

Measurements of the variation in hygroscopic growth of organic aerosol with oxygen-to-carbon ratio (O/C)

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Keywords: hygroscopicity, kappa, O/C, single particle analysis.

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Aerosols play a vital role in influencing radiative forcing through both the direct and indirect effect. The radiative forcing due to the indirect effect, where the aerosol droplets act as cloud condensation nuclei, has been shown by the IPCC to have an uncertainty similar in magnitude to the effect from carbon dioxide and to be of opposite sign (Forster et al., 2007). To reduce this uncertainty it is important to characterise how aerosol droplets of different compositions grow in size when exposed to increasing relative humidity (RH). This is referred to as aerosol hygroscopicity, and quantifies the equilibrium size of particles and also the extent of their light extinction.

Hygroscopic growth can be represented by a radial growth factor (GF). This is the ratio of the wet to dry particle sizes, and varies as a function of RH. To create a universal measure of hygroscopicity, Petters and Kreidenweis (Petters & Kreidenweis, 2007) have parameterised the GF in terms of a hygroscopicity parameter kappa, κ , and RH. It has been suggested in various studies that κ correlates with the magnitude of the m/z 44 ion fragment expressed as a fraction of the total organic ion signal, taken from aerosol mass spectrometry measurements. This ion fragment is usually attributed to the presence of a CO_2^+ ion, and has in turn been suggested to correlate with the oxygen to carbon ratio (O/C), indicative of the photochemical age of secondary organic aerosol (SOA) (Duplissy et al., 2011).

In this study, hygroscopicity measurements on single aerosol droplets of known composition were made using both aerosol optical tweezers (AOT) and an electrodynamic balance (EDB). The AOT allowed simultaneous determination of droplet size and refractive index at a particular RH through analysis of whispering gallery modes in the Raman spectra. This could then be converted into a radial GF. Kinetic measurements of the evaporative flux and equilibration of initially dilute droplets were made using the EDB at a well-defined RH. The mass flux equations of Kulmala et al. (Kulmala, Vesala, & Wagner, 1993) were employed to calculate the droplet water activity during evaporation, and thus deduce the hygroscopicity up to water activities approaching saturation. Initial focus was on compounds with O/C = 1, with the aim of determining how tightly constrained κ is for a fixed O/C ratio. The research was then expanded to look at compounds with a significantly higher and lower O/C to determine whether these were distinguishable from compounds with O/C = 1 on the basis of κ . Figure 1 shows an example of a GF measurement for the compound galactose.

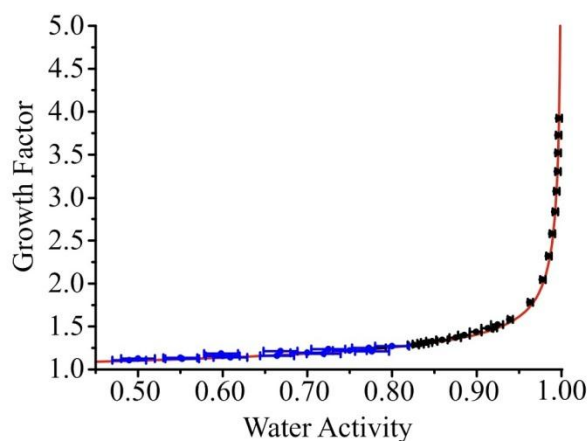


Figure 1. Experimental GF data for galactose from AOT (points below 0.8) and EDB (points above 0.8) compared to the AIOMFAC prediction (solid line).

In addition, published experimental data for κ were compiled and compared against O/C. The reported aerosol κ values include studies at subsaturated conditions and supersaturated conditions, single particle measurements and ensemble measurements, and a variety of experimental systems from field measurements to chamber SOA.

Experimental data and comparison with literature results strongly suggests the use of O/C as an indicator of κ should be more fully evaluated. O/C is a coarse parameter and ignores differences in chemical structure that may affect hygroscopicity.

This work is funded by the EPSRC and the NERC.

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