Liquid-liquid phase separation in mixed organic-inorganic aerosols exposed to hygroscopic cycles

G. Ciobanu, C. Marcolli, U. K. Krieger, U. Weers , Th. Peter

Institute for Atmospheric and Climate Science, ETH Zurich, 8092, Zurich, Switzerland

The phase changes of single polyethylene glycol 400/ammonium sulfate droplets deposited on a hydrophobic substrate have been investigated during hygroscopic cycles, using a combination of two techniques, optical microscopy and micro-Raman spectroscopy. A liquid-liquid phase separation has been observed both upon moistening (~80 % RH) and drying (~90 % RH) the particles. The composition of the two liquid phases has been identified using micro-Raman spectroscopy. The organic phase was at the surface of the droplet, while the inner core was mainly aqueous ammonium sulfate. This morphology was found for a 50:50 wt% mixture of PEG 400/ AS to be present between 80-90 % RH and 90 % RH and the efflorescence of ammonium sulfate for increasing and decreasing relative humidity, respectively. The presence of a liquid-liquid phase separation may change the partitioning of semivolatile species between the gas and condensed phase as well as the hygroscopic properties of the inorganic components, while the presence of the organic phase at the aerosol surface may influence the heterogeneous chemistry. Two different mechanisms leading to phase separation have been identified according to the droplet's morphology at the onset of phase separation: spinodal decomposition and nucleation and growth. The route that the system chooses when separating was found to depend on the organic to inorganic ratio. Our results together with the bulk measurements performed by Marcolli & Krieger (2006) were used to construct the phase diagram of the PEG 400/AS/H_2O system which shows the phase changes as a function of relative humidity and the fraction of inorganic component.

References:

Marcolli, C. & Krieger U. K. (2006), Phase Changes during Hygroscopic Cycles of Mixed Organic/Inorganic Model Systems of Tropospheric Aerosols, *J. Phys. Chem. A*, 110, 1881-1893.