium vapor pressure of semi-volatile mixture substances (here water) over a curved droplet surface, which increases the concentration of dissolved solutes (here ammonium sulfate and PEG-400), and (ii) the change of surface tension at the gas-droplet interface upon LLPS. Both of these effects typically tend to increase the RH of LLPS onset and therefore partially or fully counteract (and potentially exceed) the effect of an interfacial energy penalty. Thus, knowledge of the interfacial energy contribution alone is not sufficient to accurately determine the droplet size effect on phase separation onset and the deviation of a size-dependent phase diagram from the bulk phase diagram, such as the one shown in Figure 3-5. However, the magnitude of the interfacial energy contribution as a function of droplet size allows an estimation of the change in expected LLPS onset RH if this were the dominant size effect. Table 4-1 lists calculated interfacial energy contributions for the water + PEG-400 + ammonium sulfate system (1:1 mass ratio of PEG-400 to ammonium sulfate) for a selection of droplet sizes.
ranging from 1 µm to 10 nm in diameter. The given values are calculated based on measured solution densities and surface tensions by Song et al. and other mixture properties and assumptions given in Table 4-2. Combining the phase diagram information shown in Figure 3-5 for the bulk system with Table 4-1 shows that the interfacial energy contribution leads to a shift of the onset water activity (equivalent to the onset RH at bulk conditions) of phase separation to a lower RH value. This is seen from the location of the dashed white curves in Figure 3-5, which are contour lines of constant Gibbs energy difference between a (forced) single phase state and the stable (two-phase) state at thermodynamic equilibrium. The interfacial energy penalty to be overcome for LLPS in a small droplet means that this energy barrier to separation needs to be compensated by a reduction in the system’s Gibbs energy due to phase separation, which is achieved with a reduction in equilibrium water activity of the droplet. For example, with the interfacial tension of $1.07 \times 10^{-3} \text{ J/m}^2$, a droplet of 90 nm diameter is predicted to have an interfacial energy contribution of ~2 J/mol, which can be compared to the molar Gibbs energy shown in Figure 3-5. Such a droplet will undergo LLPS at a RH approximately 2.5 % lower than the corresponding bulk solution (both with a 1:1 mass ratio of PEG-400 to ammonium sulfate). Taking, for comparison, the lower range of the interfacial tensions given by Song et al. as $0.08 \times 10^{-3} \text{ J/m}^2$, the 90 nm diameter droplet would experience an interfacial energy contribution of ~ 0.15 J/mol and a shift in LLPS onset of approximately 0.7 % RH. In conclusion, Table 4-1 shows that the interfacial energy contribution increases with a decrease in droplet size and overcoming this energy barrier for phase separation therefore requires a reduction in the onset RH of LLPS, typically of less than 10 % RH even for rather small droplets. As mentioned above, other droplet size effects tend to counteract this reduction in onset RH of LLPS. We note
that the interfacial energy contribution calculated in this section for a certain droplet size relates to the equilibrium thermodynamic state of that system and is different from an activation energy for nucleation and growth of a new phase that starts as a critical cluster of distinct composition within a homogeneous droplet, because the size of a critical cluster will be different from the size of the core or shell phases of the droplet at equilibrium.

Table 3-1: Calculated droplet size dependence of the interfacial energy contribution to the system’s Gibbs energy.

<table>
<thead>
<tr>
<th>Droplet diameter [nm]</th>
<th>Droplet volume [m³]</th>
<th>Substance amount in droplet volume [mol]</th>
<th>Core phase surface area [m²]</th>
<th>Interfacial energy (a) [J/mol]</th>
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</thead>
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<td>1.151E-14</td>
<td>1.979E-12</td>
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</table>

(a) This is the interfacial energy contribution per overall molar amount of substance in the phase-separated droplet based on a value of 1.07×10⁻³ J/m² for the interfacial surface tension and the given assumptions about the volume ratio and average density of the droplet phases.
Table 3-2: Component and system parameters used to determine the interfacial energy contribution as a function of size in Table 4-1.

<table>
<thead>
<tr>
<th>System or component property</th>
<th>Numeric value and unit</th>
</tr>
</thead>
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<td>Molar mass of water</td>
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</tr>
<tr>
<td>Molar mass of PEG-400</td>
<td>0.400000 [kg/mol]</td>
</tr>
<tr>
<td>Molar mass of ammonium sulfate</td>
<td>0.132139 [kg/mol]</td>
</tr>
<tr>
<td>Average molar mass (estimated for a system with PEG-400 and ammonium sulfate mixed 1:1 by mass and a water content of 80 mol-%)</td>
<td>0.054143 [kg/mol]</td>
</tr>
<tr>
<td>Overall solution density (a)</td>
<td>1190 [kg/m³]</td>
</tr>
<tr>
<td>Average molar density of solution (droplet)</td>
<td>21978.9 [mol/m³]</td>
</tr>
<tr>
<td>Core/shell volume ratio of the phases</td>
<td>1.0 [-]</td>
</tr>
<tr>
<td>Interfacial surface tension (b)</td>
<td>1.07 [mN/m] (c)</td>
</tr>
</tbody>
</table>

(a) Value based on data given in Table 2 of Song et al. (2013) for this system.
(b) Song et al. (2013) list a range of values for the interfacial tension between 0.08 and 1.07 [mN/m] at different water activities (i.e. different RH levels). Here the largest measured value is taken, which applies to conditions at 82 % RH.
(c) An interfacial surface tension of 1 mN/m is equivalent to 10⁻³ J/m².

Experimental Methods: Aerosol Particle Generation and Cryogenic-Transmission Electron Microscopy

Solution preparation and aerosol particle generation

Aerosol particles composed of ammonium sulfate (> 99.0%, EMD) and poly(ethylene glycol) 400 (PEG-400; BioUltra, Sigma-Aldrich) were generated from aqueous solution without further purification. Aqueous solutions with 0.015 wt.% to 0.0625 wt.% solute were prepared for the mixtures of PEG-400 with ammonium sulfate at either a 80/20, 60/40, 52/48, 50/50, or 45/55 mass ratio of PEG-400/ammonium sulfate. These solutions were prepared using ultrapure water (high-performance liquid chromatography grade). Aerosol particles were generated at a high relative humidity (RH ≥ 96%) from the aqueous solutions using a constant output atomizer (TSI 3076, Shoreview, MN). Nitrogen flow through the atomizer was approximately 1.5 L/min. The wet aerosol particles were dried to less than 2% RH (with a drying rate of 87.2% RH/s and at a
temperature of 295 K) using a diffusion dryer filled with molecular sieves (13X mesh size, Sigma Aldrich). The dry aerosol particles were collected onto TEM grids for imaging.

**Cryogenic-Transmission Electron Microscopy (cryo-TEM)**

To prepare samples for imaging, a cascade impactor (PIXE International Corp., Tallahassee, FL) was used to collect dry aerosol particles onto 200 mesh copper TEM grids coated with continuous carbon (Electron Microscopy Science, Hatfield, PA). The impactor was backed by a mechanical pump to provide a flow rate of 1.0 L/min. The particles were imaged using cryo-TEM at an accelerating voltage of 120-200 kV. Prior to imaging, the samples were transferred to a cryo-TEM holder and cooled in the microscope to approximately 93 K using liquid nitrogen. Cryogenic conditions were used to minimize electron beam damage to the samples.\textsuperscript{10-12}

Collected TEM images were analyzed using ImageJ (National Institutes of Health, Bethesda, MD). The areas of thousands of particles were determined for each sample. Assuming the particles are spherical, the calculated area is converted to an area equivalent diameter. The total number of particles at each area equivalent diameter can be used to plot the distribution of particle sizes as a function of their morphology.

**Particle Composition Information**

Due to the procedure by which the aerosol particles are generated, we assume that the overall chemical composition of homogeneous and phase-separated particles is the same for a given organic/inorganic mass ratio. We have used energy dispersive X-ray spectroscopy (EDS) to obtain composition information for the particles studied and have shown that regardless of particle size and morphology, the overall composition is uniform.
Although the particles undergo electron beam damage even at cryogenic temperatures (93 K), we can still obtain elemental composition. Specifically, we are interested in detecting sulfur and carbon, which are not vaporized during the process of acquiring an EDS spectrum. We note that although we use carbon-coated TEM grids, the carbon present in the particles yields additional signal over the relatively constant background levels, and thus we can use the sulfur to carbon ratios to determine if the particles have uniform composition. Figure 3-6 shows sample EDS spectra for two 60/40 PEG-400/ammonium sulfate particles: one phase-separated and one homogeneous. The homogeneous and phase-separated particles presented in the spectra below are approximately the same size and have an identical EDS spectrum. We note that the copper signal results from the cryo-TEM sample holder and the TEM grid support film, while the silicon signal is primarily from the TEM grid background.
We have obtained EDS spectra for the 60/40 PEG-400/ammonium sulfate system and analyzed a total of 62 particles (29 homogeneous and 33 phase-separated) with particle sizes ranging from 105 nm to 426 nm. We note that the sulfur peak becomes difficult to detect for particle diameters less than 100 nm. The peak areas from the EDS spectra were analyzed using DeskTop Spectrum Analyzer II (DTSA-II; National Institute of Standards and Technology, Gaithersburg, MD). The average sulfur to carbon ratios are presented in Figure 3-7. In addition to the identical EDS spectra observed for homogeneous vs. phase-separated particles, we have shown that regardless of particle morphology, we obtain similar sulfur to carbon ratios for the particles studied, indicating uniform overall particle composition.
Figure 3-7: Sulfur to carbon ratios derived from EDS spectra peak areas using DTSA-II for 60/40 PEG-400/ammonium sulfate phase-separated and homogeneous particles. The error bars result from the measurement of sulfur to carbon ratios for multiple particles.

Data for the 60/40 and 45/55 PEG-400/Ammonium Sulfate Systems

The 60/40 and 45/55 PEG-400/ammonium sulfate systems behave similarly to the 80/20 PEG-400/ammonium sulfate mixtures in terms of the size dependent behavior observed. The samples analyzed for the 60/40 PEG-400/ammonium sulfate system consisted of 2968 particles (266 homogeneous and 2702 phase-separated). The smallest phase-separated particles are 80 nm in diameter, and the largest homogeneous particles are 198 nm in diameter (Figure 3-8). Particles larger than these size regimes are phase-separated, and those that are smaller are homogeneous.
Figure 3-8: Histogram showing the size dependent behavior of the morphology of the 60/40 dry mass ratio PEG-400/ammonium sulfate mixture. Large particles are phase-separated (blue), while smaller particles have a homogeneous morphology (red).

The samples analyzed for the 45/55 PEG-400/ammonium sulfate system consisted of 2436 particles (575 homogeneous and 1861 phase-separated). The smallest phase-separated particles are 64 nm in diameter, and the largest homogeneous particles are 214 nm in diameter (Figure 3-9). Particles larger than these size regimes are phase-separated, and those that are smaller are homogeneous.
Figure 3-9: Histogram showing the size dependent behavior of the morphology of the 45/55 dry mass ratio PEG-400/ammonium sulfate mixture. Large particles are phase-separated (blue), while smaller particles have a homogeneous morphology (red).

The results for the 60/40 and 45/55 PEG-400/ammonium sulfate mixtures can be explained by considering the bulk phase diagram and the activation barrier as we approach the critical point. The predicted phase diagram shows that inside the composition space where two liquid phases are stable, the same final compositions of the liquid phases can be reached from different initial single phase compositions located along the same tie-line (i.e. when they are located approximately at the same water activity), including from points with 60/40 or 80/20 overall PEG-400/ammonium sulfate dry mixtures initially. That is, the difference in the initial mixture composition may not translate into different final phase compositions; rather, the different initial compositions will lead to different final volumes of the two liquid phases. If the nucleation barrier is associated directly with the final liquid
phase composition, for example, by nucleating a PEG-rich phase from the initial one-phase system, the nucleation barrier could be similar for both 60/40 and 80/20 mixtures. As a result, if the phase separation mechanism for both 60/40 and 80/20 mixtures is by nucleation-and-growth, it is possible that the histograms for both cases look similar. The difference as seen from the predicted phase diagram, is that one could expect that the 80/20 mixture can only phase separate by nucleation-and-growth, while in the case of the 60/40 mixture, the spinodal limit is crossed during drying, which then would allow for phase separation by spinodal decomposition. The reason that did not occur in many cases for very small particles in the experiments could be related to the time scale for drying of the particles.

