Role of organic and inorganic salts in atmospheric nanoparticle growth: a modelling study

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New particle formation, i.e. formation of new nanometer sized particles from gas phase precursors and their subsequent growth towards larger sizes, is a significant source of aerosol particles in many atmospheric environments. Condensational growth is a critical step on the way of these nanoparticles to climate forcers, and growth rate of particles determines to a large extend their survivor probability to cloud condensation nuclei sizes. Large fraction of the condensational growth of atmospheric nanoparticles is due to organic vapors, but not all the vapors and processes related to their condensation are identified yet (Riipinen et al., 2012). In order to grow the nanoparticles, the compounds need to either be low-volatile or transferred into low-volatile substances through particle phase processes. Existence of semi-volatile organic acids and amines in nanoparticles has suggested that particle phase salt formation may play an important role in nanoparticle growth (Smith et al., 2010).

In this study we used particle growth model MABNAG (Model for Acid-Base Chemistry in Nanoparticle Growth) to study the importance of salt formation on nanoparticle growth. We focused on the effect of salt formation on condensation of organic acids and the relative roles of ammonia and amines for particles of 3-20 nm in diameter. MABNAG is a condensational particle growth model for monodisperse aqueous particles where particle phase acid dissociation and base protonation are accounted for. The model is based on bulk thermodynamics and utilizes Extended Aerosol Inorganic Model (E-AIM; Clegg et al. 1992; Clegg and Seinfeld, 2006) for calculating the particle phase chemistry. MABNAG predicts the particle size and composition evolution in time based on gas phase concentrations of vapors and initial particle size and composition. In this study, modelled system included five vapors: sulfuric acid, ammonia, an organic acid, an amine and water. When calculating the condensation of vapors, both size and composition dependence is taken in to account for the equilibrium vapor pressures.

At typical boreal forest conditions the model predicted the effect of dissociation, and thereby salt formation, to be small for the condensation of organic acid. As most of the growth was due to condensation of the organic acid, salt formation affected the particle growth rates only little The relative roles of the two bases were rather similar at all particle sizes between 3-20 nm, and depended on their relative gas phase concentrations, while the absolute contribution of the bases increased with particle size. At base-rich conditions (amine conc. > 10^9 cm^{-3} / ammonia conc. > 10^{10} cm^{-3}) significant fraction of the organic acid was predicted to dissociate which further increased the particle growth rate. In all cases, all the amine and ammonia was predicted to protonate in particle phase – indicating the importance of salt formation for the condensation of the bases.

Comparison of MABNAG to a quantum chemistry based modelling approach on salt formation in nanoparticles during the growth (Riipinen et al., 2012) revealed a difference between the two approaches in predictions for condensation of amines. Further study is thus needed on the applicability of bulk thermodynamics (used in MABNAG) in the nanoparticle size range.

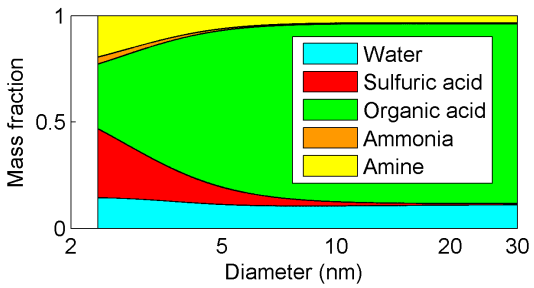

Figure 1. Predicted mass fractions at typical ambient conditions at boreal forest site Hyytiälä.

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