



Impeded ice nucleation in glassy and highly viscous aerosol particles: the role of water diffusion

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In situ and remote observations in the upper troposphere have disclosed the existence of water vapor pressures up to and even above water saturation. Under such conditions ice particle formation by homogeneous nucleation is expected to set in followed by ice crystal growth until the supersaturation is consumed. While the highest measured water vapor values might not withstand rigorous quality checks, values up to water saturation seem to be occurring. Since air masses appear to contain sufficient numbers of aerosol particles for cloud formation, the question arises why these aerosols are not successful at nucleating ice.

The atmospheric aerosol is a complex mixture of various inorganic and organic components, whereas the organic fraction can represent more than 50% of the total aerosol mass. The homogeneous ice nucleation threshold was established for atmospherically relevant salt solutions and sulfuric acid, but only for a few organic species. The organic aerosol fraction tends to remain liquid instead of crystallizing as the temperature is decreased and, thus, organic aerosol particles may form highly viscous liquids. When the viscosity of such liquids reaches values in the order of 10^{12} Pa s, the molecular motion becomes so slow, that the sample vitrifies at the glass transition temperature T_g . If aerosol particles were present as glasses, this would influence several physical and chemical processes in the atmosphere significantly: Water uptake from the gas phase would be drastically impeded and ice nucleation inhibited.

We investigated the glass transition temperature of a series of aqueous organic solutions such as polyols, sugars and dicarboxylic acids as a function of the solute concentration using a differential scanning calorimeter (DSC). These measurements show that the higher the molar mass of the organic solutes, the higher T_g of their respective solutions at a given water activity. Aerosol particles containing larger (≥ 150 g mol $^{-1}$) organic molecules are therefore likely to form glasses in the upper troposphere. If aerosol particles are highly viscous or glassy, the equality between relative humidity of an air mass and water activity of the contained particles is no longer fulfilled because water diffusion within the particles is too slow to follow RH changes in the atmosphere. There is a lack of literature data for water diffusion within organic glasses at low temperatures. We therefore measured hygroscopicity cycles of aerosol particles with an electrodynamic balance (EDB) at temperatures between 220 – 291 K and developed a microphysical model to calculate diffusion coefficients of water within the particles based on the EDB results together with available literature data. As model substance we chose sucrose, a substance that has been identified in biomass burning aerosols and may represent the high molecular weight constituents of the organic aerosol fraction. We indeed observed a hysteresis between water uptake and release for levitated sucrose particles that is due to slow water diffusion within the glassy particle and can be used to derive water diffusion coefficients at low temperatures with our microphysical model.