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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Water activity and activation diameters from hygroscopicity data – Part I: Theory and application to inorganic salts" *by* S. M. Kreidenweis et al.

S. M. Kreidenweis et al.

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Comment 1 - The authors compare against published assessments of the Sc based on laboratory CCN measurements. Most (all ?) of these are linked to models of supersaturation in the cloud chamber which itself is dependent on a priori knowledge of the Sc-Ddry relationship.

The reviewer is absolutely correct. This point is often not made explicitly in those experimental papers.

There are two consequences: 1) The "uncertainty ranges" emphasized at the end of sections 3.1.2 and 3.2.2 do not include bias coming from the predicted

Sc-Ddry relationship, and 2) the "uncertainty ranges" referred to, may reflect the width of a Gaussian used to fit data consisting of activation fraction and Ddry and as such the uncertainties are more a consequence of broadening in an electrostatic classifier rather than measurement error.

Without knowing the source of uncertainties reported by others, we do not feel justified in commenting on this. We simply report the range as given by previous workers whose results we cite.

Comment 2 - I feel that more attention should be given to the GF measurements. First, I do not think that the introduction is the place to include a description of the apparatus.

If the Editor so instructs, we can move the description into the Methodology section.

Second, how confident are the authors that the particles are equilibrated in the Perma Pure tubing? Have experiments been conducted with differing lengths of Perma Pure tubing, different residence times, etc?

We do not feel a lengthy description of the HTDMA is warranted. We have published a number of papers reporting results with the same apparatus. Prior testing, and the consistency of our data for the salts reported here with expected results, indicate that we can have confidence in our instrument. More importantly, the focus of this paper is intended to be the technique of fitting HTDMA data (whether from our device or others') and using the fits to predict CCN activity.

Comment 3 - Since calculations for bulk systems, for which the Kelvin effect can be ignored, are the basis for you aw-x validation, I feel that the Kelvin correction should be explicit in Equation 17. In contrast, you discuss three different results: 1) the uncorrected activities, 2) the Kelvin-corrected activities assuming pure water surface tension, and 3) the Kelvin corrected activities assuming concentration-dependent solution tensions. I feel that these three options over-

burden both the discussion (bottom of page 296 and the end of section 4 on page 305) and the graphics (Figures 4, 5 and 6). In my opinion the Kelvin effect be accounted for using concentration-dependent solution tensions and presented as such without recourse to the intermediate step of Kelvin-uncorrected activities.

First, equation (17) is the basis of the discussion. Water activity properly appears there. The question then becomes how to relate a measurement - relative humidity - to water activity. Certainly the most correct assumption is to use equations (19) and (20), with data for composition-dependent solution surface tension. However, one of the points of this work is to be able to use the same methodology for compounds for which surface tension is unknown. In such cases, we can imagine 2 limiting assumptions: (1) the surface tension is approximately equal to that for pure water; (2) the surface tension is suppressed due to surface-active compounds, and the Kelvin effect is negligible. We included both assumptions here, even though we know the "right" answer for these compounds, so the reader can get a feel for how much difference it makes in the fits and predictions when we don't know the right answer a priori. So in response to this comment, our position is that we need to consider the limiting cases because of the intended future applications of this technique (which may, or may not, prove to work as hoped - it has not yet been tested for ambient aerosols).

Comment 4 - Section 6 (Summary and Conclusions) left me with several questions. Clearly, the proposed approach does not require dry particle density to predict critical dry size but this result is expressed in the following way, "It also does not require the dry particle density to predict CCN activity". I find this vague and recommend a more direct statement.

We have modified the text to be more clear and direct.

I have the same comment about the usage "dry material". Perhaps "solute mass" is more definitive.

We have made some changes in how we refer to the initial dry particle, also in accord

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with another reviewer's comments.

Finally, the terminology "dry particle weight percent" is confusing because I believe you are referring the composition of the dry particle, not the liquid solution, but you use weight percent to describe the composition of both. My general comment is that the semantics both here (Conclusions) and in the body of the text need to be coordinated.

We are referring to the composition of the solution. We have attempted to make this more clear in our revision.

Comment 5 - I have several comments about the formulism. First, the authors present Equation (2) without any reference or justification. Specifically, I am referring to the use of the partial molar volume in the Kelvin term; what is the basis for this?

We did not think Equation (2) needed a reference as it is the expression of equilibrium. Partial molar volume is the correct term in this equation. It has often appeared incorrectly in the literature (Brechtel and Kreidenweis, 2000a discuss this further, but is not the only reference to point this out).

Second, below Equation (12) we are presented the formulation, and are told that Equation (12) "is the same expression that would be obtained from " in the dilute limit. Are you sure about this?

The reviewer has a point. We should have stated this is true if the mole fraction is computed using the assumption of complete dissociation of the solute. We have removed this statement as it is not central to the discussion anyway.

