

Composition and Size Effects on the Phase of Mixed Organic/Inorganic Particles

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Aerosol particles have an impact on climate through directly scattering light, heterogeneous chemistry, and influencing cloud formation [1]. These climate effects depend greatly on particle phase which is governed by composition and environmental processing. With increasing relative humidity (RH) particles will start to uptake water and fully dissolve (deliquescence relative humidity, DRH). Conversely, as the RH is decreased, the particles will shrink until they crystalize (efflorescence relative humidity, ERH). It has been observed previously that the organic composition has only a small effect on the water uptake, but it can dramatically affect the efflorescence depending on the amount and type of organic present [2]. Previous experiments have shown that the ERH for ammonium sulfate is dependent on particle size. The largest ammonium sulfate particles (17 μm) effloresced at 47% RH [3] and the smallest particles (0.043 μm) effloresced at 31% RH [4]. Because of the effect of composition on the phase of the particles, the hygroscopic properties of particles in the atmosphere must be well understood to help model atmospheric processes.

The ERH behavior of ammonium sulfate and various dicarboxylic acid particles were studied individually and in mixtures. Samples were prepared by atomizing a solution of the analyte dissolved in water. The particles were subsequently dried in a flow diffusion dryer and impacted on continuous carbon TEM grids. Each sample was loaded into the WetSTEM sample stage in a Quattro ESEM (ThermoFisher, Hillsboro OR). The chamber water vapor pressure was kept constant through the experiment and the RH was changed by adjusting the temperature of the sample. While initially decreasing the temperature (increasing the RH), the water uptake events were observed, but due to possible beam damage to the particles no quantitative data was acquired. An area not previously exposed to the electron beam was then chosen for each ERH experiment. For each experiment the samples were initially exposed to 95% RH before the temperature was increased slowly until all particles in the field of view were crystallized. After the experiment, MIPAR analysis package was used to automate the segmentation and analysis of particles in each image.

Utilizing *in-situ* SEM capabilities, the ERH of individual particles was analyzed for a range of particle sizes. We observed a difference in the ERH as a function of droplet size with the largest droplets crystallizing first followed by the smallest particles crystallizing last. There was some variability between experiments when the RH was increased near water saturation, but keeping the maximum RH exposure to 95% led to repeatability in the experiments with droplet size vs. ERH. Figure 1 shows a subset of the observed crystallization of multiple particles with decreasing humidity. The first crystallization event occurred at 33.7% RH and the last at 30.1%. The largest particles generally effloresced first followed by the smaller particles, though there is a distribution of particle sizes at each humidity. The ERH for individual particles is plotted in Figure 2 and additionally binned every 0.5% RH to show the trend of larger particles efflorescing at higher RH. Differences in the ERH were observed not only with the size of the particle, but also between particle types. It is observed that with only a small change in relative humidity, there is a drastic change in the phase of the particles depending on the size and composition of the particles [5].

