

Size Dependence of the Structure of Organic Aerosol

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S Supporting Information

ABSTRACT: The effects of aerosol particles on heterogeneous atmospheric chemistry and climate are determined in part by the internal arrangement of compounds within the particles. We have used cryo-transmission electron microscopy to investigate the phase separation behavior of model organic aerosol composed of ammonium sulfate internally mixed with succinic or pimelic acid. We have found that no particle with a diameter <170 nm for succinic acid and 270 nm for pimelic acid is phase separated. Larger particles adopt a phase separated, partially engulfed structure. We therefore demonstrate that phase separation of aerosol particles is dependent on particle size and discuss implications for aerosol–climate interactions.

The greatest uncertainties in our understanding of the climate system are aerosol interactions with light and clouds.¹ In particular, organic aerosol particles have been the focus of much current scientific interest due to their chemical complexity and importance in the troposphere.² Organic aerosol reactivity, optical properties, and ability to participate in cloud formation are determined in part by the internal arrangement of compounds within the particle. This morphology is governed by the degree of phase separation between the particle components.

Theory of bulk solutions and experiments on particles micrometers in diameter has shown that aqueous solutions of atmospherically relevant compounds can undergo liquid–liquid phase separation to form coexisting liquid phases when these compounds are present in sufficiently high concentration.^{3–11} Specifically, solutions of ammonium sulfate and organic molecules composed of C, H, and O that have a ratio of O to C atoms of < ~0.7 undergo liquid–liquid phase separation,³ though molecular structure also impacts which compounds phase separate.⁴ As a particle is dried, phase separation may occur through nucleation and growth or spinodal decomposition mechanisms.⁵ Possible morphologies that have been observed for laboratory proxies for aqueous organic aerosol include homogeneous, partially engulfed, and core–shell structures (Figure 1).^{3,5–8}

Current technologies are limited in their ability to characterize particle morphology in the accumulation mode size regime (100 nm to 2.5 μm), which corresponds to the particles with the longest atmospheric residence time.¹² We note that liquid–liquid phase separation has also been studied extensively by the biochemistry community.¹³ The advent of new bioimaging analysis techniques and laser methods has led to the rise of

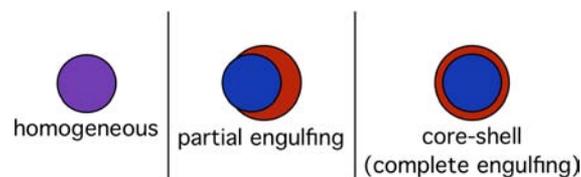


Figure 1. Three major types of observed particle morphologies for model aqueous aerosol particles composed of salt and soluble or insoluble organic compounds at a fixed relative humidity.

super resolution techniques, which allow for imaging at length scales below 100 nm, but generally require the use of fluorescent dyes.¹⁴ In contrast to these technologies, we would ideally like to obtain information on unaltered aerosol particles at length scales smaller than the diffraction limit. Cryo-transmission electron microscopy (cryo-TEM) provides a method to characterize the structure of organic aerosol in the accumulation mode size regime that is dried in the gas phase.¹⁵

In this paper, we report on the size dependence of aerosol morphology observed in the accumulation mode size regime. We use particles generated from aqueous solutions composed of equal weight percents of ammonium sulfate and succinic or pimelic acid that are dried in the gas phase and collected on transmission electron microscopy grids. Samples were analyzed at approximately 104 K to minimize electron damage of these fragile samples.¹⁶ We use image contrast and particle electron beam damage to characterize the phase separation.¹⁵ We have shown that substrate effects and the low imaging temperature have little effect on our results.¹⁵

In order to compare the structures we observe in our TEM images to the optical microscopy data provided in the literature, we have used optical microscopy to investigate phase separation and drying of particles ~100 μm in diameter that are composed of ammonium sulfate and pimelic or succinic acid (Figure 2). For particles composed of pimelic acid and ammonium sulfate, we observe phase separation of the liquid components prior to crystallization. In contrast, in particles composed of succinic acid and ammonium sulfate, crystallization occurs prior to any observation of phase separation. These results are consistent with the literature.^{3,6}

In the cryo-TEM images, we observe that large particles have partially engulfed, phase separated structures and that small particles are homogeneous (Figure 3). We analyzed four samples of each composition, which consisted of 519 pimelic acid/ammonium sulfate particles (440 homogeneous and 79

