Towards an understanding of the impact of chemical functionality on aerosol hygroscopicity

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Aerosol hygroscopicity affects both the aerosol direct effect, via control of particle size and refractive index, and the indirect effect, through its impact on the critical supersaturation required for atmospheric aerosol to activate in to cloud droplets. Hygroscopicity can be represented in terms of a reduced kappa parameter based on κ-Köhler theory (Petters and Kreidenweis, 2007), and is often inferred from measurements of aerosol composition in terms of the O:C ratio (Duplissy *et al.*, 2011). Recent work has shown that the correlation between kappa and O:C is only approximate (Rickards *et al.*, 2013), highlighting the importance of considering chemical functionality and oxidation history on aerosol hygroscopicity. Here, we use a recently developed comparative kinetics technique (Davies *et al.*, 2013) to compile a database of hygroscopic growth curves for a wide range of organic solutes with varied chemical functionality, seeking new ways in which to correlate aerosol composition with particle hygroscopicity.

In this work, a cylindrical electrodynamic balance is used to trap single, aqueous aerosol particles (30 μm to 4 μm in radius) as they evaporate into a nitrogen flow of controlled temperature (245 – 325 K) and relative humidity (RH; 0 to > 90 %). Elastic light scattering from the trapped particle is used to monitor its evaporation, with an accuracy in radius of < 50 nm and a time resolution of < 5 ms. The RH of the nitrogen flow is determined with an uncertainty < 0.5 % by sequential trapping of a calibrant droplet (Davies *et al.*, 2013).

From the particle radius vs time data, the mass flux of water leaving the aerosol can be calculated at all times, allowing the water activity within the evaporating droplet to be determined with high temporal resolution (Kulmala *et al.*, 1993). Knowledge of the mass fraction of solute in the particle at the point of capture allows both mass and radial growth factors, kappa values and osmotic coefficients to be determined with high accuracy. Single droplet evaporation events take on the order of ~ 30 s, with individual aerosol particles being reproducibly generated using a droplet-on-demand generator loaded with the solution of interest. Hygroscopicity measurements are averaged over hundreds of droplets, increasing instrument sensitivity.

Benchmarking measurements on the growth curves for well characterised inorganics (NaCl, $(NH_4)_2SO_4$, $NaNO_3$) and organic acids (Glutaric acid, Succinic acid, Oxalic acid) show excellent agreement between experiment and theory over a wide RH range (Figure 1). By tuning the starting solution concentration and gas phase RH, hygroscopic data up to 99.9 % RH can be measured with high precision (inset, Figure 1). Systematic measurements for functional groups including alcohols, carboxylic acids and nitrogen containing species have so far been performed and will be presented, with measurements on multifunctional compounds due to begin shortly.
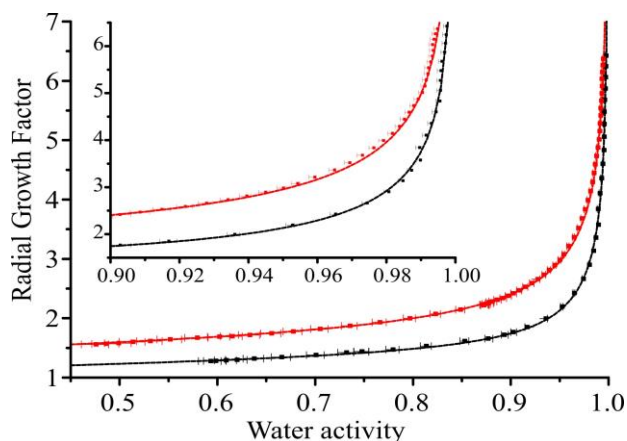

Figure 1. Measured hygroscopic growth curves for NaCl (red squares) and $(NH_4)_2SO_4$ (black squares) compared with E-AIM model predictions (dashed lines). Inset: High water activity data.

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