It is also important to note that the activation barrier for phase separation decreases near the critical point.\textsuperscript{1,15} Our results suggest that a 60/40 mixture is likely not close enough to the critical point to have a significant effect on the activation barrier. This may also explain why as we move to the 45/55 mixture (which is slightly closer to the critical point than the 60/40 mixture), we are nearing the threshold where the activation barrier decreases and phase separated particles are observed at slightly smaller diameters compared to the 60/40 case.

Distinguishing between Homogeneous and Phase-Separated Particles

In our cryo-TEM experiments, we use image contrast and electron beam damaging behavior to characterize the morphology of the aerosol particles studied. For phase-separated particles with a resulting core-shell morphology, we are able to see an organic-rich shell that surrounds the inorganic-rich core down to particle diameters on the order of
20 nm. We note that in these experiments we study particles only down to ~20 nm. Particles smaller than this size regime become difficult to distinguish from the background at higher magnifications in addition to undergoing immediate electron beam damage.

The homogeneous particles appear spherical and are uniform in morphology. We can further distinguish the two observed morphologies (i.e. core-shell and homogeneous) using the electron beam damaging behavior. Although we image our particles at approximately 93 K to minimize electron beam damage, longer exposure times will eventually damage the particles. Figure 3-10 shows the damaging behavior of a phase-separated and a homogeneous PEG-400/ammonium sulfate particle. As the phase-separated particles damage, voids begin to form in the particle core and around the perimeter of the core. The voids slowly move towards the outer diameter of the particle but do not fully form throughout the entire particle. As seen in Figure 3-10a, there is an organic shell that is still clearly visible even after the particle has undergone electron beam damage. From the electron beam damaging behavior of the phase-separated particle, it appears that the particle is divided into three sections: the inorganic-rich core, the voids around the core, which may consist of both the organic and inorganic phase, and the pure organic shell surrounding the voids and the core. We note that despite the three regions that are observed upon electron beam damage, the phase-separated particle is still a two-phase system. Since PEG-400 is a surfactant and is surface active in aqueous solution droplets, the organic-rich phase has a PEG-400 rich exterior and a salt-containing area near the core. Raman microscopy of dry particles containing an organic/inorganic component has shown that surface active organics have a higher concentration near the particle edge while the inorganic component decreases in concentration at the air/particle interface.13,14
The homogeneous particles, on the other hand, damage uniformly through the formation of voids. As seen in Figure 3-10b, the homogeneous particle forms voids throughout the entire particle. Thus, in addition to the clearly visible core and shell for the phase-separated particles (and a lack of these morphology features in homogeneous particles), we are also able to use electron beam damage to distinguish between phase-separated and homogeneous particles.

![Figure 3-10: Cryo-TEM images of electron beam damage to (a) a phase-separated PEG-400/ammonium sulfate particle, and (b) a homogeneous PEG-400/ammonium sulfate particle. The time of exposure under the electron beam and particle damage increases from left to right.](image)

In addition to using phase contrast and electron beam damaging behavior to distinguish between phase-separated and homogeneous particles, we also use scanning TEM high angle annular dark field (STEM HAADF) imaging. STEM HAADF imaging is sensitive to the mass of the element being detected. A higher atomic (Z) number leads to a greater loss of energy as electrons interact with the sample. Thus, regions with high Z
atoms appear bright as they scatter more strongly. As seen in Figure 3-11, we can distinguish between a homogeneous and core-shell morphology based on mass contrast. The core-shell particle (Figure 3-11a) has a bright core and a shell that becomes darker near the outer regions of the particle, indicating that PEG-400 is surface active. The homogeneous particle shown in Figure 3-11b appears uniform throughout and does not show any phase separation.

![80/20 PEG-400/Ammonium Sulfate](image)

**Figure 3-11:** Scanning TEM high angle annular dark field (STEM HAADF) image of (a) an 80/20 dry mass ratio PEG-400/ammonium sulfate phase-separated particle and (b) an 80/20 mass ratio PEG-400/ammonium sulfate homogeneous particle.

**Resolution of Cryo-TEM below 100 nm**

As shown in the histogram plots for the PEG-400/ammonium sulfate systems in the main text, cryo-TEM allows us to characterize the morphology of particles studied at diameters well below 100 nm. Through the use of the cryo-TEM technique, we observe both phase-separated and homogeneous morphologies at particle diameters on the order of 50 nm and less. As seen in Figure 3-12, a core and shell is visible in the case of a phase-separated particle (Figure 3-12a) and a lack of phase separation is evident in the homogeneous particle (Figure 3-12b).
**Figure 3-12**: Cryo-TEM images of (a) a phase-separated PEG-400/ammonium sulfate particle, and (b) a homogeneous PEG-400/ammonium sulfate particle showing the resolution of cryo-TEM at diameters on the order of 50 nm.

**Supplementary Information References**


Chapter 4

Effect of Drying Rate on Aerosol Particle Morphology

Introduction

Aerosol particles have increasingly been the focus of atmospheric chemistry research due in large part to their complex effects on the Earth’s climate. Unlike greenhouse gases, which have been shown to cause a net warming effect on climate, it is known that aerosol particles have a net cooling effect, but the magnitude of cooling remains highly uncertain.\(^1\) Aerosol particle properties such as composition, morphology, and size play a large role in determining aerosol-climate interactions.\(^1\)\(^-\)\(^5\) It is important to accurately determine these properties in order to incorporate them into climate models that are designed to understand the aerosol direct and indirect effects. The aerosol direct effect accounts for the absorption and scattering of light by aerosol particles, while the aerosol indirect effect describes the ability of aerosol particles to act as cloud condensation nuclei and impact cloud formation and precipitation.\(^1\)\(^,\)\(^2\)

Aerosol particle morphology has been a topic of recent interest as it plays a critical role in the heterogeneous chemistry that occurs in our atmosphere.\(^1\)\(^-\)\(^5\) Aerosol particle morphology has been investigated from the submicron to the supermicrometer size regime
using a wide range of analytical techniques. In our previous work, we probed aerosol particle morphology using cryogenic-transmission electron microscopy (cryo-TEM) and discovered a size dependent morphology of organic aerosol among systems that undergo phase separation.\textsuperscript{6,7} We observed that large particles were phase separated while small particles remained homogeneous. In these studies, we worked with model organic aerosol systems, where a dicarboxylic acid (either pimelic acid or succinic acid) was mixed with ammonium sulfate.\textsuperscript{7} Figure 4-1 shows optical microscopy images of the dicarboxylic acid systems undergoing phase separation at a distinct separation relative humidity (SRH). The pimelic acid mixture undergoes liquid-liquid phase separation prior to crystallization, while the succinic acid system phase separates upon crystallization.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-1.png}
\caption{Optical microscopy images illustrating phase separation as relative humidity is decreased for 1:1 mixtures of ammonium sulfate/pimelic acid (top panel) and ammonium sulfate/succinic acid (bottom panel). For the ammonium sulfate/pimelic acid mixture, the initial particle is shown in (a), followed by liquid-liquid phase separation (b), and crystallization (c). For the ammonium sulfate/succinic acid mixture, the initial particle is shown in (d), followed by the start of crystallization (e), and complete crystallization (f).}
\end{figure}
Although we observed a size dependent morphology for the organic aerosol systems investigated, the observed transition region (i.e. the size regime where both phase separated and homogeneous structures are observed) occurred at particle sizes greater than 100 nm.\(^7\) We note that size dependent aerosol phase transitions such as efflorescence and deliquescence have previously been observed for particles with diameters on the order of 40 nm.\(^8\) Thus, the transition region we observe for size dependent phase separation is larger than the size regime where aerosol nanoscale effects have previously been observed. In this work, we explore the potential role of kinetics and thermodynamics in the presence of a size dependent morphology. For instance, depending on the drying rate, the viscosity of a particle may impact its ability to nucleate a new phase (kinetic effect). Thus, particle drying rate may be a key parameter in determining the width and size regime of the transition region. To examine this possibility and determine whether our results are due to a purely kinetic phenomenon or impacted by underlying thermodynamics, we have carried out a series of experiments that study a range of particle drying rates and their impact on the resulting morphology.

**Experimental Methods**

**Solution preparation and aerosol particle generation**

Aerosol particles composed of ammonium sulfate (> 99.0%, EMD) mixed with either pimelic acid (>98%, Acros Organics) or succinic acid (>99%, Sigma Aldrich) were generated from aqueous solution. Aqueous solutions with 0.05 wt.% to 0.3 wt.% solute were prepared for the individual components and for mixtures of each organic compound with ammonium sulfate at a 1:1 ratio by mass. These solutions were prepared using
ultrapure water (high-performance liquid chromatography grade). Aerosol particles were generated at a high relative humidity (RH ≥ 96%) and at a temperature of 295 K from the aqueous solutions using a constant output atomizer (TSI 3076, Shoreview, MN). Nitrogen flow through the atomizer was approximately 1.5 L/min. Depending on the drying rate required for a particular experiment, the wet aerosol particles were dried using either a diffusion dryer filled with molecular sieves (13X mesh size, Sigma Aldrich; drying rate of 87.2% RH/s), a nafion tubing dryer (Permapure, Toms River, NJ), a 300 mL round bottom flask (RBF) dryer filled with molecular sieves, or a Tedlar bag (New Star Environmental, Roswell, GA). The drying rate in the nafion dryer was controlled by adjusting the nitrogen sheath flow over the nafion tubing. For our experiments, the drying rate in the nafion dryer ranged from 19-27% RH/s. The drying rate in the RBF dryer was adjusted to 5% RH/s. In the case of the Tedlar bag (with a volume of approximately 500 L), aerosol particles were introduced into the bag at a flow rate of 1.5 L/min over the course of approximately 2 hours. Following particle collection, nitrogen (1-4 L/min) was introduced into the bag in 5 to 40 min intervals over the course of 2-4 hours. In between each drying interval in the bag, time was allowed for mixing and RH equilibration. The drying rates in the Tedlar bag ranged from 3.5 x 10^{-3} to 0.08% RH/s at the point of separation relative humidity (SRH). In these experiments, we note that we work at a constant drying rate at relative humidities ±20% of the SRH. After undergoing drying at the experimentally required drying rate, the dry aerosol particles were collected onto TEM grids for imaging. Figure 4-2 illustrates our setup for the experiments discussed in this work.
Figure 4-2: Experimental schematic for preparation and collection of laboratory generated aerosol particles at varying drying rates.

Cryogenic-Transmission Electron Microscopy (cryo-TEM)

We have discussed the use of cryo-TEM to image submicron aerosol particles in detail in an earlier publication. Briefly, to prepare samples for imaging, a cascade impactor (PIXE International Corp., Tallahassee, FL) was used to collect dry aerosol particles onto 200 mesh copper TEM grids coated with continuous carbon (Electron Microscopy Science, Hatfield, PA). The impactor was backed by a mechanical pump to
provide a flow rate of 1.0 L/min. The particles were imaged using cryo-TEM at an accelerating voltage of 120-200 kV. Prior to imaging, the samples were transferred to a cryo-TEM holder and cooled in the microscope to approximately 93 K using liquid nitrogen. Cryogenic conditions were used to minimize electron beam damage to the samples.

Collected TEM images were analyzed using ImageJ (National Institutes of Health, Bethesda, MD). The areas of several hundred to thousands of particles were determined for each sample. Assuming the particles are spherical, the calculated area is converted to an area equivalent diameter. The total number of particles at each area equivalent diameter can be used to plot the distribution of particle sizes as a function of their morphology.

**Results/Discussion**

In our earlier work, where we discovered the presence of a size dependent morphology for organic aerosol, our experiments utilized a diffusion dryer (drying rate of ~99.7% RH/s) to dry the laboratory generated aerosol. This drying rate is orders of magnitude larger than that experienced by particles in the ambient atmosphere. We have repeated the initial diffusion dryer experiments with ammonium sulfate mixed with either pimelic acid or succinic acid. Figure 4-3 shows the results for similar diffusion dryer experiments where a greater number of particles (~1000s) were studied. We note that the particle size distributions shown in the histograms are not lognormal as the particle counts depend on particle collection time and concentration of the aqueous solution from which the aerosol is generated. As seen in the cryo-TEM images for the two dicarboxylic acid
systems in Figure 4-3a and 4-3c, a partially engulfed morphology is observed at large sizes, while a homogenous morphology is seen at small particle sizes. We note that in the experiments described in this work, we have analyzed a much greater number of particles to obtain a more accurate representation of the width of the transition region. In our original work, which reported the discovery of a size dependent behavior, we studied ~300-500 particles. In these earlier experiments (with a diffusion dryer drying rate of 99.7% RH/s), for the 50/50 ammonium sulfate/pimelic acid mixture, the largest homogeneous particles were 276 nm in diameter, and the smallest phase separated particles were 270 nm in diameter. For the 50/50 ammonium sulfate/succinic acid system we found that the largest homogeneous particles were 196 nm in diameter, while the smallest phase separated particles were 170 nm in diameter. Though we have a more accurate understanding of the transition region due to the significantly larger number of particles imaged, it is clear that the transition region still occurs at particle sizes above 100 nm. For the 50/50 ammonium sulfate/pimelic acid system, the largest homogeneous particles were 243 nm in diameter, while the smallest phase separated particles were 122 nm in diameter. In the case of the 50/50 ammonium sulfate/succinic acid system, the largest homogeneous particles were 214 nm in diameter, while the smallest phase separated particles were 129 nm in diameter.
Figure 4-3: Cryo-TEM images of (a) 50/50 ammonium sulfate/pimelic acid and (c) 50/50 ammonium sulfate/succinic acid. In (b) and (d), histograms show the size dependent behavior of the morphology of the two organic aerosol systems studied using a diffusion dryer. Large particles are phase separated (blue), while smaller particles are homogeneous (red).

