

# The Impact of Molecular Structure and Chemical Functionality on Aerosol Hygroscopicity

J.P. Reid<sup>1</sup>, A. Cowling<sup>1</sup>, R.E.H. Miles<sup>1</sup>, A. Marsh<sup>1</sup> and G. Rovelli<sup>1,2</sup>

<sup>1</sup>School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

<sup>2</sup>Department of Environmental and Earth Science, Università degli Studi di Milano-Bicocca, Milan, Italy

Keywords: hygroscopicity, kappa parameter, single particle, electrodynamic balance.

Presenting author email: J.P.Reid@bristol.ac.uk

Aerosol hygroscopic growth affects both the aerosol direct effect, via particle size and refractive index, and the indirect effect, through the critical supersaturation required for aerosol activation in to cloud droplets. Hygroscopicity, represented by a reduced kappa parameter (Petters and Kreidenweis, 2007), is often inferred from aerosol composition using measurements of the O:C ratio, although the correlation between O:C and kappa has recently been shown to be only approximate (Rickards *et al.*, 2013). This highlights the importance of understanding the precise impact of chemical functionality on solute hygroscopicity.

Here, we use a comparative kinetics technique (Davies *et al.*, 2013) to measure hygroscopic growth curves for organic solutes with varied chemical functionality over wide ranges in temperature (245 – 325 K) and RH (<5% to >99.5%). The objective is to provide a large library of hygroscopic growth measurements for a wide range of organic compounds that will allow refinement of predictive models and from which elementary insights can be gained through the influence of molecular structure on hygroscopicity.

A cylindrical electrodynamic balance is used to trap single, aqueous aerosol particles (30  $\mu\text{m}$  to 4  $\mu\text{m}$  in radius) as they evaporate into a nitrogen flow of controlled temperature and relative humidity. 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 < 10 ms. The RH of the nitrogen flow is determined with an uncertainty < 0.5 % by sequential trapping of a water or NaCl calibrant droplet (Davies *et al.*, 2013). The mass flux of water leaving the aerosol can be calculated at all times from the evolution in droplet radius, allowing the water activity (aw) within the evaporating droplet to be determined with high temporal resolution (Kulmala *et al.*, 1993). Knowledge of the mass fraction of solute (MFS) in the particle at the point of capture allows both mass and radial growth factors, kappa values, osmotic coefficients and MFS vs aw curves to be determined with high accuracy. Individual aerosol particles are reproducibly generated using a droplet-on-demand generator loaded with the solution of interest, increasing instrument sensitivity by allowing hygroscopicity measurements to be averaged over many tens of droplets.

In the work reported here, the effect of chemical functionality on solute hygroscopicity is systematically studied for two atmospherically relevant classes of chemical compounds; dicarboxylic acids and amino

acids. Experimentally determined MFS vs aw curves recorded in the range 45 to 99.9% RH are compared with theoretical models (eg. AIOMFAC) to determine the accuracy with which changes in hygroscopicity due to chemical structure are currently represented. Measurements on sixteen dicarboxylic acids (C<sub>2</sub> to C<sub>7</sub> backbone) show a clear trend of decreasing hygroscopicity with the addition of multiple methyl and ethyl substituents. MFS vs aw data for unbranched dicarboxylic acids agree well with AIOMFAC predictions, with the model found to less well represent the hygroscopicity of the branched diacids (Figure 1). A similar impact of structure on hygroscopicity is observed for the amino acids.

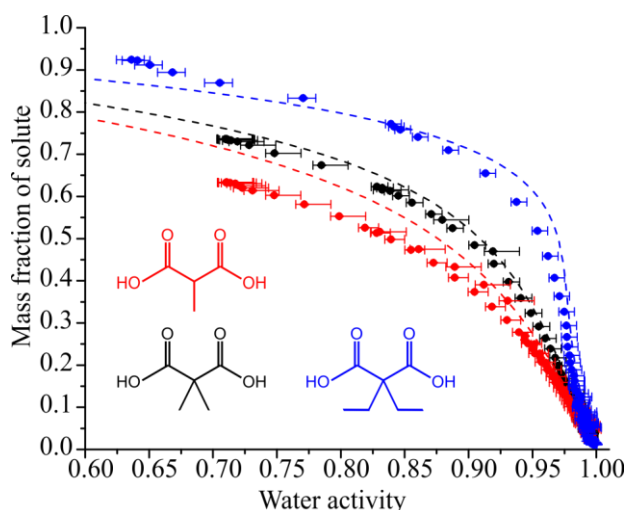


Figure 1. Examples of measured hygroscopicity curves (circles) for a series of branched dicarboxylic acids; methylmalonic acid (red), dimethylmalonic acid (black), diethylmalonic acid (blue). AIOMFAC, dashed lines.

This work was supported by the Natural Environment Research Council (NE/L006901/1, REHM and JPR) and an Italian Ministry of Education Scholarship (GR).

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