The Pennsylvania State University

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FACTORS THAT INFLUENCE AEROSOL PARTICLE LIQUID-LIQUID PHASE SEPARATION

A Dissertation in

Chemistry

by

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ABSTRACT

Aerosol particles can have a variety of compositions which determines their origin and their phase transitions. They can exist in the atmosphere where they are emitted from a variety of natural and anthropogenic sources. Aerosol particles can impact the climate directly though interacting with radiation or indirectly by nucleating cloud droplets and the clouds interacting with the sun. Aerosols can also impact health through the respiratory system. Additionally, aerosols can be used for synthetic purposes where they are created purposely for pharmaceutical or material creation along with many other applications. Understanding the factors that influence phase transitions that a particle may undergo is a prerequisite to understanding both atmospheric aerosol and synthetic aerosol. Several of these factors are investigated.

First, the impact of the average ratio of oxygen to carbon (O:C) atoms in the organic molecules through the addition of sucrose to aerosol particles is studied using optical microscopy. A variety of organic molecules and salts combinations which are able to undergo phase separation were studied. The organic/inorganic mixtures exhibit a mixture both high and low separation relative humidities. Then sucrose was added until the particles no longer exhibit phase separation. Particles with higher separation relative humidities in the absence of sucrose required larger quantities of sucrose in order to inhibit phase separation. Additionally, phase separation was seen at higher O:C values than published previously, showing that while average O:C is a good indicator of phase separation, the precise composition of the particles is more important.

The morphology of polymer/polymer aerosol particles according to their size was determined. In agreement with previous work, large particles undergo liquid-liquid phase separation while small particles remain homogeneous. Polyethylene glycol with dextran was used as well as polystyrene sulfonate with polyvinyl alcohol. Both of these systems inhibited phase separation at small sizes. To understand the size dependent morphology of polymer/polymer systems, different molecular weight mixtures of the polymers were studied. As the molecular weight of the polymers increased, smaller and smaller aerosol particles were able to undergo phase separation. This was further confirmed with a simple model based on the equations of phase separation and Flory-Huggins theory of a binary system which also showed the decrease in the size of the smallest phase separated particle as the molecular weight of the polymers increase in the size regime studied. The project created novel polymer materials and investigated the phase separation of polymer/polymer systems in confinement.

The phase separation of submicron aerosol particles with different salts was investigated to determine the influence of different anions on the size dependent morphology of aerosol particles. The ammonium, sodium, chloride and sulfate ions were used. TEM was used to determine that sodium salts transition to homogenous particles at smaller sizes than their comparable ammonium salt. This difference is likely due to the softness of the ammonium ion when compared to the hardness of the sodium ion. This study provides insights into the size dependent morphology of sea spray aerosol may differ from that of continental aerosol in addition to increasing our understanding of how cations and anions impact phase transitions under confinement.

These studies combined increase knowledge of confined phase transitions. While the O:C ratio has been studied before, the importance of the actual composition over the average O:C ratio has now been shown which is useful in understanding atmospheric aerosol particles. The presence of a size dependent morphology for polymer-polymer systems has been shown and modeled in addition to the development of novel polymeric materials. The phase separation differences between ammonium containing aerosols and sodium containing aerosols provides key insights into the differences between continental aerosol and sea spray aerosol in addition to contributing new information about the importance of cations in liquid-liquid phase separation of confined systems. Through these studies both atmospheric aerosol and synthetic aerosol are now better understood.

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Chapter 1

Introduction

Aerosol particles are any solids or liquids that are suspended in a gas. This can look like using a can of spray paint or the wind blowing sand off the desert into the atmosphere. Aerosol particles can come from natural sources as well as anthropogenic sources. They can be created with a purpose or created accidentally. No matter where aerosol particles come from, they can have interesting morphology, reactivity, and in some cases interesting uses. The aerosol particles discussed here, while varying in composition, have one important thing in common. The particles that all start as homogeneous liquid aerosol, can change to a liquid particle with a variety of different phase separated structures. This change is called liquid-liquid phase separation.

Liquid-Liquid Phase Separation

Liquid-liquid phase separation (LLPS) has been studied for over a century.¹⁻² It has applications in materials science, atmospheric science, and biological systems just to name a few.³⁻ ⁸ LLPS often occurs when two components in a solution reach a concentration where they become insoluble with each other. The concentration where this occurs is dependent on the compounds, but also changes as the ratios of the compounds are varied. As aerosol particles, these systems typically exist in one of three morphologies, homogenous, core-shell, and partially engulfed. Homogeneous particles are well mixed particles that have not undergone LLPS where both components are available at the air water interface. A core-shell morphology exists when a particle phase separates with one phase completely surrounding another phase. This typically occurs where an aqueous and salt core is surrounded by an organic shell. A partially engulfed morphology is when LLPS has

occurred, but both phases are exposed to air. The physical properties of the organic coating determine which phase separated morphology is favorable.

Some organic and salt combinations are able to undergo LLPS when dissolved in water. This is called salting out.² The Hofmeister series is used to predict the salting out behavior of various cations and anions.^{2, 9-10} Figure 1-1 shows the order of the ions. Anions are typically a much stronger controller of salting out than cations.² Anions such as F^{-} and SO_4^{2-} are strongly salting out.² This means that they strengthen hydrophobic interactions.² This causes a decrease in surface tension and a decrease in the solubility of nonpolar molecules. Anions at the other end of the spectrum such as ClO_4^{-} and SCN^{-} are salting in.² The means that they increase the solubility of nonpolar molecules, weaken hydrophobic interactions, and increase surface tension.² These interactions are true in bulk as well as in aerosol particles.¹⁰ The molecules mixed with the salts, undergoing these interactions, can be small chain organics or large macromolecules or in some cases even other salts.² The interactions hold true across the molecular weight and size spectrum.⁹⁻¹⁰



Figure 1-1: Hofmeister series shows the order that different cations and ions salt other components in and out of solution.

LLPS can occur with polymer-polymer systems. This transition happens when the molecular weights are significantly large. These systems can have an upper critical solution

temperature (UCST) or a lower critical solution temperature (LCST).¹¹⁻¹² An UCST occurs when polymers phase separate below a certain temperature, with the separation temperature differing with changing mass fractions of each polymer in the solution. A LCST occurs when polymers phase separate above a certain temperature and, once again, this temperature changes with changing mass fraction of the polymers. A LCST often occurs for high molecular weight systems, while a UCST occurs for short polymer chains.¹³ Some polymer systems have both a UCST and an LCST.¹¹

LLPS can occur via two different mechanisms. Nucleation and growth or spinodal decomposition.¹³⁻¹⁵ An example liquid-liquid phase diagram is shown in Figure 1-2. The x-axis shows the mass fraction of one component of the mixture, whereas the y axis can show a variety of different variables with water activity and temperature being two of the most common. The critical point of this curve is where mixtures that can undergo LLPS will undergo spinodal decomposition instead of nucleation and growth.¹³ The phase separation method of spinodal decomposition has no energy barrier, whereas nucleation and growth has an energy barrier.¹³ In an aerosol particle, spinodal decomposition will look like the whole particle undergoing phase separation all at one time. Nucleation and growth in an aerosol particle occurs via the formation of nuclei which will frequently all accumulate together.⁵



Figure **1-2**: A phase diagram of PEG 400 and ammonium sulfate in terms of fraction of ammonium sulfate and water content. If this was a polymer-polymer phase diagram, it would likely exist in terms of fraction of polymer and temperature. Figure from Altaf et al. 2016.¹⁴

This work focuses on the phase separation of aerosol particles. The particles studied have fall into two main categories, model systems for atmospheric aerosol and aerosols for materials applications. While the systems and the applications may vary, many of the underlying processes are the same.

Aerosols in the Atmosphere

Aerosol particles are ubiquitous in the atmosphere. This makes them available to interact with radiation from the sun. Aerosols can interact directly with the radiation by absorbing or scattering it. Aerosols can also become part of a cloud, and the cloud can absorb or scatter radiation, allowing the aerosol particles to interact indirectly with radiation. These interactions are all highly uncertain and additional studies are needed to better predict the effect of aerosol particles on Earth's climate.¹⁶ The particles in the atmosphere are a complex variety of compositions and morphologies. Understanding the composition and morphologies is vital to understanding how the aerosol

particles are interacting with the environment that surrounds them and how they are impacting the climate.

Liquid-Liquid Phase Separation in Atmospheric Aerosol

LLPS occurs in atmospheric aerosol particles.¹⁷ A homogenous particle and a phase separated particle will have different heterogenous chemistry, different optical properties, and different water uptake.¹⁸⁻²³ This makes it necessary to understand what types of systems will undergo LLPS and what factors can influence LLPS. Phase separation in model atmospheric aerosol has been studied primarily on two different particle types, organic/inorganic particles and secondary organic aerosol (SOA) particles independent of salts. Organic/inorganic particles can undergo phase separation of the organic acid from the inorganic salt, creating an organic coating around an inorganic/aqueous core.^{10, 17, 24-27} SOA in the absence of salt can undergo liquid-liquid phase separation at high relative humidities (RHs) with the secondary organic material phase separating from an aqueous phase.^{25, 28-30}

Model atmospheric aerosol is studied in terms of its morphology in terms of the relative humidity. Organic/inorganic particles typically exist in one of four morphologies: Liquidhomogeneous, liquid-phase separated, effloresced-homogeneous, or effloresced-phase separated. These transitions can all be seen in Figure 1-3 where these supermicron particles have been studied with an optical microscope. The relative humidity (RH) where a particle transitions from liquidhomogenous to liquid-phase separated is the separation relative humidity transition (SRH) and usually occurs with lowering of the RH. After a particle is phase separated, the RH surrounding the particle can be raised, causing the particle to undergo a mixing transition where the RH is the mixing relative humidity (MRH). A particle can transition from the liquid state to a crystallized state from either the liquid-homogenous morphology or the liquid-phase separated morphology. The humidity where this occurs is called the efflorescence relative humidity. The reverse transition can also occur and is called deliquescence, with the assigned relative humidity called the deliquescence relative humidity (DRH).



Figure 1-3: An organic/inorganic aerosol can undergo four major transitions between its three common morphologies. SRH is the separation relative humidity, MRH is the mixing relative humidity, ERH is the efflorescence relative humidity, and DRH is the deliquescence relative humidity. All scale bars are $100 \mu m$.

Some of the most studied factors that affect LLPS in organic/inorganic aerosol are the oxygen:carbon (O:C) ratio, the speciation of the inorganic salt, and the pH of the aerosol.^{25, 30-34} While there are a variety of options for looking at the molecules that undergo LLPS such as polarity, solubility, hydrophobicity, and Hansen solubility parameters, these methods are difficult to use on actual atmospheric aerosol due to complex and largely unknown composition. The O:C ratio can be easily measured by aerosol mass spectrometry which makes it a practical method for prediction LLPS. The O:C ratio has been studied fairly extensively. Original studies looked at single organic molecules with ammonium sulfate and found that compounds with an O:C of less than 0.5 always undergoes phase separation, compounds between 0.5 and 0.8 sometimes undergo phase separation, ^{5, 26, 33, 35-36}

This was expanded to complex mixtures and the same parameters were found to hold true.^{25, 28-29, 34-35, 37} The O:C ratios were then used to create parameterizations for SRH, DRH, and ERH.³³ A parameterization was also made for the organic : sulfate ratio and the influence of the hydrogen : carbon ratio was investigated.^{24, 33} O:C ratios will be further discussed in chapter 3 of this work.

The effect of inorganic salt was studied. (NH₄)₂SO₄, NH₄HSO₄, NaCl, and NaNO₃ were compared with several organics.²⁴ The salts were found to salt out in aerosol particles following the trends from the Hofmeister series.²⁴ This was true in the ability to phase separate at all as well as the SRH where different salts with each organic phase separated.²⁴

The pH studies first studied in our lab investigated the effect of raising the pH of the aerosols by adding sodium hydroxide. While raising the pH did not significantly influence the deliquescence or mixing relative humidities, it did lower the separation RH and raise the efflorescence relative humidity.³² This caused the first reported hysteresis between the SRH and the MRH.³² The second pH study in our lab looked at the effect of lowering the pH on LLPS.³¹ Losey and I found that the impact of pH depended on the SRH of the organic with ammonium sulfate. Organic/ammonium sulfate particles that had a high SRH did not experience a strong impact by the increasing pH compared to organic/ammonium sulfate particles that had a low SRH.³¹ This study was done by stoichiometrically changing the amount of sulfate in the particles through the use of sulfuric acid starting (NH₄)₂SO₄, to (NH₄)₃HSO₄)₂ and then to NH₄HSO₄. Excess sulfuric acid was also used to study a more general low pH. It found that ammonium sulfate is the most salting out, followed an intermediate ammonium sulfate ratio of 1.5, followed by ammonium bisulfate with a highly sulfate containing system.³¹ This paper showed that it is likely that high pH in aerosol particles keeps many particles from undergoing phase separation.³¹

Synthetic Aerosol Particles

In addition to particles that are created for simplified studies of atmospheric aerosol particles, particles can also be created for other purposes such as materials science and medical applications. These particles vary widely in composition, size, and purpose. Common materials science applications of aerosol particles include spray paint and air fresheners. In the medical field, frequent aerosol particle applications are inhalers and nebulizers which can distribute medications directly to the lungs. Both of these fields require a strong understanding of the composition, morphology, and reactivity of the aerosol particles.

Aerosol Particles in Materials Science

Aerosol particles in material science can have a wide variety of compositions depending on their designated uses. The process of creating the aerosol particles is directly related to the designated purposes of the aerosol particles. For instance, the composition and creation of an aerosol that is designed to provide a protective coating on a surface will be different than those that are a synthetic route to create nanoparticles with applications in areas such as optics.

One of the most prevalent uses for aerosol particles in materials science is using them to synthesize nanomaterials. Some of the methods used for these processes include spray pyrolysis, salt assisted decomposition, and aerosol-assisted molten salt syntheses.³⁸ The desired product type dictates which of these methods will be the best synthesis route. Hexaferrite particles can be synthesized using aerosolization followed by heating, or spray pyrolysis, and the particles have applications in recording products.³⁹ Droplet hydrolysis been used as a method to create TiO powders with the process providing basic chemistry information as well as sol-gel applications.⁴⁰

In other cases, changing the outside of the powder coating particles that are aerosolized to coat a surface can change the finished product from a glossy finish to a matte finish.⁴¹ Aerosol assisted synthesis can also be used to "freeze" particles in a metastable state which can be useful for catalysts, bioceramics and even for making "inks" that can pattern organic, inorganic, and composite materials on diverse surface types.⁴² While the use of aerosol particles in materials science may be diverse, understanding the composition and morphology of the particles is always key to their applications.

Aerosol Particles in Medicine and Biology

Aerosol particles are important to medicine in two different ways. The first of these ways is how aerosols in the surrounding atmosphere can influence health and the second is how aerosolization of solutions can be used as a medical treatment. Since aerosols in the atmosphere are ubiquitous, they are inhaled into and exhaled from the lungs constantly. This allows air pollution to enter the body and cause health effects such as heart and lung disease.⁴³⁻⁴⁴ Additionally, airborne diseases can also enter the body and cause sickness such as the flu.⁴⁵⁻⁴⁶ This makes it important to understand the composition, the morphology, as well as the viability of living aerosol to understand how atmospheric aerosol particles impact human health.

Aerosol particles are a commonly used method for providing medications to the body. Inhalers and nebulizers provide a method for the delivery of drugs to the body. There are two major types of inhalers, the pressurized metered dose inhaler and the dry powder inhaler.⁴⁷ It is important for inhalers to produce a consistent and specific range of aerosol sizes to properly deliver medications.⁴⁸ Inhalers and nebulizers are common treatment methods for lung diseases such as asthma, chronic obstructive pulmonary disease, and fibrotic lung disease.⁴⁹ Another use for aerosols in medicine that is currently under development is the use of tracer aerosol particles. Magnetic aerosols are being studied as a possible tracer which can be detected using magnetic imaging.⁵⁰

Material Properties Under Confinement

When materials are confined to small sizes, the properties and phase transitions may differ from those in bulk. A well-studied material that exhibits different properties at small sizes is gold. Gold nanoclusters (which are in the tens to hundreds of molecules range) are able to exhibit molecular like optical properties whereas gold nanocrystals (in the thousands to millions of molecules range) exhibit unique surface plasmonic properties.⁵¹ The properties of small objects are not just studied for elements like gold, but also for mixtures. Studied mixtures of confined materials include metals such as InAs with semiconductor applications and polymer blends such as poly(D,Llactide-co-glycolide), lecithin, and poly(ethylene glycol) with applications including drug delivery.⁵²⁻⁵³ Even something as simple as organic/inorganic mixtures can exhibit changed phase transitions when confined in nanoparticles around 30 nm or less.^{14, 54-55}

Droplet Confinement

Water soluble polymers such as poly(ethylene glycol) and dextran are able to undergo phase separation and have been studied for over a century. In addition to bulk, these systems are also studied under droplet confinement. These droplets are studied for possible uses in biomedicine such as vessels for protein delivery, templates for biomaterial fabrication or microreactors for enzyme reactions, but they could also have uses in the food industries and cosmetic formulations.⁵⁶⁻⁵⁷ One important feature of the PEG and dextran system, and others like it, is their solubility in

water which prevents the need for organic solvents that are not biocompatible.⁵⁶⁻⁵⁸ Microfluidics are a common method for the creation of these droplets.⁵⁶⁻⁵⁹

Thin Film Confinement

Polymer thin films have been studied to understand how confinement influences the phase transitions and are an important step in understanding the different between bulk systems in highly confined aerosol systems. Thin film confinement can change both the morphology and phase transitions in polymer systems. The process of creating a thin film is typically done through one of two different methods: annealing or solvent evaporation. Annealing involves heating the polymer film whereas solvent evaporation uses polymer solutions where the solvent evaporates away to crate the thin film.⁶⁰⁻⁶⁶ The morphology types of a thin film can include lamellar, islands, block, and dendritic (Figure **1-4**).



Figure 1-4: Some common morphologies of phase separated polymer thin films include a) two layered, b) islands, c) lamellar, and d) dendritic.

A variety of factors can influence the morphology types. Changing the solvent can dramatically change the morphology of the film due to its influence on the polymer solubility.⁶⁷ The molecular weight, the ratio of the two polymers in the film or the patterning of the substrate can change the morphology from lamellar to islands or dendritic structures or even combination structures.⁶⁸ Nucleation mechanism is thought to impact the morphology of the thin film.⁶⁹ Film thickness changes the morphology due to changes in the forces the polymers experience with the substrates.⁴ Many solvent evaporation films are made through spin coating, and the speed of the spin coater changes the morphology due to the changing quench times in addition to changing the thickness of the film.⁷⁰ These are just a few of the factors that can influence the structure of a thin film. Due to the diversity in the composition and morphology of thin films, they have applications in a wide variety of fields including nanodevice templates, optics, and photovoltaics.^{64, 69} An

understanding of size dependent structures and properties could allow a material to be created with the ideal properties for a specific application.

Aerosol Confinement

It has been shown that small organic/inorganic aerosol particles will not undergo phase separation.^{14, 55, 71} Many of these experiments were done at fast drying rates (98%RH/sec), but the inability of small particles to undergo phase separation was shown to be true at slower drying rates and is expected to continue to infinitely slow drying rates.⁵⁵ One factor that can allow all particles to undergo phase separation mechanism. When particles undergo spinodal decomposition instead of nucleation and growth, the particles can phase separate at all sizes.¹⁴ This has also been shown to be true when made from complex mixtures of organic as well as SOA, implying that this size dependence would be true in the atmosphere.⁷² This research shows that particles that previously would have been thought to be phase separated may in fact sometimes be homogenous in the atmosphere, which could change the optical properties and the heterogenous chemistry that the particles may undergo.

Scope of Dissertation

This dissertation looks at different factors that can influence the size of submicron and supermicron aerosol particles. Chapter 2 explores the different techniques used throughout the course of all studies in this dissertation. The use of TEM for organic aerosol particles and the role damage can play in the interpretation of results is discussed in Chapter 3. Chapter 4 explores the influence of the average O:C on the liquid-liquid phase separation of supermicron organic/inorganic aerosol particles using sucrose. The effect of confinement on the liquid-liquid

phase separation of submicron polymer-polymer aerosol particles is studied in Chapter 5. In Chapter 6, the impact of cations and anions on the size dependent morphology of submicron organic/inorganic aerosol particles is investigated.

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Chapter 2

Instrumentation and Experimental Methods

Optical Microscopy

The optical microscope used in Chapter 4 of this work is a Nikon Eclipse Ti2 inverted microscope. This means that the camera images from underneath the sample, while the light comes from above the sample. A LED light source is used. Most often, the 10X objective is suitable for imaging a diverse size population at one time. If particles are small or a phase transition is difficult to see, then the 20X objective can be used. The sample is placed in an environmental chamber on the stage of the microscope. Then a bubbler and nitrogen lines are used to control the relative humidity (RH) inside the chamber. A RH probe sits on the out-flow nitrogen lines to measure the humidity of the air the particles are exposed to. The microscope and experimental setup are shown in Figure **2-1**.



Figure 2-1: The experimental setup for super micron aerosol particles uses an inverted optical microscope. The sample sits inside a chamber that has nitrogen flows in on one side and out on the other side which allows the humidity inside the chamber to be monitored. A relative humidity probe on sits on the exit flow for the nitrogen from the chamber to allow us to monitor the humidity

The humidity is controlled manually and usually changes at a rate of 1% RH/min. When working with samples that will deliquesce, it is useful to first effloresce the particles and then deliquesce the particles before studying their separation and mixing. This helps to prevent the excess water from artificially lowering the SRH value when the particle is not in equilibrium.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) works similarly to a traditional upright microscope, but replaces the beam of light with a beam of electrons. Using an electron beam allows the user to see below the diffraction limit of light. This type of microscopy is conducive to high throughput imaging so many particles can be studied in a short period of time. In a TEM, electron sources can vary from thermionic sources to cold field emission sources.¹ Thermionic sources are less expensive and are used at a lower emission voltage which provides better contrast, whereas cold field emission sources produce higher emission voltages which equates to lower contrast in the images but a better resolution.¹ The FEI Tecnai TEM used in Chapter 5 this work uses a LaB_6 (lanthanum hexaboride) filament which is a thermionic source, but does provide more electron voltage and more resolution than a traditional tungsten filament. For the work done in Chapter 6, most TEM images were taken with the FEI Talos C instrument which uses an X- Field Emission Gun (X-FEG) emission source. In both instruments, a series of apertures are used to focus the beam of electrons. The sample is placed in the middle of the column, with apertures and condensers both above and below the sample. Near the sample is a cold finger which uses liquid nitrogen to provide a cold surface to collect contamination that is created by interactions between the beam and the sample. Below the apertures is a phosphorescent screen where the grid and contents can be seen. The screen also is used to protect an undermount camera, which was the primary camera for this work. A simplified schematic of the TEM can be seen in Figure 2-2. Additionally, the Talos C has a cryo-box which can be inserted around the sample for cryogenic imaging. This prevents the sample from developing ice even on humid days.