To examine the effect of changing drying rate on the observed size dependence, we used two nafion dryers connected in series, where the drying rate was 19% RH/s for ammonium sulfate/succinic acid to 27% RH/s for ammonium sulfate/pimelic acid. Figure 4-4 summarizes the results obtained for the systems dried with the nafion dryer. A size dependent morphology is still observed, where large particles are partially engulfed and those that are smaller are homogeneous. However, the most discernable change that takes place is the shift of the transition region to smaller diameters. Furthermore, the width of the transition region also becomes narrower due to the slower drying rate. As a result of
the slower drying rate, phase separated particles are now observed at ~60 nm (average of smallest phase separated particles observed for the 50/50 ammonium sulfate/pimelic acid and ammonium sulfate/succinic acid systems) compared to the ~125 nm when the particles are dried using the diffusion dryer.

Figure 4-4: Cryo-TEM images of (a) 50/50 ammonium sulfate/pimelic acid and (c) 50/50 ammonium sulfate/succinic acid. In (b) and (d), histograms summarize the size dependent behavior of the morphology of the two organic aerosol systems studied using a Nafion dryer. Large particles are phase separated (blue), while smaller particles are homogeneous (red).
Given the significant change observed in the transition region as a result of the nafion dryer experiments, further studies were designed to investigate drying rates that were orders of magnitude lower. The round bottom flask (RBF) setup yielded a drying rate of 5% RH/s. As Figure 4-5a and 4-5c illustrate, we observed phase separated particles down to approximately 35-50 nm. Although the transition region shifted to slightly smaller diameters, the width was still quite large (~70 nm), indicating that the particles are undergoing drying too quickly and kinetics still play an important role in the observed size dependence. Following these studies, we carried out Tedlar bag experiments that allow particles to be dried over the course of hours, thus resulting in much slower drying rates than we have previously examined. The Tedlar bag experiments consisted of an intermediate drying rate (~0.04-0.08% RH/s; Figure 4-5 b and 4-5d)) and an extended experiment which yielded our slowest experimental drying rates ranging from $3.5 \times 10^{-3}$ to $5.5 \times 10^{-3} \%$ RH/s at the point of separation relative humidity (Figure 4-6). The Tedlar bag experiment results provide great insight into the physical chemistry that plays an important role in the observed size dependence. At the intermediate Tedlar bag drying rates, we observe a very sharp transition region that is ~3-10 nm in width. Moreover, the smallest phase separated particles have shifted to ~30 nm range for both organic aerosol systems.
Figure 4-5: Histograms illustrating the size dependent behavior of the morphology of the 50/50 ammonium sulfate/pimelic acid and 50/50 ammonium sulfate/succinic acid systems using a RBF dryer (a) and (c), and a Tedlar bag (b) and (d). Large particles are phase separated (blue), while smaller particles are homogeneous (red).

Figure 4-6 shows a similar effect on the transition region for the slowest Tedlar bag drying rate experiment, in addition to the cryo-TEM images that illustrate the observed size dependence at particle sizes below 50 nm.
Figure 4-6: Cryo-TEM images of (a) 50/50 ammonium sulfate/pimelic acid and (c) 50/50 ammonium sulfate/succinic acid (c). In (b) and (d), histograms summarize the size dependent behavior of the morphology of the two organic aerosol systems resulting from the slowest experimental drying rate using a Tedlar bag. Large particles are phase separated (blue), while smaller particles are homogeneous (red).

The shift in the transition region to smaller particle diameters, the significant decrease in the width of the transition region, and the persistence of a size dependent morphology as the drying rate is decreased by over four orders of magnitude indicate that both kinetics and thermodynamics play an important role in our size dependence experiments. Figure 4-7 summarizes the data from all drying rate experiments and illustrates the impact of changing drying rate on particle morphology for both dicarboxylic acid mixtures. The largest homogeneous and smallest phase separated diameters are plotted at each drying rate studied for the ammonium sulfate/pimelic acid and ammonium sulfate/succinic acid systems. The shaded gray region represents the width of the transition
region, considering the largest homogenous and smallest phase separated particle observed at a given drying rate. The results presented in Figure 4-7 indicate that, for the drying rates studied in this work, the width of the transition region changes from 121 nm at the fastest drying rate to 3 nm at the slowest drying rate.

![Figure 4-7](image-url)

**Figure 4-7:** A summary of the effect of varying experimental drying rates (spanning over four orders of magnitude) on the resulting particle morphology and transition region.

As we have hypothesized in earlier work, the width of the transition region likely results from the viscosity of the particles at the point of phase separation and the stochastic nature of the phase separation process.\textsuperscript{10} When particles are dried rapidly, as done in our previous work, particles at small sizes that have a high viscosity may not have enough time to nucleate a new phase during the timescale of the experiment. Thus, by slowing down
the drying process and allowing particles to experience sufficient compositional fluctuation
events may result in phase separation at smaller sizes which ultimately leads to a shift in
the transition region, as observed in our experiments. Though this may explain the kinetic
effect in our drying experiments, it is also important to note the continued presence of a
size dependent morphology even at the slowest drying rates and the shift in the mean size
of particles in the transition region. The fact that we obtain a size dependent morphology
for both systems studied regardless of the timescale of the experiment and observe a
plateauing effect as we move towards slower drying rates (as seen in Figure 4-7) suggests
a size dependence would persist at infinitely slow drying rates. This result indicates that
the size dependence results from an underlying thermodynamic effect rather than solely a
kinetic phenomenon. Thus, it is likely that the presence of a nanoscale confinement effect
dictates particle morphology in our experiments. We note that the size regime where we
observe this effect closely resembles where nanoscale confinement effects have previously
been observed. For example, a size dependence has been observed for the deliquescence
(DRH) and efflorescence (ERH) phase transitions for sodium chloride aerosol particles,
where particles with diameters <40 nm undergo deliquescence and efflorescence at
increased relative humidities. This size dependent behavior has been explained by the
Kelvin effect and an extension of Köhler theory. As described in our previous work,
the size dependent morphology we observe is not due to the Kelvin effect, but rather the
activation energy needed to form a new phase. We note that nanoscale effects related to
the control of particle morphology and size have also been of great interest in the materials
community. Development of methods for mixing of immiscible substances that result in
size dependent phase separation have received increasing attention due to their role in allowing tunability of a material’s function such as its thermal properties.  

Conclusions and Atmospheric Implications

For the systems investigated in this work, we have shown that particle drying rate has a significant impact on the resulting particle morphology. At the fastest experimental drying rates, we observe a large transition region (121 nm) where both phase separated and homogeneous morphologies exist. However, as the drying rate is slowed down over several orders of magnitude, the location of the transition region shifts to smaller diameters and the width narrows to 3 nm. The presence of a size dependent morphology even at the slowest drying rates indicates an underlying thermodynamic effect that controls particle morphology at the smallest particle sizes. Constraining aerosol particle morphology at the submicron size regime should remain a central focus of investigation primarily because of the role submicron aerosol (especially < 200 nm) play in heterogeneous chemistry, cloud condensation nuclei (CCN) activity and new particle formation. By parameterizing aerosol particle morphology with atmospherically relevant meteorological conditions (e.g. temperature and relative humidity), it will be possible to accurately assess aerosol optical properties and CCN activity which are key variables in helping constrain the aerosol related radiative forcing.
References


Chapter 5

Effect of Particle Morphology on Cloud Condensation Nuclei Activity

Introduction

Organic aerosol particles are chemically complex and ubiquitous in the Earth’s atmosphere. Recently, a central focus of the atmospheric science community has been to understand the climate effects of complex organic aerosol systems. For instance, the impact of the aerosol indirect effect (i.e. the ability of aerosol particles to serve as cloud condensation nuclei, CCN) on climate forcing remains highly uncertain.\textsuperscript{1,2} It is essential to obtain a clear understanding of the population of aerosol that serves as cloud condensation nuclei, as CCN play a critical role in cloud formation, lifetime, reflectivity, and precipitation.\textsuperscript{1-4}

The effectiveness of an aerosol particle to activate and grow by condensation to form cloud droplets is controlled by a number of chemical and physical properties of the particle. Aerosol particle size and composition are key parameters in CCN activation that have received increasing attention in the literature.\textsuperscript{1-4} The abilities of species such as sulfates and abundant inorganic salts to serve as CCN are relatively well understood.\textsuperscript{1,2} However, our understanding of the ability of organics to serve as CCN is quite limited and
has resulted in a large uncertainty in the global modeling of cloud droplet nucleation and indirect forcing.\textsuperscript{1} Recently, within the atmospheric chemistry community, there has been an emerging interest in investigating the role of particle mixing state and surface active organics on CCN activity.\textsuperscript{5-7} In order to accurately determine the role of aerosol particles on atmospheric CCN concentrations, a comprehensive approach that includes the measurement of CCN and size distribution as a function of water vapor supersaturation is needed. Though a number of laboratory and field measurements have worked towards this objective, the reliability of instruments that measure CCN concentrations as a function of water vapor supersaturation has been a main concern.\textsuperscript{3-4} Recently, a commercially available continuous-flow streamwise thermal-gradient CCN instrument (cloud condensation nuclei counter, CCNC) has allowed extremely precise and reliable CCN measurements.\textsuperscript{3,4,8}

To better constrain the indirect effect related to CCN, global models must represent the complexity of organic species and the degree of mixing of individual species in a given aerosol mass. Thus, studies of parameters such as particle morphology which involve understanding the physics and chemistry of aerosol particles may be useful approximations to incorporate into models representing a range of aerosol particle physical and chemical properties. As shown in our previous work, we have observed a size dependent morphology of organic aerosol, where small particles are homogeneous and large particles are phase separated.\textsuperscript{9} Furthermore, we have previously demonstrated that for a given system, phase separated and homogeneous particles have the same composition.\textsuperscript{10} In this work, we apply our results from earlier experiments that allow us to take advantage of our ability to control particle morphology for model organic aerosol systems. With the
capabilities of the CCNC in mind, we designed a study to probe the effect of particle morphology on cloud condensation nuclei activity. Specifically, we have worked with ammonium sulfate mixed with either pimelic acid or succinic acid, and have investigated whether a differing morphology for a given system (i.e. phase separated vs. homogeneous) impacts CCN activity.

**Experimental Methods**

**Solution preparation and aerosol particle generation**

Aerosol particles composed of ammonium sulfate (> 99.0%, EMD), pimelic acid (>98%, Acros Organics) or succinic acid (>99%, Sigma Aldrich) were generated from aqueous solution. Solutions for mixtures of each organic compound mixed with ammonium sulfate (at a 50/50 mass fraction) were also prepared and aerosolized. The concentrations of the aqueous solutions (prepared using high-performance liquid chromatography grade ultrapure water) ranged from 0.05 wt.% to 0.3 wt.% solute. Aerosol particles were generated at a high relative humidity (RH ≥ 96%) and at a temperature of 295 K from the aqueous solutions using a constant output atomizer (TSI 3076, Shoreview, MN). Nitrogen flow through the atomizer was approximately 1.5 L/min.

**Controlling Particle Morphology**

As discussed in our previous work, we are able to control particle morphology for the systems described above by altering the drying rates particles experience in a given experiment. To obtain a homogeneous morphology in the ~50 – 100 nm size regime, we use a diffusion dryer filled with molecular sieves (13X mesh size, Sigma Aldrich; drying rate of 87.2% RH/s). A Tedlar bag setup (New Star Environmental, Roswell, GA) can be
used to slow down the drying rate by several orders of magnitude. The drying rates in the Tedlar bag range from 3.5 x 10^{-3} to 0.08\% RH/s. For a given system, the slowest drying rate yields phase separated (partially engulfed morphology) particles in the ~50 – 100 nm size regime. Thus, by employing this method, we can effectively control the morphology of particles used in our CCN studies.

