#### Hygroscopicity of aminium sulphates from comparative kinetics measurements in a cylindrical electrodynamic balance <u>G Rovelli</u>, REH Miles, JP Reid

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# Summary

Comparative kinetic evaporation measurements in a cylindrical electrodynamic balance (EDB) were performed at 273 K between 0.47 and 0.999 water activity values on five aminium sulphates.

### Introduction

Aerosol hygroscopicity influences its activity as cloud condensation nuclei (CCN) and therefore its indirect effect on the atmosphere radiation budget. Since there are still uncertainties in the understanding of the microphysical properties of mixed inorganic/organic aerosols and the processes that lead to cloud droplets formation, a better knowledge of aerosol hygroscopic properties is needed.

A previously developed comparative kinetics technique in an EDB [1] was widened to allow hygroscopic growth curves measurements down to about 0.47 water activity (a<sub>w</sub>) and up to a<sub>w</sub> values close to saturation (0.999). The obtained method was used to measure five aminium (methyl, dimethyl, trimethyl, diethyl and triethyl) sulphates hygroscopic growth curves at 273 K, because they have been proved relevant products of the acid-base chemistry between amines and sulphuric acid in environmental aerosol [2].

### **Methods and Materials**

Comparative kinetics evaporation measurements were performed in a cylindrical EDB, which allows confinement of single charged aerosol droplets in an electrical field [1]. Thanks to 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 one (water or NaCl). The RH in the chamber is estimated from the evaporation kinetics of the probe and the application of Kulmala et al.'s treatment for mass and heat transport [3] allows to determine aerosol hygroscopicity curves from evaporation measurements.

### Results

Expanding the previous comparative kinetic approach was possible thanks to measurements on three wellcharacterized aerosol components (NaCl, NaNO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). The obtained radial hygroscopic growth curves were compared to predictions from AIM model and an empirical criterion to evaluate the accuracy of high  $a_w$ radial grow factors (GFs) measurements into low RHs was established. A surface-normalised mass flux is calculated for a sample droplet in every instant during its evaporation and the calculated GF is accepted only when the normalised mass flux derivative is negative. Applying this criterion on the three reference compounds, the measured hygroscopic growth curves are in very good agreement with AIM model simulations.

First results on aminium sulphates have shown an interesting hygroscopic behaviour for this class of compounds. First of all, their GF curve is found to be very similar to the one predicted from ammonium sulphate by AIM model, especially at  $a_w < 0.8$ . The measured GF values are significantly higher than those measured by Qui and Zhang [4] in HTDMA experiments. In addition, an interesting trend can be individuated from methylaminium sulphate to triethyleaminium sulphate. 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 kind of behaviour is thought to be determined by the increasing hydrophobicity of the nitrogen substituents in the cation going from methylamine to triethyl amine.

# Conclusions

The range of applicability of a previously developed comparative kinetics evaporation in an EDB was broadened to 0.47-0.999 a<sub>w</sub> with measurements on three very well characterized aerosol compounds and the comparison of the experimental GF curves with AIM model simulations. With the presented method, the hygroscopic growth curves for five aminium sulphates have been measured at 273 K. Ethylaminium sulphate hygroscopicity is going to be measured too, together with temperature dependence measurements.

### References

[1] Davies, J. F.; Haddrell, A. E.; Rickards, A. M. J.; Reid, J. P. Anal. Chem. 2013, 85, 5819–5826.

- [2] Ge, X.; Wexler, A. S.; Clegg, S. L. Atmos. Env. 2011, 45(3), 524-546.
- [3] Kulmala, M.; Vesala, T.; Wagner, P. E. Proc. R. Soc. Lond. A 1993, 441, 589–605.
- [4] Qiu, C.; Zhang, R. Environ. Sci. Technol. 2012, 46, 4474-4480