Study of Hygroscopic Properties of Four Alkyl Aminium Sulphate Salts Using Micro-Raman Spectroscopy

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As one of the organic nitrogen compounds, amines are the most important category of alkaline gases besides ammonia in the atmosphere. Among ~150 amine compounds, short-chain alkyl amines with low molecular weight are the most common and abundant, such as mono-methylamine (MMA), di-methylamine (DMA), tri-methylamine (TMA) and mono-ethylamine (MEA) (Ge et al., 2011). These gaseous amines can enter the particle phase through nucleation processes (Murphy et al., 2007) or gas–particle partitioning (Rehbein et al., 2011). Aminium sulphates, which can be formed via acid–base neutralization between amines and sulphuric acid, will affect physicochemical properties of aerosols such as hygroscopicity. By measuring water activities of aminium sulphate bulk solutions, our earlier study (Sauerwein et al., 2015) showed that aminium sulphates are more hygroscopic than ammonium sulphate. Besides, measured water contents of aminium sulphate solutions were higher than the results of Clegg et al. (2013). However, these findings were confined to concentrations below saturation. Therefore, water contents of aminium sulphates in the super-saturated region are of great interest to discover.

In this study, hygroscopic properties of four atmospherically relevant alkyl aminium sulphates at different aminium-to-sulphate mole ratios (A/S) from dilute to super-saturated concentrations were investigated. Sample droplets with ~60 μm in diameter were deposited in air-flow cells and characterized by micro-Raman spectroscopy. The normalized area of water stretching peaks in Raman spectra was converted to water-to-solute mole ratios (WSR) at various relative humidity (RH). A/S of samples were determined using ion chromatography. Experimental results showed that mono-methylaminium sulphate (MMAS) and mono-ethylaminium sulphate (MEAS) were stable at A/S=2.0 and did not exhibit amine evaporation. However, DMA and TMA evaporated from di-methylaminium sulphate (DMAS) and tri-methylaminium sulphate (TMAS) salts, which eventually equilibrated at A/S of 1.5 and 1.0, respectively. Hygroscopic measurements were done with these stable/equilibrium salt compositions and we also estimated the hygroscopicities of DMAS and TMAS beyond the equilibrium compositions. In general, within experimental uncertainty all the studied aminium sulphates had consistent hygroscopic trends with corresponding bulk solutions and were more hygroscopic than their respective ammonium counterparts, especially at low RH. The WSR uncertainties with unstable DMAS and TMAS salts were large and further investigation is warranted to accurately determine the hygroscopic properties of those unstable alkyl aminium sulphates.

Recently, it has been reported that the modelled concentrations of methylamines (MMA, DMA and TMA) in the global atmosphere are substantially lower than the observed values (Yu and Luo, 2014). The gap between modelled and observed concentrations of methylamines would reduce if the re-evaporation of amines after amine uptake by aerosols is taken into consideration.

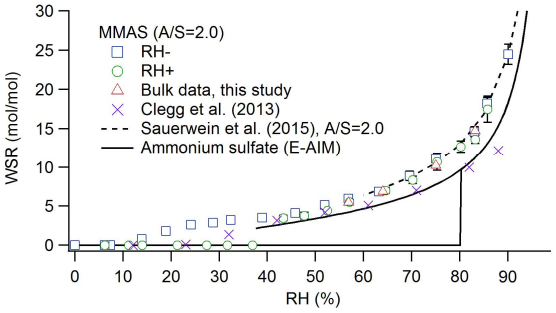

Figure 1. Hygroscopicity of MMAS (A/S=2.0) and comparison with literature data. RH+ and RH- indicate data points obtained during humidification and dehumidification in the RH cycle, respectively.

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