SUPPORTING INFORMATION

Experimental Determination of Chemical Diffusion within Secondary Organic Aerosol Particles

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TITLE RUNNING HEAD: SOA: viscosity and diffusivity

Experimental Setup

Figures 1a and 1b provide a schematic of the experimental setup used to generate pyrene-coated pure SOA particles and SOA particles formed in the presence of PAHs vapors, respectively.

In experiments with pyrene-coated pure SOA particles, pure SOA particles are generated in a smog chamber by injecting 200 ppb of α-pinene, ~500 ppb of O_3, and ~250 ppm of cyclohexane, used as an OH scavenger, into a 100 L Teflon bag.[1-3] Particle size distributions are periodically monitored using a scanning mobility particle sizer (SMPS, TSI Inc., Model 3936). All SMPSs and differential mobility analyzers (DMAs) used to select aerosol samples with narrow distributions of mobility diameters (d_m) are calibrated using NIST-certified size standards, spherical polystyrene latex (PSL) beads of known diameters.. Once SOA particles stop growing, they are classified with the first DMA (DMA1, TSI Inc., Model 3081) and the mono-disperse particles are passed through a coating chamber containing pyrene vapor, whose vapor pressure is controlled by varying the pyrene source temperature. When SOA is passed over the pyrene source held at room temperature (RT), the SOA particles acquire a sub-nanometer thick pyrene coating, producing SOA particles that contain slightly less than ~2% pyrene by weight.

This coating thickness is determined by measuring the vacuum aerodynamic diameter (d_{va}) of the DMA-classified particles before and after coating process. Using measured changes in d_{va} and the SOA density, determined from measured d_m and d_{va},[3] we calculate thickness of 0.8±0.3 nm for the thin pyrene coating.

To generate SOA with a thicker pyrene coating, the pyrene source is heated to generate supersaturated pyrene vapor that condenses on the SOA seed particles as they pass through it. The coating process is monitored with DMA2 and the coating "thickness" is controlled by varying the source temperature. The coated particles are classified with DMA2 to select mono-disperse particles with uniform SOA core and uniform coating thickness.

Coated SOA particles are passed through the two inline denuders filled with activated charcoal, and loaded into the evaporation chamber that is partially filled with activated charcoal and kept at RT. Particle shape, morphology, d_{va}, precise density, and composition through individual particle mass spectra are periodically measured with our single particle mass spectrometer, SPLAT II.[1-6] Typical evaporation experiments take ~24 hours.[1] The evaporation of SOA particles coated with a sub-nanometer of pyrene was monitored for 2 hours, until pyrene had evaporated to below detection.

A detailed description of SPLAT II, its characteristic measurement capabilities, and a complete account of RT evaporation kinetics experiments are provided elsewhere.[1-6] Here we provide only a very brief description.

SPLAT II uses an aerodynamic lens inlet to efficiently transport particles into the vacuum and generate a collimated particle beam, in which particle velocity is related to particle vacuum aerodynamic diameter, d_{va}. Each particle is detected in two optical detection stages and the measured particle time-of-flight between the two stages is used to calculate particle velocity, yielding particle d_{va}. The relationship between particle velocity and d_{va} is calibrated using NIST-certified PSL particles. SPLAT II has sizing precision that is better than 0.5%,[4, 7] making it possible to measure the density of particles classified by a DMA with precision of ±0.5%.[3, 8]

The two optical detection events are also used to generate triggers to the pulsed infra-red (IR) and ultra-violet (UV) excimer lasers. The IR laser (GAM Lasers, Model EX5/200, 9.4 µm) is used to evaporate the volatile fraction of each particle and the time-delayed UV laser (GAM Lasers, Model EX5/300, 193 nm) is used to ionize the molecules in the expanding plume of evaporating gas. The ions are detected and analyzed with an angular reflectron time-of-flight mass spectrometer (TOF-MS, R. M. Jordan, Inc., Model D-850). The two-step ion generation scheme, provides significant improvement on the instrument quantitative capabilities.[9] Moreover, in SPLAT II the line-shape and position of the d_{va} distribution of mono-disperse particles can be used to determine particle shape and high precision density, with spherical particles having narrow line-shape and aspherical particles exhibiting broad d_{va} size distributions.[3] Particle morphology is characterized by utilizing a depth-profiling approach.[2, 6]

Figure 2a shows that the d_{va} distribution of pure SOA core particles classified with DMA1 at d_m=175 nm (green shaded peak) peaks at 207 nm and has a narrow line-width (full width at half maximum, FWHM, of 6.5%), consistent with spherical particles whose density is 1.18 g/cm^3, in agreement with our previous measurements.[1-3, 10, 11] The d_{va} distribution of pyrene-coated SOA particles classified at d_m=400 nm peaks at 308 nm and has FWHM of 28%, providing unequivocal evidence of particle asphericity and large dynamic shape factor. As pyrene coating evaporates, the line-width of the d_{va} distribution decreases, indicating a transformation of aspherical pyrene-coated particles into spherical pure SOA particles, consistent with the mass spectra.