Figure 2-2: Schematic that shows the layout of the TEM instrument.

While a variety of imaging methods and compositional analysis tools exist for the TEM, the primary technique used here is brightfield microscopy. Using this technique, the electrons move through the sample and in an image, lighter areas are where more electrons come through. Typically, the background is light and the sample appears dark. A variety of factors influence the darkness of the sample including the composition, a composition with higher Z-number elements will be darker than those with low Z-numbers. Thicker samples will also appear darker than thinner samples, which is one of the reasons that larger aerosols are typically easier to see than smaller aerosols. The substrate used for TEM can change the contrast the sample. Changing the substrate thickness or composition can change the contrast of the particles. Additionally, apertures in the microscope can be adjusted to influence the contrast.

Many organic containing samples are not stable under the electron beam. The sample will start to sublimate upon exposure. This can hide the morphology of the sample, change the size of the sample, or even make the sample disappear before it can be imaged. In order to elongate the life the sample, a cryo-holder can be used. A cryo-holder uses a dewar of liquid nitrogen to keep the sample frozen, making it take longer until the sample damages. This technique was used for the TEM studies in this work. While not typical of cryo-holder use, the sample is loaded warm and then the liquid nitrogen is added. This helps minimize the amount of ice that will develop on the sample. The moisture that is not entirely sucked out by the vacuum does accumulate on the sample over time which limits the imaging time and makes it more difficult to image samples during the warm and humid days. Further description and examples of particle damage and ice can be found in Chapter3.

Atomic Force Microscopy

Atomic force microscopy uses a laser and a pointed tip to trace the surface of a sample. As the tip moves on the surface of the sample, the computer registers the movement of the laser and correlates it to the height of the sample. This technique can be used to look at sample heights, phase of material, and molecular interactions along with many other effects. An AFM sample, often a sample on a silicon substrate is attached to a magnetic disk. The magnetic disk can then be held in place on top of the AFM scanner though a magnet in the scanner. The scanner is a tube that contains a piezo electric material. The scanner moves the sample in a set pattern in the x and y directions, which will allow the AFM tip to trace over the surface. The tip holder is inserted into the head of the AFM. This will allow the laser inside the head to be set to reflect off of the tip and into the photodetector. The movement of the laser on the photodetector during scanning allows the AFM change the voltage assigned to the piezo electric, which will move the sample up and down. This is then translated by the computer into height information about the sample. Figure **2-3** shows the parts of the AFM.



Figure 2-3: The equipment of a Multimode AFM with a schematic of the workings inside the AFM head.

In order to study aerosols, a setup for controlling humidity was created. The area where the sample sits needs to be enclosed to minimize the exchange of air with the room. To do this, the top of a water balloon is cut off and the balloon is rolled up. Then the rolled balloon is placed around

the peg that holds the sample (Figure 2-4). This minimizes the air flow that can enter the AFM head from the bottom. A plexiglass cover has been designed to cover the front of the sample holder box. This plexiglass cover has an O-ring built into it, and is held in place by two rubber bands. There is an inlet hole and an outlet hole on the front of the plexiglass cover to allow the humidity inside the chamber to be controlled using mass flow controllers. The air flow must be slow to prevent the flow from moving the AFM tip and impacting the image quality. Additionally, there is a humidity and temperature probe built into the inside of the cover so that the humidity can be monitored. This setup can be seen in Figure 2-5.



Figure **2-4**: Images of the balloon seal which is used to minimize air exchange through the bottom of the head.



Figure 2-5: Images of the AFM humidity cover built for the multimode AFM with A) showing a front view with hoses attached for nitrogen flow in and out of the chamber and B) showing a back view where the humidity and temperature sensor inside the cover can be seen along with the O-ring that helps to seal off the chamber from outside air.

Aerosol Generation and Collection for Optical Microscopy

The aerosol particles studied using the optical microscope vary from 20 to 250 micrometers in diameter. The actual size range studied will vary some depending on the objective that is used in the experiments. Aerosols for these experiments are made by creating at 5 wt.% solution of the compounds. Usually, 25 mL of water is used. The solution is then put in a standard spray bottle, which is used to aerosolize the particles. The particles are impacted on hydrophobic glass slides. To make the hydrophobic glass slides, a regular glass slide is first cleaned using soapy water, followed by HPLC water, and then ethanol. Finally, Rain-X glass cleaner + water repellent is used to coat the slide. The slide is left to rest overnight before use, using it to soon after treating can cause a decrease in contrast for phase separation.

Aerosol Generation, Drying, and Collection for TEM and AFM

Aerosol generation and collection for TEM and AFM are done following the same method with different substrates used for the collection. A solution (typically around 0.03 wt. % for concentration) is atomized using a constant output atomizer. This means that the solution is pumped into the atomizer, where a nitrogen flow breaks the solution stream into thousands of aerosol particles. The particles are then dried using diffusion dryers or a Tedlar bag. All research in this work is done using diffusion dryers. If the particles are composed of an organic/inorganic mixture and dry easily one diffusion dryer is used, which dries the particles at ~98%RH/sec. Polymer-polymer systems are more hydrophilic, making them harder to dry. To overcome these drying issues, multiple diffusion dryers can be used (the work in Chapter 4 used up to 4 diffusion dryers in series to dry the particles.) A tedlar bag can be used to slow dry the aerosol particles when the influence of fast drying the particles needs to be eliminated.

The aerosol particles are then impacted using an impactor. This can be done using a PIXIE cascade impactor (PIXIE International Corp., Tallahassee, FL) or a MOUDI cascade impactor (Micro orifice uniform deposit impactor, TSI Shoreview MN). These impactors can be used interchangeably, though collection times will differ. The impaction time for the mini MOUDI is usually about 30x's the collection time for the same sample using the PIXIE. For TEM, the aerosols are impacted on 200 mesh, carbon film, copper grid TEM grids (Electron Microscopy Sciences, Hatfield, PA). For AFM a silicon substrate is used for impaction. The silicon surface should be cleaned before use and the typical method is to sonicate the substrate in water, followed by acetone, finishing with methanol, with each solvent being sonicated for 5 minutes. The substate should be allowed to dry before placing it in the impactor. All samples should be stored in a desiccator until use and should be used within 3 days if possible.

Tensiometer

Surface tension is an important factor in understanding the morphology of aerosol particles. Surface tension is the Gibbs surface free energy of a solution, though more frequently thought of as how strongly the molecules at the surface will hold together. There are three common methods for measuring surface tension: the pendent drop method, the Wilhelmy plate method, and the Du Noüy ring method. The method used in this work is the Wilhelmy plate method. In order to take surface tension measurements, first the density of the sample must be determined.

The density is measured using a hook and a reference weight with a known density. The balance in the tensiometer first measures the mass of the hook, then measures the mass of the hook with the reference weight on it. Next the empty hook is submerged in the solution and the mass is determined. Finally, the hook with the reference weight on it is submerged in the solution and the

density of the solution is determined by the instrument. With these measurements, Equation (1) is used by the tensiometer software to determine the density of the sample.

(1)
$$\rho_L = \rho_{MP} \frac{G_{MPL} + G_{MPA}}{G_{MPA}}$$

Where ρ_L is the density of the liquid, ρ_{MP} is the density of the measuring probe, G_{MPL} is the weight of the measuring probe in liquid, and G_{MPA} is the weight of the measuring probe in air.² This procedure is followed three times for each solution, and two solutions with the same composition and concentration are used for each published value.

The Wilhelmy plate method uses a platinum plate to measure the surface tension. Before each use, the plate is washed with hot water and then spun in a propane torch flame until the plate glows yellow. This process removes any surfactants from the surface so they do not contaminate the sample by altering its surface tension. The sample is raised until it comes into contact with the plate which causes the force of the liquid to act on the plate and is measured with a force sensor. Equation 2 is then used by the instrument to calculate surface tension.

(2)
$$\sigma = \frac{F}{L\cos\theta}$$

Where σ is the surface tension, F is the force acting on the force sensor, L is the wetted length, and θ is the contact angle.² The surface tension is measured 3 times for each of two samples to obtain a published value.

Rheometer

A rheometer is used to understand how a fluid flows, and for a simple solution this is often represented as a value for viscosity. In this work the instrument was used to obtain the viscosity values of organic/salt/sucrose solutions. The instrument used is an Ares RFS -3 rheometer with a RSF-2 cylindrical geometry. Using this setup 1.5 mL of solution is placed inside the geometry, a cylinder is lowered into the solution and is spun by the instrument. The instrument then measures the forces involved in spinning the cylinder. The rate of spinning, the measurement time, and the direction of measurement can all be adjusted to obtain higher quality data. Steady motor mode on the instrument was used which changes exposes the sample to a sheer strain in a linear fashion as opposed to dynamic motor mode with a sheer strain exposure in a sinusoidal fashion. The data collected showed Newtonian behavior in the sheer range studied of 10 to 100 s^{-1} . If non-Newtonian behavior is seen, then the viscosity is not only influenced by the temperature, but also on the sheer rate. This can be determined by looking at a graph of viscosity vs sheer rate. A Newtonian fluid will appear as a straight, flat line, whereas a non-Newtonian fluid will appear as an exponential or angled line due to the presence of sheer thickening or sheer thinning. ³

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Chapter 3

Use of Transmission Electron Microscopy for Analysis of Aerosol Particles and Strategies for Imaging Fragile Particles.

Author Contributions: Ott and Freedman co-wrote manuscript. Ott supplied most figures, with Kucinski and Dawson supplying remaining figures and assisting with outline development.

Abstract

For over 25 years, Transmission Electron Microscopy (TEM) has provided a method for the study of aerosol particles with sizes from below the optical diffraction limit to several microns, resolving the particles as well as smaller features. The wide use of this technique to study aerosol particles has contributed important insights about environmental aerosol particle samples and model atmospheric systems. Particles with sizes that can be below the diffraction limit of light are imaged via the transmission of electrons through the sample. TEM produces an image that is a 2D projection of aerosol particles that have been impacted onto grids, and through associated techniques and spectroscopies, can contribute additional information such as the determination of elemental composition, crystal structure, and 3D particle structures. Soot, mineral dust, and organic/inorganic particles have all been analyzed using TEM and spectroscopic techniques. TEM, however, has limitations that are important to understand when interpreting data including the ability of the electron beam to damage and thereby change the structure and shape of particles, especially in the case of particles composed of organic compounds and salts. In this paper,

we concentrate on the breadth of studies that have used TEM as the primary analysis technique. Another focus is on common issues with TEM and cryogenic – TEM. Insights for new users on best practices for fragile particles, that is, particles that are easily susceptible to damage from the electron beam, with this technique are discussed. Tips for readers on interpreting and evaluating the quality and accuracy of TEM data in the literature are also provided and explained.

Aerosol Particles and Atmospheric Chemistry

Aerosol particles are ubiquitous in the air, making their study important for understanding the Earth's climate as well as necessary for characterizing their implications for human health. As energy from the Sun enters Earth's atmosphere, it can interact with aerosol particles in two ways. When particles absorb or scatter energy, they have a direct effect on radiative forcing; whereas when a particle nucleates a cloud droplet and the cloud interacts with the Sun's energy, they have an indirect effect. The magnitude of the net cooling effect of aerosol particles is still highly uncertain, and additional studies are required to help reduce this uncertainty.¹

Inhalation of aerosol particles is associated with many negative human health outcomes. A variety of medical conditions have been linked to high air pollution such as cardiovascular disease, respiratory disease, and cancer.²⁻⁵ Depending on aerosol particle size, deposition can take place in the upper or lower respiratory tract, and particles < 100 nm in diameter can cross the blood-air barrier into the bloodstream.⁶ A fraction of particles in the bloodstream can cross the bloodbrain barrier and have been found in patients with dementia.⁶ Of particular current concern is the role of aerosol particles in disease transmission, for example in superspreader events of SARS-CoV-2.⁷ Because of the climate and health effects of aerosol particles, it is necessary to know their origins and transformations and how each type impacts the human body.⁸ One way that the particles can be directly speciated is through transmission electron microscopy (TEM).

Several reviews have discussed the use of TEM for atmospheric chemistry.⁹⁻¹³ Buseck et al. 2000 primarily focused on how mineral aerosol particles can be studied with TEM, whereas Buseck 2010 describes many types of aerosol particles that can be analyzed with TEM, some of the associated techniques, and how the information gained can be applied.^{9, 12} Among others, Laskin et al. 2006 and 2019, Tang et al., and Ault and Axson all provide brief overviews of TEM and its relationship with other techniques.^{10-11, 13-14} Similar to previous reviews, we give an overview of the types of particles on which TEM can be used. We then expand on associated analysis techniques, providing a more comprehensive overview of these techniques than in previous reviews. In contrast to previous reviews, our main interest is in the study of aerosol particles composed of organic compounds and salts, which are very fragile in the electron beam, that is, the particles are easily damaged by the electron beam. One impetus for this article is the fact that when these particles are presented in the literature, their images often show signs of damage, which limits the conclusions that can be drawn from these samples. We review our and other's work in this area and demonstrate explicitly the types of damage that can occur to these samples, and the origins of this damage. We intend this article for researchers who are interested in using TEM to study particles containing organic compounds and/or salts as well as readers of the atmospheric literature, in order that researchers can more easily identify and avoid damage to samples, and understand the impact of damage on their analysis. For readers of the atmospheric literature, a general overview of TEM and associated techniques with comparison to commonly used techniques in the atmospheric community is provided.

TEM Technique

TEM uses an electron beam to image samples. In brightfield imaging, the light regions of the image indicate where all the electrons are transmitted through the sample, whereas the darker regions are where some portion of the electrons are not able to pass through the sample. This typically leads to a light background with a dark object. The contrast of the object against the background is influenced by several factors such as the thickness of the object and the Z-number, or atomic number, of the elements in the sample. As the thickness or Z-number increases, the sample becomes darker in the image. Traditional TEM is performed under extremely high vacuum conditions, often reaching pressures as low as 10⁻¹² torr.¹⁵ An exception to this is environmental TEM (E-TEM) where samples can be kept at atmospheric pressure, while the rest of the instrument is under vacuum. E-TEM experiments are frequently performed using a sample holder that is a gas or liquid cell, allowing processes such as aerosol particle efflorescence or deliquescence to be observed in submicron particles.¹⁶⁻¹⁸ These cells typically provide decreased resolution, however, when compared to standard TEM experiments because of the reduced mean free path of the incoming or transmitted electrons due to interactions with molecules in the air.¹⁹ Additionally, many organic compounds (composed of primarily carbon, oxygen, and nitrogen) are unstable when exposed to a room temperature electron beam and will be damaged, and as a result, they cannot easily be studied with this technique. To minimize or delay damage to particles from the electron beam, a cryogenic holder, or a cryo-holder, can be used. A cryo-holder works with both a room temperature sample or a pre-frozen sample. Pre-frozen samples are prepared by cooling the holder down with liquid nitrogen and then inserting the sample into the holder while keeping it immersed in a liquid nitrogen bath. Then the holder can be inserted into the instrument. A room temperature sample can be placed in the holder, inserted into the instrument and then frozen or can be prepared in the same manner as a pre-frozen sample. The samples are then imaged using the same process used for non-cryo samples.

TEMs can be equipped with a variety of associated instruments for spectroscopy and diffraction. These include selected area electron diffraction, or SAED, which is used to determine the crystal lattice structure of nanoparticles. As the atoms in the sample interact with the electron beam, they scatter some electrons resulting in an electron diffraction pattern that can be analyzed for specific structural information. High angle-angular dark field (HAADF) images come from operating the instrument in scanning transmission electron microscopy (STEM) mode. The images from HAADF are commonly known as z-contrast images. In this technique, the detector is placed at an angle under the sample, allowing only the small amount of inelastically scattered electrons that are transmitted through the sample to reach the detector as the electron beam scans the sample. This type of imaging can cause increased contrast for some samples.²⁰ Energy dispersive x-ray spectroscopy (EDS or EDX), electron energy loss spectroscopy (EELS), and energy filtered transmission electron microscopy (EF-TEM) are all methods used to determine the elemental composition of a sample. These techniques can be qualitative or quantitative depending on the method of imaging, sample stability, and the elemental composition. EDS and EF-TEM can be done with or without STEM, but EELS typically is performed with the TEM in STEM mode. EDS can be used to analyze a single point or create an elemental map of the whole sample, but is not generally used quantitatively.¹⁵ EF-TEM can provide elemental information as well as some chemical bonding information, but may damage the sample more than EDS or EELS.²⁰ EELS can be used to provide quantitative elemental data as well as occasionally provide chemical bonding information and has high spatial resolution.²¹ Electron tomography is used to create a 3D image of the sample from many 2D images in TEM. By using a specialized holder, the TEM grid can be tilted into two directions, allowing a sample to be imaged at many different angles. These images are then combined to create a 3D image. Associated techniques and spectroscopies increase the variety of samples that can be studied with TEM and diversify the type of data that can be obtained for each sample.

Advantages of TEM for Atmospheric Chemistry Research and Examples

TEM has many advantages over other methods including ease of sample collection. Methods for collection include cascade impactors for size-selected samples, thermophoretic sampling, and nucleopore filtration sampling²²⁻²³ Some sampling methods collect all particles sizes, while others collect a specific size range. The small size of many aerosol particles makes them ideal for TEM due to their thinness. If a sample is too thick, it will not be transparent to the electron beam, making it impossible to image directly with this technique. TEM allows for high throughput imaging. Around one hundred particles per hour can be imaged by hand, though particle density on the grid and necessary magnification may lower this number, compared to measurements of single digit numbers of particles per hour for atomic force microscopy (AFM). Additionally, a diverse size range can be studied with TEM. Submicron particles, which are generally difficult to study due to their size below the diffraction limit of light, can be imaged in addition to particles that are several microns in diameter, or until the sample becomes too thick. These are just a few of the advantages of TEM.

TEM is a powerful tool for the study of atmospheric aerosol particles. To know how and when to apply this tool, it is important to understand how TEM compares to other techniques that are commonly used in the field of atmospheric chemistry. One frequently used technique is the scanning mobility particle sizer (SMPS) which can provide real time data with very high throughput and without any substrate effects. The limitations of SMPS are that only sizing data is obtained and that the theory for SMPS is based on the assumption that the particles are spherical. Aerosol mass spectrometry (AMS) is frequently used to study the composition of aerosol particles and is used both online and offline with high throughput. Extensions to certain types of AMS have been made to give optical property data and differentiate core-shell structures from other morphologies.²⁴⁻²⁶ Scanning electron microscopy (SEM) is used as an alternative to TEM and

provides images showing the surface of the particles. SEM can be used on fragile samples with minimal damage due to low field electron emission detectors. AFM can provide high resolution sizing of the x, y, and z directions of an aerosol particle and does not require a sample to be under vacuum.²⁷⁻²⁹ Optical microscopy provides an accessible method to study aerosol particles with control of factors such as temperature and humidity, and can be coupled to Raman or FTIR to provide information on functional group composition. Scanning transmission x-ray microscopy coupled with near-edge x-ray absorption fine structure (STXM-NEXAFS) is a highly powerful tool that accomplishes much of the same analysis of aerosol particles as TEM, but requires a synchrotron that is capable of generating tunable X-rays.³⁰⁻³² In some cases, TEM has advantages over these techniques. SMPS and AMS do not provide any of the morphology information that can be retrieved from TEM. Combined electrostatic mobility and aerodynamic diameter measurements have been used to characterize fractal from non-fractal particles.³³⁻³⁴ Additionally, TEM can be used accurately on all particle shapes, unlike the SMPS, and can couple morphology information with some elemental data unlike most AMS instruments. When looking for the internal structure of an aerosol particle, TEM should be used in place of SEM. When compared to AFM, TEM collects data much more quickly and TEM can provide elemental analysis and direct internal structure information. For high-throughput characterization in which the morphology and elemental analysis of submicron particles is desired, TEM is preferred over other techniques. A variety of samples have been studied with TEM as detailed below.

The distinctive shape of some types of particles can give information on speciation. Soot and fly ash particles are often characterized by their fractal components and their different size spherules. Cubic crystals like sodium chloride can be differentiated from other salts and in general, some salts can be differentiated by their shape and crystal structure. Mineral dust is often irregularly shaped compared to nearly spherical organic/inorganic aerosol particles. Visual identification is often combined with elemental analysis for conformation. Below, we provide information on the types of aerosol particles that have been investigated with example studies that demonstrate the breadth of the TEM technique. While hundreds of papers studying aerosol particles have used TEM, those mentioned in this paper typically use TEM as a primary technique in the study.

Soot and heavy metal containing particles have been visually studied to understand their general structure, fractal dimension, and degree of aggregation. HAADF-STEM, high resolution TEM, and EDS have been used to characterize metals such as gold, iron, arsenic, and uranium in aerosol particles collected near a coal-fired power plant, developing a method for future characterization of heavy metals that are found as minority components in atmospheric nanoparticles. ³⁵ These metals, which originated from the coal, are often incorporated in soot particles. The morphology of soot particles can be indicative of their source and their aging in the atmosphere.³⁶⁻³⁹ There is a long-standing interest in the study of soot particles due to their existence in varying concentrations in urban environments, air pollution events, volcanic plumes, and biomass burning. Soot has been proposed as the second largest atmospheric warmer after CO_2 due to the presence of highly absorbing elemental carbon with additional warming coming from the lensing effect, where a non-absorbing, lower scattering coating can lead to enhanced absorption of an absorbing, higher scattering core.⁴⁰ An example of a soot particle is shown in Figure 1a, which has the characteristic overlapping spherules and is relatively spread out. This morphology is an indication that the soot particle is not yet highly aged. The particles that arise from different composition sources were characterized by Xiong and Friedlander, improving the understanding of the diverse nature of atmospheric aggregates such as soot.⁴¹ Electron tomography has also been used on soot particles to better understand structure and aging.⁴²⁻⁴³ A variety of sampling methods have been compared by Ouf et al. who showed that similar soot samples can be prepared using different methods, and confirmed that the collection method has minimal influence on the appearance and composition of the samples indicating that studies using different collection methods can be directly compared.²³ The lattice fringe structure of the soot particles has been

investigated by Wentzel et al. to determine how artificial soot structure differs from that of a diesel engine.⁴⁴ The lattice fringe structure shows the spacing of the lattice planes of the crystalline sections of the sample. In China et al., TEM is used to investigate how soot becomes impacted in supercooled droplets and ice crystals in order to determine the impact of this type of aging on soot morphology.⁴⁵ The unique morphology of soot particles makes it easy to classify them in mixed ambient particle samples.



Figure **3-1**: Particle type examples that include a) a fractal particles, b) a mineral dust particle, c) a homogenous organic/inorganic containing particle, and d) a core-shelled organic/inorganic particle.

Mineral dust aerosol is the second largest emission by mass into the atmosphere and is often composed of a mixture of mineral species. Figure 3-1b shows a mineral dust particle. Pósfai et al. characterized Middle East desert dust and found a range of different mineral types including smectites, illite, silicates (feldspars, quartz), and calcite.¹⁸ To determine the types of minerals, TEM, SAED, and EDS were used, and to explore water uptake properties, E-TEM was used to study dust

mixed with pollution. Half of the mineral particles were mixed with ammonium sulfate or soot, though most did not take up water until > 90 %RH. The abundance of mineral dust in the atmosphere makes for a large variety of these types of particles in the atmosphere.