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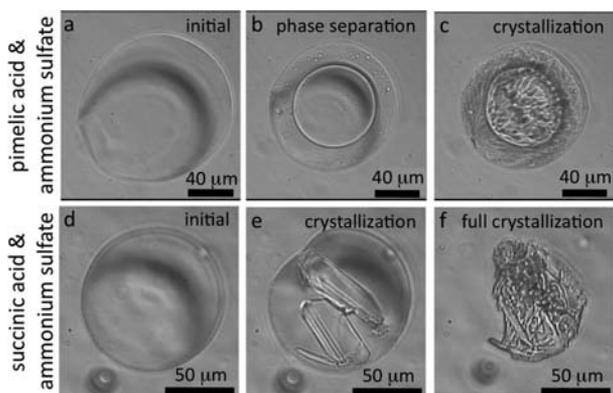


Figure 2. Optical microscopy images of the time evolution of particles drying for internal mixtures of ammonium sulfate with pimelic acid (top) and succinic acid (bottom). For pimelic acid, we show the (a) initial particle, (b) liquid–liquid phase separation, and (c) crystallization. For succinic acid, we show (d) the initial particle, (e) crystallization, and (f) complete crystallization.

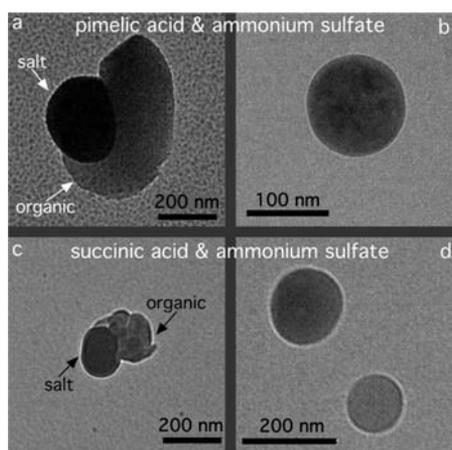


Figure 3. Particle morphology observed using cryo-TEM for internally mixed particles composed of ammonium sulfate and (a and b) pimelic acid or (c and d) succinic acid. (a and c) Larger particles are phase separated, where the organic component may contain some ammonium sulfate (see text). (b and d) Smaller particles are homogeneous.

phase separated) and 324 succinic acid/ammonium sulfate particles (234 homogeneous and 90 phase separated). For particles composed of succinic acid and ammonium sulfate, the smallest phase separated particles are 170 nm in diameter, and the largest homogeneous particles are 196 nm in diameter. For particles composed of pimelic acid and ammonium sulfate, the smallest phase separated particles are 270 nm in diameter, and the largest homogeneous particles are 276 nm in diameter (Figure 4). Particles larger than these size regimes are partially engulfed, and smaller particles are homogeneous. The region in Figure 4 where both morphologies are observed may result from plotting area equivalent diameters for nonspherical, phase-separated particles. We note that cryo-TEM can resolve phase separated particles <200 nm in diameter as shown for internally mixed particles composed of ammonium sulfate and adipic or azelaic acid (Figure S1). Because the O:C ratio of pimelic acid is in between that of adipic and azelaic acids, our results do not suggest a shift in the O:C ratio at which liquid–liquid phase separation occurs. Based on the optical properties of the particles that we have measured using cavity ring-down

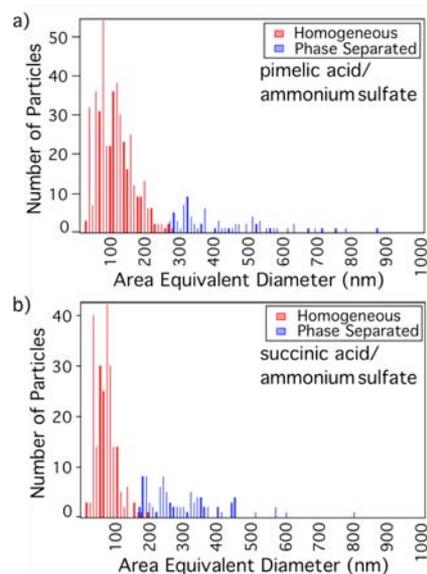


Figure 4. Morphology of internally mixed particles composed of ammonium sulfate with (a) pimelic acid and (b) succinic acid vs area equivalent diameter.

spectroscopy and the electron beam damaging behavior of the particles, we conclude that the homogeneous particles are internally mixed (see Supporting Information).

