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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake" *by* E. Mikhailov et al.

Anonymous Referee #2

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The authors introduce a mass based parameterisation of aerosol particle water uptake and demonstrate its applicability to measurements of sodium chloride water uptake and samples from two field measurements sites. Generally speaking the paper is very well written and describes the work concisely but with adequate detail. The science in this paper is relevant to ACP's audience. A number of points in the paper do however require clarification, some more detail and / or context.

General points: Measurements

A number of questions arise after reading the manuscript as to the relevance of the FDHA technique to probing the hygroscopic properties of atmospheric particles, or at

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least the limitations of the technique employed (some of which are mentioned briefly in the manuscript). Each point is covered in more detail below. I would suggest these points could be resolved by adding some more specific details to the paper and extending the discussion sections. Given that the cited article on the FDHA technique is "in press" at the time I am writing this review, more details of the method must be given for this work to stand up in its own right.

How long are the samples given to equilibrate at each relative humidity? In HTDMA studies the "residence time" (nominally the time for which the humidified size sample is exposed an given relative humidity prior to reclassification) can be an important variable in interpreting the results. HTDMA residence times of less than the order of 10's seconds have been shown to produce growth factors in a transient regime for particles composed of secondary organics (Duplissy et. al., 2009, Sjogren et. al, 2007), although artefacts attributable to evaporation have been observed at residence times of around 60 seconds (Gysel et. al., 2007). In EDB studies where it is possible to hold a particle at a given relative humidity for much longer e.g. for hours / days it has been observed that equilibrium is only achieved after much longer time (of the order of minutes and longer) for certain compounds e.g. Chan et. al., 2006. Given these previous findings it is clearly important that the residence time is well defined. Has the rate of water uptake been recorded and if so what does this tell us about the nature of the sample?

The volatility of the sampled particles could be an issue. As the sample is heated and the helium is continuously purging the chamber there is the potential to remove particulate material from the filter. The key question here is if this is a significant process for the experiments in the manuscript. For the sodium chloride it will not be an issue, for the field samples the authors should justify why they believe evaporation will have a negligible effect. (N.B. as an aside: this type of apparatus might be useful for experiments designed to look at hygroscopicity and volatility).

These two previous points lead on to a question on the dry sample treatment. At what

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RH is the sample deemed dry (I assume <1

The authors justify the applicability of their bulk sampling method by noting that the mode of the mass size distributions sampled tend to be above 250 nm (for the AMAZE sample) and hence the Kelvin effect can be ignored. The discussion on the applicability of the bulk sampling method should be expanded to address other factors that may limit the method:

i. The characteristics of the boreal mass size distributions should be mentioned briefly. ii. Ignoring the Kelvin effect will bias the derived hygroscopicity to a lower value. Could the authors calculate how big an effect this is for the typically observed number size distributions e.g. from the difference in the theoretical size resolved vs. bulk water content or some other metric? It might also to useful for future reference if the limits of the applicability of the assumption are tested (theoretically). To be more complete the authors could consider the impact of size dependent composition on the hygroscopicity in more detail (an issue that is mentioned in the manuscript) and the hygroscopic mixing state (is there any information on this available for the ambient samples? Is there an implication for the FDHA technique? Is the FDHA technique sensitive to mixing state and how might an externally mixed particle population manifest itself in the KIM analysis?). iii. The filter sampling duration should be stated in the paper. Values for the mass collected, dry mass and wetted mass of the samples could be given. Any temporal variability in the particle's hygroscopicity cannot be captured using this method. If online hygroscopicity measurements are available these should be discussed in the context of the FDHA measurements i.e. any smearing of the hygroscopicity. Composition measurements could also be used to infer temporal variation in the hygroscopicity to some extent if a more direct measure is not available.

A final point on the measurement technique is how well the integrity of the individual particles is conserved on the filter as it is put through drying and humidifying cycles? If the sample is put through a number of cycles are the results the same? Perhaps microscopy could be used to look at this point.

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General points: Parameterisation

My main query here is on the purpose of the KIM parameterisation. Is it just a method to provide a fit to the measurement data? The authors state it performs well compared to a rigorous thermodynamic approach (for the sodium chloride sample), but is this not simply due to the measurements being consistent with the rigorous thermodynamic model rather than any predictive skill of the model. You would always expect the KIM to perform well provided the measurements agree with the rigorous thermodynamic approach if there are enough inflection points.

Regarding the three defined KIM regimes. I find the generality of these definitions questionable and find the question of their relevance unanswered. Whilst pure substances undergo abrupt phase changes others (multi-component) may be more gradual and the relative humidities at which the phase changes / dissolution etc take place may cover a wide range and be highly variable from mixture to mixture.

Specific points:

P 30879 – line 6 – definition of critical diameter – I don't think it is the measured critical diameter that is, rather it is the smallest dry diameter at which particles activate at a given super-saturation measured (sometimes called the activation diameter). The authors make this clearer later in the manuscript e.g. using the term critical dry diameter in the caption of figure 4. The difference between the conventional definition of critical diameter should be made clear throughout the paper to avoid confusion.

P 30882 – line 18 – idealality – this is an example of where the authors need to be more precise when talking about idealality. I don't believe that anyone is seriously assuming constant activity coefficients of unity. Rather it is the change in non-idealality that is not dealt with rigorously when simply adding up volumes (e.g. when using ZSR type approaches to interpret HTDMA data). With this in mind the statement on line 18 (p 30882) is probably not the most informative way of illustrating the advantage gained from a mass based hygroscopicity metric. Perhaps, calculating the change in kappa

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derived from a volume additive approach vs. a mass based approach for some relevant binary and ternary systems would be more informative (e.g. sodium chloride + water and sodium chloride + water + X).

Minor points

There is some mixing of US and UK English in the manuscript.

P 30879 – line 15 – the use of "etc" here makes the sentence somewhat colloquial. I would suggest making this a full sentence explaining precisely what is meant.

P 30889 – line 13 – Spelling of Setschenow – references I have seen to this author spell it "Setschenov".

P 30901 – lines 6 to 7 - this should be one paragraph

P 30901 – line 14 – "along these lines" sounds this sounds somewhat colloquial. As the final statement in the paper this sentence should be reworded to be neater and more precise.

References

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