Estimation of viscosity of SOA particles based on coalescence times

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Secondary organic aerosol (SOA) formed from partitioning of oxidation products of volatile organic compounds (VOC) accounts for a significant portion of atmospheric particulate matter. The phase of SOA particles affects their behaviour in the atmosphere and ultimately also the climate in ways that fall under topical scientific interests (Riipinen *et al*., 2012).

Virtanen *et al.* (2010) concluded that biogenic SOA particles can be amorphous solids. In a recent study, Abramson *et al.* (2013) estimated that the viscosity of α-pinene SOA particles is approximately 10^8 Pa·s, implying highly viscous (*i.e.* semi-solid) liquid particles. In this study we analyze the coalescence of agglomerates to estimate the viscosity of SOA particles. In the coalescence process, the (surface) free energy of agglomerated particles is minimized by reconstruction of the particles into spheres. For viscous amorphous particles, the characteristic time for coalescence is (Frenkel, 1945)

$$\tau = \mu d_p / \sigma, \qquad (1)$$

where μ is the viscosity of particles, d_p particle diameter, and σ surface tension. A similar analysis recently used for levitated polystyrene microspheres was by Trevitt *et al.* (2009).

We performed chamber experiments using living Scots Pine (*Pinus sylvestris* L.) trees as a biological source of VOCs (Hao *et al.*, 2009). Other precursors (α-pinene, SO_2) were also investigated and the levels of ozone and trimethylethylene (TME), to produce OH, were controlled. The filter samples for scanning electron microscope (SEM) analysis were collected from the chamber (flow 0.2 l/min, sampling times 5–10 min).

The results of scanning mobility particle sizer (SMPS), aerosol mass spectrometer (AMS) and SEM were compared to characterize the particle size, O:C-ratio, SO_4/ORG-ratio, NH_4/SO_4 ratio and particle shape. O:C-ratio was calculated to be around 0.3 for every samples. Scanning electron microscope images of the SOA particles are shown in Figure 1. In Fig. 1a individual agglomerates with primary particle size around 40–80 nm and in Fig. 1b spherical SOA particles with particle size around 30–90 nm are shown. The storage time of these samples was two (2) months before image analysis was performed and agglomerates were still observed. Thus the structural deformation from agglomerates to spheres is remarkably slow and the characteristic coalescence time, τ, is longer than two months.
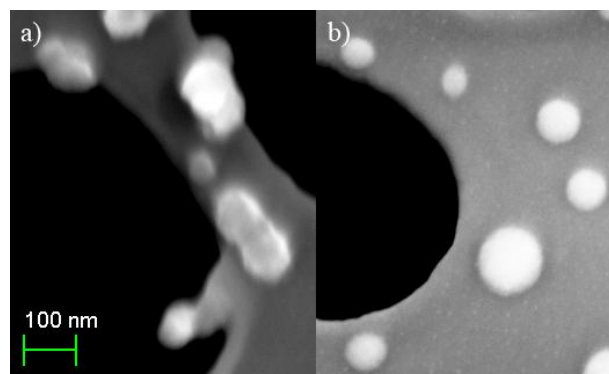

Figure 1: SEM images of the agglomerated SOA particles formed from pine + SO_2 + TME **(a)** and spherical SOA particles formed from oxidation of α-pinene **(b)**.

By using the equation (1), the viscosity of SOA particles can be estimated. As we do not know the detailed molecular composition of SOA, we used the estimated O:C-ratio to pinpoint a suitable model compound, *cis*-pinonic acid, with $\sigma = 35$ mJ/m^2. (www.chemspider.com/Chemical-Strucure.209536.html) This yields $\mu \geq 10^{12}$ Pa·s for SOA particles from pine + SO_2 + TME, and $\mu \ll 10^{12}$ Pa·s for SOA from pure α-pinene oxidation products. These results are consistent with earlier research (Virtanen *et al.,* 2010: Saukko et al., 2012; Abramson *et al*., 2013), and bear out the hypothesis of highly viscous or even glassy SOA particles in the ambient atmosphere.

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