It is possible to use the known SOA and pyrene densities, the size of the SOA core, and the measured d_m and d_{va} for pyrene-coated particles to calculate the pyrene volume fraction and the average particle dynamic shape factor[6] following the equations below.

$$m_p = \frac{\pi}{6}(d_{ve})^3 \rho_p \tag{S1}$$

Where m_p is particle's mass, d_{ve} is particle's volume equivalent diameter, and ρ_p is particle's density.

$$d_m = d_{ve}\chi_t \frac{C_c(d_m)}{C_c(d_{ve})} \tag{S2}$$

Where, d_m is particle's mobility diameter, χ_t is the dynamic shape factor (DSF) in the transition regime, and $C_c\,(d_m)$ and $C_c\,(d_{ve})$ are the Cunningham slip correction factors.

$$d_{va} = \frac{\rho_p}{\rho_0}\frac{d_{ve}}{\chi_v} \tag{S3}$$

Where d_{va} is particle's vacuum aerodynamic diameter and χ_v is the particle DSF in the free-molecular regime.

For spherical particles $\chi_v = \chi_t = 1$, $d_m = d_{ve}$, and $d_{va} = \frac{\rho_p}{\rho_0} d_{ve} = \frac{\rho_p}{\rho_0} d_m$

When particle d_{ve} is unknown, Equations S1-S3 can be used to calculate an average DSF,[6, 12, 13] under the approximation that $\chi_v = \chi_t = \overline{\chi}$ according to:

$$\frac{d_{va}}{d_m} = \frac{\rho_p}{\rho_0}\frac{1}{\chi_v\chi_t}\frac{C_c(d_{va}\chi_v\,\rho_0/\rho_p)}{C_c(d_m)} = \frac{\rho_p}{\rho_0}\frac{1}{\overline{\chi}^2}\frac{C_c(d_{va}\overline{\chi}\,\rho_0/\rho_p)}{C_c(d_m)} \tag{S4}$$

Using volume and mass additivity, for pyrene-coated particles

$$m_p = \frac{\pi}{6}\left[\rho_{SOA}(d_{ve}^{SOA})^3 + \rho_{PAH}\,(d_{ve}^{PAH})^3\right] \tag{S5}$$

$$(d_{ve})^3 = (d_{ve}^{SOA})^3 + (d_{ve}^{PAH})^3 \tag{S6}$$

Where, d_{ve}^{SOA} is the volume equivalent diameter of the SOA seed of the pyrene-coated particle, d_{ve}^{PAH} is volume equivalent diameter of pyrene of these particles, ρ_{SOA} is SOA density, and ρ_{PAH} is pyrene density.

For pyrene-coated particles with d_m = 400 nm, d_{va} = 308 nm, d_{ve}^{SOA}=175 nm, ρ_{SOA}=1.18 g cm^{-3}, and ρ_{PAH}=1.27 g cm^{-3}, Equations S1 to S6 yield an average DSF of $\overline{\chi}$=1.32, pyrene volume fraction of 84%, and pyrene weight fraction of 85%.

SOA particles formed in the presence of PAHs vapors are generated under conditions identical to those for pure SOA particles, except that prior to the experiment small amount of bulk PAH sample is loaded into the smog chamber filled with particle-free zero-air and left for ~24 hours to equilibrate. Once SOA formation is complete, particles are classified, passed through the denuders into the evaporation chamber and characterized as function of evaporation time as described above.

Aged SOA particles are generated by leaving the particles in the smog chamber for ~24 hours before they are studied.

To determine the particles' pyrene content, mono-disperse samples of pure pyrene, pure SOA particles, and pyrene-containing SOA particles with known diameters and loadings were characterized by the Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc.),[14, 15] which was used to quantify the relative and absolute intensities of non-overlapping peaks characteristic of pyrene and SOA. Based on the mass-spectral calibrations of pure SOA and pure pyrene particles the relative content of pyrene trapped in SOA particles was determined to be ~5%.

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