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Water interactions of aerosol particles composed of protein macromolecules and salts: hygroscopic growth, microstructural rearrangement, electric and kinetic effects

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Proteins and related organic macromolecules account for a significant fraction of water-soluble organics in fine air particulate matter (10-20% in urban, rural, and high alpine PM2.5). They influence the physicochemical properties of aerosol particles and thus their effects on the atmosphere, climate, and public health (Mikhailov et al., 2004; Franze et al., 2005; and references therein).

The interaction of aerosol particles composed of the protein bovine serum albumin (BSA) and the inorganic salts sodium chloride and ammonium nitrate with water vapor has been investigated by hygroscopicity tandem differential mobility analyzer (H-TDMA) experiments complemented by transmission electron microscopy (TEM) and Köhler theory calculations (100–300 nm particle size range, 298 K, 960 hPa). BSA was chosen as a well-defined model substance for proteins and other macromolecular compounds, which constitute a large fraction of the water-soluble organic component of air particulate matter.

Pure BSA particles exhibited deliquescence and efflorescence transitions at $\sim$35% relative humidity (RH) and a hygroscopic diameter increase by up to $\sim$10% at 95% RH in good agreement with model calculations based on a simple parameterisation of the osmotic coefficient. Pure NaCl particles were converted from near-cubic to near-spherical shape upon interaction with water vapor at relative humidities below the deliquescence threshold (partial surface dissolution and recrystallisation), and the

diameters of pure NH_4NO_3 particles decreased by up to 10% due to chemical decomposition and evaporation.

Mixed NaCl-BSA and NH_4NO_3-BSA particles interacting with water vapor exhibited mobility equivalent diameter reductions of up to 20%, depending on particle generation, conditioning, size, and chemical composition (BSA dry mass fraction 10–90%). These observations can be explained by formation of porous agglomerates (envelope void fractions up to 50%) due to ion-protein interactions and electric charge effects on the one hand, and by compaction of the agglomerate structure due to capillary condensation effects on the other. The size of NH_4NO_3-BSA particles was apparently also influenced by volatilisation of NH_4NO_3, but not as much as for pure salt particles, i.e. the protein inhibited the decomposition of NH_4NO_3 or the evaporation of the decomposition products NH_3 and HNO_3. The efflorescence threshold of NaCl-BSA particles decreased with increasing BSA dry mass fraction, i.e. the protein inhibited the formation of salt crystals and enhanced the stability of supersaturated solution droplets.

The H-TDMA and TEM results indicate that the protein was enriched at the surface of the mixed particles and formed an envelope, which inhibits the access of water vapor to the particle core and leads to kinetic limitations of hygroscopic growth, phase transitions, and microstructural rearrangement processes.

The Köhler theory calculations performed with different types of models demonstrate that the hygroscopic growth of particles composed of inorganic salts and proteins can be efficiently described with a simple volume additivity approach, provided that the correct dry solute mass equivalent diameter and composition are known. A parameterisation for the osmotic coefficient of macromolecular substances has been derived from an osmotic pressure virial equation. For its application only the density and molar mass of the substance have to be known or estimated, and it is fully compatible with traditional volume additivity models for salt mixtures.

References:

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