**Measuring Cloud Condensation Nuclei Concentrations**

As seen in Figure 5-1, once the aerosol particles are generated and undergo drying, we can size select the aerosol flow using a differential mobility analyzer (DMA). After size selection, the aerosol flow enters the cloud condensation nuclei counter (CCNC). The detailed design and operation of the Droplet Measurement Technologies-CCNC (DMT-CCNC; Longmont, Colorado) has been previously published and thus, only a brief overview will be provided here. The CCNC consists of a cylindrical vertical flow tube in which the aerosol flows from top to bottom. A near-linear positive temperature gradient is established in the column by thermoelectric coolers. As the laminar flow travels down the column, heat and water vapor move from the inner column walls towards the column centerline. The faster diffusion of water molecules (as compared to heat) results in a constant water vapor supersaturation centerline. As aerosol particles travel through the vertical column and become progressively supersaturated with water vapor, the particles with a critical supersaturation less than that of the centerline become activated as CCN. The aerosol sample enters the column at the center, where supersaturation is highest. Filtered humidified sheath air (ratio of 1 part of sample air to 10 parts of sheath air) surrounds the sample to ensure the aerosol flow is exposed to a uniform supersaturation profile. An optical particle counter is used to size and count the activated droplets. As
shown in Figure 5-1, a condensation particle counter (CPC) is included in the experimental setup to determine the total number of particles (i.e. those that activated as CCN, in addition to those that did not). With this information, the fraction of particles that activated as CCN can be determined as a function of particle size.

![Figure 5-1: Schematic of the cloud condensation nuclei counter experiments.](image)

### Results/Discussion

Before investigating the cloud condensation nuclei activity of organic aerosol mixtures, the CCNC instrument was calibrated with ammonium sulfate, a system that has been well characterized in the literature. In each calibration experiment, four different temperature gradient values ($\Delta T$) were used to check the linearity between critical supersaturation and temperature gradient. A large deviation from linearity indicates possible malfunction in the instrument, such as a faulty humidifier. Our experiments resulted in a linear calibration curve between the supersaturation and temperature gradient.
and thus did not indicate any issues with the operation of the instrument. For the ammonium sulfate CCN experiments, 30 different dry diameter ($D$) values were size selected by the DMA in the range of 15-220 nm. We note that we employed this method rather than scanning a range of particle diameters to allow for increased averaging time and adjustment for particle concentration as the diameter is changed. At each $D$, the total number concentration of aerosol particles, $N_{CN}$, was measured with a condensation particle counter. The number concentration of CCN, $N_{CCN}$, was measured with the CCNC. By combining these measurements, the CCN efficiency (activated particle fraction; $N_{CCN} / N_{CN}$) was calculated from the averaged concentrations and a CCN efficiency spectrum of fraction activated vs. $D$ was plotted. The CCN efficiency spectrum for ammonium sulfate at a 0.35% supersaturation is shown in Figure 5-2a. A cumulative Gaussian distribution function is applied to each CCN efficiency spectrum using a non-linear least squares fit

$$f_{N_{CCN}/N_{CN}} = a(1 + \text{erf}(\frac{D-D_a}{\sigma\sqrt{2}}))$$

where $\text{erf}$ is the error function, $a$ is half the maximum value of $f_{N_{CCN}/N_{CN}}$, $D_a$ is the particle diameter at $f_{N_{CCN}/N_{CN}} = a$, and $\sigma$ is the standard deviation of the cumulative Gaussian distribution function. Under ideal conditions, all particles activate as CCN once a threshold diameter is reached and a maximum activated fraction of 1 and $a = 0.5$ should be obtained. However, particle losses and counting efficiencies of the CPC and CCNC lead to deviations from these values. Thus, in order to account for such deviations, the maximum value in the CCN spectra can be normalized to 1. This is done by multiplying the experimental values of activated fraction by $0.5/a$. We note that this normalization procedure does not impact the $D_a$ as the change is symmetric with respect to the midpoint of the CCN spectra. In addition to normalizing the CCN spectra to unity, it is also important to correct for
multiply charged particles. Size selection of particles of a given electrical mobility by the DMA results in particles that are multiply charged. Though the multiply charged particles have the same electrical mobility as singly charged particles, multiply charged particles are larger in diameter and therefore activate at a lower supersaturation. As seen in Figure 5-2a, these particles appear in the CCN spectra as a plateau at smaller diameters. Since multiply charged particles can alter the CCN spectra and affect the $D_a$, it is essential to apply a correction to the experimental data. The probability of particles with three or more charges is generally low, and thus only the fraction of doubly charged particles is accounted for in the correction process. The fraction of activated doubly charged particles $(N_{CCN}/N_{CN})_2$ from the height of the lower plateau is used to calculate the activated fraction of singly charged particles $(N_{CCN}/N_{CN})_1$

$$(N_{CCN}/N_{CN})_1 = \frac{N_{CCN} - N_{CN} \cdot (N_{CCN}/N_{CN})_2}{N_{CN} - N_{CN} \cdot (N_{CCN}/N_{CN})_2} \quad (2)$$

The corrected and normalized CCN spectrum is then fit with the Gaussian function described in equation 1. Figure 5-2b illustrates this process for ammonium sulfate, where the closed symbols represent the raw CCN data, the open symbols represent the normalized and corrected data, and the solid lines depict the Gaussian fit to the experimental data which is used to derive the activation diameter, $D_a$, where 50% of particles activate as CCN. We have obtained a $D_a = 58 \pm 0.6$ nm for ammonium sulfate, which agrees well with the calculated literature value of 58 nm at a 0.35% supersaturation. The activation diameter can be converted to a hygroscopicity parameter, $\kappa$, using $\kappa$-Kohler theory, as shown by Petters and Kreidenweis, 2007

$$\kappa = \frac{4A^3}{27D_a^3 \ln \frac{2S_c}{3}} ; \text{where } A = \frac{4M_W \sigma_W}{RT \rho_W} \quad (3)$$
$M_w$ is the molecular weight, $\rho_w$ is the density of water, $R$ is the universal gas constant, $T$ is the ambient temperature, $\sigma_w$ is the surface tension of the droplet (assumed to be pure water), and $S_c$ is the critical supersaturation for a dry particle of diameter $D_a$.

The hygroscopicity parameter, $\kappa$, provides a quantitative measure of aerosol physicochemical properties such as water uptake and CCN activity. For ammonium sulfate, the CCN derived $\kappa$ in our experiments is $0.566 \pm 0.017$, which is close to the literature value of $\sim 0.6$.$^{14}$

**Figure 5-2:** CCN efficiency spectra for ammonium sulfate. In (a), the raw, uncorrected ammonium sulfate data is shown. (b) shows the normalized CCN spectrum that has been corrected for doubly charged particles and fit using a Gaussian error function.

Following the ammonium sulfate experiments, the CCN activity of the pure organic compounds, pimelic acid and succinic acid was investigated at a supersaturation of 0.35%. Pimelic acid had an activation diameter of 79 nm ($\kappa = 0.225$), while the $D_a$ for succinic acid was 67 nm ($\kappa = 0.370$). These results agree with the general solubilities of the two compounds, where succinic acid is more soluble than pimelic acid and thus activates at a smaller diameter. Figure 5-3 summarizes the CCN data for the pure organic compounds.
Figure 5-3: Normalized CCN spectra that have been corrected for doubly charged particles and fit using a Gaussian error function for (a) pimelic acid and (b) succinic acid.

Since the goal of this work was to probe the effect of particle morphology on CCN activity, 50/50 mixtures by weight of each organic and ammonium sulfate were run through the CCNC. By controlling the particle drying rate for a given system, either a homogeneous or phase separated morphology was obtained and investigated with the CCNC. As shown in Figure 5-4a, a phase separated morphology for the 50/50 ammonium sulfate/pimelic acid system yielded an activation diameter of 57 nm ($\kappa = 0.617$). However, for the same system, a homogeneous morphology resulted in a $D_a = 65$ nm ($\kappa = 0.403$).
Figure 5-4: Normalized CCN spectra that have been corrected for doubly charged particles and fit using a Gaussian error function for the 50/50 ammonium sulfate/pimelic acid system with two distinct morphologies, (a) phase separated and (b) homogeneous.

As highlighted in Figure 5-5, for the 50/50 ammonium sulfate/succinic acid system, an activation diameter of 59 nm ($\kappa = 0.551$) was obtained for phase separated particles, while a homogeneous morphology resulted in a $D_a = 62$ nm ($\kappa = 0.473$).

Figure 5-5: Normalized CCN spectra that have been corrected for doubly charged particles and fit using a Gaussian error function for the 50/50 ammonium sulfate/succinic acid system with two distinct morphologies, (a) phase separated and (b) homogeneous.
The CCNC data for the 50/50 mixtures surprisingly showed that, given a system of the same composition, particle morphology has a noticeable effect on the activation diameter and κ value. Thus, the mechanism of water uptake and efficiency of a particle to serve as a CCN changes with a phase separated vs. a homogeneous morphology. Generally, the activation diameter of phase separated particles is similar to that of ammonium sulfate for the systems studied in this work. Homogeneous particles, on the other hand, have an activation diameter that is in between the pure inorganic and organic components. This result may partly be understood by examining the specific morphology of the two organic aerosol mixtures. As shown in the insets in Figures 5-4a and 5-5a, both pimelic acid and succinic acid mixtures with ammonium sulfate yield a partially engulfed morphology upon phase separation. Given this morphology, the ammonium sulfate component (which is more hygroscopic than the organic phase) is available to the air interface and can freely uptake water and allow the particle to grow as a cloud droplet. Molecular-scale observations in previous studies have shown that small amounts of inorganic salts can significantly enhance the CCN activation of organic compounds.\textsuperscript{15-17} In the case of a homogeneous morphology, the particle is uniformly mixed and the ammonium sulfate component does not contribute as strongly to water uptake and CCN activation as in the case of a phase separated morphology. Surface partitioning of organics (as observed for succinic acid in the literature) also impacts CCN activation and hygroscopic growth of organic aerosol.\textsuperscript{5,15,18-20} Surface-active organics can affect cloud droplet formation by inhibiting water uptake, reducing surface tension, and causing activation to occur at a larger diameter.\textsuperscript{5,15,18-20}
Conclusions and Atmospheric Implications

We have investigated the effect of particle morphology on cloud condensation nuclei activity. By using our results from earlier work where a size dependent morphology was observed for mixtures of organic aerosol, we have specifically studied the difference in activation caused by a homogeneous vs. a phase separated morphology. Surprisingly, for a system of similar composition, distinct morphologies lead to noticeable changes in CCN behavior. For 50/50 mixtures of ammonium sulfate/pimelic acid and ammonium sulfate/succinic acid, a phase separated morphology results in activation diameters close to that of ammonium sulfate, while a homogeneous morphology yields an activation diameter in between the pure components. The data presented in this study indicate that morphology is an important parameter in determining CCN activity for the systems investigated in this work. By accurately assessing and accounting for the effect of morphology, cloud microphysics models will be able to better predict the CCN activity of mixed atmospheric particles containing complex organics. Furthermore, by combining particle composition information and morphology-resolved CCN data, we can compute multicomponent hygroscopicity parameters for complex particles containing varying amounts of inorganic and organic compounds. In order to better predict the impact of aerosol particles on cloud properties and the radiative balance of the Earth, our experiments suggest that it is essential that models incorporate the complex physical and chemical parameters of cloud droplet formation.
References


Chapter 6

Morphology Dependent Optical Properties of Mixed Inorganic/Organic Aerosol Particles

Introduction

The impacts of aerosol particles are the most uncertain aspect in our understanding of the climate system.\(^1\) Aerosol particles have a direct effect on climate through the absorption and scattering of incoming solar radiation. In addition, aerosol particles have an indirect effect on climate by acting as cloud nuclei, which alters cloud lifetime, reflectivity, and precipitation.\(^2\) Currently, the extent to which aerosol particles cool the climate system is uncertain,\(^1\) in part because we do not completely understand the physics and chemistry of aerosol processes. Two factors that influence aerosol properties are the composition and morphology of the particles. In particular, organic aerosol has been a focus of current research because of its ubiquity and chemical complexity.\(^3-5\) Organic aerosol is formed from natural and anthropogenic processes, and can be divided into primary organic aerosol (POA) and secondary organic aerosol (SOA).\(^5\) Primary organic aerosol is directly emitted into the atmosphere from sources such as combustion of fossil fuels, biomass burning, cooking, biogenic emissions, and biological matter.\(^6,7\) Secondary
organic aerosol, in contrast, is formed from the oxidation of gas species and evolution of particle phase species.\textsuperscript{4,7,8}