The speciation of mixtures of particles is useful in determining the types and sources of pollution. Pósfai used TEM with EDS to study the composition of smoke from biomass burning in southern Africa that contained organic, inorganic, and soot particles.⁴⁶ The young smoke contained largely organic particles, aged smoke changed to contain high amounts of tar balls, and the haze afterward consisted of primarily sulfate and organic/sulfate particles.⁴⁶ In Li et al. the potassium and sulfur ratios calculated from EDS and SAED information provided insight into the difference in the haze composition in the presence and absence of biomass burning in Beijing.⁴⁷ These studies provide important information about the variety of aerosol particles in ambient samples and how it varies with location and pollution.

Sea spray aerosol is the largest emission by mass into the troposphere, and consists of a range of salts, primarily sodium chloride, and organic compounds.⁴⁸ Aerosol particles created by marine aerosol reference tanks also investigated organic species found in marine environments of biological origin such as those studied by Patterson et al.⁴⁹ Pósfai et al. characterized the composition of Equatorial Pacific aerosol particles, and found NaCl as well as sulfates of sodium, calcium, magnesium, and potassium.⁵⁰ Los Angeles coastal aerosol was also investigated as part of the CalNex campaign.⁵¹ Sodium containing aerosol from the CalNex campaign was found using EDS to often be highly reacted to form sulfur-containing compounds rather than chloride containing ones. E-TEM was used to understand the phase transitions of model sea spray aerosol.⁵²⁻

Aerosol particles that contain organic compounds are less studied with TEM than other aerosol types due to their fragility in the electron beam. Mixed organic/inorganic aerosol is of interest due to its ubiquity in the environment, and its importance in air pollution events, new particle formation, and cloud droplet formation. In addition, the composition of organic aerosol that results from the oxidation of volatile and semivolatile organic compounds is of continued interest. Lauraguais et al. used TEM to identify the structure of secondary organic aerosol particles and found both spherical and irregular particles, all of which were amorphous. ⁵⁴ Our group has used cryogenic-TEM (cryo-TEM) extensively to determine the morphology of model organic/inorganic aerosol particles, as discussed below.⁵⁵⁻⁶⁰ Figure 3-1 shows examples of a homogenous organic/inorganic particle (Figure 3-1c) and a core-shell organic/inorganic particle (Figure 3-1d). One of the commonly studied types of organic compounds is brown carbon. The formation pathways that produce brown carbon in air pollution and biomass burning are of current interest in the atmospheric chemistry community, as light-absorbing aerosol particles can limit ozone concentrations and impact radiative effects of aerosol particles. This occurs when black and brown carbon particles absorb photons and prevent NO₂ from undergoing photolysis, which can result in ozone production. To characterize the composition of brown carbon, Alexander et al. performed TEM and EELS on brown carbon spheres.⁶¹ While imaging and analysis of organic compounds can be complicated due to their fragility and volatility, it provides important information about true sample morphology and composition. These fragile particles will be the primary focus below.

Our group has used TEM extensively to characterize the optical properties of mineral dust aerosol when combined with other techniques and to characterize the internal structure (morphology) of aerosol particles composed of organic compounds and salts. Initially, we used TEM to complement our measurements of the optical properties of mineral dust particles. Our technique for measuring aerosol optical properties is cavity ring-down spectroscopy, which often uses size-selected samples to constrain the effective refractive index of the particles of interest. Accurate and low dispersity size selection with a differential mobility analyzer requires the use of spherical particles. When non-spherical particles are used, the size distribution for a given mobility diameter of the sample has a larger dispersity. To characterize the sizes of particles selected, we used TEM for samples with aspect ratios near unity (calcite, hematite, quartz) and a combination of SEM and TEM for samples with aspect ratios that deviated from unity (aluminosilicate clay minerals).⁶²⁻⁶⁵ We also worked with mixtures of different types of mineral dust particles, including Arizona test dust and NX illite.⁶⁵ The characterization of the size distribution then allowed us to model the optical properties retrieved from cavity ring-down spectroscopy through use of Mie theory or the discrete dipole approximation. The advantage of using TEM for these studies is that it is a high-throughput method, the shape of particles can be easily determined (with the caveat that SEM or another technique that is capable of both top down and side images is also needed when working with high aspect ratio samples), and we experienced no charging effects with our thin samples.

These initial studies led to work on two field studies. In Hasenkopf et al., aerosol particles from Ulaanbaatar, Mongolia were organized into broad classes: fractal (soot and fly ash), irregular (mineral dust), spherical (organic or organic/salt).⁶⁶ EDS was used to obtain the elemental content of a subset of particles, especially focusing on sulfur content as a function of season. Sulfur content was used as a marker for increased coal burning and was found to be higher during the colder months.⁶⁶ Alstadt et al. used TEM to characterize changes to ambient aerosol particle types as a university campus moved from coal to natural gas as a power plant fuel source, especially focusing on soot aerosol particles and soot mixing state.²² As natural gas rose in usage, less soot was observed, and it was often more aged because it was no longer produced locally and was a result of long range transport, as judged based on morphology and mixing state.²²

Concurrently to the studies of mineral dust aerosol particles, we began to use cryo-TEM to determine the morphology of aerosol particles composed of organic compounds and salts to understand previous results for the optical properties of these systems that were hypothesized to result from the internal structure of the particles.⁶⁷ These particles often undergo liquid-liquid

phase separation.⁶⁸⁻⁶⁹ We initially worked with individual dicarboxylic acids mixed with ammonium sulfate, where we found that liquid-liquid phase separation was inhibited at small particle sizes.^{58, 70} We have subsequently used cryo-TEM extensively to characterize the size dependence of the phase separation. In particular, we have investigated the origins of the size dependence, specifically investigating the role of drying rate and the mechanism of phase separation on the size dependence.⁵⁶⁻⁵⁷ We have worked with different systems including dicarboxylic acids/ammonium sulfate, polymer/salt, and polymer/polymer, as well as complex mixtures of organic compounds with ammonium sulfate.^{57, 59, 70-71} We have recently expanded our preparation technique to vitrify aqueous aerosol particles to determine the relative humidity at which phase separation occurs.^{60, 72} Through these studies, we have shown the origins and applicability of the size dependence of phase separation on atmospheric chemistry. TEM has allowed us to characterize the morphology of hundreds of particles for each study, allowing for accurate and comprehensive analysis.

Secondary Characterization

As mentioned above, TEM is powerful not just as an imaging technique, but also because of additional characterization that can be performed within the instrument. In particular, a host of associated spectroscopic and spectrometric techniques are commonly available on TEM instruments. Additionally, samples can be manipulated within the TEM holder, for example, by exposing to heat or purposeful radiation damage.

STEM takes the electron beam, condenses it to a point, and raster scans it across the sample which can increase image resolution.¹⁵ This can provide additional contrast when imaging with HAADF which uses a detector placed at an angle to collect the scattered electrons, such as was

done in the work of Utsunomiya and Ewing and by Patterson et al.,^{20, 35, 49} These techniques can be used on both fragile and stable samples. Additionally, EDS can be performed using STEM. In EDS, the sample is exposed to X-rays, which excite core electrons. When higher energy electrons fill the holes created in the core levels of the atoms, X-ray radiation is emitted and detected. This light provides elemental information about the samples due to the characteristic signature of X-ray wavelengths that are emitted by atoms of a given element and has been used extensively in the study of atmospheric aerosol particles.^{18, 20, 46-47, 49, 51, 73-95} This technique works best on high atomic weight elements and samples that are beam stable. Fragile samples are frequently destroyed before a full analysis can be obtained.

EF-TEM provides elemental information, is performed in regular microscope mode, and does not require the TEM to have STEM mode, with the added feature that it can be done with a range of filaments. EELS uses the inelastic scattering of electrons to obtain elemental information in spectral form and can also provide information about sample thickness.²⁰ This technique has been commonly used in place of EDS for samples with low atomic number elements.^{46, 49, 79, 82, 84,} ^{89, 96-98} Another method for particle identification is SAED. This technique is used to determine which samples are crystalline and which samples are not crystalline.^{47, 73, 75-76, 89, 91, 94, 98-99} EF-TEM, EELS, EDS, and SAED are primarily used on electron beam stable samples, but qualitative information can, in some cases, be obtained for fragile samples. Electron tomography works by changing the angle that the sample is held within the instrument and taking pictures at many different angles. Then these 2D images can be combined to create a 3D image of the sample.^{42-43,} ^{81-82, 84} Tomography can be performed using a standard room temperature holder or using a cryotomography holder depending on the durability of the sample. Cryogenic-TEM is used on sensitive samples to improve their stability in the electron beam.^{49, 56-60, 70} This method cools the samples to below -180°C which makes them more stable to the electron beam allowing them to be imaged for longer time periods without damage to the sample. For highly sensitive samples, this can be combined with a low dose of electrons by increasing the spot size or by using low-dose mode on the TEM.

E-TEM is useful for controlling the environment to which a TEM grid is exposed. Using this method, factors such as temperature and humidity are controlled. E-TEM allows for transitions such as efflorescence and deliquescence of submicron aerosol particles to be studied in addition to watching the water uptake of the particles.^{52-53, 82, 100-103} Pósfai et al. used E-TEM to study water uptake of mineral dust particles, but found that the particles collected in Saudi Arabia did not uptake enough water to change the appearance of the particle.¹⁸ Semeniuk et al. compared soot particles, tar ball particles, and organic particles as humidity was raised from 0% to 100% RH and then returned the particles back to 0% RH to understand the hygroscopicity of biomass burning aerosol particles.⁷⁷ Wise et al. studied NaCl containing particles from laboratory samples and samples collected in pollution plumes in coastal areas to understand the influence of pollution on the hygroscopicity of sea spray aerosol particles.¹⁶ E-TEM provides important information on efflorescence and deliquescence for submicron and supermicron particle sizes. Note, however, that the extended exposure of the particle to the electron beam over the course of an experiment can cause damage to the aerosol particles, particularly to fragile samples.

Information can also be gained through unique treatment of the samples either inside the TEM instrument or in the grid collection process. Three examples stand out for how samples have been manipulated in the TEM to give additional information on particle chemical and physical properties. In Adachi et al., particles are heated between 25 and 600°C to understand how particles decompose with heating.¹⁷ In Geng et al., bubbling due to sublimation, caused by radiation damage, is used as a method to help speciate particles. EDS is used as well to confirm composition.¹⁰⁴ In Hara et al., a chemical test incorporated onto the grids is used to speciate particles.¹⁰⁵ BaCl₂ grids were used for identification of sulfate, Ca-coated grids were used to identify acidic sulfate, and nitron coated grids were used to detect nitrate.¹⁰⁵ The use of Ca-coated grids to identify acidic

sulfate has been performed repeatedly in the literature.^{76, 85, 89, 105} These experiments typically by work by coating the grid with a chemical compound. The aerosol particles then interact with the coating on which they are impacted and produce crystallization rings which can be viewed using TEM. These forms of sample manipulation help to increase the data that can be obtained from a TEM.

Identifying Damage to Particles

Some samples are fragile in TEM due to the potential for damage from the electron beam. Damage comes from the scattering of electrons both elastically and inelastically. Elastic scattering causes electrostatic charging, atomic displacement, and electron beam sputtering.¹⁰⁶⁻¹⁰⁷ Inelastic charging also causes electrostatic charging in addition to specimen heating, structural damage, mass loss, and deposition. ¹⁰⁶ In samples such as NaCl this can initially be seen as degassing of the material.¹⁰⁸⁻¹⁰⁹ If a sample is solely composed of metals, mineral dust, or soot, it will likely be stable for imaging. Any aerosol particles composed of organic compounds or salts can be damaged. As a result, damage can affect organic, brown carbon, and sea spray aerosol particles, as well as particles with organic coatings. One often unseen method of damage occurs through the evaporation of volatile organic compounds due to the vacuum conditions of the instrument. If the experimental data may be influenced due to this type of damage, in some cases E-TEM data may be compared to traditional TEM data to understand the impacts of volatility. Damage in organic particles often occurs as the particle shrinks due to the sublimation from exposure to the electron beam, whereas salt particles often appear to bubble.¹⁰⁸ In some cases, damage is used as a tool to speciate aerosol particles, more often, damaged particles are published and not acknowledged as damaged.^{18, 41, 44,} 47, 50, 54, 61, 85-86, 89, 96, 110-116 It is important to recognize damage to ensure that data from images are correctly interpreted and that accurate data are collected. If the damage occurs quickly, it can obscure the true morphology or size of the particle, as seen in the image of a particle composed of 3,3 – dimethylglutaric acid and ammonium sulfate in Figure 3-2. In Figure 3-2a the particle is shown in its undamaged form. Figure 3-2b shows the beginning signs of damage where there are slight circles appearing across the particles and the core looks larger and is less defined. Figure 3-2c shows more and more circles appearing and the presence of the core disappears more. Additionally, the particle in 3-2c is larger than the original particle in 3-2a because damage frequently causes changes in the size of particles. This 3,3-dimethylglutaric acid and ammonium sulfate particle is an example of why it can be misleading to assume the size or the morphology of a damaged particle. This particle was imaged using cryo-TEM, because standard (non-cryo) TEM would cause the particle to undergo damage faster than it could be imaged. When reading TEM literature, it is important to check for the appearance of texture due to bubbling in the particle such as found in Figure 3-2 b and c. Typically, the more a particle is covered with these features, the less accurate an analysis of the particle will be. In exceptional cases, the author should provide an explanation for why these features are not signs of damage or why they do not impede analysis. In cases when the composition of the particle is important, damage can make quantitative composition information difficult though some qualitative information may still be possible. While the amount of the components in the particle may change, the presence of some elements in the particle may still be detectable. Using cryo-imaging can help prevent or slow damage, as shown in Figure 3-3. When imaging ammonium sulfate particles using cryo-TEM, a user can easily obtain an undamaged image as shown in Figure 3-3a. When imaging this moderately beam stable compound with noncryo TEM, damage occurs rapidly, which limits the usability of the image (Figure 3-3b). Note that the particles imaged for this paper all show a bright white ring around them. This ring is the Fresnel fringe and is visible because the images are taken with the particle slightly under focused for improved contrast. This ring is not a part of the particle, and instead just surrounds the particle.



Figure 3-2: Electron beam damage to particles over time with estimated electron doses of a) 7.34×10^6 electrons, b) 103×10^6 electrons, and c) 159×10^6 electrons. All scale bars are 100 nm.



Figure 3-3: a)Ammonium sulfate that shows no damage due to cryogenic imaging while b)shows ammonium sulfate that is imaged without cryogenic conditions and particles show significant damage. Scale bars are 100 nm.

When looking at the morphology of phase separated particles it is important to know when small circles within the particle are indicative of damage and when they instead show inclusions within the particle. Inclusions can be a sign that the particle was not able to reach its equilibrium morphology and could cause the particle to have different optical properties than a core-shell particle. Because of these implications it is important not to confuse inclusions with damage. Figure 3-4 shows examples of both a diethylmalonic acid and sodium acetate beam damaged particle and some undamaged particles of the same composition that contain inclusions. Figure 3-4a shows more pitting, or small brighter spots, in the particle image which is often indicative of damage with the white arrow in the image pointing out an example of one of the brighter spots. Additionally, when imaging, the particle continually changed appearance as the particle was exposed to the electron beam which means the particle was undergoing damage. In the case of Figure 3-4b and 3-4c, the particles have some circles in them, but continual exposure to the beam did not change the size, location, or appearance of the circles. Since the amount of time it takes for a particle to damage was already known for particles of this composition, the inclusions are not signs of damage that occurred before the study occurred. Additionally, other signs of damage such as increased texture and constantly changing particle size were not observed. For a situation like this, we suggest the author include images showing a time lapse of the particles, which can help the reader be confident in an accurate assessment of the images. A constant appearance shows that the circles in the particle are inclusions and are not due to damage. Additionally, the particles in Figure 3-4b and 3-4c do not show the texture due to bubbling indicative of electron beam damage. Since homogenous, core shell, and partially engulfed particles can damage, an untrained user may falsely interpret damage as the particle itself having a more complex morphology.



Figure 3-4: a) A damaged particle with the white arrow pointing to texture due to bubbling that is indicative of damage, b, c) Undamaged particles with inclusions. All scale bars are 100 nm.

Other common issues can occur in addition to beam damage of particles. These issues include the development of ice on cryo-TEM grids, wet impaction, and splattering (Figure 3-5). Ice

is a common problem when using a cryo-holder in a standard TEM. The cryo-holder cools down to below -180°C, making it the coldest spot inside the TEM vacuum column. As a result, any moisture in the column moves preferentially to the sample and the ice shows in the images. Ice crystals can hide the morphology of a particle. The 2-methylglutaric acid and ammonium sulfate particles in pictures Figure 3-5a and 3-5b show large amounts of ice. Ice often starts as small crystals that cover the entire grid and cause a decrease in the contrast of the aerosol particles. Ice can be minimized by imaging on cool days with low humidity, storing samples in a desiccator, or using a TEM that has been designed for cryogenic imaging and contains special features such as a cryo-box. Whenever possible, it is best to avoid ice buildup on a sample since it may not only hide the morphology of a particle but also can hide the presence of small particles, or if the ice has grown sufficiently large, it can itself appear like one of the collected particles.

Wet impaction of particles can lead to samples easily icing over. It can also lead to excess frozen water sitting on the grids which will freeze and become visible when imaged cryogenically. Figure 3-5c shows an example of particles composed of poly(ethylene) glycol and dextran that still contained water when they were impacted. The particles are surrounded by large circles of frozen water and the morphology of the particles is hidden by the presence of frozen water. Additionally, when particles are impacted wet, they can splatter on the grid. Figure 3-5d shows the evidence of secondary organic aerosol (SOA) with an ammonium sulfate seed particles splattering on a grid when impacted on an angle with some light water splatter around them. In this case, the morphology and size of the particles were likely changed by their wet impaction.



Figure **3-5**: All images are examples of cryo-TEM with a and b showing large ice crystals. C shows an example of wet impaction and D shows examples of particle splatter that can occur on grids

In this section, a few of the pitfalls a TEM user may experience have been discussed as well as how a reader can spot them; other problems are possible and depend on the system of interest. These issues can have a significant impact on studies where the size or morphology of the particles is characterized. If a study is solely focused on the qualitative composition of a sample, then these limitations will be less important. However, qualitative studies will still be influenced by the rate that particles damage. In addition, the composition of a particle will influence its hygroscopicity which can impact the likelihood of wet impaction. While TEM is a versatile tool for atmospheric chemistry, it is important to remember its limitations, particularly for many of the easily damaged types of particles found in atmospheric and model atmospheric systems.

Conclusions & Best Practices for TEM Imaging

To summarize, TEM is a technique that can provide a 2D structure of submicron atmospheric aerosol particles by transmitting electrons through the sample. This technique provides images of samples below the optical diffraction limit and can be combined with techniques such as EDS, EF-TEM, EELS, SAED, and HAADF which provide additional information about features such as chemical composition and crystal structure. The studies of types of aerosol particles such as soot, mineral dust, salt, and organic/salt particles have been outlined. Studying fragile particles can result in damage and contribute to loss of data. This loss is often caused by the vacuum of the instrument, the electron beam, or from ice that develops on the samples. In this section we outline methods that both readers of TEM literature and users of TEM can use to increase the quality of TEM studies in atmospheric literature.

Best practices for TEM readers

To assess the quality of TEM literature data

- Check images for texture due to bubbling which is indicative of damaged particles.
- Look for signs of ice on the images or evidence of splattering which could be indicative of wet impaction. If these features exist in the images, the text should be searched for an explanation of the presence of the features. Is the use of the TEM image quantitative or

qualitative? If quantitative data was collected, is there any signs that particle damage may be preventing accuracy?

Best Practices for new TEM users

To best use these TEM and associated techniques, it is necessary to understand the limitations of TEM such as beam damage or with cryo-TEM, the presence of ice. Some suggestions for ensuring proper use of the TEM on aerosol particles include:

- Initially, image a fragile material(e.g. ammonium sulfate) without causing damage. It is possible to image ammonium sulfate with standard (non-cryo) TEM without inducing damage. This step teaches a user about what damage can look like as well as providing practice on quick imaging for minimizing sublimation of beam sensitive samples.
- Work with laboratory samples and determine how much exposure is needed for damage to occur with each sample type. Using a laboratory sample can help determine what damage will look like and how much electron dosage the particle can withstand. This helps prevent waste on ambient samples because it will give an approximate starting point for minimizing damage.
- Use cryo-TEM when needed to avoid damage to organic compounds. Both a cryo-holder for a standard TEM and a cryo-TEM work well. Many organic compounds will still damage when using cryo-TEM, but with a decreased electron dosage it is possible to image these particles before they damage, giving a better understanding of the morphology of the particle.
- Recognize signs of damage and adjust interpretation of results appropriately. Damage typically looks like the sublimation or shape change of the particle while it is occurring, but may look different after the particle is completely destroyed. Sometimes it can be difficult to determine what is leftover particle residue and what is organic or water that remains on the grid. If in doubt, try to compare with a cryo-TEM sample.
- . Use low-dose TEM when searching for particles to minimize the number of electrons that interact with the sample. After a particle is selected, the TEM will increase the beam intensity to take the image. This mode, widely available on TEM instruments, helps to minimize the amount of electron dosage while providing a good contrast photo.

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Chapter 4

Effects of Sucrose on Phase Transitions of Organic/Inorganic Aerosols

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Author Contributions: Ott is responsible for most of the data collection, the experimental design and is the primary author. Tackman collected remaining data as well as assisting with discussions and editing.

Abstract

Aerosol morphology influences the interactions of particles with light, water uptake, and heterogeneous chemistry. Through these mechanisms, morphology may be important to the role of aerosol particles on the climate system. A factor that impacts morphology is the diverse and complex mixture of organic compounds that make up the aerosol particles in the atmosphere. In this paper, we investigate the effect of sucrose on liquid-liquid phase separation. As the amount of sucrose is increased, the oxygen to carbon ratio (O:C) of the particles increases. We show that the morphology of the particle changes as O:C is increased with phase separation causing the particle to take on a textured appearance due to large or small inclusions, as opposed to a coreshell particle. As a result of the increased O:C ratio, the separation relative humidity (SRH) of the particles decreases and, in all cases, the SRH can be completely arrested with the addition of a sufficiently large concentration of sucrose. The quantity of sucrose required to arrest phase separation of the particles shows a direct correlation with the SRH of the system without sucrose. The identity of the salt also impacts the amount of sucrose required to arrest phase separation and is controlled more strongly by the identity of the anion. When the mixture contains an organic/inorganic combination that is strongly phase separating, phase separation is observed at an O:C of 0.92 which is a higher O:C value than previously shown (O:C > 0.8). Sucrose is compared with several other high O:C compounds to confirm the influence of the average O:C ratio. In all, these effects could drastically influence aerosol processes in the climate system.