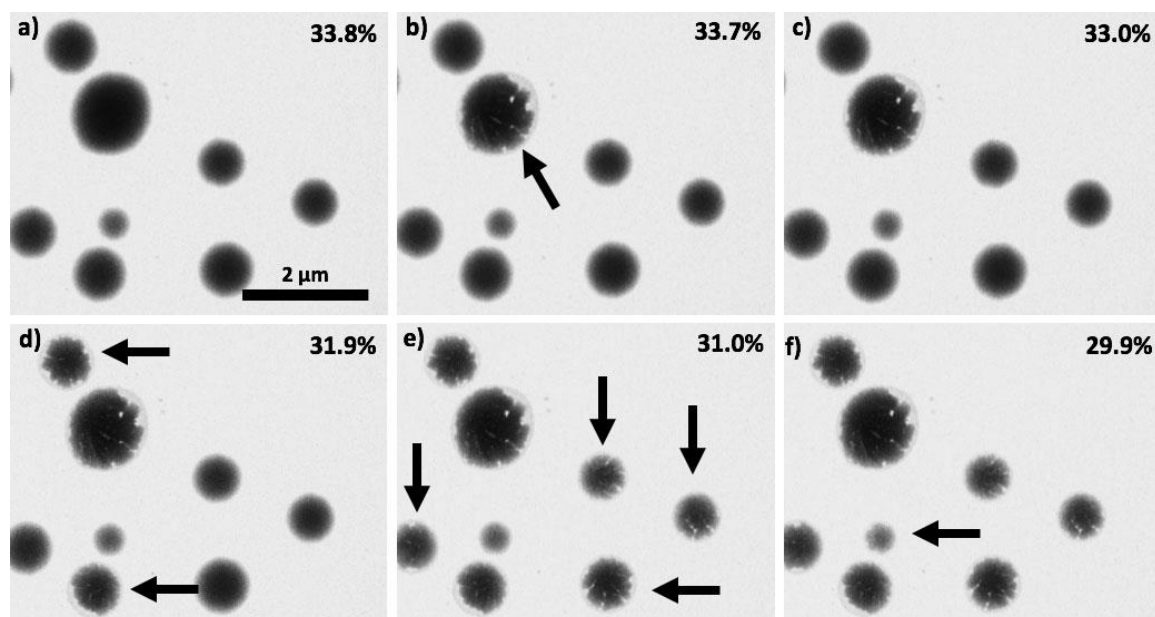


Figure 1. BF SEM images of 50:50 wt. % ammonium sulfate:pimelic acid particles originally exposed to 95% humidity a) just prior to first crystallization event (33.8% RH), b) first crystallization event (33.7%) RH, and c-f) subsequent crystallization event binned at 0.5% RH each. Arrows indicate crystallization of given particle.

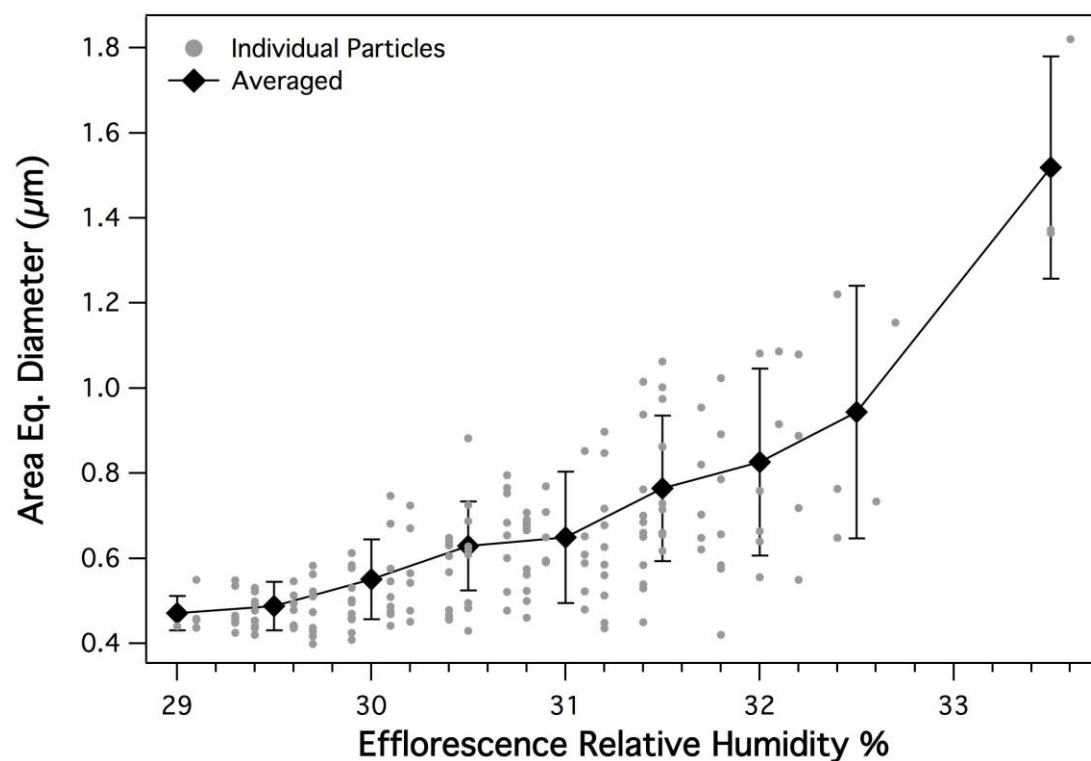


Figure 2. Area equivalent diameter of each particle of 50:50 wt. % ammonium sulfate:pimelic acid particles just prior to the crystallization event compared to the ERH for each particle (grey dots) and binned every 0.5% RH.

References

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