Previous studies have shown that many aerosol particles are commonly present in the atmosphere as complex inorganic/organic mixtures.\textsuperscript{9-12} As the relative humidity (RH) is cycled within the atmosphere, these mixed particles can undergo liquid-liquid phase separation to form coexisting liquid phases.\textsuperscript{13-27} Particle morphology plays an important role in the formation of aerosol particles and can affect heterogeneous chemistry in the atmosphere (e.g. through the reactive uptake of gas-phase species such as N\textsubscript{2}O\textsubscript{5}).\textsuperscript{28-33} Moreover, particle morphology may affect mass accommodation coefficients, a parameter which determines the transfer rate of gases into aqueous droplets for organic aerosol loading levels.\textsuperscript{33} It is also possible that aerosol optical properties could be impacted as a result of liquid-liquid phase separation in mixed particles.\textsuperscript{34} Because the optical properties of particles in the Mie scattering regime are dependent upon morphology, the extinction cross section of mixtures of aerosol particles with different components may aid in the understanding of complex composition.\textsuperscript{34-42}

Several particle morphologies have been observed in aqueous particles including homogeneous, core-shell, and partially engulfed structures (Figure 6-1).\textsuperscript{14,15,17,24} In contrast to previous studies of particles several to tens of micrometers in diameter, we have applied cryogenic-transmission electron microscopy (cryo-TEM) for the study of the morphology of dry, submicron organic aerosol, in which we observe the general morphologies shown in Figure 6-1.\textsuperscript{43} We note that Figure 6-1 depicts aqueous particles with liquid phases. The submicron particles we have studied, however, are dry and will therefore have at least one solid/crystalline phase. Furthermore, the three morphologies
shown in Figure 6-1 are what we observe for our dry particles, though a larger range of morphologies has been observed for supermicron dry particles.\textsuperscript{14,15,17,24} We have discovered that the morphology of some systems is dependent on particle size and have previously shown that both thermodynamic and kinetic effects result in the observed size dependence.\textsuperscript{44} In terms of kinetic effects, in particular, the viscosity and stochastic nature of phase separation likely influence the size dependent behavior of the particles.\textsuperscript{44}

![Figure 6-1: Types of morphologies of mixed inorganic/organic aqueous aerosol particles. Internally mixed particles can be homogeneous, core-shell (with an inorganic core and organic shell, or vice versa), or partially engulfed.](image)

To better understand the structure and optical properties of organic aerosol at the submicron scale, and further investigate the size dependence of morphology for a wider range of organic/inorganic mixtures, we have used cavity ring-down spectroscopy (CRDS), cryo-TEM, and optical modeling. Specifically, we have studied ammonium sulfate, a common salt found in the troposphere, mixed with two different dicarboxylic acids (either pimelic acid or succinic acid), or an organic alcohol (1,2,6-hexanetriol). All of these systems have previously been shown to undergo phase separation.\textsuperscript{15,18,44} We discuss the impact of organic aerosol structure on aerosol optical properties by calculating the differences in radiative forcing caused by a phase separated vs. a homogeneous particle morphology.
Experimental Methods

Cavity ring-down spectroscopy (CRDS) and cryogenic-transmission electron microscopy (cryo-TEM) were used to characterize the phase separation behavior and optical properties of internally mixed aerosol particles composed of organic compounds (1,2,6-hexanetriol, pimelic acid, and succinic acid) with ammonium sulfate. Figure 6-2 is a schematic of our experimental instrumentation. Aerosol particles are generated from aqueous solution, dried to less than 2% relative humidity (RH) using a diffusion dryer, and then size selected with a differential mobility analyzer. The extinction coefficient of the particles is measured through the cavity ring-down spectrometer and the particle number concentration is measured with a condensation particle counter. For imaging, particles are collected on TEM grids after the diffusion dryer using an impactor.

Figure 6-2: Schematic of the cavity ring-down spectrometer and the setup for preparing TEM samples.
**Solution preparation and aerosol particle generation**

Aerosol particles composed of ammonium sulfate, dicarboxylic acids, and organic alcohol were generated from aqueous solution. Ammonium sulfate (> 99.0%, EMD), pimelic acid (>98%, Acros Organics), succinic acid (>99%, Sigma Aldrich), and 1,2,6-hexanetriol (>97%, Acros Organics) were used without further purification. Aqueous solutions with 0.025 wt.% to 0.05 wt.% solute were prepared for the individual components and for mixtures of each organic compound with ammonium sulfate at varying mass fractions. These solutions were prepared using ultrapure water (high-performance liquid chromatography grade). Aerosol particles were generated from the aqueous solutions using a constant output atomizer (TSI 3076, Shoreview, MN). Nitrogen flow through the atomizer was approximately 1.5 L/min. The wet aerosol particles were dried to less than 2% RH using a diffusion dryer filled with molecular sieves (13X mesh size, Sigma Aldrich). The dry aerosol particles were either collected onto TEM grids for imaging, or size selected and directed through the cavity ring-down spectrometer.

**Cryogenic-Transmission Electron Microscopy (cryo-TEM)**

To prepare samples for imaging, a cascade impactor (PIXE International Corp., Tallahassee, FL) was used to collect dry aerosol particles onto 200 mesh copper TEM grids coated with continuous carbon (Electron Microscopy Science, Hatfield, PA). The impactor was backed by a mechanical pump to provide a flow rate of 1.0 L/min. The particles were imaged using a Philips EM420T TEM at an accelerating voltage of 120 kV. Prior to imaging, the samples were transferred to a cryo-TEM holder and cooled in the microscope to approximately 100 K using liquid nitrogen. Cryogenic conditions were used to minimize electron beam damage to the samples.\textsuperscript{43-45} We note that we are looking for size dependence
of morphology of the systems studied down to ~50 nm diameter particles. It is difficult to image particles smaller than ~50 nm due to the fragility of the particles in the electron beam at higher magnifications.

Collected TEM images were analyzed using ImageJ (National Institutes of Health, Bethesda, MD). The areas of over several hundred to thousands of particles were determined for each sample. Assuming the particles are spherical, the calculated area is converted to an area equivalent diameter. The total number of particles at each area equivalent diameter can be used to plot the distribution of particle sizes as a function of their morphology.

**Cavity Ring-Down Spectroscopy**

We have described the design of our home-built cavity ring-down spectrometer and verified its accuracy in an earlier publication.\(^46\) Thus, only a brief overview will be given here. Prior to entering the cavity ring-down spectrometer, the aerosol particles are size selected using an electrostatic classifier (TSI 3080, Shoreview, MN) and a differential mobility analyzer (DMA; TSI 3081, Shoreview, MN). With this setup, it is possible to size select aerosol particles from 10 nm to 1 µm. In the electrostatic classifier, aerosol particles are exposed to a sealed \(^{85}\)Kr neutralizer. Although most particles exposed to the \(^{85}\)Kr are neutralized, a small fraction become charged (±1, ±2, ±3, etc.) according to a known charge distribution.\(^47\) The charged particles are size selected based on their electrostatic mobility, which is inversely proportional to the diameter of the particles.\(^48\) For spherical particles, the particles that leave the DMA are primarily monodisperse, singly charged particles with a small population of larger doubly charged particles with the same electrostatic mobility. We note that the fraction of multiply charged particles compared to that of singly charged
particles is size dependent. In addition, the correction for the presence of larger multiply charged particles generally increases as particle size increases.\(^{47}\) We correct for doubly charged particles by taking into account the fraction of doubly charged particles in the retrieval of the effective refractive index. When selecting a particular mobility diameter, we obtain a range of different sizes, resulting in a degree of polydispersity that depends on the aerosol flow and sheath flow selected within the DMA. To ensure the best size selection and reduce polydispersity, various sheath flow and aerosol flow rates were tested. An aerosol to sheath flow of 1:10 is generally used to produce the smallest polydispersity for the size selection of a particular diameter. However, we have used a higher aerosol to sheath flow ratio for our systems. We have found that an aerosol flow rate of 1.5 L/min and a sheath flow rate of 5 L/min allows us to provide an inlet flow of 1.5 L/min required by the CPC without sample dilution, and be able to size select up to 500 nm. The larger aerosol flow rate allows us to ensure that the purge flow on the mirrors results in only a small perturbation and does not significantly affect the particle number concentration. For instance, when an aerosol flow rate of 0.3 L/min is used instead of 1.5 L/min, the purge flow (which is approximately 0.025 L/min) becomes a larger perturbation. We avoid using an aerosol flow rate of 0.5 L/min along with the 5 L/min sheath flow, as that would require dilution of our sample before the CPC, and significantly reduce the total particle number concentration. We use the same sheath flow (5 L/min) for the particles we size select from 100-500 nm. We have shown in a previous publication that when working with nearly spherical particles (e.g. ammonium sulfate), the aerosol polydispersity agrees with the theoretical transfer function and we are able to model the extinction cross sections as monodisperse spheres.\(^{46}\) Since the particles we are working with are spherical or nearly
spherical, we expect a size distribution that agrees with the theoretical transfer function. However, when working with irregular particles (as shown for calcium carbonate in our previous work), the sizing is more polydisperse and thus microscopy is used to incorporate polydispersity to characterize the optical properties.\(^{46}\)

After the particles are size selected by the DMA, the aerosol flow enters the cavity ring-down spectrometer. This instrument has a cavity that is capped with highly reflective mirrors at each end (≥ 99.998% reflective). As light from a 643 nm diode laser propagates through the cavity, the light that is transmitted through the back mirror on each pass decays in intensity. When a sample enters the cavity, the extinction (i.e. scattering and absorption) of light by the sample increases the rate of decay, which is termed the ring-down time. The ring-down time for our spectrometer, with no particles present in the cavity, is 150-170 µs, which corresponds to an effective path length of approximately 45-51 km. Using the difference in the ring-down times measured with and without sample, the extinction coefficient, \(b_{\text{ext}}\), is measured according to the equation

\[
b_{\text{ext}} = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\]

where \(R_L\) is the ratio of the cavity length to the sample length, \(c\) is the speed of light, \(\tau_0\) is the ring-down without any particles in the cavity, and \(\tau\) is the ring-down time when particles are present. For our system, the cavity length is 90.8 cm and \(R_L\) is 1.18. After the measurement of extinction coefficient, the particle concentration, \(N\), is measured using a condensation particle counter (CPC; TSI 3775, Shoreview, MN). The extinction coefficient and particle concentration are used to determine the extinction cross section, \(\sigma_{\text{ext}}\), where \(\sigma_{\text{ext}} = b_{\text{ext}}/N\).
While refractive indices are a property of a pure material, we can retrieve effective refractive indices for internally mixed particles by comparing the experimental extinction coefficients to those predicted by Mie scattering theory. To determine the theoretical extinction efficiencies, $Q_{\text{ext}}$, for a particular range of particle sizes, we use Mie scattering theory for particles that we assume are spherical and homogeneous. The Mie scattering calculations are performed using a code written for MATLAB, adapted from Bohren and Huffman.\textsuperscript{34,49} The extinction efficiencies can be converted to extinction coefficients with the equation

$$b_{\text{ext}} = Q_{\text{ext}} r^2 N$$

where $r$ is the particle radius and $N$ is the particle number concentration measured from the CPC.