Introduction

Aerosol particles influence the climate through their interactions with radiation from the Sun and Earth. Particles affect the climate directly through the absorption and scattering of radiation and indirectly as seeds for cloud droplets.¹ Particles often are composed of a combination of organic and inorganic components.²⁻⁴ When the particles lose water content, the organic and inorganic components can become immiscible, at which point particles undergo liquidliquid phase separation (LLPS) where they form an inorganic core with an organic coating.⁵⁻⁸ This change in morphology can alter the optical properties of the particles as well their heterogenous chemistry and water uptake behavior.^{4, 9-15} Phase separation has been shown to be influenced by variables such as the type of salt, the oxygen to carbon (O:C) ratio of the organic components, particle size, drying rate, and pH.¹⁶⁻²⁰

The O:C ratio is one of the most commonly studied influencers of phase transitions because it can be easily measured in atmospheric samples using mass spectrometry and is an indicator of solubility and hygroscopicity, but it does not account for the differences between functional groups.²¹⁻²³ Its influence on efflorescence, deliquescence, and LLPS have all been studied.^{16, 24-26} Past studies investigated how changing the O:C ratio regulates the phase separation of particles in the absence of salt.²⁷⁻³⁰ Some researchers previously studied particles composed of a single organic compound and a salt. They found that particles always phase separate when the O:C ratio is below 0.5, sometimes separated between 0.5 and 0.8, and never phase separate when it is above 0.8.¹⁶ Additional research has expanded this work to study mixtures of organics as well as secondary organic material.^{4, 7, 24-25, 31} The ranges in which separation can occur from these more complex systems agree with the results from the single organic/salt systems, in that the average O:C ratio dictates whether phase separation will occur. This research has also created parameterizations for predicting phase transitions, provided an understanding of the effect of the Hofmeister series on phase separation, and highlighted how factors such as functional groups can regulate phase separation when combined with the O:C ratio.^{16, 31-32}

Sucrose is often used by the atmospheric community as an example of a glassforming organic compound. It has been used to study the effects of viscosity on diffusion, the transition from liquid-like particles to glassy particles, mass transfer, and kinetics.³⁴⁻³⁵ It has also been added to particles that contain salts to characterize the effect of sucrose on efflorescence behavior. Wang et al. added sucrose to ammonium sulfate particles and studied their efflorescence using optical microscopy coupled with FTIR.³⁶ They found that as they increased the organic to inorganic ratio (from 1:4 to 1:1), the percent crystallinity decreased and the efflorescence relative humidity (ERH) also decreased until at the 1:1 ratio they found that crystallization no longer occured.³⁶ Liquid-liquid phase separation of sucrose and ammonium sulfate was studied by You et al. and found not to occur under any RH conditions, which is consistent with what is expected based on its O:C ratio.³⁷

In this paper, we add sucrose (O:C = 0.92) to organic/inorganic systems that undergo LLPS to understand the influence of the increasing average O:C ratio on the phase transitions of the particles. We study the effect of sucrose on phase transitions for systems that span a broad range of SRH values prior to the addition of sucrose. The effect of increased sucrose concentration on the morphology of the aerosols is described. Additionally, we study the influence of different salts on the phase separation of these particles.

Experimental Methods

Particles were prepared by spraying aqueous solutions onto hydrophobic glass slides. The solutions used were 5.0 wt.% of inorganic and organic components combined in a 1:1 ratio (i.e. each component at 2.5 wt.%) in HPLC grade water (Fisher Chemical). The one exception was ammonium sulfate and 2,2-bis(hydroxymethlyl)butyric acid, which were used in a 0.6:0.4 ratio to maintain consistency with our previous study and to ensure the presence of phase separation which may require more salt due to the O:C ratio of the organic compound.^{19, 32} The organic compounds used were 2-methylglutaric acid (> 98%, Alfa Aesar), 4-methylglutaric acid (> 99%, TCI), 3,4-dimethylglutaric acid (> 98%, Alfa Aesar), 2,2-bis(hydroxymethyl)butyric acid (> 97%, TCI), poly(ethylene) glycol 1000 (PEG 1000) (Alfa Aesar), and poly(ethylene) glycol 12000 (PEG 12000) (Alfa Aesar). The inorganic components were ammonium chloride (> 99.5%, VWR), sodium chloride (> 99%, Millipore), sodium sulfate (> 99%, Fisher Chemical), and ammonium sulfate (> 99%, Millipore). The weight percent of sucrose (> 99%, Fisher Chemical) was calculated independently of the organic/inorganic quantities for sucrose containing solutions. The crystalline sucrose was then added to the premade 5.0 wt.% organic/inorganic systems. 2.2-Bis(hydroxymethyl)butyric acid, 2-methylglutaric acid, and 4-methylglutaric acid have O:C ratios of 0.667, 3,4-dimethylglutaric acid has an O:C of 0.571, PEG 1000 and PEG 12000 have O:C ratios of 0.523 and 0.502, respectively and sucrose has an O:C of 0.920. In this procedure, the mass of organic and inorganic components and the amount of water remained constant and the quantity of sucrose added was variable. Increasing quantities of sucrose were added until the particles no longer showed phase separating behavior. The average O:C of the particles was calculated using the following equation:

Average
$$0: C = \frac{(moles_{Organic} \times 0: C_{Organic}) + (moles_{Sucrose} \times 0: C_{Sucrose})}{moles_{Organic} + moles_{Sucrose}}$$

To determine the influence of the average O:C ratio, sucrose was replaced with other organic compounds that have high O:C ratios. The compounds used were succinic acid (> 99%, Sigma Aldrich), glycerol (> 99.0%, Affymetrix), glutaric acid (99%, Alfa Aesar), raffinose (97%, Dot Scientific), citric acid (>99.5%, Sigma Aldrich), and malonic acid (99%, Alfa Aesar). Succinic acid and glycerol both have O:C values of 1.00, glutaric acid has an O:C of 0.800, raffinose has an O:C ratio of 0.875, and citric acid and malonic acid have O:C ratios of 1.167 and 1.333, respectively.

The particles were studied using a Nikon Eclipse Ti2 microscope with a 20X objective, observing phase transitions of particles 20-200 μ m in diameter. This inverted microscope has a depth of field between 3.2 and 5.4 microns and was typically focused near the center of the particle. The resolution is submicrometer for existence of inclusions in larger particles, but details of inclusions less than 3 microns in diameter cannot be observed.

The slides were placed in a home-built environmental chamber where the relative humidity (RH) was controlled by flowing a mixture of wet and dry nitrogen into the chamber. A Vaisala HMP60 probe was used to measure the RH with $\pm 3\%$ RH uncertainty between 1% and 90% RH and ± 5 %RH uncertainty between 90% and 100% RH. While these are the related uncertainties for the technique and are typical with these types of probes, those reported in the paper are the standard deviation of the data collected in keeping with the literature.^{19-20, 38} The standard deviations account for any size effects a given system may experience for a phase transition. The humidity was ramped at a rate of approximately 1% RH/min until the region of the phase transition was reached and the

rate was decreased to ~0.5% RH/min until the phase transition finished. Decreasing the ramp rate near phase transitions allows for the reported RH values to be more accurate but is not expected to influence the RH where the transition takes place.

For each phase transition listed in Table 4-1, a minimum of 30 particles were studied and the particles were generated from two or more solutions. All the intermediate data points shown in Figures 4-1,4-2 4-3, 4-4, and 4-5 can be found in Table 4-4 along with the number of particles studied in each case. For the purposes of this paper, the point of phase separation is the RH at which the initial appearance of the changes associated with the processes of phase separation become visible. In addition, the point when signs of phase separation are not seen in particles 50 µm in diameter and smaller using a 20X objective is identified as arrested phase separation. This identity comes from the resolution limit of the microscope. If a higher resolution objective was used, we would expect some additional sucrose to be required to arrest phase separation until the limit of that lens is reached and until the point occurs when phase separation is no longer seen. To understand how the end point of phase separation is influenced by the magnification, a 10X objective was compared with the 20X objective for several systems. The PEG 1000/sodium chloride system appears to no longer phase separate at a sucrose dry mass fraction of 0.233 whereas it requires a 0.263 sucrose dry mass fraction at the 20X objective. This is a difference of 0.25 wt% in the initial solution. The same concentration difference (in terms of wt. %) was required for the 4-methylglutaric acid/sodium chloride system which appeared to stop phase separation at 0.263 sucrose dry mass fraction at 10X but required 0.290 sucrose dry mass fraction at 20X. Additionally, the 4-methylglutaric acid/ammonium sulfate system phase separation was arrested at the sucrose dry mass fraction of 0.202 for both the 10X and 20X objectives. As a result, even with higher magnification, eventually phase separation would be arrested. Regardless of the magnification, the trends for the relative amounts of sucrose needed between the different organic compounds should still hold true.

Results and Discussion

Liquid-Liquid Phase Separation of Organic/Salt Aerosols with Added Sucrose

The addition of sucrose to the particles influences both their SRH and appearance. As sucrose is added to each system, the core-shell morphology of the particles is inhibited and multiple inclusions form instead. In some cases, distinct inclusions are observed, and in other cases, the surface of the particle takes on a textured appearance, which we attribute to inclusions throughout the particles. The degree and appearance of the inclusions is dependent on the system that is studied. In Figure 4-1 row 1, the 3,4-dimethylglutaric acid/ammonium sulfate system is shown. This system starts with a core shell morphology (Figure 4-1a), retains the core shell morphology when the sucrose dry mass fraction is increased to 0.382 (Figure 4-1b), and eventually phase separation appears as a very fine texture, likely very small inclusions, as seen in Figure 4-1c, at the last point before phase separation is inhibited. PEG 1000/ ammonium sulfate is shown in Figure 4-1 row 2 with a core shell morphology in the absence of sucrose (Figure 4-1d); a very fine textured surface, small inclusions, at a midway point (Figure 4-1e); and finally, with a mixture of small and larger inclusions causing a more irregular looking surface in the final phase separation (Figure 4-1f). In the studied systems, the location of the inclusions on the particles may move from the center to the edges; the location is not necessarily indicative of their location in ambient aerosol due to the presence of the substrate. These two samples are indicative of the phase separation of all samples with three exceptions which are 2,2-bis(hydroxymethyl)butyric acid/ammonium sulfate because the addition of any sucrose caused an immediately arrested phase separation, as well as PEG 12000/sodium chloride, and PEG 12000/ammonium chloride. The PEG systems are shown in Figure 4-1, rows 3 and 4 respectively. The PEG 12000/sodium chloride system shows the presence of large inclusions (Figure 4-1g); however this system (containing no sucrose) did not reach a core-

shell morphology even when held near the point of phase separation for close to 20 minutes. The addition of sucrose causes these particles to appear to have a mixture of sizes of inclusions causing a more irregular texture at first (Figure 4-1h), and finally a uniform texture of small inclusions before the inhibition of phase separation (Figure 4-1i). The PEG 12000/ammonium chloride system starts with the appearance of large inclusions shown as an irregular texture (Figure 4-1j) and the inclusions become smaller with the addition of more sucrose, changing the appearance to look more uniform (Figure 4-1k), and finally smaller inclusions causing an almost smooth looking surface just before the end of phase separation (Figure 4-11). These two systems are particularly interesting because they do not start with a core shell morphology. The two systems have relatively low starting SRH values with PEG 12000/ammonium chloride at 57.8 \pm 1.0% RH and PEG 12000/sodium chloride at $66.6 \pm 0.9\%$ RH. Owing to the size of the PEG 12000 molecule, it is expected that diffusion would be limited and the viscosity higher than when compared to a small molecule such as 4-methylglutaric acid.³⁹⁻⁴⁰ These images show that it *could* be possible for liquid particles to exist in a phase state that is neither homogeneous or core shell due to an increased viscosity or other effects in the particle at the point of phase separation.⁴¹ The presence of inclusions in phase separated aerosols has been previously shown.^{6, 41-42} Ciobanu et al. found for supermicrometer droplets that smaller particles had fewer inclusions, and as a result, it is unclear if this result can be extended to the submicrometer size regime.⁶



Figure 4-1: a, b,c) The phase separation of 3,4-dimethylglutaric acid/ammonium sulfate with different levels of sucrose showing the loss of core shell morphology and the addition of surface texture. d,e,f) the phase separation of PEG 1,000/ammonium sulfate showing the loss of core shell to texture with the surface roughness increasing with sucrose concentration. In f, the circle indicates a larger inclusion and the arrow points to an area with smaller inclusions. g,h,i) the phase separation of PEG 12000/sodium chloride showing the sucrose-free particle not able to reach a core shell morphology and the addition of sucrose allowing this to progress to textured particles. j,k,l) the phase separation of PEG 12000/ammonium chloride showing texture without sucrose with

increasing sucrose causing the texture to get smoother. All scale bars are 50 μ m. Images c, f, i, k, and l have had contrast and brightness adjusted to show texture in the images more clearly.

In the Figure 4-2 panels a and b, we display the value of SRH as a function of sucrose dry mass fraction. The last nonzero points shown on the plot are for a sucrose dry mass fraction equivalent to a sucrose concentration that is 0.25 wt.% before phase separation is arrested. This inhibition of phase separation is represented by the drop off in the SRH values. We find that as the SRH of the organic/inorganic solution at 0.000 sucrose dry mass fraction increases, more sucrose is needed to lower the SRH and finally arrest phase separation (Figure 4-2). Figure 4-2a shows the phase separation data for systems containing ammonium sulfate. 2,2-Bis(hydroxymethyl)butyric acid/ammonium sulfate does not phase separate when an amount as small as 0.25 wt.% sucrose is added to it, giving a sucrose dry mass fraction of 0.048, and this system has the lowest SRH at 0.000 sucrose dry mass fraction, just below 48% RH. 2-Methylglutaric acid/ammonium sulfate and 4methylglutaric acid/ammonium sulfate have starting SRH values of 79.4 %RH and 72.6 %RH and at sucrose dry mass fractions of 0.233 and 0.202, respectively, experience arrested phase separation. 3,4-Dimethylglutaric acid/ammonium sulfate has a starting SRH at 90 %RH and requires a 0.772 sucrose dry mass fraction solution to prevent phase separation. PEG 1000 and PEG 12000 both have starting SRH values above 95 %RH and require the highest sucrose dry mass fractions of 0.908 and 0.912, respectively, to arrest phase separation. The high starting SRH values also indicate that the system is strongly driven to phase separate and, as a result, a large quantity of sucrose is required to influence that driving force.

The effect of sucrose on SRH is also studied with sodium chloride using the same organic compounds (Figure 4-2b). 2,2-Bis(hydroxymethyl)butyric acid is not studied because it does not undergo phase separation with sodium chloride. 4-Methylglutaric acid/sodium chloride and PEG 1000/sodium chloride have starting SRH values of 55 % RH and only require 0.290 and 0.263 sucrose dry mass fraction solutions, respectively, to arrest phase separation. We note that for the PEG 1000/sodium chloride/1.75 wt.% sucrose system which has a sucrose dry mass fraction of 0.263, less than 5% of particles undergo phase separation before efflorescence in a 68 particle study. Therefore, we consider phase separation to be arrested for this system for the size range studied in this paper. The starting SRH values for 2-methylglutaric acid/sodium chloride and PEG 12000/sodium chloride are 61.7 %RH and 66.6 %RH respectively and these systems take 0.561 and 0.550 dry mass fraction sucrose solutions to prevent phase separation. 3,4-Dimethylglutaric acid/sodium chloride has a starting SRH of 87.5 %RH and required a 0.886 sucrose dry mass fraction solution to prevent its phase separation. Overall, the primary factor for determining how much sucrose is required to arrest phase separation is the SRH of the system without sucrose.



Figure 4-2: a) Phase separation of particles composed of organic compounds and ammonium sulfate vs dry mass fraction of sucrose. The SRH of the PEG 12000 system and the PEG 1000 systems are both marked as 95 to represent their >95% values. b) Phase separation of the same organic compounds with sodium chloride vs mass fraction of sucrose. In both a and b, the last nonzero point (i.e. the last point before the line goes to zero) is 0.25 wt. % sucrose below where phase separation is inhibited.

Table **4-1**: The SRH, ERH, and DRH Values, Sucrose Dry Mass Fraction and the Average O:C for the 0 Wt.% Solution, Last Sucrose Concentration Before the End of Phase Separation, and the Sucrose Concentration after Phase Separation is Inhibited for Each Organic/Salt Combination in this Study

Salt	Organic Component	% Sucrose	Dry Mass Fraction Sucrose	Av. O:C	% SRH	% ERH	% DRH
fate	2-Methylglutaric Acid	0.00%	0.000	0.667	79.4 ± 1.0 *	40.6 ± 3.9 *	81.2 ± 1.1 *
		1.25%	0.202	0.711	56.3 ± 1.7	38.0 ± 5.1	81.9 ± 0.6
		1.50%	0.233	0.718		39.9 ± 4.0	81.5 ± 1.0
	3-Methylglutaric Acid	0.00%	0.000	0.667	$72.9 \pm 0.7 *$	42.8 ± 3.6 *	81.0 ± 1.1 *
		1.00%	0.168	0.703	58.5 ± 1.9	37.1 ± 3.8	82.3 ± 0.6
		1.25%	0.202	0.711	_	39.3 ± 4.4	83.1 ± 0.4
	3,3-Dimethylglutaric Acid	0.00%	0.000	0.571	$90.3 \pm 3.7*$	40.9 ± 4.7 *	*
Sul		14.25%	0.769	0.833	57.9 ± 0.6	43.4 ± 7.0	_
mium 3		14.5%	0.772	0.834	—	45.5 ± 4.0	—
	2,2-Bis(hydroxymethyl)butyric Acid	0.00%	0.000	0.667	47.7 ± 1.3 *	$38.2 \pm 2.0 *$	81.3 ± 2.5 *
m		N/A	N/A	N/A	N/A	N/A	N/A
Am		0.25%	0.048	0.677	_	38.1 ± 2.1	81.2 ± 0.4
	PEG 1000	0.00%	0.000	0.523	>95	40.6 ± 2.5	83.8 ± 1.1
		32.75%	0.907	0.910	31.0 ± 1.9	_	_
		33.0%	0.908	0.910	_	—	—
	PEG 12000	0.00%	0.000	0.500	>95	39.6 ± 2.5	84.7 ± 0.9
		34.75%	0.914	0.916	66.1 ± 1.5	_	_
		35.0%	0.915	0.916	_	_	_
	2-Methylglutaric Acid	0.00%	0.000	0.667	61.7 ± 4.7	56.1 ± 6.6	80.4 ± 0.4
		5.75%	0.550	0.794	46.0 ± 3.4	45.6 ± 8.7	77.3 ± 0.2
		6.00%	0.561	0.797	_	45.5 ± 8.1	78.3 ± 0.5
	3-Methylglutaric Acid	0.00%	0.000	0.667	55.2 ± 1.2	56.3 ± 5.5	80.5 ± 1.6
e		1.75%	0.263	0.725	49.7 ± 1.7	53.8 ± 6.1	80.6 ± 0.7
orid		2.00%	0.290	0.731		47.2 ± 4.3	79.1 ± 1.1
hlc	3,3-Dimethylglutaric Acid	0.00%	0.000	0.571	87.5 ± 0.1	56.2 ± 6.5	—
n C		27.75%	0.885	0.875	49.5 ± 2.8	_	—
liur		28.0%	0.886	0.875		_	_
Soc	PEG 1000	0.00%	0.000	0.523	55.2 ± 0.8	56.8 ± 4.3	81.5 ± 1.2
		1.50%	0.233	0.775	47.8 ± 0.3	51.4 ± 5.2	81.5 ± 0.3
		1.75%	0.263	0.789	_	49.3 ± 4.0	81.5 ± 0.1
	PEG 12000	0.00%	0.000	0.502	66.6 ± 0.9	48.7 ± 6.9	79.3 ± 0.9
		5.50%	0.538	0.912	39.2 ± 1.3	40.9 ± 5.2	75.3 ± 1.5
		5.75%	0.550	0.912		38.5 ± 5.8	75.0 ± 0.6
e	3,3-Dimethylgluartic Acid	0.00%	0.000	0.571	91.0 ± 1.0	63.9 ± 2.7	86.8 ± 2.8
ılfa		19.5%	0.823	0.854	52.9 ± 1.2	22.7 ± 8.4	—
Sodium Su		19.75%	0.831	0.855		30.6 ± 5.4	_
	PEG 12000	0.00%	0.000	0.502	>95%	61.6 ± 2.5	89.2 ± 2.9
		55.0%	0.961	0.916	68.3 ± 0.6	_	—
		55.25%	0.961	0.916		_	_
onium oride	3,3-Dimethylgluartic Acid	0.00%	0.000	0.571	71.3 ± 1.2	48.7 ± 2.3	—
		30.25%	0.897	0.879	46.0 ± 0.4	34.7 ± 11.2	_
		30.5%	0.899	0.880	_	_	_
Thl Thl	PEG 12000	0.00%	0.000	0.502	58.7 ± 1.0	51.9 ± 3.9	83.2 ± 1.3
AI AI		4.50%	0.485	0.910	21.9 ± 1.1	27.4 ± 5.1	69.5 ± 0.5
		4.75%	0.499	0.911	_	27.6 ± 5.2	69.8 ± 0.6

* represents data from Losey et al. 2018

- represents data points for phase transitions the systems were not observed to undergo

Liquid-Liquid Phase Separation of Organic/Salt Aerosols with Added Sucrose and Salt Identity

While the primary factor regarding the amount of sucrose required to arrest phase separation is SRH, the salt composition also has an effect. Some compounds mixed with sodium chloride require more sucrose to arrest phase separation than solutions containing the same compound and ammonium sulfate, while in other systems the opposite is true. For example, 3,4-dimethyglutaric acid requires a 0.886 sucrose dry mass fraction solution to prevent phase separation with sodium chloride whereas it requires only 0.772 sucrose dry mass fraction solution when mixed with ammonium chloride. Conversely, PEG 1000 needs 0.263 sucrose dry mass fraction to arrest phase separation with sodium chloride.

Particles that contain dicarboxylic acids require more sucrose to arrest phase separation when the particle contains sodium chloride than when the particle contains ammonium sulfate. In contrast, when the particles contain PEG, they need more sucrose to arrest phase separation when the particle contains ammonium sulfate than when the particle contains sodium chloride. To understand the influence of each ion contributed by the salt component on this trend, we studied one dicarboxylic acid and one molecular weight of PEG with ammonium chloride and sodium sulfate. 3,4-Dimethylglutaric acid and PEG 12000 were selected (Figure 4-3). For the PEG systems, the amount of sucrose needed to prevent phase separation for PEG 12000/ammonium chloride < PEG 12000/sodium chloride < PEG 12000/ammonium sulfate < PEG 12000/sodium sulfate. For the 3,4-dimethylglutaric acid systems the weight percent sucrose is ordered 3,4dimethylglutaric acid/ammonium sulfate < 3,4-dimethylglutaric acid/sodium sulfate < 3,4dimethylglutaric acid/sodium chloride < 3,4-dimethylglutaric acid/sodium sulfate < 3,4dimethylglutaric acid/sodium chloride < 3,4-dimethylglutaric acid/sodium sulfate < 3,4dimethylglutaric acid/sodium chloride < 3,4-dimethylglutaric acid/ammonium chloride. We see that the amount of sucrose required to prevent phase separation for each salt is different between the two organic compounds in both quantity of sucrose required and the order that the salts arrest phase separation. We find that in both cases that the anion is the primary controller of how much sucrose is needed to prevent phase separation because the salts are grouped by anion in both cases. For the 3,4-dimethylglutaric acid, the two sulfate systems require less sucrose than the two chloride systems, and for the PEG 12000 system, the two chloride systems both require less sucrose than the two sulfate systems. The variance in the behavior of the PEG system and the dicarboxylic acid is unsurprising due to the variety of conformations in which the polymer can exist and the difference in total intramolecular forces that it may experience when compared to a small molecule.



