Physical, Chemical, and Hygroscopic Properties of Submicrometer Particles Studied by X-ray Spectro-Microscopy

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Atmospheric aerosols are a complex micro-structured mixture of inorganic and organic components, where organics can represent more than 50% of the aerosol mass depending on location. Understanding and predicting the climate effects due to atmospheric aerosols requires quantitative knowledge of their hygroscopic and chemical properties. The ability of aerosols to absorb water influences their optical and cloud forming properties, ice nuclei formation and transformation, atmospheric lifetime, and chemical reactivity. The presence of organic carbon in aerosols has a complex effect on their physical-chemical and reactive properties that is poorly understood. In particular, there is a lack of robust quantitative measurements on how properties of organic components (such as particle size, morphology, chemical composition, concentration and type of mixing) influence the rate and amount of water uptake on aerosols.

Here we present a unique application of single particle Scanning Transmission X-ray Microscopy (STXM) and Atomic Force Microscopy (AFM) for quantitative analysis of density, elemental and chemical compositions, type of mixing, and hygroscopic properties of individual submicron particles. The approach utilizes AFM for direct determination of three-dimensional shape of substrate-deposited particles followed by STXM spectro-microscopy analysis performed during exposure to water vapor at different relative humidity (RH). The hygroscopic properties of atmospherically-relevant NaCl, NaBr, NaI, $NaNO_3$, malonic acid and glutaric acid, as well as several mixed organic and inorganic submicron particles were measured to evaluate the utility of the approach. A model was developed that allows quantitative determination of the mass of liquid water and water-to-solute ratio(WSR) in a submicron aerosol. The results for the deliquescence and efflorescence phase transitions and quantitative measurements of water-to-solute ratios are found in excellent agreement with available literature data.[1] Near edge X-ray absorption spectroscopy (NEXAFS) was utilized to determine and quantify efficient keto-enol tautomerization of malonic acid, with the enol form dominating at higher RH. The keto-enol equilibrium constants were calculated using the NEXAFS spectra as a function of RH and were found to be up to four orders of magnitude higher than the solution equilibrium constants. Our results suggest that in deliquesced particles, carboxylic acids may exist in their enol forms that need to be explicitly considered in atmospheric aerosol chemistry.[2]

References

(1) S. Ghorai, A.V. Tivanski *Anal. Chem* **2010**, 82, 9289-9298.
(2) S. Ghorai et al *J. Phys. Chem. A* **2011**, 115, 4373-4380.