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Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures

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Abstract

The hygroscopic growth of solid aerosol particles consisting of mixtures of ammonium sulfate and either adipic acid or Aldrich humic acid sodium salt was characterized with a hygroscopicity tandem differential mobility analyzer and an electrodynamic balance. In particular, the time required for the aerosol particle phase and the surrounding water vapor to reach equilibrium at high relative humidity (RH) was investigated. Depending on the chemical composition of the particles, residence times of > 40 s were required to reach equilibrium at 85% RH, yielding up to a 7% reduction in the measured hygroscopic growth factors from measurements at 4 s residence time compared to measurements at equilibrium. We suggest that the solid organic compound, when present as the dominant component, encloses the water-soluble inorganic salt in veins and cavities, resulting in the observed slow water uptake. Comparison with predictions from the Zdanovskii–Stokes–Robinson relation shows enhanced water uptake of the mixed particles. This is explained with the presence of the salt solution in veins resulting in a negative curvature of the solution meniscus at the opening of the vein. In conclusion, it is important for studies of mixtures of water soluble compounds with insoluble material to allow for sufficient residence time at the specified humidity to reach equilibrium before the hygroscopicity measurements.

Keywords: HTDMA; EDB; ZSR; Hygroscopicity; Mass transfer limitation; Kelvin effect

1. Introduction

Aerosol particles in the atmosphere affect the earth's radiation balance in various ways (IPCC, 2001). Firstly, aerosol particles absorb and scatter radiation. This *direct aerosol effect* is influenced by the hygroscopicity of the aerosol

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particles, which is determined mainly by their chemical composition. Secondly, the tendency for cloud formation and resulting cloud properties similarly depends on the chemical composition as well as on the size distribution of the aerosol particles (e.g. McFiggans et al., 2006). Thus, the cloud albedo and the radiative properties of cloud droplets are influenced, coined the *indirect aerosol effect*.

Atmospheric aerosol components can be classified into inorganic and organic components (e.g. Kanakidou et al., 2005). The hygroscopic properties of most inorganic salts present in the atmosphere are well known (e.g. Ansari & Pandis, 1999; Colberg, Luo, Wernli, Koop, & Peter, 2003). Of the many organic species identified in the aerosol (e.g. Putaud et al., 2004), the hygroscopic properties of quite a few pure substances have been characterized. However, to date the hygroscopic properties of only a few mixtures have been investigated. Inorganic salts (for instance ammonium sulfate (AS) and sodium chloride) can show a hysteresis behavior during uptake and loss of water, i.e. by exhibiting a difference between the deliquescence and efflorescence relative humidities (DRH/ERH), and with a higher water content of the deliquesced than the effloresced particles in this relative humidity (RH) range. Conversely, organic constituents of the aerosol without hysteresis behavior can contribute to an uptake of water at lower RH than the DRH of inorganic salts. This has been reported by Dick, Saxena, and McMurry (2000) and is also theoretically expected, as such complex mixtures can remain in the liquid state and exchange water with the gas phase at lower RHs (Marcolli, Luo, & Peter, 2004).

The response of aerosol particles to changes in RH can be measured by a variety of instruments. The particle levitation technique using an electrodynamic balance (EDB) has been demonstrated to be a valuable method for studying the hygroscopic properties of single aerosol particles (Davis, Buehler, & Ward, 1990). This technique has the advantage that the particle mass can be monitored continuously as a function of RH, thus providing unambiguous in situ characterization of the particle mass growth due to water uptake. It can be used for particles with diameters larger than a few micrometers. A different method for characterizing water uptake is the hygroscopicity tandem differential mobility analyzer (HTDMA, Rader & McMurry, 1986).

In this paper, measurements performed by two HTDMAs are compared with each other and with results obtained with an EDB. One of the HTDMAs is from the University of Manchester (UMan), UK (Cubison, Coe, & Gysel, 2005), the other one from the Paul Scherrer Institute (PSI), Switzerland (Weingartner, Gysel, & Baltensperger, 2002), while the EDB is from ETH Zurich (Colberg, Krieger, & Peter, 2004). Hygroscopicity measurements for a variety of mixtures are presented. The growth of AS is compared with the theoretical prediction using the aerosol diameter-dependent equilibrium model (ADDEM) (Topping, McFiggans, & Coe, 2005a, 2005b) developed at the UMan. In the case of mixtures of different components (AS with organics), the hygroscopic growth was predicted using the Zdanovskii–Stokes–Robinson (ZSR) relation for water activities of mixed particles (Stokes & Robinson, 1966).

Mass transfer effects in hygroscopic measurements of aerosol particles have recently obtained more attention. It has been discussed whether organic/inorganic aerosol mixtures show mass transfer limitations of water (contrary to pure inorganic salts which equilibrate very fast, within timescales of < 1 s). Kerminen (1997) considered the gas-phase transfer to particles before cloud activation, and reported calculated equilibration times < 1 s. However, a field study by Chuang (2003) found that a fraction of the particles exhibited a slower water uptake than the majority of particles sampled, which was explained by a low mass accommodation coefficient in that study. Chan and Chan (2005) did a review of the different hygroscopicity studies with possible mass transfer effects for water uptake of aerosol particles, concluding the need for further investigation. Cubison (2005) described an experimental set-up and results for several systems. Our study further investigates and analyzes the results from measurements with varying residence times at elevated RH. In order to evaluate the water vapor equilibration time, the residence time of the particles at high RH was varied from seconds to minutes.

AS was chosen as the inorganic salt in this study, as its hygroscopicity is well known and it is a common constituent in the atmosphere. Adipic acid (AA) was chosen as an organic constituent. AA has a low vapor pressure and is only moderately soluble in water (high DRH). At the RHs studied here it is present in its crystalline form, which is assumed to contribute to a prolonged water uptake equilibration time. AA has also been identified in atmospheric samples (Ray & McDow, 2005). Furthermore tests were carried out with the commercially available Aldrich humic acid sodium salt (NaHA). This compound serves as a proxy for humic-like substances that were identified as a major component of the isolated organic matter in the atmospheric aerosol (Graber & Rudich, 2006; Kiss, Tombacz, Varga, Alsberg, & Persson, 2003).