Figure 4-3: a) The SRH data for 3,4-dimethylglutaric acid and four different salts. b) The SRH data for PEG 12000 and four different salts. The ammonium sulfate and sodium sulfate systems both undergo phase separation at >95 %RH but are shown in the Figure as 95 %RH. In both a and

b, the last nonzero point is 0.25 wt. % below the point of arrested phase separation which is represented by the line going to 0.

Additional Considerations Regarding Sucrose Effects on Liquid-Liquid Phase Separation of Organic/Salt Aerosols with Added Sucrose

In addition to the effect of the different salts, sucrose could influence the solubility of the organics and impact their phase separation behavior. The presence of sucrose does change the composition of the particles and is likely soluble in both phases. It may be acting as a plasticizer in the particles, which would result in a decrease in SRH, as observed. Note, however, that we observe a sharp drop-off in SRH at sufficiently high concentrations of sucrose, indicating that the phase separation process is arrested rather than only being slowly lowered. Additionally, the concept of sugaring-out is studied as an alternative for salting out in biological and manufacturing purification processes.⁴⁴⁻⁴⁵ The kosmotropic (water ordering) properties of sugars such as sucrose allow them to be used for separation and purification. Many systems studied so far involve solvents other than water such as t-butanol, acetone, isopropyl alcohol, and ethyl acetate.⁴⁵ In Sun et al. they found that the phase separation abilities of sugars with t-butanol were galactose > glucose > fructose > mannose \approx sucrose > xylose.⁴⁵ Other factors such as concentration and pH were also found to influence the extraction yield of the system.⁴⁵ It is unknown how this may influence the phase separation of the particles studied in this paper. The gradual decrease and then sharp arrest in the phase separation lead to the conclusion that O:C will become more important than these other factors as additional sucrose is added. The effects of water activity in the particles as well as the influence of viscosity will be discussed later.

MRH/SRH Hysteresis in Organic/Salt Aerosols with Added Sucrose

The mixing relative humidity (MRH) for most systems matches within uncertainty with the SRH values. For the PEG 1000/ammonium sulfate system and the PEG 12000/ammonium sulfate system, a hysteresis is induced when sucrose is added to the system as reported in Table 4-2. In addition to those two points, we also observed a hysteresis for 0.896 sucrose dry mass fraction for PEG 1000/ammonium sulfate and for 0.833 and 0.896 sucrose dry mass fractions for PEG 12000/ammonium sulfate. We previously reported a hysteresis between SRH and MRH for higher pH values of the 4-methylglutaric acid/ammonium sulfate/NaOH system in Losey et al. 2016.²⁰ All other systems studied have SRH values and MRH values that matched within their standard deviations.

	Sucrose Dry	SRH (%)	MRH
	Mass Fraction		(%)
PEG 1000/ ammonium sulfate	0.907	31.0 ± 1.9	49.9 ± 3.9
PEG 12000/ ammonium sulfate	0.914	66.1 ± 1.5	71.9 ± 1.1

Table 4-2: The SRH and MRH Data for Systems Where a Hysteresis was Induced with the Addition of Sucrose

Efflorescence of Organic/Salt Aerosols with Added Sucrose

Figure 4 shows the data for efflorescence. The trends show that there is a slight decrease in ERH as sucrose is added, but the decrease is not significant in most cases. In Figure 4-4a, the data for 2,2-bis(hydroxymethyl)butyric acid/ammonium sulfate, 2-methylglutaric acid/ammonium sulfate, and 4-methylglutaric acid/ammonium sulfate all show no significant decrease in ERH in the ranges studied. Note, however, that these systems are only studied in the range where relevant information is available for the SRH. No additional studies are performed to continue studying the ERH. Wang et al. found that after the ammonium sulfate : sucrose ratio reached 1:1, crystallization no longer occurred.³⁶ 3,4-Dimethylglutaric acid/ammonium sulfate is still undergoing efflorescence at the ammonium sulfate : sucrose ratio of 1: 6.8. As a result, we conclude that, for this system, the organic compound influences the ability of the particle to effloresce. PEG 1000 and PEG 12000 are not shown because they do not undergo efflorescence at 0.833 sucrose dry mass fraction and higher concentrations, which is the region that these particles were studied. At 0 %RH, the particles appear liquid-like, likely becoming highly viscous due to the high concentration of sucrose.

Figure 4-4b shows the data for systems containing sodium chloride. 3,4-Dimethylglutaric acid/sodium chloride is the only system that shows a significant decrease in ERH before efflorescence is arrested. PEG 1000/sodium chloride and 4-methylglutaric acid/sodium chloride exhibited no significant changes in the range studied. PEG 12000/sodium chloride, 2methylglutaric acid/sodium chloride, and 3,4-dimethylglutaric acid/sodium chloride all show a decreasing average ERH with increasing sucrose concentration, though the change is not statistically significant. The data point for 3,4-dimethylglutaric acid at 0.689 sucrose mass fraction is lower, though still within a standard deviation, than the surrounding data points due to the limited number of particles analyzed for this data point and with additional data collection would be expected to average to an ERH value closer to 45%. 3,4-Dimethylglutaric acid/sodium chloride does reach the point where it no longer undergoes efflorescence between 0.857 and 0.885 sucrose dry mass fraction. Additionally, in the 3,4-dimethylglutaric acid/ sodium chloride system, when the solutions contained between 0.382 and 0.749 sucrose dry mass fraction, the particles were found to undergo two distinct efflorescence events, and can be seen in Figure 4-9. The first efflorescence is the presence of one or more distinct sodium chloride crystals in the center phase of the particle. Later, the rest of the particle undergoes efflorescence. The reported values are for the whole particle

efflorescence. To determine how different the ERH values between the two events are and what effect changing the organic to inorganic ratio has on the efflorescence mechanism, additional experiments would be required.



Figure 4-4: a) ERH data for systems containing ammonium sulfate. The PEG systems are not included because they do not undergo efflorescence with the sucrose dry mass fraction studied in this paper. b) ERH data for systems containing sodium chloride. The downward sloping line towards 0 %RH for the 3,4-dimethylglutaric acid/sodium chloride system indicates where the system no longer undergoes efflorescence.

Deliquesence of Organic/Salt Aerosols with Added Sucrose

The deliquescence data also show no significant trend with the addition of sucrose in the sucrose ranges used to investigate SRH. Figure 5a shows data for systems that are mixed with ammonium sulfate that undergo a deliquescence transition. The PEG systems are not shown because they do not effloresce in the regions studied and thus cannot undergo deliquescence. No 3.4-dimethylglutaric acid systems are reported here because this organic compound does not exhibit consistent deliquescence even in the presence of sucrose at all particle sizes, though an occasional small particle may undergo deliquescence. In the 3,4-dimethylglutaric acid /ammonium chloride systems deliquescence was seen in particles that are below 50 μ m in diameter at first, with increasingly larger particles able to deliquesce with increasing concentrations of sucrose. The 2,2bis(hydroxymethyl)butyric acid/ammonium sulfate, 2-methylglutaric acid/ammonium sulfate, and 4-methylglutaric acid/ammonium sulfate systems show no significant changes with increasing sucrose concentration across all ranges studied. In Figure 4-5b, the data for sodium chloride containing systems similarly show no significant changes in DRH with increasing sucrose concentration. 3,4-Dimethylglutaric acid/sodium chloride is not shown because no consistent deliquescence across all size ranges was found for this system; only an occasional deliquescence event occurred in small particles. PEG 1000/ sodium chloride, PEG 12000/sodium chloride, 2methylglutaric acid/sodium chloride, and 4-methylglutaric acid/sodium chloride systems all remain relatively linear in the sucrose concentration regions studied.



Figure 4-5: a) DRH data for systems that contain ammonium sulfate. b) DRH data for systems that contain sodium chloride.

Viscosity and Surface Tension of Organic/Salt Aerosols with Added Sucrose

To better understand the viscosity of these systems, we equilibrate the particles at 90 % RH as well as at SRH at the sucrose concentration just before phase separation is arrested, then estimate the concentration of the particles based on their diameter (Tables 4-5 and 4-6). Solutions are made at the concentrations of the 90 % RH data and viscosity measurements, surface tension and density measurements are taken (Table 4-5). Similarly, the viscosities of the particles can also be estimated
at both 90% RH and at the SRH using a fit equation of sucrose solution data from literature.⁴⁶ Solution data was used because the viscosity data taken for particles that is available in the literature is outside the estimated concentration range of our particles.^{34, 47-49} Using data fit curves, we calculate the viscosities of the particles based on their sucrose concentrations and find a linear correlation between the estimated viscosities and the measured viscosities at 90% RH (Figure 4-10). Using these estimates without the linear correlation, we see that the changes in viscosity are within 1 order of magnitude or less between the estimated viscosity at 90% RH and the estimated viscosity at the SRH and the maximum estimated viscosity is only 0.0683 Pa s. On the basis of these viscosity estimates, it is unlikely that viscosity is playing a significant role in our results.

Water Activity of Organic/Salt Aerosols with Added Sucrose

The addition of large amounts of sucrose to the particles dramatically changes the composition and brings into question the influence of the sucrose on the water activity of the particles. From the work of Starzak and Peacocok, we can see that the water activity of a solution is not expected to have a significant effect until the sucrose concentration exceeds 60 wt.%, higher than that of particles near the SRH for most systems in this study.⁵⁰ This result is in agreement with the AIOMFAC water activity data shown in Figure 4-6 for the 2-methylglutaric acid/sodium chloride system where very minimal changes occur for all additions of sucrose, with the values only ranging from 0.981 to 0.965.⁵¹⁻⁵⁴ The PEG 1000/AS system, PEG 12000/AS system, 3,4-dimethylglutaric acid/AS system and the 3,4-dimethylgutaric acid/sodium chloride system may experience some influence from changes in water activity because their sucrose concentrations are near the 60 wt. % sucrose at the SRH, however these changes are expected to be small because the activity coefficient for water should still be approximately 0.9. Below the SRH, the water activity is expected to decrease significantly and become a more important factor.



Figure **4-6**: Water activity vs the dry mass fraction for 2-methylglutaric acid/sodium chloride where no significant changes in water activity are found for the whole range of sucrose additions.

Influence of the Average O:C Ratio in Organic/Salt Aerosols with Added Sucrose

The high O:C ratio of sucrose (0.920) means that as sucrose is added to the phase separating organic/salt systems, the average O:C ratio of the solution is increasing. The relationship between the O:C ratio of the solution and the phase separation behavior can be found in Figure 4-7. The system with the lowest starting SRH, 2,2-bis(hydroxymethyl)butyric acid/ammonium sulfate, has a starting O:C ratio of 0.667. This system stopped phase separating at a 0.048 sucrose dry mass fraction, giving an average O:C ratio of 0.677 which is still well below the O:C ratio limit for phase separation. Additionally, 2-methylglutaric acid/ammonium sulfate and 4-methylglutaric acid/ammonium sulfate stop phase separating when their average O:C ratios reach 0.718 and 0.711, respectively. These systems also have starting SRH values of 79.4 %RH and 72.9 %RH and do not reach the cut off point for average O:C. That is, they stop phase separating before an O:C ratio of 0.8 is expected to end phase separation. 3,4-Dimethylglutaric acid/ammonium sulfate, PEG 1000/ammonium sulfate, and PEG 12000/ ammonium sulfate have initial SRH values of 90.3 %RH, >95 %RH, and >95 %RH. These systems are all able to undergo phase separation beyond the typical O:C range, with 3,4-dimethylglutraic acid/ammonium sulfate undergoing phase separation until it reaches an O:C ratio of 0.834, PEG 1000/ammonium sulfate undergoing phase separation until an O:C ratio of 0.910 is reached, and PEG 12000/ammonium sulfate phase separates until the solution has an O:C ratio of 0.916. For the sodium chloride systems, 2-methylglutaric acid has a staring SRH of 61.7 %RH, 4-methylglutaric acid has a starting SRH of 55.2 %RH, and PEG 1000 has a starting SRH of 55.2 %RH, and PEG 1000 has a starting SRH of 55.2 %RH, and these systems all stop phase separation are 0.797, 0.731, and 0.781, respectively. 3,4-Dimethylglutaric acid/sodium chloride has a starting SRH of 87.5 %RH and reaches an average O:C ratio of 0.875 before phase separation is arrested. Similarly, PEG 12000/sodium chloride has a starting SRH of 66.6 %RH and reaches an O:C ratio of 0.912 to prevent phase separation. Compounds with higher SRH values with 0.000 sucrose dry mass fraction are more likely to cause phase separation as a component of a high O:C mixture than compounds with a low SRH with 0% sucrose, but the exact composition is important to this trend.



Figure 4-7: SRH vs. average O:C ratio of systems at all data points studied with a) ammonium sulfate and b) sodium chloride.

To better understand the influence of the average O:C, sucrose is exchanged for other high O:C organics that do not undergo phase separation. 2-Methylglutaric acid/ ammonium sulfate and 3,4-dimethylglutaric acid/ammonium sulfate are mixed with glutaric acid (O:C = 0.800), raffinose (O:C = 0.889), succinic acid (O:C = 1.00), glycerol (O:C = 1.00), citric acid (O:C = 1.17), and malonic acid (O:C = 1.33) in addition to sucrose. These compounds are added to solutions at the same concentration as the sucrose at the point of arrested phase separation for the organic/salt

combination. Specifically, 1.5 wt.% of the high O:C compounds is used for 2-methylglutaric acid/ammonium sulfate and 14.5 wt.% of the high O:C compounds is added for 3,4dimethylglutaric acid/ammonium sulfate. Each system is then checked for phase separation. These data are shown in Figure 4-8 and Table 4-3. When glutaric acid and raffinose are added to the 2methylglutaric acid/ammonium sulfate system, the particles are still able to undergo phase separation; whereas when sucrose, succinic acid, glycerol, citric acid, and malonic acid are added, phase separation is arrested. The 3,4-dimethylglutaric acid/ammonium sulfate system undergoes phase separation with raffinose, but not with glutaric acid, sucrose, glycerol, citric acid, or malonic acid. Glutaric acid and raffinose both have O:C ratios below that of sucrose though both are not expected to undergo phase separation due to their O:C ratio, but both are able to phase separate under some conditions. Glutaric acid can undergo phase separation at an average O:C of 0.720 for the 2-methylgutaric acid/ammonium sulfate system but is arrested at O:C of 0.775 for the 3,4dimethylglutaric acid/ammonium sulfate system. Raffinose can undergo phase separation at an O:C of 0.698 for 2-methylglutaric acid/ammonium sulfate and at 0.779 for 3,4-dimethylglutaric acid/ammonium sulfate. These results show that while the average O:C of the particles is a useful parameter for predicting the phase separation behavior, the exact composition of the particles, impacting how strongly the two or more components of the system want to separate, is more important.

Table **4-3**: The phase separation behavior of the 2-methylglutaric acid/ammonium sulfate system and the 3,4-dimethylglutaric acid/ammonium sulfate system with added organics with varying O:C values.

Added Organics	O:C of added Organic	2-methylglutaric acid/ammonium sulfate/ 1.5% added organic	3,4-dimethylglutaric acid/ammonium sulfate/14.5% added organic
Glutaric Acid	0.80	Phase Separating	Not Phase Separating
Raffinose	0.88	Phase Separating	Phase Separating
Sucrose	0.92	Not Phase Separating	Not Phase Separating

Succinic Acid	1.00	Not Phase Separating	Not Phase Separating
Glycerol	1.00	Not Phase Separating	Not Phase Separating
Citric Acid	1.17	Not Phase Separating	Not Phase Separating
Malonic Acid	1.33	Not Phase Separating	Not Phase Separating



Figure **4-8**: The separation relative humidity of two systems mixed with a constant weight percent of different O:C compounds. The 2-methylglutaric acid/ammonium sulfate system is mixed to a 0.233 mass fraction of the non-phase separating organic compounds and 3,4-dimethylglutaric acid/ammonium sulfate is mixed to a 0.772 mass fraction of the non-phase separating organic compounds.

Conclusions

We demonstrate that the addition of sucrose impacts the phase separation of aerosol particles. As the average O:C of the particles undergoing phase separation increases, the morphology of the particles changes. Low concentration sucrose particles undergo phase separation to form a core-shell morphology, as viewed in optical microscopy. Particles with an intermediate sucrose dry mass fraction can exist in what appears as a textured morphology which may affect the optical properties of the particles as well as the heterogenous chemistry due to possible variations in the compositions of the phases. Finally, when particles reach a high sucrose dry mass fraction, they exist as a homogenous morphology and do not undergo phase separation at all.

As the sucrose concentration is increased, the SRH of the particles decreases until the point that the particles no longer undergo phase separation. The amount of sucrose required to prevent phase separation is related to the SRH of the system when no sucrose is present. The systems shown in this paper show no distinct trends for the ERH and DRH values as the sucrose concentration is increased.

Mixed particles with average O:C ratios beyond 0.8 have been shown to undergo phase separation with the most phase separating system able to undergo phase separation up to an O:C of 0.920. Since the particles that undergo LLPS in the atmosphere are all mixtures, we show that more than just the average O:C ratio is important. If a strongly phase separating component is present in the particle, the particle may still be able to undergo LLPS even though the average O:C says that is should not be able to undergo this phase transition.

Supporting information

		% Sucrose	Average O:C	% SRH	% ERH	% DRH
0	2-Methylglutaric Acid	1.00%	0.703	63.7 ± 0 (15) ^a	37.7 ± 2.6 (17)	85.9 ± 1.1 (19)
fate	2.4	3.00%	0.698	84.9 ± 0 (14)	42.8 ± 2.3 (16)	^b
Sul	5,4- Dimethylaluterie	7.00%	0.773	72.0 ± 0.5 (20)	N/A	
Ш		10.00%	0.805	63.4 ± 0.1 (13)	44.3 ± 4.4 (12)	
niu	Aciu	13.75%	0.830	60.7 ± 1.3 (16)	46.4 ± 2.8 (15)	
mo	DEC 1000	20.00%	0.904	52.2 ± 0.3 (21)		
TUN I	PEG 1000	30.00%	0.909	$39.2 \pm 0.7 (11)$		
Ą	DEC 12000	20.00%	0.915	83.6 ± 0 (24)		
	PEG 12000	30.00%	0.916	68.6 ± 0.1 (12)		
		1.00%	0.703	54.9 ± 1.0 (23)	57.0 ± 5.2 (16)	81.9 ± 0.3 (16)
	2 Matheulalateria	1.50%	0.718	54.0 ± 0.1 (12)	54.7 ± 5.5 (17)	81.8 ± 0 (17)
		1.75%	0.725	52.8 ± 1.0 (15)	53.6 ± 5.8 (30)	77.5 ± 1.8 (30)
	Acia	2.00%	0.731	57.3 ± 1.6 (21)	53.3 ± 5.2 (23)	$78.3 \pm 0.1 (17)$
		5.00%	0.785	44.8 ± 3.4 (11)	45.8 ± 8.2 (22)	77.1 ± 0.1 (22)
	4-	1.00%	0.703	52.3 ± 1.1 (14)	51.4 ± 5.8 (17)	$78.3 \pm 0.1 (17)$
a	Methylglutaric Acid	1.50%	0.718	51.2 ± 1.4 (12)	50.4 ± 5.3 (14)	78.4 ± 0.2 (14)
rid		3.00%	0.698	76.0 ± 0 (12)	51.5 ± 2.9 (20)	
hlo		7.00%	0.773	74.3 ± 0 (12)	45.2 ± 6.4 (21)	
C	3,4- Dimethylglutaric Acid	10.00%	0.805	68.3 ± 1.3 (12)	35.6 ± 6.5 (10)	
un		13.00%	0.826	65.1 ± 0 (10)	45.1 ± 4.7 (6)	
odi		17.00%	0.845	62.1 ± 1.1 (22)	44.1 ± 2.4 (7)	
S		20.00%	0.856	54.5 ± 0.5 (23)	44.2 ± 5.6 (7)	
		23.00%	0.864	50.1 ± 0.2 (10)	$36.2 \pm 11.1 (15)$	
	DEC 1000	1.00%	0.736	47.9 ± 0.5 (37)	49.4 ± 5.0 (59)	82.8 ± 0.2 (30)
	PEG 1000	1.25%	0.758	47.0 ± 0.2 (13)	51.3 ± 5.3 (25)	81.2 ± 0.2 (14)
		1.50%	0.898	63.5 ± 0.8 (30)	49.9 ± 5.7 (30)	$80.3 \pm 0.2 (15)$
	PEG 12000	2.00%	0.903	60.8 ± 0 (11)	56.3 ± 5.3 (13)	77.2 ± 0 (13)
		3.00%	0.907	56.9 ± 0.6 (55)	49.3 ± 6.0 (40)	$77.6 \pm 0.3 (44)$
	3,4-	10.00%	0.805	73.0 ± 0 (16)	(0) ^c	
um te	Dimethylgluartic	14.00%	0.831	50.0 ± 1.6 (10)	42.2 ± 2.7 (11)	91.7 ± 0 (5)
diu Ilfa	Acid	17.00%	0.845	54.7 ± 1.3 (17)	(0)	(0)
S.S.C	DEC 12000	20.00%	0.915	87.7 ± 0.0 (15)		
	FEG 12000	40.00%	0.916	71.7 ± 1.6 (23)		
•		2.00%	0.667	69.5 ± 0.1 (16)	(0)	
ride	3,4-	5.00%	0.743	64.33 ± 0 (13)	48.55 ± 4.9 (2)	
Iolu	Dimethylgluartic	10.00%	0.805	63.8 ± 1.1 (12)	46.8 ± 5.3 (12)	
C	Acid	28.25%	0.875	47.7 ± 1.6 (15)	41.4 ± 0 (1)	
um		30.00%	0.878	46.3 ± 1.0 (11)	55.1 ± 0.3 (2)	
inc		1.00%	0.889	$50.89 \pm 0(3)$	44.9 ± 3.7 (5)	74.5 ± 0.1 (6)
Ammo	PEC 12000	2.00%	0.903	47.3 ± 0 (5)	39.3 ± 2.9 (6)	$74.2 \pm 0.9 (11)$
	110 12000	3.00%	0.907	42.6 ± 0 (9)	35.5 ± 2.2 (9)	$72.9 \pm 0.2 (12)$
-		4.25%	0.910	33.5 ± 0.2 (9)	31.5 ± 2.9 (6)	70.1 ± 0.2 (9)

Table 4-4: The SRH, MRH, and DRH and average O:C values for all intermediate data points

^a the values in parenthesis are the number of data points taken. ^b -- represent when no phase transition was found ^c (0) are when no data was collected for that phase transition

	Organic Component	Wt% Sucrose	Sucrose Dry Mass Fraction	Organic / Sucrose	Av. O:C	OIR
		0.00%	0.000	0.000	0.667	1.00
	2 Mathedalistania Asid	1.00%	0.168	0.712	0.703	1.404
	2-Methylgiutaric Acid	1.25%	0.202	0.664	0.711	1.51
		1.50%	0.233	0.621	0.718	1.61
		0.00%	0.000	0.000	0.667	1.00
	4-Methylglutaric Acid	1.00%	0.17	0.72	0.703	1.41
		1.25%	0.20	0.66	0.711	1.51
		0.00%	0.000	0.000	0.571	1.00
		3.00%	0.382	0.447	0.698	2.24
		7.00%	0.601	0.249	0.773	4.01
ate	3,4-Dimethylglutaric Acid	10.00%	0.690	0.184	0.805	5.44
ulfi		13.75%	0.761	0.136	0.830	7.38
J S		14.25%	0.769	0.136	0.833	7.65
iun		14.5%	0.772	0.128	0.834	7.78
uo	2.2 Pig(hudroyumothul)huturio	0.00%	0.000	0.000	0.667	1.00
uu	2,2-Bis(ilydroxymethyl)butylic	N/A	N/A	N/A	N/A	N/A
Ar	Acid	0.25%	0.048	0.909	0.677	1.10
		0.00%	0.000	0.000	0.523	1.00
	PEG 1000	20.00%	0.833	0.091	0.904	11.00
		30.00%	0.896	0.055	0.909	18.2
		32.75%	0.907	0.049	0.910	20.5
		33.0%	0.907	0.048	0.910	20.7
		0.00%	0.000	0.000	0.500	1.00
		20.00%	0.833	0.091	0.915	11.0
	PEG 12000	30.00%	0.896	0.055	0.916	18.1
		34.75%	0.914	0.045	0.916	22.3
		35.0%	0.915	0.044	0.916	22.5
		0.00%	0.000	0.000	0.667	1.00
		1.00%	0.168	0.712	0.703	1.40
		1.50%	0.233	0.621	0.719	1.61
	2 Methylalutaric Acid	1.75%	0.263	0.584	0.725	1.71
	2-Weinyigiutane Acid	2.00%	0.290	0.551	0.731	1.82
		5.00%	0.513	0.322	0.785	3.11
e		5.75%	0.550	0.291	0.794	3.44
brid		6.00%	0.561	0.281	0.797	3.55
hlc		0.00%	0.000	0.000	0.667	1.00
C		1.00%	0.168	0.712	0.703	1.40
iun	4-Methylglutaric Acid	1.50%	0.233	0.621	0.718	1.61
po		1.75%	0.263	0.584	0.725	1.71
S		2.00%	0.290	0.551	0.731	1.82
		0.00%	0.000	0.000	0.571	1.00
		3.00	0.382	0.447	0.698	2.24
	2.4 Dimetholabet in Arid	7.00	0.601	0.249	0.773	4.01
	3,4-Dimethylglutaric Acid	10.00	0.690	0.184	0.805	5.44
		13.00	0.749	0.143	0.826	6.98
		17.00	0.804	0.109	0.845	9.19

Table **4-5**: The wt% sucrose, sucrose dry mass fraction, phase separating organic to sucrose ratio, average O:C, and the organic : inorganic ratio for all systems.

