Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 9, 721-732, 2009
www.atmos-chem-phys.net/9/721/2009/

Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles

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Abstract. The volatile and hygroscopic properties of ammonium sulphate seeded and unseeded secondary organic aerosol (SOA) derived from the photo-oxidation of atmospherically relevant concentrations of α-pinene were studied. The seed particles were electrospray generated ammonium sulphate ($(NH4)_2SO_4$) having diameters of approximately 33 nm with a quasi-mono-disperse size distribution (geometric standard deviation σ_g=1.3). The volatile and hygroscopic properties of both seeded and unseeded SOA were simultaneously measured with a VH-TDMA (volatility – hygroscopicity tandem differential mobility analyzer). VH-TDMA measurements of unseeded SOA show a decrease in the hygroscopic growth (HGF) factor for increased volatilisation temperatures such that the more volatile compounds appear to be more hygroscopic. This is opposite to the expected preferential evaporation of more volatile but less hygroscopic material, but could also be due to enhanced oligomerisation occurring at the higher temperature in the thermodenuder. In addition, HGF measurements of seeded SOA were measured as a function of time at two relative humidities, below (RH 75%) and above (RH 85%) the deliquescence relative humidity (DRH) of the pure ammonium sulphate seeds. As these measurements were conducted during the onset phase of photo-oxidation, during particle growth, they enabled us to find the dependence of the HGF as a function of the volume fraction of the SOA coating. HGF's measured at RH of 85% showed a continuous decrease as the SOA coating thickness increased. The measured growth factors show good agreements with ZSR predictions indicating that, at these RH values, there are only minor solute-solute interactions. At 75% RH, as the SOA fraction increased, a rapid increase in the HGF was observed indicating that an increasing fraction of the $(NH_4)_2SO_4$ is subject to a phase transition, going into solution, with an increasing volume fraction of SOA. To our knowledge this is the first time that SOA derived from photo-

oxidised α-pinene has been shown to affect the equilibrium water content of inorganic aerosols below their DRH. For SOA volume fractions above ~0.3 the measured growth factor followed roughly parallel to the ZSR prediction based on fully dissolved $(NH_4)_2SO_4$ although with a small difference that was just larger than the error estimate. Both incomplete dissolution and negative solute-solute interactions could be responsible for the lower HGF observed compared to the ZSR predictions.

Final Revised Paper (PDF, 4290 KB) Discussion Paper (ACPD)

Citation: Meyer, N. K., Duplissy, J., Gysel, M., Metzger, A., Dommen, J., Weingartner, E., Alfarra, M. R., Prevot, A. S. H., Fletcher, C., Good, N., McFiggans, G., Jonsson, Å. M., Hallquist, M., Baltensperger, U., and Ristovski, Z. D.: Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles, Atmos. Chem. Phys., 9, 721-732, 2009. Bibtex EndNote Reference Manager