The experimental and theoretical extinction coefficients are compared using a reduced cumulative fractional difference, $CFD_r$

$$CFD_r = \frac{1}{p} \sum_{i=1}^{p} \left| \frac{b_{\text{ext( theoreticld) } - b_{\text{ext( measured) }}}}{b_{\text{ext( measured) }}} \right|$$

where $p$ is the number of particle sizes used in the experiment. The $CFD_r$ is similar to the chi square goodness of fit parameter, $(\chi^2/p^2)^{1/2}$, in that the minimum of both functions occurs at the same value of the domain.\textsuperscript{50,51} For the systems in this paper, $CFD_r$ values are calculated from $n=1.2$ to $n=1.8$ in increments of 0.001. The refractive index that best fits the data is found by determining the theoretical refractive index that gives the minimum $CFD_r$.\textsuperscript{50,51}
Results and Discussion

Organic Aerosol Particle Morphology

Cryo-TEM was used to image the inorganic/organic systems to obtain qualitative structural information about the morphology (i.e. core-shell vs. partially engulfed) and size dependence of the laboratory generated aerosol particles. Ammonium sulfate was mixed with two different dicarboxylic acids (either pimelic acid or succinic acid), or an organic alcohol (1,2,6-hexanetriol). We note that for dry particles > 1 µm, a complex array of morphologies has been reported in the literature, but we observe only the structures shown in Figure 6-1 for dry submicron particles. We observed partially engulfed and homogeneous morphologies for pimelic and succinic acid, and a core-shell morphology for 1,2,6-hexanetriol. We note that, as shown in our previous publication, based on the optical properties measured using CRDS and electron damaging behavior of the particles in TEM, the homogeneous particles are internally mixed. Furthermore, based on phase diagrams reported by Song et al., the two phases for the systems studied likely consist of an organic-rich phase and ammonium sulfate (Figure 6-3). Pimelic acid and succinic acid also show a size dependence of morphology, where small particles are homogeneous and larger particles are phase separated. In Figure 6-3, for example, the 50/50 and 25/75 mixtures by weight of ammonium sulfate/pimelic acid show that large particles are phase separated, while smaller particles are homogeneous. We hypothesize that this observed size dependence of morphology is at least in part due to kinetic effects such as the viscosity of the particles as they undergo rapid drying in the diffusion dryer. Increasing viscosity inhibits both nucleation and growth of a new phase and water evaporation. As the RH is decreased, the viscosity increases. Once the viscosity reaches a threshold to inhibit phase
separation, we hypothesize that phase separation will continue to be inhibited as the RH is further decreased. Nucleation and growth can occur in the volume or surface of a particle. Water evaporation, on the other hand, depends on the diffusion of water through the volume to the surface of the particle. We hypothesize that the observed size dependence originates from the interplay of these two effects. For instance, considering a small particle at a given RH, water can move from the center of the particle to the surface faster than for a large particle due to the difference in diameter. Thus, if water evaporates more quickly from a smaller particle, the smaller particle will experience a faster increase in viscosity and will have a greater probability of being unable to nucleate a new phase and be trapped in a non-phase separated state. As a result, we would expect these effects to be important at small particle sizes, especially under rapid drying conditions.

For the 75/25 ammonium sulfate/pimelic acid mixture (as seen in Figure 6-3a), we cannot say with certainty if there is any size dependent behavior. For this system, we have observed TEM images that show phase separated particles down to 100 nm (note, however, that we show an approximately 150 nm particle in Figure 6-3a). The smaller phase separated particles can appear to have a thin shell of one of the two phases, which becomes difficult to distinguish from the homogeneous particles at small sizes due to immediate electron damage at long imaging times or higher magnifications. It is important to note that, although both partially engulfed and core-shell structures are observed in the TEM images for this system, thermodynamically, the particles can only form one type of phase separated structure (i.e. core-shell or partially engulfed).\textsuperscript{14} Since our particles are impacted onto TEM grids in random orientations, the projection of partially engulfed particles on to two dimensions will sometimes appear as partially engulfed and sometimes as core-shell.
However, when a particle has a core-shell morphology, its projected image will always appear as core-shell in the TEM, regardless of its orientation. Thus, we note that the 75/25 ammonium sulfate/pimelic acid system only has a partially engulfed morphology. It is possible that particle viscosity results in phase separated structures at all sizes. Previous studies have shown that, when considering individual organic compounds, composition, molecular structure, and hydrogen bonding are important factors in determining viscosity. We note that the morphology of the particles is likely determined by the drying process and the viscosity of the particles around the separation relative humidity (SRH). Since the 75/25 ammonium sulfate/pimelic acid mixture has a smaller weight fraction of organic present, the particles generated from this mixture may have a lower viscosity around the SRH, which allows phase separation to occur at all particle sizes.

**Figure 6-3:** Cryo-TEM images of a) 75/25 ammonium sulfate/pimelic acid mixture, b) 50/50 ammonium sulfate/pimelic acid mixture, and c) 25/75 ammonium sulfate/pimelic acid mixture. In (a), particles are phase separated at all sizes. For (b) and (c), images at the top are phase separated, while smaller particles (b and c bottom) are homogeneous. We note that the color/brightness of the TEM images will vary slightly from day-to-day and from sample-to-sample. The objective lens used on a specific day will also affect the image contrast.
Table 6-1 summarizes the size dependence results for the 50/50 and 25/75 ammonium sulfate/pimelic acid systems as a function of the area equivalent diameter. For the 50/50 ammonium sulfate/pimelic acid mixture, the largest homogeneous particles are 243 nm in diameter, while the smallest phase separated particles are 122 nm in diameter. For the particles composed of the 25/75 ammonium sulfate/pimelic acid mixture, the largest homogeneous particles are 270 nm in diameter, while the smallest phase separated particles are 180 nm in diameter. Particles larger than the size regimes discussed above are phase separated, and those that are smaller are homogeneous. We note that the transition region (i.e. the range where phase separated and homogeneous particles overlap) for the systems described above is larger than the transition ranges we have previously reported. This difference is due to the much larger number of particles studied in our most recent experiments which result in better statistics and give a more accurate representation of the width of the transition region.

**Table 6-1:** Size dependent morphology of ammonium sulfate/pimelic acid mixtures. The smallest phase separated and largest homogeneous particle diameters are reported for systems that exhibit a size dependence. No size dependence is observed for the 75/25 AS/PA system.

<table>
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<tr>
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<td>180 nm</td>
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<td><strong>largest homogeneous particle</strong></td>
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<td>243 nm</td>
<td>270 nm</td>
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In addition to the pimelic acid system, we also investigated the size dependent behavior of the morphology of ammonium sulfate/succinic acid system (Figure 6-4). For the 50/50 ammonium sulfate/succinic acid internal mixture, the morphology is dependent on particle size (as seen in Figure 6-4b). No size dependent behavior was observed for the 25/75 and 75/25 mixtures, as smaller particles, on the order of ~50 nm in diameter were phase separated. We did, however, observe some unusual structures in the case of the 25/75...
and 75/25 ammonium sulfate/succinic acid mixtures. In particular, we observe that some particles were spherical while others were more rod-like in shape (Figure 6-4c). It is possible that these internal mixtures of succinic acid exhibit an unusual behavior, as compared to the pimelic acid system, because of the mechanism of phase separation of succinic acid. Succinic acid phase separates during crystallization, while pimelic acid undergoes liquid-liquid phase separation.\textsuperscript{15,18} Succinic acid has been shown to increase the efflorescence relative humidity (ERH) of ammonium sulfate.\textsuperscript{53} Previous studies have hypothesized that as the ammonium sulfate/succinic acid mixture phase separates, the slightly soluble succinic acid crystallizes and forms nuclei for the efflorescence of ammonium sulfate.\textsuperscript{53} That phase separation occurs at crystallization may cause the wide range of structures we observe during the phase separation of the succinic acid system.

We note that the physical properties of dicarboxylic acids such as solubility and vapor pressure exhibit an even-odd dependence due to a difference in crystal structures.\textsuperscript{61} The even-odd effect causes succinic acid (C_4H_6O_4) and pimelic acid (C_7H_{12}O_4) to have similar solubilities even though their chain lengths are different. We expect, however, that the even-odd dependence of dicarboxylic acids likely does not play a major role in LLPS. LLPS is caused by salting out effects.\textsuperscript{23,25,62} Pimelic acid (C_7) is salted out due to its low oxygen:carbon (O:C) ratio and its large hydrophobic carbon chain. Succinic acid is not salted out, but it is also not soluble enough to retain water during crystallization.\textsuperscript{53}
Figure 6-4: Cryo-TEM images of particles obtained from a) a 75/25 ammonium sulfate/succinic acid mixture, b) a 50/50 ammonium sulfate/succinic acid mixture, and c) a 25/75 ammonium sulfate/succinic acid mixture.

Table 6-2 illustrates the size dependent behavior of the morphology of particles generated from a 50/50 ammonium sulfate/succinic acid mixture. The largest homogeneous particles are approximately 214 nm in diameter, whereas the smallest phase separated particles are 129 nm in diameter. Particles larger than this size regime are phase separated, and those that are smaller have a homogeneous morphology. As noted for the ammonium sulfate/pimelic acid system, due to a significantly greater number of particles studied, a slightly different transition region range for size dependence was observed for the 50/50 ammonium sulfate/succinic acid system than we have previously reported. In our previous work, we found that the largest homogeneous particles were 196 nm in diameter, while the smallest phase separated particles were 170 nm in diameter.
Table 6-2: Size dependent morphology of ammonium sulfate/succinic acid mixtures. The smallest phase separated and largest homogeneous particle diameters are reported for systems that exhibit a size dependence. No size dependence is observed for the 75/25 and 25/75 AS/SA systems.

<table>
<thead>
<tr>
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<th>75/25 AS/SA</th>
<th>50/50 AS/SA</th>
<th>25/75 AS/SA</th>
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<tr>
<td>smallest phase separated particle</td>
<td>N/A</td>
<td>129 nm</td>
<td>N/A</td>
</tr>
<tr>
<td>largest homogeneous particle</td>
<td>N/A</td>
<td>214 nm</td>
<td>N/A</td>
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For the 1,2,6-hexanetriol system, although a core-shell morphology was observed for all ratios (1:1, 1:2, and 2:1) of ammonium sulfate/1,2,6-hexanetriol (Figure 6-5), no size dependence of morphology was observed down to sizes of ~100 nm. We note that if strong substrate effects influence the phase separation behavior of a viscous liquid such as 1,2,6-hexanetriol with ammonium sulfate, we would expect to see a wide range of structures when imaging this system. In particular, core-shell, partially engulfed, and other irregular structures should be obtained. However, we obtain uniform structures, and therefore conclude that we must be forming core-shell structures prior to interaction with the substrate. As seen in Figure 6-5, the core-shell structure consists of an organic-rich shell and an ammonium sulfate core. The thin organic shell of core-shell particles and immediate electron damage at higher magnifications made it difficult to discern if particles at smaller diameters (less than 100 nm) are phase separated or homogeneous. Thus, based on the particles imaged, no size dependence of morphology was observed for the 1,2,6-hexanetriol system down to diameters of ~100 nm.
Figure 6-5: Cryo-TEM image of a particle obtained from a 50/50 mixture of ammonium sulfate/1,2,6-hexanetriol. A core-shell morphology is observed for all mixtures of ammonium sulfate/1,2,6-hexanetriol, where the core is ammonium sulfate and the shell is an organic-rich phase.

Organic Aerosol Optical Properties

Although cryo-TEM is useful for obtaining information about the morphology of individual aerosol particles, we wanted to determine the deviations that will arise from treating phase separated particles as homogeneous particles in the refractive index retrieval process. Recent studies have focused on modeling complex morphologies such as partially engulfed structures using discrete dipole approximation (DDA). The modeled results from these studies show that the optical properties (especially light absorption) differ when considering a spherical volume-weighted particle vs. a phase separated one. We also note that previous studies of internally mixed aerosol optical properties have retrieved refractive indices assuming that the particles are spherical and homogeneous, as the exact particle morphology was not known. In some cases in the literature, the experimental results deviate from the homogeneous (volume-weighted) approximation. Thus, it is important to explore whether or not the observed deviations are due to particle morphology. Specifically, we are interested in determining if different morphologies and/or mechanisms of phase separation (i.e. liquid-liquid phase separation or phase separation upon
crystallization) result in varying degrees of deviation or behavior of optical properties. CRDS has been shown to be a sensitive technique for the study of the optical properties of aerosol particles.\textsuperscript{35-42,50,51} In these experiments, we obtain experimental extinction cross sections at varying particle sizes and retrieve the effective real refractive index of internally mixed aerosol particles. We also use the CRDS data to determine the potential impact of particle morphology on radiative forcing.

To illustrate the degree to which our experimental data obtained from the cavity ring-down instrument agrees with the theoretical data predicted by Mie scattering theory, we show the experimental and theoretical extinction cross sections for ammonium sulfate (Figure 6-6a) and 50/50 ammonium sulfate/pimelic acid (Figure 6-6b). The theoretical extinction cross sections were calculated using the experimentally retrieved refractive indices. A refractive index of 1.531 was obtained experimentally for ammonium sulfate, compared to a literature value of 1.535.\textsuperscript{42} The experimentally retrieved refractive index for the pure organic components was 1.480 for pimelic acid, 1.481 for 1,2,6-hexanetriol, and 1.482 for succinic acid, compared to a literature value of 1.476 for 1,2,6-hexanetriol, an experimentally derived value of 1.473 for succinic acid, and an extrapolated literature value of 1.452 for pure organic acids.\textsuperscript{50,58,59} We show theoretical extinction cross sections with and without a correction for multiply charged particles. We have discussed the correction for multiply charged particles in detail in an earlier publication.\textsuperscript{44} As seen in Figure 6-6, the experimental results are an excellent fit to the theoretical data once the correction for multiply charged particles is applied. Figure 6-6 demonstrates that the correction for multiply charged particles has the greatest effect at smaller diameters due to a larger percentage of multiply charged particles at these sizes.
Figure 6-6: Extinction cross section vs. diameter data for a) ammonium sulfate and b) 50/50 ammonium sulfate/pimelic acid. The red squares are the experimental extinction cross sections. The dashed blue line and black solid line are the theoretical Mie scattering calculations that are either uncorrected or corrected for multiply charged particles.