		20.00	0.833	0.091	0.856	11.0
		23.00	0.857	0.077	0.864	12.9
		27.75%	0.885	0.061	0.875	16.4
		28.0%	0.886	0.060	0.875	16.6
		0.00%	0.000	0.000	0.523	1.00
		1.00%	0.168	0.712	0.736	1.40
	PEG 1000	1.25%	0.202	0.664	0.758	1.51
		1.50%	0.233	0.621	0.775	1.61
		1.75%	0.263	0.584	0.789	1.71
		0.00%	0.000	0.000	0.502	1.00
		1.50%	0.233	0.621	0.898	1.61
	DEG 10000	2.00%	0.290	0.551	0.903	1.81
	PEG 12000	3.00%	0.382	0.447	0.907	2.24
		5.50%	0.538	0.300	0.911	3.33
		5.75%	0.550	0.290	0.912	3.44
		0.00%	0.000	0.000	0.571	1.00
	3,4-Dimethylgluartic Acid	10.00%	0.689	0.184	0.805	5.44
		14.00%	0.765	0.133	0.831	7.51
ate		17.00%	0.804	0.109	0.845	9.19
llu		19.5%	0.833	0.094	0.854	10.7
n S		19.75%	0.831	0.092	0.855	10.8
liui		0.00%	0.000	0.000	0.502	1.00
Soc	PEG 12000	20.00%	0.833	0.091	0.915	11.0
		40.00%	0.930	0.036	0.916	27.7
		55.0%	0.961	0.020	0.916	49.9
		55.25%	0.961	0.020	0.916	50.4
		0.00%	0.000	0.000	0.571	1.00
	3,4-Dimethylgluartic Acid	2.00%	0.290	0.551	0.667	1.82
		5.00%	0.513	0.332	0.743	3.11
		10.00%	0.690	0.184	0.805	5.44
ide		28.25%	0.887	0.060	0.875	16.8
llor		30.00%	0.896	0.055	0.878	18.1
Ð		30.5%	0.898	0.054	0.879	18.6
um		30.75%	0.899	0.053	0.880	18.8
inc		0.00%	0.000	0.000	0.502	1.00
m		1.00%	0.168	0.712	0.889	1.40
An		2.00%	0.290	0.551	0.902	1.82
	PEG 12000	3.00%	0.382	0.447	0.907	2.24
		4.25%	0.470	0.360	0.910	2.78
		4.50%	0.485	0.347	0.910	2.88
		4.75%	0.499	0.334	0.911	2.99



Figure **4-9**: The first efflorescence and appearance of sodium chloride crystals in 3,4dimethylglutaric acid/sodium chloride 7 wt.% sucrose solution b) the complete efflorescence of the same particle

Viscosity and Surface Tension

Viscosity measurements were taken using an Ares RFS-3 rheometer with cylindrical RSF-2 geometry in steady motor mode. The solutions showed Newtonian behavior between 10 and 100 s⁻¹ sheer rate with eleven measurements taken in this range. The value reported is the average of these eleven measurements. Non-sheering solutions have an error of 5%, and the uncertainty reported reflects that error. The concentration of the solutions measured is the estimated concentration of particles equilibrated at 90% RH. The concentration of the equilibrated particles was estimated by spraying the slides and immediately imaging the particles to obtain their initial volume. The particles were allowed to equilibrate at 90% until they showed no change in diameter and imaged to determine their volume change from their initial values. Then the particles were lowered to their SRH and allowed to equilibrate at that point after which their volume was determined and its change from the initial value was once again calculated. The initially sprayed particles were assumed to have the concentration of the solution they were sprayed from and using $M_1V_1 = M_2V_2$, where M_1 is the 5.0 wt.% organic/inorganic solution with its respective quantity of sucrose, V_1 is the volume of the particles sprayed from the initial solution, and M_2 is the concentration of the particle after equilibration at 90% or SRH, and V_2 is the volume of the particle after equilibration, the estimated concentration of the equilibrated particles was determined. The same procedure was used for both the 90 %RH concentration estimates and the SRH concentration estimates. This procedure is shown in Figure 4-10. The density and surface tension of these solutions was measured using a Krüss K11 force tensiometer using a density attachment and a Wilhelmy plate, with three measurements taken for each surface tension and density reported.



Figure **4-10**: A flow chart summarizing the process used to determine the estimated viscosities of the particles.

To better understand the viscosity of these systems, we equilibrated the particles at 90 % RH and estimated the concentration of the particles based on their diameter. In these calculations, we assumed that the particles exist as perfect half spheres, will shrink equally in all directions other than where the surface is exposed to the substrate, no significant evaporation occurs from spraying, and no density changes occur in the particles. The contact angle is assumed to be 90° and constant

throughout the experiment, which is unlikely to be true. If the contact angle is less than 90° the concentration estimate will be high whereas if the angle is greater than 90° the concentration estimated will be low. A changing contact angle over the course of the experiment would also shift the concentration estimates either high or low. While contact angles were not measured in this paper, the work of Song et al. was taken into consideration for our error analysis discussion.⁷ We chose to use the 90 % RH mark because this is above the DRH for all solutions, allowing us to make these solutions in bulk because the particles are not supersaturated in solute. In addition to viscosity measurements, surface tension and density measurements were taken for these solutions. These data are summarized in Table 4-6. We see that there are no obvious trends between the surface tension or density with the wt.% sucrose, the starting SRH values, or the ending SRH values. Similarly, the viscosities of the particles can also be estimated at both 90% RH and at the SRH using sucrose solution data from literature.⁴⁶ Research in the atmospheric community has been performed on the viscosities of sucrose particles using a variety of methods such as florescence recovery after photobleaching, droplet coalescence using optical tweezers, and the poke-flow technique.^{34, 47-49} Most of the data obtained in these papers is outside of the range of sucrose concentrations estimated in this paper due to the low concentrations needed to arrest phase separation making it difficult for us to compare our sucrose values with those reported.^{34, 47-48} The sucrose concentrations are estimated using the time-mode 60 µW data from Cha et al.⁴⁶ We fit the data using a symmetric sigmoidal curve with the 0-40 wt.% modeled with one curve and the 40-60 wt.% modeled with a second curve. Using these curves, we calculated the viscosities of the particles based on their sucrose concentrations and found a linear correlation between the estimated viscosities and the measured viscosities at 90% RH (Figure 4-11). The modeled sucrose concentration curves were also used to estimate the sucrose viscosity at the SRH of each system at the last point before phase separation is arrested (Table 4-7). The correlation between the measured and estimated sucrose viscosities shown in Figure 4-11 was not used in the estimates and the

particles are assumed to contain only sucrose. Using these estimates, we see that the changes in viscosity are within one order of magnitude or less between the estimated viscosity at 90 %RH and the estimated viscosity at the SRH. The estimated viscosity values are one to three orders of magnitude different from those estimated in Fard et al. because these values are estimated for the homogenous particle as opposed to the different phases of the phase separated particles.⁴¹ The order of magnitude of our values is supported by modeled viscosities of dicarboxylic acid particles which had estimated viscosities at 0% RH from 10⁻³ to 10^{-1.5} Pa s.⁵⁵ All estimated viscosities at the point where phase separation is arrested are below 0.1 Pa s showing that viscosity is not likely to be a large factor in the phase separation of these systems. If the salt and organic components were included in the viscosities, we would expect the values to remain within the liquid-like aerosol regime, for most if not all data. We were unable to measure the actual viscosity at the SRH values because we measured the bulk viscosities and the particles are supersaturated at that point making it impossible to make those concentrations of solutions in bulk. We looked for correlations between the starting relative humidity of the systems when they have no sucrose with the last point before phase separation is arrested and included particle viscosity estimates, but did not observe any direct correlations for these data. Additionally, Table 4-7 provides estimates the concentrations of the sucrose, salt, and organics at the SRH values. From the viscosity data obtained and estimated for the systems studied in this paper, we conclude that it is unlikely that viscosity causes the inhibition of phase separation at the sucrose concentrations studied.

Table **4-6**: Estimated concentrations at 90 % RH for the sucrose, salt, and organic components and corresponding viscosity, density, and surface tension measurements of solutions of those concentrations as well as estimated sucrose viscosities.

	90% Relative Humidity									
		Wt.% Sucrose	Wt.% Salt	Wt.% Organic	Estimated Sucrose Viscosity (Pa s)	Measured Viscosity (Pa s)	Density (g/cm ³)	Surface Tension (dynes/cm)		
	2-Methylglutaric Acid	8.1 ± 1.4	15.4 ± 2.6	15.4 ± 2.6	0.00105	$\begin{array}{c} 0.0029 \ \pm \\ 0.001 \end{array}$	1.146 ± 0.004	45.7 ± 0.1		
ate	4-Methylglutaric Acid	$\begin{array}{rrr} 3.6 & \pm \\ 0.5 & \end{array}$	8.6 ± 1.3	8.6 ± 1.3	0.00102	$\begin{array}{r} 0.0017 \ \pm \\ 0.0001 \end{array}$	$\begin{array}{c} 1.078 \pm \\ 0.001 \end{array}$	53.2 ± 0.2		
ո Sulfն	3,4-Dimethylglutaric Acid	$\begin{array}{rrr} 33.8 & \pm \\ 2.2 \end{array}$	$\begin{array}{c} 2.9 \ \pm \\ 0.2 \end{array}$	$\begin{array}{cc} 2.9 & \pm \\ 0.2 \end{array}$	0.00507	$\begin{array}{r} 0.0043 \ \pm \\ 0.0002 \end{array}$	$\begin{array}{c} 1.158 \pm \\ 0.001 \end{array}$	54.9 ± 0.1		
monium	2,2- Bis(hydroxymethyl) butyric Acid	0	12.1 ± 4.5	8.1 ± 3.0		$\begin{array}{c} 0.0017 \ \pm \\ 0.0001 \end{array}$	$\begin{array}{c} 1.091 \pm \\ 0.001 \end{array}$	56.2 ± 0.4		
An	PEG 1000	41.8 ± .5	3.0 ± 0.5	$\begin{array}{rrr} 3.0 & \pm \\ 0.5 & \end{array}$	0.00801	$\begin{array}{r} 0.0077 \ \pm \\ 0.0004 \end{array}$	$\begin{array}{c} 1.191 \pm \\ 0.001 \end{array}$	62.0 ± 0.1		
	PEG 12000	55.8 ± 6.6	4.0 ± 0.5	$\begin{array}{rrr} 4.0 & \pm \\ 0.5 & \end{array}$	0.0384	$\begin{array}{ccc} 0.044 & \pm \\ 0.002 & \end{array}$	$\begin{array}{c} 1.267 \pm \\ 0.001 \end{array}$	55.6 ± 0.1		
de	2-Methylglutaric Acid	$\begin{array}{rrr} 11.5 & \pm \\ 1.8 \end{array}$	4.8 ± 0.7	$\begin{array}{rrr} 4.8 & \pm \\ 0.7 & \end{array}$	0.0011	$\begin{array}{c} 0.0017 \ \pm \\ 0.0001 \end{array}$	$\begin{array}{c} 1.083 \pm \\ 0.001 \end{array}$	49.0 ± 0.2		
Chlori	4-Methylglutaric Acid	$\begin{array}{cc} 4.3 & \pm \\ 0.3 \end{array}$	5.8 ± 0.4	$\begin{array}{ccc} 5.8 & \pm \\ 0.4 \end{array}$	0.00102	$\begin{array}{r} 0.0015 \ \pm \\ 0.0001 \end{array}$	$\begin{array}{c} 1.067 \pm \\ 0.001 \end{array}$	56.8 ± 1.7		
Sodium (3,4-Dimethylglutaric Acid	$\begin{array}{rrr} 32.2 & \pm \\ 6.9 \end{array}$	$\begin{array}{c} 2.8 \ \pm \\ 0.6 \end{array}$	$\begin{array}{ccc} 2.8 & \pm \\ 0.6 \end{array}$	0.00451	$\begin{array}{r} 0.0040 \ \pm \\ 0.0002 \end{array}$	$\begin{array}{c} 1.154 \pm \\ 0.001 \end{array}$	54.8 ± 0.1		
	PEG 1000	$\begin{array}{rrr} 3.7 & \pm \\ 0.6 \end{array}$	5.9 ± 1.0	5.9 ± 1.0	0.00102	$\begin{array}{c} 0.0017 \ \pm \\ 0.0001 \end{array}$	$\begin{array}{c} 1.062 \pm \\ 0.001 \end{array}$	61.5 ± 0.1		
	PEG 12000	$\begin{array}{rrr}12.5 & \pm\\ 0.3\end{array}$	5.4 ± 0.1	5.4 ± 0.1	0.00115	0.0056 ± 0.0003	$\overline{\begin{matrix} 1.089 \pm \\ 0.001 \end{matrix}}$	60.0 ± 0.1		



Figure **4-11**: Comparison of the estimated and measured viscosity of the solutions at the 90 %RH equilibration concentration.

	SRH				
		Wt% Sucrose	Wt% Salt	Wt% Organic	Estimated Sucrose Viscosity (Pa s)
	2-Methylglutaric Acid	10.2 ± 1.5	19.3 ± 2.8	19.3 ± 2.8	0.00105
umonium Sulfate	4-Methylglutaric Acid	5.4 ± 0.5	13.0 ± 1.2	13.0 ± 1.2	0.00103
	3,4-Dimethylglutaric Acid	46.8 ± 2.6	4.0 ± 0.2	4.0 ± 0.2	0.0133
	2,2-Bis(hydroxymethyl)butyric Acid	0	23.7 ± 7.5	15.8 ± 5.0	0
An	PEG 1000	55.4 ± 9.0	4.0 ± 0.7	4.0 ± 0.7	0.0367
	PEG 12000	60.7 ± 6.6	4.2 ± 0.5	4.2 ± 0.5	0.0683
	2-Methylglutaric Acid	20.9 ± 2.7	8.7 ± 1.1	8.7 ± 1.1	0.00182
Sodom Chloride	4-Methylglutaric Acid	8.7 ± 0.7	11.8 ± 0.9	11.8 ± 0.9	0.00105
	3,4-Dimethylglutaric Acid	52.5 ± 10.5	4.5 ± 0.9	4.5 ± 0.9	0.0259
	PEG 1000	8.2 ± 1.3	13.0 ± 2.1	13.0 ± 2.1	0.00105
	PEG 12000	25.8 ± 0.1	11.2 ± 0.5	11.2 ± 0.5	0.00270

Table 4-7: Estimated concentrations of sucrose, salt, and organic combinations at their SRH values and estimated sucrose viscosity values of those solutions

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Chapter 5

The Inhibition of Phase Separation in Aerosolized Water-Soluble Polymer-Polymer Nanoparticles at Small Sizes and the Effects of Molecular Weight

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[Post publication additions to the paper are underlined in the text and enclosed in brackets.]

Abstract

The effects of confinement on the phase separation behavior of polymer-polymer mixtures have been frequently studied in morphologies such as thin films and rods, but little research exists with respect to the nanoscale droplet size regime. This paper addresses the phase separation of water-soluble polymers in submicron aerosol droplets. Atomized aerosol particles were prepared from aqueous solutions and dried using diffusion dryers. For poly(ethylene) glycol/dextran and poly(vinyl alcohol)/poly(5-styrene sulfonic acid) systems, small particles remain homogenous while larger particles undergo phase separation within a single particle. As the molecular weight of the polymers increases while a constant ratio between monomers of polymers A and B is maintained, phase separation occurs in smaller diameter particles. These trends are modeled using a combination of equations describing the nucleation of a new phase and Flory-Huggins theory and provide qualitative agreement. These results provide insight into the phase separation of aqueous

nanoscale polymer-polymer systems. Potential exists to make new polymer materials with unique properties due to the mixing of polymer combinations that normally undergo phase separation.

Introduction

Phase separation of polymer-polymer-water ternary systems into a polymer A rich phase and a polymer B rich phase has been studied for over 70 years with applications in protein purification, metal extraction, and microparticle synthesis.¹⁻⁵ Much of the recent work has moved on from such bulk studies to microdroplets and thin films which have potential applications in photovoltaics and drug delivery.⁶⁻⁸ These microdroplets and thin films can experience confinement effects.

Materials can exhibit different properties under confinement than in bulk, causing them to undergo altered phase transitions.⁹⁻¹⁴ Phase separation of polymer-polymer systems under confinement in thin films has been extensively studied through annealing and solvent evaporation.¹⁵⁻²¹ Film thickness, atmospheric conditions, molecular weight, surface tension, composition, and surface effects are factors that impact the morphology of the phase separated film.²²⁻²⁶ These films can be used in applications such as optics and photovoltaics as well as provide a template for creating nanodevices.^{19, 24} Microparticles are another confined structure where phase separation has been studied as a potential route for drug delivery or as self-assembling materials.^{27-²⁹ To best use confined phase separated polymer systems, it is necessary to understand their different structures and size dependent properties.}

Many core-shell nanoparticles may not exhibit phase separation confinement effects due to their synthesis process. Polymer-polymer core-shell nanoparticles are frequently synthesized using traditional nanoparticle synthesis routes, including emulsion solvent evaporation, laser ablation, and nanoprecipitation.³⁰⁻³² In addition, aerosol assisted synthesis can be used to create

core-shell particles with an organic coating (frequently a polymer) around an inorganic nanoparticle.³³⁻³⁶ This paper focuses on polymer-polymer nanoparticles created through atomization. Atomization of a solution containing two polymers creates homogenous particles that must undergo phase separation while suspended in nitrogen gas.

Previously, our research group has studied liquid-liquid phase separation of aerosolized nanoparticles composed of water, small organic molecules, and salts. Characterization of particle morphology with respect to size after drying the particles found that small particles (< 30 nm) remain homogeneous while large particles (> 30 nm) undergo liquid-liquid phase separation.³⁷⁻³⁹ Almost all systems tested were found to have homogenous particles at small sizes and phase separated particles at larger sizes. The phase separated particles could occur as core-shell particles or as partially-engulfed particles, depending on the balance of surface tensions of the different components. When particles were first studied with a rapid drying rate (88-99 % relative humidity (RH)/s), an overlap region with both homogeneous particles and phase separated particles existed. As the drying rate is slowed, the phase separation behavior shifted to smaller particles and the overlap decreased until both started to plateau, indicating that the presence of the homogeneous particles persists at infinitely slow drying rates.³⁷ Phase separation mechanism experiments showed that when particles undergo spinodal decomposition, they phase separated at all sizes, but when particles undergo nucleation and growth, a size dependence of the morphology is observed due to the activation energy required for nucleation that is not required for spinodal decomposition.³⁸ This size dependence is a natural phenomenon that may someday be controllable with more research. We are interested in how our previous research can be expanded to understand the phase separation of polymer-polymer-aqueous systems at nanometer size scales.

