Atmos. Chem. Phys. Discuss., 6, S3423–S3428, 2006
www.atmos-chem-phys-discuss.net/6/S3423/2006/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Prompt deliquescence and efflorescence of aerosol nanoparticles" *by* G. Biskos et al.

G. Biskos et al.

Received and published: 29 September 2006

We appreciate the reviewer's effort to improve the quality of our manuscript and thank him/her for providing very useful comments. Below are detailed responses to each of his/her comments.

1. The most general of these is the size calibration of the two DMAs and the RH calibrations. These are central to the success of the experiments and as far as I can tell have been performed very thoroughly. The data do appear to be of very high quality and the authors should be congratulated. However, the only place the accuracy with which the DMA sizing is carried out and the RH repeatability is mentioned is in the final summary comments. Though this may have been stated in the authors' earlier paper on NaCl it should be included here. The authors should detail how the DMAs were size calibrated and the second DMA

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

referenced to the first. For what sizes of particle were these characterisations conducted? Does this vary with time? How repeatable were the measurements? The repeatability of the RH is mentioned but also not discussed. How was the primary RH calibrated, with what accuracy and how were all other RH measurements referenced to it? How often was the calibration repeated and how repeatable were the measurements? The day-to-day variability is mentioned but it is not discussed. What effect do the size and RH uncertainties have on your measurements?

We thank the reviewer for addressing the important issue of the calibration of the system. In the updated manuscript we have included a new paragraph in the experimental section that gives the important details of our calibration:

"*Accuracy and precision of the particle-sizing and relative humidity measurements were as follows. Regarding the accuracy of particle sizing (Kinney et al. 1991), the sheath and aerosol flows were calibrated to within 1% using a Gilibrator bubble flow meter, and the voltage of the central rod was measured to within 0.1% (up to 500 V). These uncertainties, combined with the uncertainties in the geometric dimensions of the DMA, propagated as an uncertainty of 2.5% in the classified particle diameter and, therefore, in the measured growth factor. (An alternative procedure using monodisperse polystyrene latex (PSL) spheres led to an uncertainty of 3%.) The precision of the TnDMA measurements of particle size was within 2% based upon replicate measurements, and did not change throughout the course of the experiments. As an experimental check of these accuracies and precisions, the sizing agreement of the two DMAs was within 2.5% from 10 to 100 nm using NaCl particles generated by a vaporization-condensation method and analyzed below 5% RH (cf. Biskos et al. 2006a). The two RH sensors (Omega Model HX93AV) were regularly calibrated against a chilled mirror hygrometer (Kahn Instruments Inc. Model S4000, with up to ś 2% uncertainty at 293 K) from 5 to 95% RH.*"

2. Introduction: pg 7054 line 9, 'E? .refers to continuous growth' the use of the

ACPD

6, S3423–S3428, 2006

word growth when discussing equilibrium behaviour is a little misleading.

To avoid confusion, the above mentioned sentence has been modified from:

"*Prompt deliquescence corresponds to a discontinuous increase of particle diameter during the phase transition that accompanies increasing RH, whereas nonprompt deliquescence refers to continuous growth.*"

to:

"*In an operational definition, prompt and nonprompt deliquescence respectively correspond to discontinuous and continuous increases of particle diameter during the phase transition that accompanies increasing RH.*"

3. Page 7056: lines 19-20 This means that the transfer function and absolute sizing of the DMAs will change. Does this matter? Furthermore, in earlier lines it is clear that the flow through DMA2 is actively controlled via a feedback loop to maintain the total flow. This is not done in DMA1, does volumetric flow variation in this DMA affect the results.

The fact that the settings of the two DMAs, and therefore their transfer functions, are not matched would not affect the hygroscopic growth results. In fact, the higher the sheath-to-aerosol flow ratio, the narrower the distribution of the monodisperse particles, resulting in higher accuracy of the measured growth factors.

4. Pg 7057 line 5: It is worth stressing that these particles are an external mixture of two populations.

According to the reviewer's comment, the above mentioned sentence has been modified to:

"*In some measurements, two separate peaks, which correspond to externally mixed populations of aqueous and solid particles, are observed for RHa close to DRH.*"

5. Pg 7057-8 A discussion of the numerical modelling would be very useful. It

ACPD

6, S3423–S3428, 2006

may detract from this paper but I would like to see such calculations somewhere, possibly in a technical note.

Following the reviewers suggestion, we provide numerical calculations of the RH profiles within DMA-2 for typical operating conditions of the nano-DMA as a supplement to the paper (see Figure S2). We avoid including these results in the main manuscript because doing so would depart from the main point of the manuscript.