Third, in Equation (13) the Kelvin term is formulated inversely with temperature but the authors comment above this that "a parameterization for the change in surface tension of water with temperature" is applied. If the temperature parameterization is applied should not both temperature-independent and temperature-

dependent terms be present in the middle equation of Equation (13)?

The reviewer is quite correct. This was left over from an earlier version and should have been changed - it is now corrected. Thank you for noting this.

Fourth, the transition from Equation (17) to Equation (18) is not clear. Does this follow from Equations (14) and (17)? Further, what is the relevance of Equation (18)?

We simply wish to show that equation (17), which is the one we apply to data, asymptotes to the correct limit - that is, as water activity approaches 1, the mole fraction goes to zero. Other functional forms that have been applied to growth factor data do not have this property and so cannot be used to extrapolate to dilute conditions. Of course, this does not guarantee that our fit equation will extrapolate to the correct dilute limit; our discussion in this paper is intended to evaluate this. But without an appropriate functional form, such extrapolation would not even be possible.

Fifth, Equation (25) uses “chi” for a shape factor but “chi” is also common notation for the dynamic shape factor seen in Stoke’s Law for aspherical particles. A dynamic shape factor equal to 1.08 is often referenced as the correct value for cubes leading to a mobility/sphere size ratio of 1.04. Recent work by Martin Geisel (EST) is relevant to your discussion of this issue.

The reviewer is correct. We have modified this discussion and cite the work of Gysel.

Sixth, the comment following Equation (26) would be more accessible if expressed in terms of molality, not weight percentage.

From HTDMA data, we know only volume fraction. It can be converted to weight fraction if density is assumed. To convert to molality or mole fraction, we also need molecular weights. For the salts studied here of course this is easily done. For the more general case of unknown compound(s), this introduces an additional source of error. We show all comparisons on the same basis, which seems sufficient here.

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Comment 6 - Your data is for the RH interval 75 to 90% RH, and only includes a few data values, but you are extrapolating to larger RH to infer Sc. Could the extrapolation introduce significant uncertainty in the Ddry-Sc relationship?

Of course. This is the main point of this paper: is it possible to make a few measurements with the HTDMA, and then extrapolate to dilute conditions meaningfully? This is why we show careful comparisons against expected values for two intensively-studied compounds, and also perform sensitivity studies. We also note that the approach of Rissler et al., which we now cite, uses the same idea: attempt to extrapolate HTMDA data into the dilute range (but using a different approach). In that work, they show that they are able to obtain good closure with CCN measurements made during a field study.

Comment 7 -We are told that the proposed technique avoids the need for knowledge of the molecular weight and degree of dissociation. This is an important advance, if it can be applied to ambient particles. What assumptions will be necessary to accomplish such a characterization, and how will these assumptions limit inferred ambient aerosol Sc values?

We have modified the Conclusions section to make this more clear.

Details: Why Dp, and not D with appropriate subscripting to indicate "wet", "dry", "critical" etc?

We can change the notation if the Editor feels this is not clear.

At the bottom of page 306 there is a “Dcrits”

We have reworded this.

You are plotting continuous functions, but I see kinks and wobbles (i.e. Figures 2, 3, 5, 7 and 8)

This is due to the number of computed values and the software idiosyncracies. We don't believe the plots will be misinterpreted.

Figures 4 and 6 are difficult to interpret - where is the "AIM" line in Figure 6, where is "Low" in Figure 4b, how to distinguish between Debye-Huckel and "Uncorrected" in Figures 4 and 6? Since you are plotting continuous functions should not the use of "data points" be avoided?

Some of our results are so close they are hard to differentiate. We have tried our best to make the figure understandable given this. We do not see any occurrences of the "data points" terminology.

The usage "stable cloud droplets" is contradictory in the sense that such particles are experiencing changing size with time, as opposed to the "stable" particles whose size constrained by the Kohler curve and ambient RH.

This is a good point. We have changed this.

Why not MKS dimensions for surface tension, etc.?

We adopted commonly-used units, but as we indicated in the reply to another reviewer who also mentioned this, we can change this in the final version if the Editor so indicates.

Is the last paragraph of section 2 relevant to the NaCl and AS covered in this paper?

No. NaCl and AS do not present such challenges, fortunately. However, we encountered issues with evaporation for organic species (to be reported in Part II).

Perhaps "metastable" for what you refer to as "crystallization (hysteresis)"?

"Metastable" is appropriate for this branch of the hysteresis curve.

Section 4.2 should be revised. Specifically, the last part of the first sentence of this sec- tion ("essentially extrapolates the volume ratios to dilute solutions) and

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the following sentence ("Thus, the Kohler curves) are a perhaps too complex.

We have tried to make this more clear in the revision.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 287, 2005.

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