



Evidence for surface nucleation: efflorescence of ammonium sulfate and coated ammonium sulfate aerosol particles

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Aerosol particles are ubiquitous in the atmosphere and can undergo different phase transitions, such as deliquescence and efflorescence. Using optical microscopy, we investigated the efflorescence of ammonium sulfate (AS) in supersaturated AS and 1:1 and 8:1 (by weight) poly(ethylene glycol)-400 (PEG-400)/AS particles, which were deposited as droplets with diameters in the 16 – 35 μm range on a hydrophobically coated slide. The PEG-400/AS particles that are exposed to decreasing relative humidity (RH) exhibit a liquid-liquid phase separation below 90 % RH with the PEG-400 phase surrounding the aqueous AS inner phase (Marcolli and Krieger, 2006; Ciobanu et al., 2009). Pure AS particles effloresced in the RH range from 36.3 to 43.7 % RH, in agreement with literature data (31 – 48 % RH). In contrast, 1:1 PEG-400/AS particles with diameters of the AS phase from 7.2 – 19.2 μm effloresced between 26.8 – 33.9 % RH and 8:1 PEG-400/AS particles with diameters of the AS phase from 1.8 – 7.3 μm between 24.3 – 29.3 % RH. Such low efflorescence relative humidity (ERH) values have never been reached before for AS particles of this size range. We show that neither a potential inhibition of water evaporation via anomalously slow diffusion through the PEG coating, nor the presence of low amounts of PEG-400 in the AS phase, nor different timescales between various experimental techniques could possibly explain the low AS ERH values of PEG-400/AS particles in our setup.

High-speed photography of the efflorescence process allowed to monitor the proceeding of the AS crystallization fronts within the particles with millisecond time resolution. The nucleation locations were deduced based on the initial crystals growth locations. Statistical analysis of 31 and 19 efflorescence events for pure AS and 1:1 PEG-400/AS particles, respectively, identified the air/droplet/substrate contact line and the air/droplet interface as preferred nucleation locations in the case of pure AS particles, whereas for 1:1 PEG-400/AS particles preferential AS nucleation in the PEG phase and at the PEG/AS/substrate contact line can be excluded. Based on this statistical analysis of efflorescence events together with the AS ERH values of pure AS and PEG-400/AS particles aforementioned, we suggest that in pure AS particles nucleation starts at the surface of the particles and attribute the lower ERH values observed for PEG-400/AS particles, to the suppression of the surface-induced nucleation process. Our results indicate that surface nucleation may indeed occur in the atmosphere, during AS efflorescence, and might constitute an important, possibly even dominating nucleation pathway.

References:

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