



The Deliquescence / Efflorescence Cycle of Organic / Ammonium Sulfate Particles: Phases, Phase Transitions, and Salt Effects

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The hygroscopic growth of liquid organic / electrolyte particles is in general well described by the Zdanovskii-Stokes-Robinson approach (Robinson and Stokes, 1966; Choi and Chan, 2002). However, little is known about the phases and phase transitions of complex organic / inorganic mixtures representing real aerosol particles. There is a lack of thermodynamic data for mixtures of organic substances with ammonium sulfate (AS) – one of the most important atmospheric salts. The salt effect of AS for liquid-liquid as well as vapor-liquid equilibria of organic / water systems has hardly been investigated.

We therefore determined the saturation concentration and water activity of organic / AS mixtures in bulk measurements and compared these results with the deliquescence / efflorescence cycles of single levitated aerosol particles of the same composition. To represent the organic fraction, we chose glycerol, 1,4-butanediol, 1,2-hexanediol, and PEG 400 as well as a mixture of five dicarboxylic acids (mixture M5 consisting of malic, malonic, maleic, glutaric, and methylsuccinic acid). Polyols together with polyethers as well as mono- and dicarboxylic acids have been identified by HNMR as main classes of the water-soluble organic fraction (Decesari et al., 2000).

We found that the aqueous solubility of ammonium sulfate is strongly reduced in the presence of polyols. Moreover, ammonium sulfate induces a phase separation in 1,4-butanediol / water and 1,2-hexanediol / water mixtures. Comparisons with other salts show that the salting-out effect of ammonium sulfate in alcohol / water mixtures is stronger than the one of e.g. sodium chloride or ammonium nitrate. In the presence of the investigated dicarboxylic acid mixture M5, the aqueous solubility of ammonium

sulfate is increased indicating that at least for some – presumably the most polar – dicarboxylic acids a salting-in effect is present. Since salt effects do not only influence liquid-liquid but also vapor-liquid phase equilibria, they also have to be considered to predict gas / particle partitioning of semivolatile organic species.

In single levitated particles consisting of PEG 400 / AS and M5 / AS, ammonium sulfate was found to effloresce at relative humidities similar or below the ones of pure ammonium sulfate, allowing to determine the water activity of the solutions at highly supersaturated concentrations. Whereas M5 does not effloresce, at least some dicarboxylic acids crystallize in the M5 / AS mixture, most probably due to heterogeneous nucleation on crystalline ammonium sulfate. Comparison with bulk data shows that the total deliquescence relative humidities of PEG 400 / AS and M5 / AS are in good agreement with the water activity of saturated solutions of the same composition. However, the hygroscopic growth before total deliquescence seems also to be influenced by the complex morphology of these mixed particles.

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