Experimental Methods

The particles in this study were produced through the atomization of aqueous solutions. The polymers used were poly(ethyne) glycol (6000 Da, Alfa Aesar, product: A17541, lot:10192844), poly(ethylene) glycol (35000 Da, Polymer Source, polymer dispersity (PI) 1.08), dextran (10000 Da, Toronto Research Chemicals, PI 1.99; 60000 Da, Toronto Research Chemicals PI 1.34), poly(vinyl alcohol) (15000 Da Electron Microscopy Sciences product 19800, lot 120111), poly(vinyl alcohol) (195000 Da, Mowiol ® 56-98 Sigma Aldrich, product 10851, lot BCBX0541), poly (5-styrene sulfonate) sodium salt (70000 Da, Alfa Aesar product 41688, lot S20D019; 1,000,000 Da, Sigma Aldrich product 434574, lot MKAA3419). Polymer dispersity information is listed when supplied by manufacturer, and in all other cases, the product and lot numbers are supplied. Product dispersity information was requested from Sigma Aldrich for the PVA products and a general dispersity, though not batch specific, of 10.5 was provided for the a 27,000 Da product which was not used in this paper, but no information was available for the 195,000 Da. On the basis of the available information for the 27,000 Da, the 195,000 Da PVA is also expected to be quite disperse, as is the 15,000 Da though it comes from a different source. The PEG/dextran solutions were made by dissolving equal masses of the polymers in HPLC grade water (Fisher Scientific). The PVA/PSS solutions were made by adding the PVA to HPLC grade water, heating to around 50° C to dissolve, cooling, and then adding an equal mass of PSS. The solutions were then atomized using a constant output atomizer (TSI 3076, Shoreview, MN). The particles then passed through diffusion dryers to dry out the particles and then were impacted on Cu TEM grids with a continuous carbon film (EMSciences, Hatfield, PA) using a cascade impactor (PIXIE International Corp., Tallahassee, FL). The particles were cryo-imaged using a Tencai LaB6 (FEI Tecnai G20 20 XTWIN TEM) with cryo-holder. The area equivalent diameters of the particles were determined using ImageJ (NIH, Bethesda, MD).

Results and Discussion

The first system we studied is the poly(ethylene) glycol (PEG) / dextran / water aqueous two-phase system. Recent research of this system includes topics such as catalytic microparticles inside droplets, synthesis of synthetic cells, and multiphase flows.⁴⁰⁻⁴² The phase separation of the PEG 6,000 Da /dextran 10,000 Da system was studied by drying atomized particles with a diffusion dryer and then using cryo-TEM and showed that these particles have a size dependent morphology similar to the organic/salt systems previously studied (Figure 5-1a).^{37-39, 43} The particles for this system are always phase separated above 85 nm in diameter and are always homogeneous below 56 nm in diameter. When the diameter is between 85 nm and 56 nm, a mixture of the two morphologies is found. All diameters are area equivalent diameters.⁴⁴ The particles exist as homogenous (Figure 5-1b), core-shell (Figure 5-1c) or partially-engulfed (Figure 5-1d) particles. The core-shell and partially-engulfed morphologies combine to make up the phase separated category. The arrangement of the PEG rich phase and the dextran rich phase within the particle is predicted on the basis of spreading coefficients that are calculated from the surface tensions of the phases.⁴⁵⁻⁴⁷ Using this method, the PEG rich phase is expected to be the shell, while the dextran rich phase is expected to be the core.



Figure 5-1: Phase separation of the PEG 6000 Da and dextran 10,000 Da system. a) The size dependent morphology of the system. Cryo-TEM images of b) a homogeneous particle, c) a coreshell particle, and d) a partially-engulfed particle. All scale bars are 50 nm.

To understand the influence of molecular weight on the phase separation of polymer nanoparticles, the PEG 35,000 Da/dextran 60,000 Da system was studied. This system was chosen because it keeps the N _{PEG}/ N _{dextran} ratio approximately equal, where N is the volumetric degree of polymerization. This helps to ensure that any differences found are a result of the changing molecular weight instead of resulting from a shift in location in the % RH vs polymer fraction phase diagram. In Figure 5-2, the size dependence of the system can be seen with only one particle remaining homogenous and having a diameter of 28 nm. All particles from 30 nm in diameter and larger remain phase separated. Similar to the PEG 6,000/dextran 10,000 system, there are both core-shell and partially-engulfed particles that combine to form the phase separated category. For both the PEG 6,000 Da /dextran 10,000 Da system and the PEG 35,000 Da /dextran 60,000 Da system, less than 10% of the particles were clear enough to image the morphology due to the large

amount of water that was retained in the particles by these highly hydrophilic polymers. The water on the particles freezes when the cryo-holder is cooled, making a coating of ice. The ice on the particles frequently concealed the morphology of the particles and all such particles were ignored. In the shown particles, the sizes of the core and shell look similar; however, the core and shell can both change size when impacted onto the substrate due to the impaction process and spreading on the substrate. While the images in this paper show a similar shell thickness, a range of thickness is observed.



Figure **5-2:** Phase separation of the PEG 35,000 Da/dextran 60,000 Da system. a) The size dependent morphology of the system. Cryo-TEM images of b) a homogeneous particle, c) a coreshell particle, and d) a partially-engulfed particle. All scale bars are 50 nm.

A second system was chosen to compare with the PEG/dextran system to investigate whether the size dependent phase separation exists in other polymer systems and to corroborate the conclusion that increasing molecular weights causes a decrease in the diameter of the smallest phase separated particle. To compare, poly(vinyl alcohol) (PVA)/poly(5-styrene sulfonic acid) (PSS) systems were used. In Figure 5-3, the results for the PVA 15,000 Da / PSS 70,000 Da are shown. Phase separated particles exist as small as 104 nm and homogeneous particles as large as 154 nm. There is a large overlap between the phase separated particles and the homogenous particles, which we attribute, in part, to the high dispersity expected for the PVA which is discussed in the Methods Section. On the basis of the surface tensions of the two polymers, the PVA is expected to be the shell, while the PSS is expected to be the core. This arrangement also holds for the second PVA and PSS system studied.



Figure 5-3: Phase separation of the PVA 15,000 Da and PSS 70,000 Da system. a) The size dependent morphology of the system. Cryo-TEM images of b) a homogeneous particle, c) a coreshell particle, and d) a partially-engulfed particle. All scale bars are 50 nm.

The high molecular weight combination is PVA 195,000 Da / PSS 1,000,0000 Da to keep the N $_{PVA}$ / N $_{PSS}$ approximately constant. For these molecular weights, we see that the smallest phase separated particle is 69 nm, while the largest homogenous particle is 128 nm (Figure 5-4). These values are both lower than those for the PVA 15,000 Da/ PSS 70,000 Da system, confirming the trend found for the PEG/dextran systems. These trends are shown with only two molecular weight combinations for each polymer-polymer mixture due to the molecular weights commercially available with constant monomer ratios, as well as to keep the homogenous/phase separated overlap region significantly different than that of the other molecular weights.



Figure 5-4: Phase separation of the PVA 195,000 Da and PSS 1,000,000 Da system. a) The size dependent morphology of the system. Cryo-TEM images of b) a homogeneous particle, c) a coreshell particle, and d) a partially-engulfed particle

Particles typically only have one of two thermodynamically determined phase separated states: core-shell and partially-engulfed.⁴⁶⁻⁴⁷ In TEM, typically core-shell particles will only look like core-shell particles, while partially-engulfed particles may look like core-shell particles or like partially-engulfed particles, depending on their orientations. It can be difficult to determine what is the thermodynamic phase separated morphology since we study the 2D projection of a 3D morphology. The systems studied in this paper all show both core-shell and partially-engulfed morphologies. Factors such as the hydrophilicity of the polymer particles and substrate effects while imaging may lead to the increased number of morphologies present. In both PEG/dextran

systems, core-shell particles are more abundant than partially-engulfed and are likely the thermodynamically stable morphology. The reason for the presence of partially-engulfed particles in this case is unknown, though it is hypothesized that they result from an inability of some particles to reach thermodynamic equilibrium. In the PVA/PSS systems, partially gulfed particles are present in higher numbers than core-shell particles, implying they are likely the thermodynamically stable morphology for these systems. In this case, the core-shell particles are hypothesized to result from their orientation on the substrate or from an inability to reach thermodynamic equilibrium due to drying rate. On the basis of previous research, the presence of a size dependence indicates that the particles are undergoing nucleation and growth instead of spinodal decomposition.³⁸ While the sizes of the smallest phase separated particle and the largest homogeneous particle may change with slower drying rates, their presence should persist to infinitely slow drying rates.³⁷

The ionic nature of PSS adds additional types of interactions that can occur in the particles, adding some complexity to the system, however, we still find that as the molecular weight of the polymers increases, the diameter of the particles that are able to undergo phase separation decreases. To better understand this phenomenon, equations describing the Gibbs free energy of nucleation of a new phase and Flory-Huggins theory were employed. In this work, Flory-Huggins theory is combined with surface energetics, as opposed to using an expansion of the theory.

The energy of phase transitions is described as

$$\Delta G_n = \frac{4\pi}{3} r^3 \Delta g_v + 4\pi r^2 \gamma \tag{1}$$

where ΔG_n is the free energy associated with the nucleation of a new phase, *r* is the radius of the nucleating phase, Δg_v is the free energy of formation of the new phase per unit volume, and γ is the surface tension.⁴⁸ To determine the minimum *r* where phase separation takes place with varying molecular weights, ΔG_n is set to 0, giving

$$\frac{4\pi}{3}r^3\Delta g_{mixing} = 4\pi r^2 \gamma. \tag{2}$$

Since the $-\Delta g_{phase separation} = \Delta g_{mixing}$, Δg_{mixing} can be substituted and determined using Flory-Huggins theory.

The Δg_{mixing} for a binary polymer-polymer system per unit volume can be written

$$\frac{\Delta g_{mixing}}{kT} = \frac{\phi_A}{N_A v_A} ln \phi_A + \frac{\phi_B}{N_B v_B} ln \phi_B + \frac{\phi_A \phi_B}{v_{AB}} \chi_{AB}$$
(3)

as:

where *k* is the Boltzmann constant, *T* is temperature, N_A , N_B are the volumetric degree of polymerization of components A and B, respectively, v_A and v_B are the segmental volumes of components A and B, respectively, and v_{AB} is the average segmental volume of components A and B, and φ_A and φ_B are the volume factions of components A and B, respectively.⁴⁹⁻⁵⁰ [Equation 3 is based on a binary system where only the two polymers are present and the solvent, water, is ignored.] Equations for calculating N_A , N_B , φ_A , and φ_B can be found in the SI. Because the PEG/dextran system was used for these models, χ_{AB} values from Clark (2000) were used for the calculations.⁵¹ By using χ_{AB} , the chemical interactions between the two polymers are taken into account in a simplified form.

In Figure 5-5, the modeled curves for the effect of molecular weight on the last point of phase separation are shown. As the molecular weight increases there is a sharp decrease, followed by a much slower decrease and then an equally slow increase in the size of the smallest phase separated particle for all χ values studied. This modeling was done with PEG molecular weights from 6,000 to 58,000 Da and dextran molecular weights from 10,000 to 98,000 Da. The Flory-Huggins interaction parameter between the two polymers in the system, χ , in literature is found to vary slightly with molecular weight for the PEG/dextran system at a constant temperature of 25 °C.⁵¹ In Figure 5-5, three different χ values (0.040, 0.032, and 0.020) were tested to see their effect on the trend. While χ strongly affects the shape of the curve and magnitude, the overall trend is maintained. These curves show qualitative agreement with the experimental data. As molecular

weight increases, χN increases, causing the polymers to prefer a phase separated state which is more ordered. This explains why increasing the molecular weight of the polymer systems causes more of the particles to exist in a phase separated morphology. The simplest model that could explain the observations was used here to show that when the surface free energy is combined with Flory-Huggins theory in polymer systems, we can predict the same type of molecular weight/particle size dependence that we see in the experiment. It is acknowledged, that by using a simpler model, factors that could be influencing the behavior, such as the solvent, dynamics of the drying process, and intermolecular interactions, that are not included in Flory-Huggins theory are not taken into account.



Increasing Polymer Molecular Weight

Figure 5-5: Modeled curves showing the effect of molecular weight on the size of particles that can undergo phase separation using several different χ values from measurements. The red curve uses a χ associated with the low molecular weights, the green curve uses a χ correlated with the midrange molecular weight, and the blue curve uses χ associated with the high molecular weight.
In summary, the liquid-liquid phase separation of polymer-polymer systems exhibits a size dependent morphology with small particles existing as homogeneous particles and large particles exhibiting a phase separated morphology. As the molecular weight of the polymers is increased, smaller particles are able to undergo phase separation. This trend can be qualitatively modeled with a combination of equations describing the nucleation of a new phase and Flory-Huggins theory. This work expands the systems in which a size dependent morphology in aerosol particles is observed in new systems, giving evidence that all systems that undergo LLPS have a size dependent morphology. In addition, this synthesis creates homogeneous polymer mixtures that were not previously possible. Our studies as a function of molecular weight provide a first step to understanding how polymer properties influence the size dependence. With additional research, the size dependence phenomenon may become controllable, allowing for the creation of designer polymeric materials. These results show that polymers can be inhibited from undergoing phase transitions in aerosol in the nanoscale size regime which may have implications for a variety of fields such as self-assembling materials, drug delivery, liquid-liquid phase separation in biological systems, and secondary organic aerosol in the atmosphere.

After Publication Correction

[After publication it was discovered that equations (1) and (2) are for the radius of the nuclei and not the radius of the particle itself. Because of this, the numbers obtained from the modeling are incorrect. We hypothesize that the correct equations to use would be related to the Laplace pressure. The Laplace pressure can be described using the following equation:

$$\Delta p = \frac{2\gamma}{R} \tag{4}$$

Where Δp is the Laplace pressure, γ is the surface tension and R is the radius of the particle. In order to use Equation (4), it is necessary to connect it to other equations that take into account the molecular weights of the polymers. The most direct way would be to connect it to the Δg_{mixing} . An in-depth study of the connections between these equations will need to be completed. While the wrong equation was used in these calculations, we expect that the trends shown in Figure 5-5 will still hold true.]

Supplemental Information

The SI contains the experimental procedure, surface tension and density measurements for polymer solutions, the surface tension and density values, and additional equations used in the calculations.

Experimental Methods

The density and surface tension of 1.0 wt % solutions of each polymer in HPLC water were measured using a Krüss K11 force tensiometer using a density attachment and a Wilhelmy plate, with three measurements taken for each of two solutions and the average surface tension and density reported (Table S1).

	Density (g/cm ³)	Surface Tension (mN/m)		
PEG 6,000	1.01 ± 0.01	62.8 ± 0.1		
PEG 35,000	1.000 ± 0.003	62.0 ± 0.1		
Dextran 10,000	1.019 ± 0.009	72.55 ± 0.06		
Dextran 60,000	1.01 ± 0.01	72.6 ± 0.2		
PVA 15,000	1.02 ± 0.02	46.4 ± 0.04		
PVA 195,000	1.02 ± 0.06	61.4 ± 0.9		
PSS 70,000	1.015 ± 0.009	57.8 ± 0.9		
PSS 1,000,000	1.01 ± 0.01	65 ± 1		

Table 5-1: Surface Tension and Density Measurements for 1.0 wt % Solutions of Polymers

Calculations

To complete the modeling of the results, additional equations were needed for the calculation of Δg_{mixing} . To calculate the volume fraction of each component the following equations were used:

$$\phi_A = \frac{n_A N_A u_A}{n_A N_A u_A + n_B N_B u_B}$$
(S1)
$$\phi_B = 1 - \phi_A$$
(S2)

where N_A , N_B are the volumetric degree of polymerization for polymers A and B respectively, n_A and n_B are the number density of molecules for polymers A and B, respectively, and u_A and u_A are the specific monomer volume of polymers A and B, respectively.⁵² These calculations assume that confinement does not alter the volume fraction. To calculate the volumetric degree of polymerization for polymers A and B, the following equation was used:

$$N = \frac{M}{\rho V \mathcal{N}}$$
(S3)

where N is the volumetric degree of polymerization, ρ is the polymer density, V is the monomer volume, assumed to be 100 A³, \mathcal{N} is Avogadro's number, and M is the molar mass.⁵⁰ The density of PEG is assumed to be 1.064g/cm³ at 413K for all molecular weights and the density of dextran is assumed to be 1.03 g/cm³ for all molecular weights.⁵³⁻⁵⁴

To determine the specific monomer volume, the following calculation was used:

$$\frac{Nu^3}{R_g^3} = N^{1-3\nu}$$
 (S4)

when *N* is the volumetric degree of polymerization, u^3 is the segmental volume, and the assumption that 1-3v = -0.77 for a real chain is made, defined as a chain where long range interactions are taken into account.⁵⁵ To determine the specific monomer volumes, the radius of gyration R_g was needed. Because the model was performed using PEG and dextran, the R_g equation for PEG is

$$R_g = 0.02M^{0.58}$$
(S5)

and the $R_{\rm g}$ equation for dextran is

$$R_a = 0.066 M^{0.43} \tag{S6}$$

where *M* is the molecular weight in both equations.⁵⁶⁻⁵⁷ Rg is assumed to remain the bulk value in these calculations. Since the Rg values are calculated to be 1 to 50% of the particle diameter, they are assumed to not have a significant effect.

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Chapter 6

Influence of Ions on the Size Dependent Morphology of Aerosol Particles

Abstract

The study of aerosol particles composed of mixtures of organic and inorganic compounds provides insights for understanding chemistry in the atmosphere as well as information about phase transitions of systems under confinement. In the submicron size regime, we have previously found that liquid-liquid phase separation can be inhibited at sufficiently small particle diameters leading to phase separated particles at larger sizes and homogeneous particles below a threshold diameter. In this paper, we have investigated the influence of cations and anions in the inorganic compound (NH⁺, Na⁺, SO₄²⁻, HSO₄⁻, and Cl⁻) on the phase separation of submicron aerosol particles. Each of five salts were studied with two different organic compounds. Surprisingly, a strong dependence on the identity of the cation is evident in the size dependence of the particle morphology and no dependence on the anion was found. Sodium containing samples exhibit phase separation in particles below 20 nm in diameter whereas ammonium containing samples cease to undergo phase separation in particles between 45 and 65 nm in diameter. The separation relative humidity for supermicron droplets also depends on the identity of the cation in the inorganic component if the anion is the same across the salts compared. In addition, the influence of the separation relative humidity on the size dependence was investigated and displays a trend, but is not a dominant feature of the data. We explain the results in terms of hard and soft ions, where the harder cation (Na⁺) leads to phase separation down to smaller sizes while the softer cation (NH₄⁺) prevents phase separation and causes larger particles to remain homogenous. This study has implications for atmospheric chemistry in regions dominated by sea spray aerosol, which

contains sodium as the primary cation, when compared to continental aerosol, where ammonium is an abundant cation. Additionally, these findings can be used in understanding the influence of cations on the phase transitions of confined materials.

Introduction

Aerosol particles are ubiquitous in Earth's atmosphere and impact human health and climate. Particles can interact with radiation from the Sun in two different ways, directly when they scatter and absorb radiation, or indirectly when they act as nuclei for cloud droplets and the clouds scatter and absorb radiation. The Intergovernmental Panel on Climate Change reports a large uncertainty in the direct and indirect radiative effects of aerosol particles.¹ This uncertainty is in part due to the diversity of aerosol particle types in the atmosphere, which leads to the necessity of simplifying particle types and processes in models. Aerosol particles differ by their composition, size, shape, and internal structure. Below, we refer to the internal structure of particle components as particle morphology. These factors also influence the water uptake and the heterogenous chemistry that the aerosol particles may undergo.²⁻⁷

Many particles are composed of mixtures of organic and inorganic compounds (organic/inorganic aerosol particles).⁸⁻¹⁰ By organic compound, we mean a compound primarily composed of carbon and hydrogen, but also frequently containing oxygen, nitrogen, and/or sulfur atoms. By inorganic compound, we are typically referring to a salt. As the relative humidity (RH) that a particle is exposed to changes, the particle may change from a solid- or semisolid-like particle to a liquid-like particle and *vice versa*. Additionally, as the water content of the particle is altered, it may undergo liquid-liquid phase separation (LLPS), where the particles form an inorganic core with an organic coating.¹¹⁻¹⁴ The common morphologies of these particles are homogeneous, core-

shell, and partially engulfed.¹⁵ LLPS has been found to occur at high RH (>90 %) in secondary organic aerosol particles in the absence of salt as well as in particles composed of organic/inorganic components at a large range of RH values (25 - 100%).^{10-13, 16-24}

The composition of a particle determines its ability to undergo LLPS. Different salts have different abilities to undergo phase separation depending on the salting out ability of their individual cations and anions. The salting out ability is commonly described using the Hofmeister series, however, other metrics such as Hansen solubility parameters can be used to describe LLPS.²⁵⁻²⁶ A previous study on aerosol particles found that as the anions become more kosmotropic (water-ordering), phase separation is less likely to occur, and that the separation relative humidity (SRH) tends to track with the Hofmeister series, that is, kosmotropic salts typically have lower SRH values than chaotropic (water-disordering) salts.^{22, 27} You et al. focused on ammonium sulfate, and primarily investigated the role of the anion.²² The salting out and SRH trends hold true when the anion is present from inorganic salts, when the anions are added via strong acids, and in systems where the anions are present from both inorganic salts and strong acids.²⁷ The cations used in the cited studies were H⁺ for the acids or a mixture of NH₄⁺ and Na⁺ with different anions.^{22, 27} Aerosol particle studies have focused on the role of the anion because anion effects are often stronger than cation effects.²⁸

Another factor that can influence the phase separation of organic/inorganic aerosol particles is the size of the particles. Previous research from our group has shown that phase separation exhibits a size dependence in the submicron size regime. While larger particles undergo phase separation, smaller particles remain homogenous.²⁹⁻³¹ This trend is expected to be maintained even at infinitely slow drying rates.²⁹ Drying rate does, however, change the size at which particles transition from homogenous to phase separated.²⁹ The size dependent morphology can also be impacted by the mechanism of phase separation.³⁰ However, to see an influence due to nucleation

mechanism, it is necessary for the sample to be in a very narrow region of the phase diagram close the critical point. Particle morphology is important for particle properties including the fact that it can influence the ability of particles to act as cloud condensation nuclei.³² Our previous studies on LLPS in submicron aerosol particles have all used ammonium sulfate as the inorganic component of the aerosol particles.

In this paper, we will outline the influence of cations and anions on the size dependence of submicron aerosol particles. The presence of a size dependent morphology with salts other than ammonium sulfate is shown for the first time with the use of ammonium bisulfate, sodium chloride, ammonium chloride and sodium sulfate. The influence of the bulk separation relative humidity on the size dependence of the morphology is also investigated.

Experimental Methods

The particles in this study are composed of an organic and an inorganic compound. The organic compounds are 2,5-hexanediol (TCI, > 98.0%) and diethylmalonic acid (Sigma Aldrich, 98%). The inorganic compounds are ammonium sulfate (EMD Millipore,> 99.0%), ammonium bisulfate (Alfa Aesar, >99.9%), sodium chloride (EMD Millipore, > 99.0%), ammonium chloride (BDH, 99.5%) and sodium sulfate (Fisher Chemicals, 99.14%). The aerosol particles were made using 0.03 wt. % solutions with a 2:1 organic to inorganic ratio in conjunction with a constant output atomizer. The particles were then dried using a diffusion dryer at a rate of ~99% RH/s. A miniMOUDI cascade impactor (TSI 135-8A) was used to collect the particles on 200 mesh copper grids with a carbon film (Electron Microscopy Sciences, Hatfield, PA). Samples were stored in a desiccator until imaging to prevent moisture from contaminating the impacted aerosol particles. The particles were then imaged using a FEI Talos C with a X-FEG source, operating at 200 kV and coupled with cryo-holder and a cryo-box to minimize radiation damage. In this study, particles analyzed were larger than 15 nm in diameter because while the TEM can clearly image smaller particles it is difficult to obtain pictures at a high enough magnification to determine internal morphology without destroying the particles. The images were analyzed using ImageJ (NIH, Bethesda, MD). The particles were characterized based on their area equivalent diameters of the particles and their morphologies.