To model homogeneous particles, we assume the mixtures of materials are evenly dispersed and the particles are spherical. The homogeneous (volume-weighted) approximation is one of the most common mixing rules used to predict the refractive
indices of mixtures of materials.\textsuperscript{36,54-56} The volume-weighted average refractive indices were calculated using the equation

\[
n_{vw} = \frac{v_{\text{inorg}}}{v_{\text{tot}}} n_{\text{inorg}} + \frac{v_{\text{org}}}{v_{\text{tot}}} n_{\text{org}}
\]

where \(n_{vw}, n_{\text{inorg}}, \) and \(n_{\text{org}},\) are the real refractive indices for the volume-weighted average, pure inorganic compound, and pure organic compound; and \(v_{\text{inorg}}, v_{\text{org}},\) and \(v_{\text{tot}}\) are the volumes of the inorganic component, organic component, and total, respectively. To calculate the volume ratios for each weight fraction, we used the bulk densities of the organic and inorganic components.\textsuperscript{36,50} The average experimental refractive indices determined for each pure component were used for \(n_{\text{inorg}},\) and \(n_{\text{org}}.\) We note that a range of particle sizes (i.e. 7 particle diameters ranging from 100 – 500 nm) is used in the retrieval of \(n_{\text{inorg}},\) and \(n_{\text{org}}.\) Thus, the actual experimental values at a particular diameter may differ from the calculated value.

The data in Figure 6-7 show the predictions for homogeneous particles with volume-weighted refractive indices (black and red lines) and experimentally retrieved refractive indices for pimelic acid and 1,2,6-hexanetriol mixed with ammonium sulfate (black and red squares, respectively). We note that, as commonly performed in the literature, the refractive index retrieval process assumes that all particles are homogeneous and spherical with a narrow size distribution.\textsuperscript{36,50} Thus, the refractive indices retrieved are underestimates because for a given refractive index, a homogeneous particle will have a higher extinction cross section than that of a core-shell particle with an inorganic core. The refractive index data show that the phase separated systems (i.e. experimental data) deviate from the calculation for homogeneous particles. Furthermore, the optical properties for a
partially engulfed morphology (pimelic acid system) and core-shell morphology (1,2,6-hexanetriol system) are approximately equal within experimental error. The error in the refractive index is from the uncertainty in the retrieval of the refractive index from the multiple trials performed for each specific experiment.

Figure 6-7: Experimental and theoretical effective real part of the refractive index as a function of the fraction of organic by weight for pimelic acid (black) and 1,2,6-hexanetriol (red) mixed with ammonium sulfate.

The optical properties of succinic acid mixed with ammonium sulfate are more difficult to understand. The refractive indices of internal mixtures of ammonium sulfate and succinic acid at varying inorganic/organic ratios do not agree with the homogeneous approximation of the refractive index (Figure 6-8). That a deviation is observed agrees with previously reported results for the ammonium sulfate/succinic acid system in the literature. At an organic weight fraction of 0.25 and 0.75, there is a positive deviation from the homogeneous approximation (i.e. the refractive index is greater than that of the pure components). At an organic weight fraction of 0.5, on the other hand, there is a
negative deviation from the homogeneous approximation. We note that the fact we observe large deviations is consistent with the literature, though the actual magnitude and sign of the deviations observed differs. This may result from slight variations in the experimental setup, such as the number and type of dryers used. It is possible that the unusual optical properties are a result of the wide range of structures observed for the ammonium sulfate/succinic acid system (Figure 6-4) and the fact that succinic acid undergoes phase separation as it crystallizes, rather than through LLPS.\textsuperscript{44}

![Figure 6-8: Experimental (black squares) and theoretical (solid line) effective real part of the refractive index as a function of the fraction of succinic acid by weight for particles composed of succinic acid and ammonium sulfate.](image)

**Organic Aerosol Hygroscopicity**

In addition to determining the morphology and optical properties of the organic aerosol systems, our recent work has focused on understanding the hygroscopicity of organic aerosol particles. Hygroscopic growth resulting from variations in ambient RH can affect a particle’s refractive index and size. Thus, water uptake can alter the optical
properties of an aerosol particle which can impact visibility and radiative effects. In order to investigate the optical properties of organic aerosol as a function of relative humidity we have used cavity ring-down spectroscopy to obtain growth factors. We can measure the extinction of dry particles and then flow the dry particles through a humidifier, exposing them to approximately 80% RH. The extinction of the wet particles can be measured in a second CRD cell. The optical growth factor ($f_{\text{RH}}$) of a system is defined as the ratio of the wet extinction coefficient (at a given RH) to the dry extinction coefficient

$$f_{\text{RH}}(\% \text{RH}, \text{Dry}) = \frac{b_{\text{ext}}(\% \text{RH})}{b_{\text{ext}}(\text{Dry})}$$  \hspace{1cm} (5)$$

where $b_{\text{ext}}(\% \text{RH})$ and $b_{\text{ext}}(\text{Dry})$ are the wet and dry extinction coefficients, respectively. We have used our experimental setup to measure the $f_{\text{RH}}(80\%, \text{Dry})$ of the mixed inorganic/organic aerosol systems discussed earlier. These preliminary experiments have allowed us to compare our results of optical growth to growth factors reported in the literature. Figure 6-9 shows that our ammonium sulfate data is a good fit to the theoretically predicted optical growth using a literature growth factor of 1.46 for ammonium sulfate (80% RH). Furthermore, pimelic acid shows almost no optical growth (growth factor is approximately 1), while 1,2,6-hexanetriol is slightly more hygroscopic than pimelic acid at the diameters studied.
Figure 6-9: Optical growth experiments for mixed inorganic/organic aerosol systems measured with cavity ring-down spectroscopy.

CRDS Error Analysis

Though CRDS is a sensitive method of measuring aerosol optical properties, it is important to note the possible sources of error. Previous studies by Miles et al. and Toole et al. have shown that errors in particle counting, size selection, and uncertainty in the length of the cavity occupied by aerosol can significantly impact the measured extinction cross sections and retrieved refractive index values.\textsuperscript{64,65} Miles et al. have shown that a $\pm 10\%$ CPC error can result in an error of $\sim 2.5\%$ in the retrieved refractive index value when using polystyrene latex spheres (PSLs).\textsuperscript{64} We have performed similar calculations to account for the accuracy of our CPC. We assume a $\pm 10\%$ error (following the manufacturer specifications) in the particle count by the CPC. For the ammonium sulfate
system we find that assuming a 10% undercount of particles, the average percent error in the refractive index is approximately 2%. Assuming a CPC overcount of 10%, the average percent error in the retrieved refractive index is 1.5%. Both of these percent errors in the retrieved refractive index are slightly lower than compared to the value in Miles et al., but this may be due to the fact that different systems are used in the experiments. Furthermore, as mentioned in Miles et al. and Toole et al, errors in particle size selection can also have a significant impact on the refractive index retrieval. For instance, Miles et al. calculate up to a 2.9% error in the retrieved refractive index for an uncertainty in particle diameter of ±6 nm when working with PSLs. To determine the effect this error may have on our data (for ammonium sulfate particles), we have calculated new refractive indices using polydispersity data from one of our previous publications.46 Our prior experiments have shown that the polydispersity of ammonium sulfate particles is size dependent and that the polydispersity is consistent with the theoretical transfer function. We used TEM to characterize the size selection by the DMA, and found that the mean diameter is approximately 20 nm too small.46 Thus, we use an uncertainty of ±20 nm in particle diameter and obtain an average error of approximately 5% in the refractive index retrieval for ammonium sulfate particles. We note that in our earlier publication we showed that the polydispersity of ammonium sulfate particles did not have an effect on the calculated extinction cross sections as the weighted average of the extinction cross sections calculated from the TEM data match those obtained from CRDS.46 That we are able to retrieve the literature refractive index values for ammonium sulfate gives us confidence that the CPC is accurate. We note that considering the combined CPC and size selection error we calculated above, in addition to the error resulting from the uncertainty in determining the
length of the cavity occupied by aerosol (which Miles et al. have shown to be ~2.5%), we obtain a total error in the retrieved refractive index value of ~9.0-9.5%. Compared to the maximum error of 0.6% shown by the error bars (calculated from repeated experiments) in our current data in Figures 6-7 and 6-8, the possible error that can result from the CPC, size selection, and uncertainty in sample length in the cavity, is higher. However, we note that though the sources of error discussed above can impact the refractive index retrieval and are important to acknowledge, they do not affect our results concerning the large deviations in optical properties observed for the systems studied. Since we have been able to retrieve the correct refractive index for multiple compounds, we have some assurance that the CPC is working accurately and the size selection error is minimal. We note that if we were not retrieving the correct refractive indices for the pure compounds due to an error in the CPC or size selection, we expect that it would be systematically high or low. Though this error would change the value of the refractive indices retrieved (i.e. shifted to higher or lower values), the large deviations from the homogeneous predictions and general trends shown in Figures 6-7 and 6-8 would still be observed. Based on the data presented in Figures 6-7 and 6-8, it is evident that each system exhibits deviations from the homogeneous predictions. It is possible that these deviations are due to morphology and the mechanism of phase separation. For instance, in contrast to pimelic acid which undergoes LLPS, succinic acid undergoes phase separation upon crystallization and shows the largest deviations (both positive and negative) from the homogeneous calculations. We conclude that the mechanism of phase separation likely plays an important role in determining the degree and overall behavior of deviation for a particular system.
Atmospheric Implications

To determine the potential impact of the observed deviation in optical properties between phase separated particles and the prediction for homogeneous particles, we have calculated the radiative forcing for the retrieved refractive indices using a one-dimensional model developed by Charlson et al.\textsuperscript{57} To perform this calculation, we first determine the asymmetry parameters based on refractive indices shown in Figure 6-7 resulting from homogeneous and phase separated particles. The asymmetry parameter quantifies the difference in forward and backward scattering by a particle. The aerosol asymmetry parameter is equal to the cosine-weighted average of the phase function, where phase function is defined as the probability of radiation that is scattered in a given direction. The asymmetry parameter ranges from -1 for completely backscattered light to +1 for completely forward scattered light.\textsuperscript{60} We performed calculations at particle diameters of 100-1000 nm and a wavelength of 643 nm. The extinction efficiencies ($Q_{\text{ext}}$) and the asymmetry parameter ($g$) were calculated from 100-1000 nm using Mie scattering theory and volume weighted average refractive indices for the internally mixed particles shown in Figure 6-7. This calculation assumes the particles are homogeneous. A similar calculation was performed using the retrieved refractive indices for the phase separated systems in Figure 6-7. After calculating the extinction efficiency and asymmetry parameter using both the volume weighted and experimentally retrieved refractive indices, a radiative forcing ratio was calculated using a simplified version of equation 3 in Charlson et al. for non-absorbing particles

\begin{equation}
\Delta F_R = \frac{1}{2} F_T T^2 (1 - A_e)(1 - R_s)^2 \beta \delta_a
\end{equation}
where $F_T$ is the radiative flux at the top-of-the-atmosphere, $T$ is the fraction of incident light that is transmitted by the atmospheric layer above the aerosol layer, $A_c$ is the fractional cloud cover, $R_s$ is the albedo of the underlying surface, $\beta$ is the fraction of radiation scattered upward by the aerosol and $\delta_a$ is the areal optical depth of the aerosol. The fraction of radiation scattered upward, $\beta$, can be approximated by (Sagan and Pollack, 1967)\(^{66,67}\)

$$\beta = \frac{1}{2} \left( 1 - g / 2 \right)$$  \hspace{1cm} (7)

where $g$ is the aerosol asymmetry parameter. This simple approximation works well as a model for radiative forcing and has been shown to provide good estimates for the radiative forcing resulting from sulfate aerosol.\(^{57}\) We have used this approximation to estimate the radiative forcing ratio for phase separated particles compared with homogeneous particles. When the ratio of $\Delta F_R$ is computed for two different refractive indices, all the terms shown in equation 6 will be constant, except $\beta$ and $\delta_a$. We use equation 7 to approximate $\beta$ and also take into account the aerosol optical depth, $\delta_a$, by using the extinction efficiencies ($Q_{\text{ext}}$) for a phase separated particle vs. a homogeneous particle

$$\Delta F_R = \frac{1 - \frac{g_{ps}}{2} Q_{\text{ext,ps}}}{1 - \frac{g_h}{2} Q_{\text{ext,h}}}$$  \hspace{1cm} (8)

where $\Delta F_R$ is the ratio of radiative forcing for phase separated particles compared with homogeneous particles, $g_{ps}$ and $g_h$ are the asymmetry parameters for phase separated and homogeneous particles, and $Q_{\text{ext,ps}}$ and $Q_{\text{ext,h}}$ are the extinction efficiencies for phase separated and homogeneous particles, respectively.\(^{57}\)

Figure 6-10 shows the results of equation 8 for the ammonium sulfate/pimelic acid and ammonium sulfate/1,2,6-hexanetriol systems at varying organic weight fractions. We
observe the largest radiative forcing ratio for the ammonium sulfate/hexanetriol mixture at an organic weight fraction of 0.33, whereas the smallest radiative forcing ratio is observed for the ammonium sulfate/hexanetriol mixture at an organic weight fraction of 0.67. In comparisons of the two different internal structures (homogeneous vs. phase separated), we calculate up to a 6% difference in the radiative forcing ratio, where phase separated structures result in additional scattering. The difference is largest for smallest sizes, and decreases at larger diameters. Although the calculated difference in the radiative forcing ratio is not large, we note that the effect of morphology on radiative forcing may be much stronger for other types of organic aerosol, which we are currently exploring.

