Hygroscopicity of aminium sulphates from comparative kinetics measurements in a cylindrical electrodynamic balance

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Hygroscopicity influences the activity of aerosol as cloud condensation nuclei (CCN) and therefore their indirect effect on the atmosphere atmospheric radiation budget. Since there are still uncertainties in the understanding of the microphysical properties that affect aerosol behaviour, a better knowledge of its hygroscopicity is needed.

Aminium sulphates are salts formed from the neutralization reaction of sulfuric acid with amines. They have been detected in atmospheric aerosols (Ge, 2011) but their physicochemical behavior is less characterized than their inorganic equivalent, ammonium sulphate.

Hygroscopic properties have been studied for six aminium sulphates (methyl, dimethyl, trimethyl, ethyl, diethyl and triethylaminium sulphates) with comparative kinetics evaporation measurements in a cylindrical Electrodynamic Balance (EDB). This instrument allows confinement of single charged aerosol droplets in an electrical field within temperature and RH (Relative Humidity) controlled conditions. A previously developed comparative kinetics technique (Davies, 2013) was widened to allow hygroscopic growth curves measurements down to water activities (a_w) of about 0.45 and up to a_w values close to saturation (>0.99). Using a two-dispenser experimental setup, two different types of droplets can be alternately levitated in a comparative experiment between a sample solution and a probe solution (water or NaCl). The RH in the chamber is estimated from the evaporation kinetics of the probe and the application of a semi-analytical treatment for mass and heat transport (Kulmala, 1993) allows the determination aerosol hygroscopicity curves from evaporation measurements.

Results of hygroscopicity growth measurements for aminium sulphates have shown interesting behaviour. First of all, their radial growth curve is found to be very similar to that predicted for ammonium sulphate (Clegg, 1997), especially at a_w<0.8. The measured grow factor (GF) values are significantly higher than those previously measured (Qui and Zhang, 2012) in HTDMA experiments. This could be a consequence of loss of amine during the drying step in HTDMA experiments. In addition, an interesting trend can be seen in the progression from methylaminium sulphate to triethyleaminium sulphate (Figure 1, just 3 aminium sulphates are shown for clarity). In effect, compounds with an increasing number of carbon atoms in the aminium cation are increasingly less hygroscopic from the previous one in the series. This behaviour is consistent with hygroscopic properties determined by the increasing hydrophobicity of the nitrogen substituents in the cation on progressing from methylamine to triethyl amine.

The temperature dependencies of these six aminium sulphates hygroscopic curves has also been evaluated and the vapour pressures of the amine in the inorganic salt particles measured from long-time trapping measurements in the EDB.

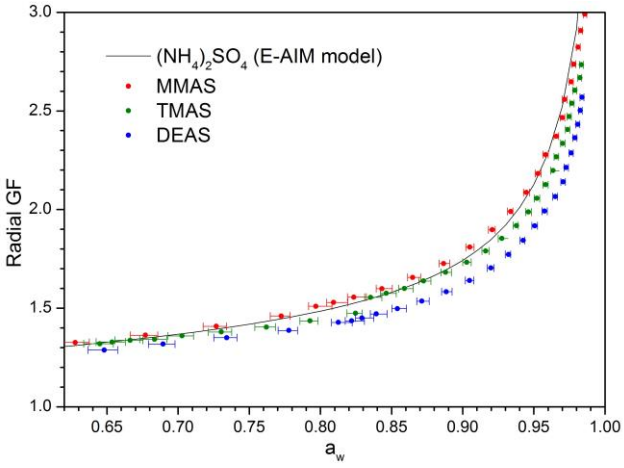

Figure 1. Radial growth curves are shown for three of the studied compounds: monomethylaminium sulphate (MMAS, red), trimethyliaminium sulphate (TMAS, green) and diethylaminium sulphate (DEAS, blue). The growth curve for (NH4)2SO4 predicted from E-AIM model data is also reported as a comparison (black line).

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