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Liquid-liquid phase separations and hygroscopic properties of internally mixed organic/inorganic aerosol particles

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In the troposphere, when the organic fraction covers a wide range from hydrophilic to hydrophobic substances, phase separations into a mainly polar (aqueous) and less polar organic phase are expected to occur (Pankow, 2003). Moreover, the interactions between organic and inorganic compounds in aerosol particles may induce liquid-liquid phase separations (LLPS) during humidity cycles (Marcolli and Krieger, 2006). Considering the compositions of the tropospheric aerosols, phase separations should indeed occur frequently when the particles are exposed to varying relative humidity (RH) (Ciobanu et al., 2009). Therefore, experimental studies are needed to obtain insight in the possible phase transitions and morphologies of more complex organic/inorganic aerosol particles relevant for the atmosphere which can further contribute to a better understanding of aerosols physical states.
In order to obtain more detailed information on LLPS and their morphologies for different organic-to-inorganic ratios (OIR) during RH cycles, we investigated three representative model systems, namely C5/ammonium sulfate (AS)/water, C6/AS/water and C7/AS/water using optical microscopy and micro-Raman spectroscopy. C5 consists of three dicarboxylic acids containing five carbon (C) atoms (glutaric, methylsuccinic, and dimethylmalonic acid), C6 of three dicarboxylic acids containing six C atoms (2-methylglutaric, 3-methylglutaric, and 2,2-dimethylsuccinic acid), and C7 of three dicarboxylic acids containing seven C atoms (3-methyladipic acid, 3,3-dimethylglutaric acid and diethylmalonic acid) atoms leading to O:C ratios of 0.8, 0.7 and 0.6, respectively.
Micrometer sized single particles of C5/AS/water showed no LLPS. The AS component effloresced at 37.9 % RH and deliquesced at 77.5 %. On the other hand, LLPS was observed for an AS dry mass fraction of 0.1 to 0.8 for C6/AS/water particles. Depending on the OIR, it occurred by fundamentally different mechanisms like growth of a second phase at the surface of the particle, spinodal decomposition and nucleation-and-growth. The onset of LLPS occurred at RHs from 71.1 to 89.6 % depending on the OIR during water evaporation. Interestingly, the inner phase that was confirmed to consist of aqueous AS by Raman spectroscopy tended to move toward the edge of the particle after LLPS had occurred. Such partial engulfing structures have also been observed by Kwamena et al. (2010). Compared to the C6/AS/water system, C7/AS/water particles showed LLPS over a wider range of OIR and up to RHs as high as 90 %. Core-shell structure was the main configuration in these systems. In conclusion, the RH range of coexistence of two liquid phases and the processes resulting in LLPS depend on the chemical compositions and the O:C ratios of the particles. The observed morphologies of the investigated particles might very likely be present in the troposphere.

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