Separation relative humidity (SRH) values measured for this paper were collected using the same equipment and methodology as outlined in Ott et al. and will only be described briefly here.³³ Particles were made by spraying a 5 wt. % solution containing a 2 to 1 organic to inorganic ratio onto a hydrophobic slide. A Nikon Ti2 inverted microscope with a 10x objective was paired with an environmental chamber. A Vaisala HMP60 humidity probe with $\pm 3\%$ uncertainty between 0 and 90% relative humidity (RH) and $\pm 5\%$ above 90% RH was used. The RH is changed at an average of 1% per minute and images were taken every 5 minutes as well as at phase transitions. The RH was changed at a rate lower than 1% per minute in the regions where phase transitions occur. Reported SRH values are an average of 30 or more particles ranging in size from 20 to 200 mm in diameter.

Results

The effects of cations and anions on the phase separation of aerosol particles are characterized below. A variety of different particle morphologies were seen in this study. Two examples of each type of particle morphology are shown in Figure 1 with (a) showing a partially engulfed particle from the diethylmalonic acid and ammonium bisulfate system and (b) representing a partially engulfed particle composed of diethylmalonic acid and sodium chloride. Figure 1c shows an inclusion-containing particle composed of diethylmalonic acid and ammonium chloride and (d) shows another inclusion-containing particle from the 2,5-hexandeiol and ammonium chloride system. Figure 3e shows a homogeneous particle from the diethylmalonic acid and ammonium chloride system and (f) shows a homogeneous particle composed of 2,5-hexanediol and sodium chloride. The particles shown in Figure 1 were chosen to be representative of all of the different types of partially engulfed, inclusion containing, and homogeneous particles for all ten systems studied in this paper. A comparison of a small phase separated particle and a small homogeneous particle is shown in Figure 6-5.



Figure 6-1: Sample images of particle morphologies where a,b) show images of partially engulfed particles, c,d) show different types of inclusions, and e,f) show homogeneous particles. All scale bars are 100 nm.

The influence of the ammonium cation with one of three different anions on the size dependence of LLPS is shown in Figure 2. Figure 2 a, b, and c show the ammonium cation with 2,5-hexanediol. Figure 2a shows 2,5-hexanediol with ammonium sulfate. 380 particles were studied between 15 and 250 nm in diameter with all particles below 65 nm being homogenous, those larger than 101 nm being phase separated, and a mixture of both between these two diameters. In this histogram, as well as all other histograms shown in this paper, it is important to note that the data for these histograms are collected with a goal of comparing where the largest homogenous particles are present and where the smallest phase separated particles are present. Because of this fact, in the transition region where both morphologies are observed, the histogram is indicative of the distribution of particle morphologies. Outside of that region, however, the histogram does not provide accurate information about the particle size distribution. This result is due to the focus on imaging particles in the transition region where both phase separated and homogeneous morphologies are found as opposed to equal amounts of imaging across all size ranges. Ammonium bisulfate with 2,5-hexanediol is shown in Figure 2b. With this mixture, 427 particles were studied and all those below 47 nm in diameter were homogenous, all those above 93 nm were phase separated, and between, a mixture of both morphologies are found. Figure 1c shows the ammonium chloride/2,5-hexanediol mixture where 393 particles were studied and all of those below 55 nm were homogenous, and all of those above 66 nm were phase separated with a small region where both morphologies are found between 55 and 66 nm. In this series of 2,5-hexanediol with ammonium salts, the region where both phase separated to homogenous particles are found remains relatively constant, with the range of diameters at which the smallest phase separated particle is observed for each system ranging only by 18 nm.

After studying 2,5-hexanediol, another organic compound was selected for comparison. The same salts were studied with diethylmalonic acid and their results shown in Figure 2 d, e, and f. 757 particles were studied for diethlymalonic acid with ammonium sulfate where the smallest phase separated particle was 51 nm in diameter and the largest homogenous particle was 83.9 nm in diameter (Figure 1d). For the ammonium bisulfate and diethylmalonic acid mixture, shown in Figure 1e, 392 particles were studied and all those below 43 nm in diameter were homogenous while all those above 80 nm in diameter were phase separated. Additionally, in Figure 2f, the diethylmalonic acid and ammonium chloride mixture was studied and the smallest phase separated particle was found to be 46 nm in diameter and the largest homogenous particle was 71 nm in diameter for the 353 particles studied. The smallest phase separated particles for the systems consisting of the three ammonium salts with 2,5-hexanediol differ by only 8 nm, and the diameters over which both morphologies are found is small for each system. To better understand the influence of the cations as well as the anions, the same anions and organic compounds were studied with the sodium cation.



Figure **6-2**: Histograms showing the number of particles with each morphology vs. area equivalent diameter for 2,5-hexanediol with a) ammonium sulfate, b) ammonium bisulfate, and c) ammonium chloride; and diethlymalonic acid with d) ammonium sulfate, e) ammonium bisulfate, and f) ammonium chloride.

The results for the sodium cation look significantly different from those systems containing the ammonium cation and are shown in Figure 6-2. When 357 particles composed of 2,5-hexanediol and sodium chloride were studied, particles as small as 16 nm were found to be phase separated.

While this histogram does not fully show the transition from phase separated to homogenous, the one phase separated particle in the 20 nm size bin, compared to the 40 homogenous particles in the same size bin indicate that the transition would occur soon if smaller particles were studied. In this system all particles above 49 nm in diameter were phase separated and all studied sizes smaller were a mixture. Similarly, the 2,5-hexanediol and sodium chloride particles do not show the complete transition to homogenous particles. The smallest phase separated particle is 16 nm in diameter. In this case, we once again see the rapidly falling off of phase separated particles with the homogeneous particles existing in a much higher abundance which is indicative of the final transition to only homogenous particles but the size range studied does not allow that transition to be fully seen. All particles above 52 nm in diameter are phase separated and the sizes studied below that are a mixture of phase separated and homogenous. The diethylmalonic acid and sodium chloride system does see the transition from phase separated to homogenous with the smallest phase separated particle having a diameter of 22 nm in diameter and the largest homogenous particles having a diameter of 46 nm. This is the one sodium system that does show the complete transition to homogenous particles in the size range studied. With a smallest phase separated particle at 17 nm in diameter, the diethylmalonic acid and sodium sulfate system does not quite see the transition to fully homogenous with the particle size range studied, but is likely sitting right on the edge of that transition. This system has a mixture of particle morphologies up to 50 nm in diameter where particles become solely phase separated. All of the sodium systems transition or are estimated to transition to fully homogenous particles in the 15 to 20 nm in diameter range based on the shape of the particle distributions. This is much lower than the range seen for the ammonium particles which transitioned between 43 and 65 nm.



Figure 6-3: Histograms showing the morphology of aerosol particles as a function of area equivalent diameter for 2,5-hexanediol with a) sodium chloride and b) sodium sulfate; and diethylmalonic acid with c) sodium chloride and d) sodium sulfate

In this study, the majority of particles that undergo phase separation exhibit a partially engulfed morphology. The one exception to this result is 2,5-hexanediol and ammonium chloride where 212 of the phase separated particles are core shell and 132 are partially engulfed. This mixture of morphologies may be due to the orientation of the particles on the substrate or due to the fast-drying rate used, which can prevent particles from reaching their thermodynamic equilibrium morphology.³⁴⁻³⁵ This mixture of morphologies has been seen previously in aerosol particles composed of polymer mixtures that undergo LLPS.³⁶ In many of the systems studied, a small number of the particles exhibited inclusions. When imaging the particles, the morphology

did not change with extended beam exposure or show increased texture or changing size, which is indicative of inclusions rather than radiation damage from the electron beam in the TEM.³⁷ In the cases of 2,5-hexanediol and ammonium bisulfate, 2,5-hexanediol and ammonium chloride, diethylmalonic acid and ammonium bisulfate, diethylmalonic acid and ammonium chloride, and diethylmalonic acid and ammonium sulfate, less than 10 of the phase separated particles contained inclusions. 2,5-hexanediol and ammonium sulfate had 32 particles with inclusions. These inclusions typically occur in particles that are greater than 100 nm in area-equivalent diameter but do not appear to have any additional dependence on size.

Discussion

The organic compounds, 2,5-hexanediol and diethlymalonic acid, were chosen for this study because of the degree of sensitivity of their separation relative humidities (SRH) to different salts. 2,5-hexanediol SRH values are highly dependent on the identity of the salts, whereas the diethylmalonic acid SRH values are largely independent of the identity of the salts. According to the work of You et al., 2,5-hexanediol has statistically different SRH values for ammonium sulfate, ammonium bisulfate, and sodium chloride, whereas diethylmalonic acid has statistically similar values for those same salts. We measured SRH values for these organic compounds with ammonium chloride and sodium sulfate; all other values used are from You et al. (Figure 4; Table 1))²². To understand the effect of SRH on the size dependence of each system, the smallest phase separated particle is used as a metric in Figure 4a. The influence of the cation is also investigated in this figure. The triangles represent systems with diethylmalonic acid while the squares represent 2,5-hexanediol systems, and the blue markers represent systems with ammonium species are all

grouped together at the top of the figure and the red shapes representing sodium are all group together at the bottom of the figure. The influence of anions is shown in Figure 4b. Note that Figure 4b is identical to Figure 4a except for the color and shape of the markers used. Blue shapes represent sulfate, red represents bisulfate, and green represents chloride in Figure 4b. Similarly to Figure 4a, triangles represent diethylmalonic acid and squares represent 2,5-hexanediol. In contrast to Figure 4a, the anions show no specific trends with color or shape of the markers observed. Comparing these figures indicates that the cations are more important when determining the size dependence of the morphology than the anions. Additionally, we can see that the diethylmalonic acid particles, those represented by triangles in Figure 4, appear to have a slight dependence on SRH with four of the five values following the trend of a decrease in the diameter of the smallest phase separated particle with a decrease in SRH. The 2,5-hexanediol markers do not appear to have a trend with SRH. From this result, we conclude that the SRH may have a slight impact on the size dependence of the particle morphology but that ultimately, the identity of the cation in the inorganic component is more important.



Figure 6-4: The smallest phase separated particle for each system vs. SRH with markers color coded according to a) the cation present in solution and b) the anion present in solution. The SRH values for ammonium sulfate, ammonium bisulfate, and sodium chloride are from You et al. 2013²²

Table 6-1 : Comparing the SRH values for different ion combinations using data from	You et
al. 2013 combined with new data.	

		Na ⁺ SRH	NH4 ⁺ SRH
Diethylmalonic acid	SO ₄ ²⁻	95	89*
Diethylmalonic acid	Cl	87*	85
2,5-hexanediol	SO ₄ ²⁻	93	88*
2,5-hexanediol	CI	74*	58

* Values come from You et al. 2013.²²

In a previous study, the influence of kinetics and thermodynamics on the size dependent morphology were studied.²⁹ The diameters of the largest homogeneous particle and the smallest phase separated particle depend on the drying rate. As the drying rate slows, the diameters of the

largest homogeneous and smallest phase separated particles decrease.²⁹ At the slowest drying rates, the size dependence persists, indicating an underlying thermodynamic origin of this phenomenon. Because fast drying rates are used in this study, the largest homogeneous particle and the smallest phase separated particle of each system are larger than they would be with a slower drying rate.

The impact of the solubility of the inorganic component was also considered. In Table 2, the CRC values for solubility are listed. The ammonium values are all higher than the sodium values, however if solubility were the reason for this trend, we would not have expected the ammonium chloride size dependence to more closely align with the sodium salts. Based on this, we conclude that solubility is not the primary controlling factor in the ability of small particles to undergo LLPS. Another factor that was investigated was the surface tension of the solutions. 8 mM salt solutions with 5 mM diethylmalonic acid were studied and values for ammonium sulfate, ammonium chloride, sodium sulfate, and sodium chloride did not show any significant differences (Table S1).

	Solubility in g/100 g H ₂ O	Smallest Phase Separated Particle Diameter (nm)	
		Diethylmalonic 2,5-Hexanedic	
		Acid	
Ammonium chloride	39.5 ^a	46	55
Ammonium bisulfate	100 ^a	43	47
Ammonium sulfate	76.4 ^a	51	65
Sodium chloride	36.0 ^a	22	17
Sodium sulfate	28.1 ^a	17	16

Table 6-2 :	CRC s	solubility	values	for	salts.
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^aCRC Handbook of Chemistry and Physics³⁸

The influence of the softness/hardness of the cations was explored. Sodium is a hard cation while ammonium trends in a softer direction. Softness/hardness also be understood as the apparent dynamic hydration of the ions. Collins studied the influence of both free ions and of charged headgroups of proteins and concluded that the apparent dynamic hydration numbers need to match

in order to interact in solution.³⁹⁻⁴¹ Mehringer et al. performed further experimental and theoretical studies on the influence of charged headgroups, investigating the role of the carbon chain length.⁴² Mehringer showed that by changing the carbon chain length attached to the charged headgroup, the affinity of the headgroup for binding to soft or hard ions can change.⁴² Based on the short carbon chain length of the diethylmalonic acid used in this study and the work of Mehringer, we anticipate that the carboxylate group interacts more strongly with the ammonium ion than the sodium ion. A similar argument can also be made for the alcohol groups on 2,5-hexanediol. We hypothesize that softer cations interact more strongly with the organic functional groups and thus impede the phase separation process. Based on this hypothesis, we would predict that the separation relative humidity is lower for softer cations and higher for harder cations. Additionally, we would predict that the aerosol particles that contain a soft cation would transition from phase separated to homogenous at a larger size than those with a hard cation because soft cation impede phase separation. The trends we see for both phase separation and for the size dependence match our hypothesis. Table 1 shows the bulk SRH values for these systems. Note that the anions dominate the trend in SRH, as shown in You et al., but when species with the same anion are compared, the trend in SRH supports the hypothesis that softer cations lead to lower values.²² In an attempt to further confirm this trend for the size dependence of particle morphology, we worked with methylammonium chloride and trimethylammonium chloride but neither showed phase separation with either diethylmalonic acid or 2,5-hexanediol. Additionally, silver sulfate was tested but it did not exhibit a traditional liquidliquid phase separation and all results were inconclusive. Potassium sulfate with diethylmalonic acid was briefly studied and its results are comparable with those of sodium sulfate (Fig. S2). While modeling studies exist on the interactions of ions with the aqueous air interface and with protein interfaces, additional studies which look at confined and phase separated interfaces are needed to better understand this role of ions in the phase separation process.⁴³⁻⁴⁴

Conclusions and Atmospheric Implications

In this paper, we investigated the influence of different salts on the size dependent morphology of submicron aerosol particles. We studied salts composed of two different cations and three different anions. Aerosol particles that contain the ammonium cation undergo their transition to all homogenous particles at a larger size than those that contain sodium as the cation. We hypothesize that the hardness or softness of the cation influences interactions with the organic compound and impacts when phase separation occurs. This effect is seen in both the size dependent morphology of submicron aerosol particles as well as in the separation relative humidity of supermicron aerosol particles.

These results have implications in atmospheric chemistry where ammonium and sodium are abundant.⁴⁵⁻⁴⁸ Sea spray aerosol particles that can undergo phase separation due to their composition are more likely to be phase separated at most sizes due to the presence of sodium as the dominant cation. Additionally, in continental aerosol where ammonium is more abundant, the size dependent phenomenon will cause a larger number of particles to be homogenous. Most atmospheric chemistry LLPS studies have focused on the influence of anions and assumed the impact of the cation is minimal. This study shows that it is important to consider both cations and anions, where the cations are the controlling factor in determining particle morphology in submicron aerosol particles. This study also has implications for our understanding of the properties of cations and anions and their interactions with organic molecules in confinement. Future studies should include additional size dependence studies with common divalent cations as well as modeling studies to investigate the role of cations and anions at interfaces and during the nucleation process.

Supporting Information



Figure 6-5: A comparison of particles composed of a mixture of diethylmalonic acid and sodium chloride with a) phase separated and b) homogeneous morphologies. Scale bars are 100 nm. The approximate particle area equivalent diameters are 30 nm.

Surface Tension Experimental Procedure:

The surface tension values were measured with a Krüss K11 tensiometer. The solutions measured contained 7.8 mmol of salt and 5.0 mmol of diethylmalonic acid. A typical optical microscopy experiment uses 0.833 g of diethylmalonic acid, which corresponds to approximately 5.0 mmol, and 0.417g of salt. This mass was converted to moles for each salt. The highest number of moles from that conversion was 7.8 mmol which was chosen as representative for these measurements. The reported values are the average and deviations for two solutions each of which were measured three times for a total of six values with each salt.

Table **6-3**: Surface tension data for diethylmalonic acid and salts with 7.8 mmol of salt and 5.0 mmol of diethylmalonic acid in 25 mL water.

	Diethylmalonic Acid
Ammonium Sulfate	49.5 ± 0.3
Sodium Sulfate	49.4 ± 0.1
Ammonium Chloride	48.0 ± 0.4
Sodium Chloride	46.6 ± 0.7



Figure 6-6: Histogram of diethylmalonic acid and potassium sulfate which is very similar to diethylmalonic acid and sodium sulfate.

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Chapter 7

Conclusions and Future Directions

This dissertation studies how the properties of aerosol particles influence their phase separation with applications in the fields of atmospheric chemistry and polymer/materials chemistry in addition to providing insights into the basic scientific understanding of liquid-liquid phase separation. Chapter 4 showed a study on the influence of the average oxygen to carbon ratio on the phase separation of supermicron aerosol particles. The ability of polymer-polymer aerosol particles to exhibit a size dependent morphology and the effect of molecular weight on the size dependance was explored in Chapter 5. In Chapter 6, the impact of ions on the liquid-liquid phase separation and size dependence was explored. Chapter 4 primarily used optical microscopy, while Chapters 5 and 6 were more focused on transmission electron microscopy.

Conclusions

Optical microscopy studies provide humidity and temperature-controlled studies of super micron aerosol particles. Using this method, the impact of the average oxygen to carbon ratio was investigated. Organic/inorganic mixtures that undergo liquid-liquid phase separation were used. Sucrose, which does not undergo LLPS with inorganic salts was added in increasing quantities to the starting organic/inorganic mixture until phase separation was no longer seen. For mixtures with a high starting relative humidity, separation was found to occur for some systems up to 0.9 O:C which was higher than previously seen. This study added to the literature by showing that while the previously shown end of phase separation at 0.8 O:C is a good guideline, the actual composition

will provide more information, if available, because a strongly separating organic, even in small quantities can sometimes drive phase separation processes.

Transmission electron microscopy allows the study of aerosol morphology to be extended to submicron aerosol particles. Previous work from our group showed that for organic/inorganic systems where LLPS typically occurs, the transition is inhibited in small aerosol particles. This research was extended to polymer-polymer systems. The inhibition of phase separation was found to also occur in the polymer systems. This inhibition produced materials that cannot be created using traditional methods due to the need of the materials to undergo LLPS. This was expanded to understand the impact of the molecular weight of the polymers on the size dependence. Increasing molecular weight correlated with more phase separation occurring at higher molecular weights in the aerosol particles. For conformation a model based on Flory-Huggins theory and the equations which govern the nucleation of a new phase was developed. This model showed the same trends in the molecular weight region probed in this study.

Additionally studied using TEM, were organic/inorganic particles with varying salts. This provided a better understanding of the influence of ions on liquid-liquid phase separation. Ammonium, sodium, sulfate, bisulfate, and chloride salts were used. Ammonium salts were shown to have a stronger impact on the size dependent morphology than sodium salts. Additionally, ammonium salts experience a higher separation relative humidity than equivalent sodium particles. These are indications that the softness or hardness of the cation controls interaction with organic molecules. This has implications for the atmospheric chemistry as sea spray aerosol is less likely to exhibit a size dependent morphology than continental aerosol due to the high concentrations of sodium in sea spray aerosol when compared to the high concentrations of ammonium in continental aerosol. Additionally, it is more important than previously understood to study the influence of cations on aerosol particle morphology. This has also shown a new principle of liquid-liquid phase

separation in general in that the typically unimportant cation can actually become a controlling factor in submicron aerosol particles.

Future Directions

In the sucrose study there are several possible avenues of future direction on the supermicron aerosol particles such as how the critical nucleation size is impacting the LLPS, trends in the slopes of the separation relative humidity values, and the mechanisms of evaporation. The data can also be studied in other terms than O:C such as solubility, polarity, and hydrophobicity. Additionally, modeling could look at the molecular interactions that occur inside these particles during phase separation. These changes will expand on and better explain the physical chemistry behind the processes. In order to directly apply the results of that study to atmospheric aerosol particles, it is necessary to understand how it translates to smaller particles. The variety of aerosol particle morphologies exhibited by the supermicron aerosol particles should be searched for in submicron particles using TEM. General O:C studies of simple organic/inorganic particles should also be conducted to confirm that the O:C range for the liquid-liquid phase separation of supermicron particles is the same as the range for submicron aerosol particles, and its influence on the size dependence phenomena can be determined.¹

The polymer/polymer phase separation study is the beginning of a method for the creation of novel materials. At this point, the creation of these materials is not controllable because many factors are not well understood. The influence of temperature on both the types of possible morphologies as well its possible control of the size dependent morphology provide some of the first steps for investigation. The influence of temperature on polymer films indicates that understanding temperature effects could have key implications to the aerosol particle morphologies of these polymer/polymer systems.² The glass transition temperature of the confined polymers is

also likely to play a role in the morphology of the particles and is known to exhibit changes under confinement.³ Features such as polymer branching and polymer shape pose possible paths of study to extend the current work. Understanding factors such as these may provide the ability to produce novel polymeric materials with predicted properties.

To continue the research of the influence the ions on the size dependent morphology, divalent cations could be investigated. Divalent cations are abundant in sea spray aerosol but their influence on the phase separation of aerosol particles when compared to monovalent cations is understudied. In order to fully understand their impact, both optical microscopy and TEM studies are needed.

Outlook

The objective of this work was to expand our knowledge about the morphology of aerosol particles. This was done on both supermicron aerosol particles which were studied using optical microscopy and submicron aerosols using TEM. Organic/inorganic aerosols were used to study the influence of average oxygen to carbon ratio on phase separation as well as the influence of different ions on the size dependent morphology of aerosol particles. Polymer/polymer aerosol particles were investigated and shown to exhibit a size dependence and to create novel polymeric materials. The study which looked at the average O:C can be expanded to submicron aerosols and other complex systems. The influence of ions on the size dependent morphology of aerosol particles were for a submicron aerosols and other complex systems. The influence of ions on the size dependent morphology of aerosol particle project can expand by changing the temperature of the particle during formation or changing features of the polymers by using chains with branching.

The average oxygen to carbon ratio study as well as the ion study provide information that can be used to understand how particles in the atmosphere are acting. This can be used to improve models that are used to understand the climate. The polymer study creates novel polymeric materials which are expected to have unique properties when compared to their individual components and is a continuing pathway to understanding polymer phase transitions under extreme confinement. Additional studies that look at the kinetic and thermodynamic influences are also necessary.

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PUBLICATIONS

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