TOWARDS CLOSING THE GAP BETWEEN HYGROSCOPIC GROWTH AND ACTIVATION FOR SECONDARY ORGANIC AEROSOL (SOA)

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1. INTRODUCTION

Atmospheric aerosol particles consist of both, inorganic and organic substances, with varying mass fractions. One way to form particulate matter is by oxidation of precursor gases. When organic compounds are formed by this process, the different products of this reaction are called SOA (Secondary Organic Aerosol). Among biogenic volatile organic compounds, monoterpenes appear to be the major precursors of SOA particulate matter [*Sun and Ariya*, 2006]. Many studies have examined SOA particles generated by the oxidation of α-pinene, which belongs to the group of monoterpenes.

For SOA particles generated from different precursor gases, in general a slight hygroscopic growth with growth factors of about 1.1 at 90% RH is observed [e.g. *Virkkula et al.*, 1999; *Varutbangkul et al.*, 2006]. Contrary to this, SOA particles are commonly found to be more CCN active than their hygroscopic growth factors would suggest [e.g. *VanReken et al.*, 2005, *Prenni et al.*, 2007, *Duplissy et al.*, 2008,]. Assuming a constant hygroscopicity derived from measured hygroscopic growth at RHs below 95% implies, that a very low surface tension of about 30 mN/m is needed to explain the measured CCN activity [e.g. *Prenni et al.*, 2007]. This is lower than values that have been measured for atmospheric rain and fog water samples [*Facchini et al.*, 2000], HULIS (HUmic LIke Substances) extracts from atmospheric samples [*Kiss et al.*, 2005; *Salma et al.*, 2006] and for different organic substances that are thought to contribute to SOA [*Huff Hartz et al.*, 2006].

Here we report measurements of hygroscopic growth at RH < 99.5% and cloud condensation nucleus activity for SOA generated via dark ozonolysis of α-pinene. Using these data we explore the potential role of surface tension for cloud droplet activation.

2. MEASUREMENTS

The SOA particles were generated via gas-phase oxidation of α-pinene and ozone. The generation was performed in a reaction vessel with a volume of about 12 dm^3. Inside the reactor the following air flows were mixed: synthetic hydrocarbon free air (hereafter synthetic air) carrying α-pinene vapor, synthetic air with ozone concentrations of 100 to 1000 ppbv, and additional pure synthetic air. The residence time in the tank was several minutes, and the generated SOA particles were directly fed to the different instruments.

For all measurements, different dry particle sizes were selected with a DMA (Differential Mobility Analyzer). LACIS (Leipzig Aerosol Cloud Interaction Simulator, [*Stratmann et al.*, 2004] and an HH-TDMA (High Humidity Tandem Differential Mobility Analyzer, [*Hennig et al.*, 2005]) measured the hygroscopic growth at high relative humidities (RHs) above 80%, with the HH-TDMA measuring up to 98% and LACIS up to 99.5% RH [*Wex et al.*, 2005]. A continuous-flow streamwise thermal-gradient CCNc (Cloud Condensation Nucleus counter [*Roberts and Nenes*, 2005]) was used for measurements of the particle activation.

3. MODELING

The modeling was based on the approach of a single parameter representation of the hygroscopicity, which is described e.g. in *Petters and Kreidenweis* [2007] and in *Wex et al.* [2007], using κ or ρ_{ion} as this single parameter, respectively. The basic assumption of these approaches is, that the number of ions/molecules in the particle/ droplet solution does not change, once the particle has deliquesced. In these approaches, this single parameter, be it κ or ρ_{ion} (both differ only by a constant), models the properties of the particle substance(s) in the Raoult (or solubility) term of the Köhler equation. Then the only other unknown in the Köhler equation is the surface tension (σ) in the Kelvin term.

For evaluating the data measured for the SOA particles in our study, hygroscopicity (i.e., κ and ρ_{ion}) was derived based on the measured hygroscopic growth and cloud droplet activation. For this, a value was ascribed to σ, and the value for the hygroscopicity was obtained, that, together with this σ, reproduced the measured values.

4. RESULTS

Figure 1 shows values of κ (and ρ_{ion}) derived from hygroscopic growth and activation measured with LACIS and with the CCNc, respectively. For the measured hygroscopic growth, the values were derived for σ of 30 and 72.8 mN/m (the latter being the value for water). The results are depicted as filled symbols. The measured activation (open symbols) was modeled assuming σ of 30, 50, 55, 60, 65, and 72.8 mN/m. Three things can be seen from Figure 1:

1) The hygroscopicity increases as the particles become more dilute, i.e. the values obtained for κ (and ρ_{ion}) are not constant but vary with the SOA concentration in the particle. This change in hygroscopicity becomes clearly obvious only at RHs above 98% and thus could not be observed in the past. This explains the low values of σ that had to be assumed in the past, when a constant hygroscopicity was assumed.

2) Looking at the grey area, it becomes obvious that a value for σ of 30 mN/m is too low to get a consistent transition from hygroscopic growth to activation data, and σ of water likely is too high. It can reasonably be assumed that σ is not lower than 50mN/m. The upper limit of σ is unclear, since it depends on the nature of the volume fraction versus hygroscopicity relationship. This will be discussed in a future publication.

3) The change in hygroscopicity can not be counteracted by a concentration dependent σ. Would the hygroscopicity be constant (a horizontal line in Figure 1), the measured activation could only be reproduced if σ was decreasing towards more diluted particle/ droplet solutions, instead of increasing towards the value of water, which usually is observed for organic solutions.

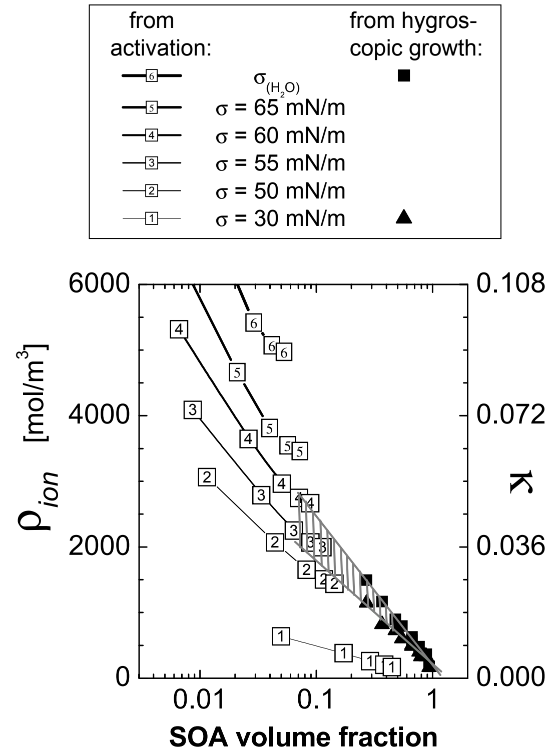

Fig. 1: *Hygroscopicity of SOA particles derived from LACIS and CCNc measurements assuming different values for σ, expressed as ρ_{ion} (and κ) as a function of the SOA volume fraction.*

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