Direct Determination of Melting Temperatures for Individual, Sub-Micron Isoprene Epoxydiol-Derived Secondary Organic Aerosol Particles

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Abstract

The phase state of atmospheric aerosol particles – solid, semi-solid, or liquid – influences their ability to take up water and participate in heterogeneous chemical reactions. Changes in phase state have been predicted by glass transition temperature (T_g) and viscosity; however, direct measurements of these properties is challenging for sub-micron particles. Historically, bulk measurements have been used, but this does not account for particle-to-particle variation or the impacts of particle size. Melting temperature (T_m) is the most significant predictor of T_g, and the two properties can be related through the Boyer-Beaman rule. Herein, we apply a recently developed method utilizing a nano-thermal analysis (nanoTA) module coupled to an atomic force microscope (AFM), to determine the T_m of individual secondary organic aerosol (SOA) particles generated from the reactive uptake of isoprene-derived epoxydiols (IEPOX) onto acidic ammonium sulfate aerosol particles. NanoTA works by using a specialized AFM probe which can be heated while in contact with a particle of interest. As the temperature increases, the probe deflection will first increase due to thermal expansion of the particle followed by a decrease at its T_m. The direct measurements are compared with model predictions based on molecular composition from hydrophilic interaction liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOF-MS) analysis. We compared the T_m of the SOA particles formed from IEPOX uptake onto acidic ammonium sulfate particles created at 30, 65, and 80% relative humidity (RH), and found that increasing RH from 30 to 80% led to an overall decrease in average T_m, indicating less viscous particles at higher RH conditions. Our measurements with this technique will allow for more accurate representations of the phase state of aerosols in the atmosphere.