**Figure 6-10:** Radiative forcing ratios for the ammonium sulfate/pimelic acid and ammonium sulfate/1,2,6-hexanetriol systems at varying organic weight fractions. The ratios are calculated according to equation 8 above.
Conclusions

Organic aerosol morphology has implications for mass accommodation, cloud condensation nucleus activity, and heterogeneous chemistry. Furthermore, particle morphology has consequences for aerosol optical properties (e.g. aerosol optical depth), since optical properties are sensitive to aerosol particle structure. By understanding the physical chemistry that plays an important role in defining the structure of aerosol particles and how they interact with radiation, we can better account for the current uncertainty in the net radiative forcing, of which aerosol particles are the largest contribution. Through the use of cryo-TEM, we have characterized the morphology of laboratory generated organic aerosol particles composed of ammonium sulfate mixed with pimelic acid, succinic acid, or 1,2,6-hexanetriol. We observe a core-shell morphology for the 1,2,6-hexanetriol system, whereas particles composed of ammonium sulfate mixed with either pimelic acid or succinic acid have a partially engulfed morphology. The morphology of pimelic acid and succinic acid particles exhibits a size dependent behavior at some mass fractions of organic to inorganic components. We have also shown that the optical properties (i.e. the effective real part of the refractive index) of phase separated systems studied deviate from the predictions for homogeneous particles. We observe that the mechanism of phase separation may determine the magnitude and behavior of such deviations. The largest deviations are observed for succinic acid which undergoes phase separation upon crystallization rather than LLPS. That the optical properties of phase separated systems deviate from the predictions for homogeneous particles may be important in calculations of radiative forcing. Specifically, our Mie scattering theory calculations show up to a 6% difference in radiative forcing resulting from phase separated vs. homogeneous particles,
with more scattering resulting from a phase separated morphology. Moreover, our results show that it does not matter, in terms of optical properties, whether a particle that phase separates by LLPS has a core-shell or partially engulfed morphology for the systems explored in this study.

References


34. Bohren, C. F., Huffman, D. R. *Absorption and Scattering of Light by Small Particles*. Wiley-VCH; Weinheim, Germany, **2004**.


59. 1,2,6-hexanetriol Technical Bulletin; Aldrich Chemical Company, Inc.: St. Louis, MO, 1996.


Conclusions and Future Directions

Conclusions

In this dissertation, we have explored the physics and chemistry of the complex morphology of organic aerosol particles and discussed the atmospheric implications. We have observed that for some systems, organic aerosol particle morphology depends on particle size, where small particles are homogeneous and large particles are phase separated. To understand the origin of this size dependent behavior, we have characterized the morphology of a model organic aerosol system, poly(ethylene glycol)-400/ammonium sulfate using cryogenic-transmission electron microscopy. We have studied a wide range of poly(ethylene glycol)-400/ammonium sulfate mixtures. Surprisingly, we observe a size dependent behavior at some compositions, but not at others. Our results indicate that a size dependence of morphology is observed where an activation barrier to phase separation is present, as in the case of a nucleation-and-growth mechanism.

We have also investigated the kinetics and thermodynamics of the phase separation process and the impact on resulting morphology by using a range of particle drying rates spanning over four orders of magnitude. In experiments with the fastest drying rates, the
width of the transition region (i.e. where both phase separated and homogeneous morphologies are observed) was larger than 100 nm in diameter. At the slowest drying rates, the transition region shifts to smaller diameters, but the size dependence still persists. Since a size dependent morphology exists at the slowest drying rates, this result is indicative of an underlying thermodynamic effect rather than solely a kinetic phenomenon.

To determine the atmospheric implications of a size dependent morphology, we have explored the effect of particle morphology on cloud condensation nuclei activity. A cloud condensation nuclei counter (CCNC) was used to study mixtures of ammonium sulfate and dicarboxylic acids. For the pimelic acid/ammonium sulfate and succinic acid/ammonium sulfate systems, we have found that for a given system, phase separated and homogeneous particles of similar composition have different activation diameters. Particles that have a phase separated morphology activate at diameters similar to that of ammonium sulfate. Homogeneous particles, on the other hand, activate at diameters in between the activation diameters of ammonium sulfate and the pure organic compound.

Since aerosol optical properties are sensitive to particle structure, it is important that models accurately depict the role of particle morphology in order to constrain the uncertainty in the direct radiative forcing of aerosol particles. To better understand the structure and optical properties of aerosol particles composed of organic compounds (pimelic acid, succinic acid, and 1,2,6-hexanetriol) mixed with ammonium sulfate at the submicron scale, we have used cavity ring-down spectroscopy, cryogenic-transmission electron microscopy, and optical modeling. We have observed a core-shell morphology for 1,2,6-hexanetriol, and a partially engulfed morphology for pimelic acid and succinic acid. From the spectroscopy data, we observed that the optical properties of core-shell and
partially engulfed particles are approximately equal, but different than the prediction for homogeneous particles. We have also calculated the differences in radiative forcing caused by a deviation of optical properties of phase separated systems from homogeneous predictions.

Among systems that undergo phase separation, a size dependent morphology should be a widespread phenomenon in the atmosphere. This result has consequences for new particle growth and impacts the formation and activation of cloud condensation nuclei. Furthermore, a size dependent morphology may impact particle hygroscopicity and influence cloud formation, albedo, and precipitation. An accurate understanding of aerosol particle morphology, optical properties, and CCN activity will allow us to better constrain the large uncertainty in the aerosol direct and indirect effects and the overall impact on climate.

**Future Directions**

Although model aerosol systems provide great insight in obtaining a fundamental understanding of aerosol particle physical and chemical properties, it is important to work with atmospherically relevant systems that capture the complexity of organic aerosol present in the Earth’s atmosphere. To work towards this, we have begun to apply our model organic aerosol experiments to biogenic secondary organic aerosol. Biogenic emissions are responsible for complex particle formation in the atmosphere. Though the amount of biogenic emissions from vegetation far exceeds that of anthropogenic emissions, there is little understanding about the climate effects of biogenic SOA.\(^1\)\(^2\) Trees and plants release large amounts of biogenic volatile organic compounds (BVOCs) such as isoprene
(C₅H₈), monoterpenes (C₁₀H₁₈), and sesquiterpenes (C₁₅H₂₈). Upon entering the atmosphere, these biogenic compounds can be photo-oxidized by nitric oxides (NOₓ), hydroxyl radicals (OH), and ozone (O₃).¹⁻²⁻³ The oxidized species undergo gas-particle partitioning processes and ultimately lead to the formation and growth of SOA. One of the main reasons that the production of SOA is poorly constrained is due to the magnitude and chemical complexity of organic compounds present in the atmosphere. Thus, to accurately understand the impact of biogenic SOA on climate forcing, there is a need to determine the sources, structure, chemistry and fate of poorly quantified organic atmospheric constituents.

We have carried out preliminary experiments with two common biogenic aerosol systems, β-caryophyllene and α-pinene secondary organic aerosol particles, which were produced in the lab and characterized using transmission electron microscopy. β-caryophyllene was oxidized with ozone in a Tedlar bag and mixed with ammonium sulfate seed particles. In the case of α-pinene SOA, the water-soluble component of α-pinene oxidation products were mixed with ammonium sulfate. α-pinene was oxidized with ozone in a flow-through potential aerosol mass (PAM) chamber that has a short residence time and is irradiated with ultraviolet light.⁴ PAM is the maximum aerosol mass that can be produced from the oxidation of precursor gases. The precursor gases (in this case, β-caryophyllene and α-pinene) are quickly oxidized with high levels of oxidants to form low volatility products which yield aerosol mass. The concept of PAM has been shown to be very useful in investigating SOA processes, as there is great control over variables such as temperature, relative humidity, and oxidant concentration.⁴ The SOA mass can be
collected onto a filter and then extracted and mixed with ammonium sulfate for further analysis.

We have characterized the morphology of the two biogenic aerosol systems described above using transmission electron microscopy. As seen in Figure 7-1, the β-caryophyllene SOA data show particles that exhibit partially engulfed and core-shell morphologies. The TEM images for the α-pinene SOA show a core-shell morphology.

![β-caryophyllene SOA](image1) ![α-pinene SOA](image2)

**Figure 7-1:** Transmission electron microscopy images showing phase separated biogenic secondary organic aerosol (SOA) particles. β-caryophyllene SOA exhibits (a) a partially engulfed morphology and (b) a core-shell morphology. (c) α-pinene SOA particles are core-shell. The dark black regions within each particle correspond to the inorganic rich phase (ammonium sulfate), while the lighter regions correspond to the organic rich phase.

These experiments illustrate our ability to successfully generate and image complex biogenic aerosol systems. In order to expand on this work, future experiments should focus on determining whether the fundamental physical chemistry results described in this dissertation can be applied to complex atmospheric systems. For example, studies at varying experimental drying rates should be performed to determine if a size dependent morphology is observed for such systems and the implications this may have on cloud condensation nuclei activity.
Investigating and accurately determining particle morphology of complex atmospheric aerosol systems may have significant implications in the calculation of accurate mass accommodation coefficients for organic aerosol loading in the atmosphere. In addition, a suite of spectroscopy techniques such as cavity ring-down spectroscopy, photoacoustic spectroscopy, and spectroscopic ellipsometry should be combined with optical modeling methods to characterize the morphology-resolved optical properties of complex organic aerosol mixtures. An improved prediction of organic particulate matter mass, composition, morphology, and optical properties will ultimately help improve climate models and constrain the large uncertainty in climate forcing.

References


VITA
Muhammad Bilal Altaf

EDUCATION
Pennsylvania State University  Ph.D. in Chemistry  August 2012 – May 2017
Saint John’s University  B.S. summa cum laude  Major: Chemistry  August 2008 – May 2012

RESEARCH EXPERIENCE
Graduate Research Assistant  Aug. 2012 – May 2017
Dept. of Chemistry, Penn State University, University Park, PA 16802

Research Assistant  Jun. 2009 – May 2012
Dept. of Chemistry, St. John’s University, Queens, NY 11439

Dept. of Chemistry, University of Memphis, Memphis, TN 38152

TEACHING EXPERIENCE
Graduate Teaching Assistant  Aug. 2012 – May 2017
Dept. of Chemistry, Penn State University, University Park, PA 16801

General Chemistry Lab Section Supervisor  Aug. 2013 – May 2017
Dept. of Chemistry, Penn State University, University Park, PA 16802

FELLOWSHIPS, HONORS, AND AWARDS
2016-2017 Scholl Award in Analytical Chemistry
2016-2017 Continuing Graduate Teaching Fellowship Award
2013-2014 Dan H. Waugh Memorial Teaching Award
2013 National Science Foundation Graduate Research Fellowship Honorable Mention

PUBLICATIONS