6. Pg 7058 line 10: The authors state that this observation rules out their earlier hypothesis. However, this could be a cause if the solutions used in the previous wok were not as pure as those used in this study.

This is true. We have replaced the sentence:

"*This explanation rules out our earlier hypothesis (Biskos et al. 2006a,b) that impurities concentrated by atomization could explain literature reports of nonprompt deliquescence of nanoparticles.*"

with:

"*This explanation makes unnecessary our earlier hypothesis (Biskos et al. 2006a,b) of impurities concentrated by atomization as the explanation for literature reports of nonprompt deliquescence of nanoparticles.*"

7. Pg 7059 line 12-13: Do the relative populations of the two fitted functions at the different RHs tell you something about the probability of crystallisation at different RH assuming that it is not due to the RH gradients mentioned.

In theory, the existence of two populations (i.e., dry and aqueous particles) at RH values close to the ERH can be an indicator of stochastic crystallization. In practice, the two populations can be the result of slightly non uniform conditions in the HTDMA system. For example, particles that have traveled through the nafion tube closer to the walls would experience a lower RH compared to those that have traveling in the centerline. With the system described in this paper it wouldn't be possible to tell whether the

ACPD
6, S3423–S3428, 2006

EGU

two modes in crystallization are due to a natural phenomenon (stochastic nucleation) or due to an experimental artifact (slightly non uniform RH conditions in the conditioner or the DMA).

8. Pg 7060 lines 7-9 Are the flow rates available for the DMAs in the Hameri study? This would help to confirm your hypothesis.

Yes, the flow rates and the basic design parameter of DMAs used by Hämeri et al 2000 are listed in their paper. Reference to that Table is made in the updated manuscript:

"*Two designs of Hauke-type DMA's (namely, one for particles smaller than 30 nm and another for those larger than 30 nm) are employed by Hämeri et al. (2000) (cf. Table 1 therein).*"

9. Pg 7060 line 24: 'E? appears to be a systematic bias of 1-2%..' in what? , you need to say. Taking as an example, there is a measured GF of 1.2 at 80% for 8 nm particles and a modelled prediction of 1.25 at the same conditions. This would give rise to wet particles of 9.6 and 10 nm diameter respectively. Can the DMAs resolve these difference, they are less than half the FWHM of the transfer function for a 10:1 flow. Are these statistically significant? These discussions need the measurement accuracies reporting as requested above.

We thank the reviewer for noting this mistake. In fact, the 1-2% bias refers to the comparison between the diameter set by DMA-1 (by adjusting the voltage and the flows) and the measured diameter of the dry particles (i.e., at RH values below DRH). This 1-2% diameter depression (which is highlighted in Fig.6 and the associated discussion in the manuscript) can explain the systematic bias of 1 to 4% between the predicted and the measured growth factors. Given that the uncertainty of the TDMA in determining growth factors is of the order of 2%, this systematic bias could be resolved with the current system. Differences of up to 4% in the growth factor may not be distinguished as two separate modes for typical operating conditions of the DMA (since they would result differences in mobility diameter that are less the the FWHM of the transfer

ACPD
6, S3423–S3428, 2006

EGU

function), but should be evident when estimating the mean mobility diameter from the measured monodisperse size distributions. We have modified the above mentioned sentence to clarify this point as follows:

"*Even so, there appears to be a systematic bias of 1 to 4% between the model predictions of the growth factor and the measurements, with slightly greater bias for decreasing particle size.*"

10. Pg The prediction of size dependent deliquescence RH for ultrafine (NH4)2SO4 particles by Ming and Russell and Topping et al is not mentioned anywhere in the text. This is an important confirmatory result of that presented by Hameri et al. The previous work should be included in the introduction and the authors' contribution highlighted in the main results section as well as the result summarised at the end.

The references to the Russel and Ming as well as the Topping et al papers are already included in the introduction and the conclusions of the manuscript.

11. Figure 1: The sheath air is left without a grey coloring. This is a minor point but it is confusing when tracing the diagrams given the comments about coloring at the bottom of the figure caption.

We appreciate the reviewer's comment. The grey color in the figure is used to distinguish the aerosol (RH-controlled flow) from the purge flows in the nafion tubes (RH-conditioning flows). The color of the sheath flow in DMA-2 is white because this is an RH-controlled. We have updated the revised manuscript accordingly to highlight this distinction.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7051, 2006.