Based on our optical microscopy results, we hypothesize that larger pimelic acid and ammonium sulfate particles undergo liquid–liquid phase separation, which then results in phase separation in the dry particle. In contrast, larger succinic acid and ammonium sulfate particles phase separate as the succinic acid crystallizes, resulting in the observed phase separation in the dry particle.¹⁷ According to phase diagrams for liquid–liquid coexistence, the primarily organic phase may also contain ammonium sulfate.⁶ Our findings also indicate that small particles composed of these organic acids do not undergo phase separation as they dry. While the salt/organic acid systems that we have worked with are unlikely to exhibit glassy dynamics at room temperature, they could be high-viscosity liquids. In a high-viscosity liquid, molecules could be hindered from initiating phase separation. Pimelic acid/ammonium sulfate is likely to undergo liquid–liquid phase separation at above 60% relative humidity (RH) based on its O:C ratio, and succinic acid/ammonium sulfate undergoes efflorescence at approximately 48% RH.^{3,17} Based on studies of secondary organic material, these relative humidities correspond to diffusion coefficients that are indicative of semisolid behavior.¹⁸ Combined with the rapid drying rates used in our particle generation setup (estimated to be 99.7% RH/s), phase separation may be inhibited in these systems. The viscosity of the particles, however, cannot solely explain the observed size dependence. Viscosity of secondary organic aerosol decreases with size for particles with diameters <30 nm.¹⁹ Because our particles are significantly larger, we do not expect that particles 100 nm in diameter have a different average viscosity than particles at larger sizes. We therefore hypothesize that another mechanism contributes to the observed size dependence. Slowing the drying process could illuminate the mechanism by which phase separation exhibits dependence on particle size and will be pursued in future studies.

We can roughly compare the surface activity of homogeneous, partially engulfed, and core–shell structures using

geometric arguments. Consider the ammonium sulfate to contain the active sites for reactive or nonreactive (e.g., water or ice) uptake. In core–shell structures, the organic coating covers all the active sites leading to suppression of reactions²⁰ and requiring higher supersaturations for cloud condensation nucleus and ice nucleus onset.²¹ We note that the molecular and mesoscale structure of the coating can limit the degree of this inhibition.²² For a partially engulfed structure, only some of the active sites are coated with the organic compound. Take $1/f$ to be the fraction of the surface area $4\pi r_{pe}^2$ of a partially engulfed particle of radius r_{pe} that is not coated. A homogeneous particle of radius r_h has active sites over its whole surface area $4\pi r_h^2$. The particles have the same activity when $r_h = f^{-1/2} r_{pe}$, meaning that a smaller homogeneous particle can have the same activity as a larger partially engulfed particle. In addition, the interaction of aerosol particles with electromagnetic radiation is determined by aerosol optical properties, which are a sensitive function of aerosol structure in the accumulation mode size regime.²³ As a result, forming partially engulfed and homogeneous structures rather than core–shell structures will impact the calculated aerosol optical depth due to organic aerosol.

In summary, through the use of cryo-TEM, we observe that the morphology of model organic aerosol particles is dependent on their size. Homogeneous morphologies are observed for aerosol particles with diameters <196 nm for particles composed of succinic acid and ammonium sulfate and 276 nm for particles composed of pimelic acid and ammonium sulfate. At diameters >170 nm for particles composed of succinic acid and ammonium sulfate and 270 nm for particles composed of pimelic acid and ammonium sulfate, partially engulfed structures are seen. These results demonstrate that for some systems liquid–liquid phase separation ceases at or below the diffraction limit. In contrast to core–shell particles, the partially engulfed and homogeneous structures we observe should increase reaction rates with the aqueous core and enhance cloud condensation and ice nucleus formation activity. In addition, homogeneous particles will have higher reaction rates and cloud/ice nucleus activity compared with partially engulfed particles. As a result, these morphology differences have consequences for heterogeneous atmospheric chemistry as well as aerosol interactions with electromagnetic radiation and clouds, which are the largest uncertainties in our understanding of the climate system. In addition to the systems studied here of relevance to atmospheric chemists, the breakdown of liquid–liquid phase separation at the nanoscale likely affects systems of interest to the wider chemistry community.

■ ASSOCIATED CONTENT

■ Supporting Information

Descriptions of methods, resolution, electron beam damage, and optical properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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