Atmos. Chem. Phys. Discuss., 8, S2679–S2687, 2008
www.atmos-chem-phys-discuss.net/8/S2679/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "CCN activation experiments with adipic acid: effect of particle phase and adipic acid coatings on soluble and insoluble particles" *by* S. S. Hings et al.

S. S. Hings et al.

Received and published: 14 May 2008

Anonymous Referee 2

We thank the anonymous referee for their careful reading of the manuscript and comments. The referee's comments are indicated in **bold**.

Abstract

1. Comment: Page 4440 Lines 11 through 14 Clarify whether lines 11 through 14 in the abstract are results related to the 'pure' adipic acid studies or the adipic acid 'coating' studies. It is a bit confusing, since these statements immediately follow a statement about the coatings experiments.

Response: This and other issues in the Abstract have been clarified by re-writing the Abstract.

Experimental

2. Comment: Page 4446 Lines 9 through 16 The generation of the 'wet' adipic acid particles is unclear. Is the CCNC used as part of the particle generation system? How do you differentiate the particle generation process from the activation process and measurement? Why was this method chosen over a humidifying system? When the dry adipic acid particles take up water to become 'wet' adipic acid particles, are there changes in diameters? If so, how did you take that into account?

Response: As stated in Section 3.3 of the text, we generate the 'wet' adipic particles by coating a small ammonium sulfate core with a mass fraction >85% of adipic acid via vapor deposition. The diameter of this dry, mixed particle is taken as the initial particle diameter. Again, as stated in the text, we postulate that in the CCNC apparatus, the water vapor encounters the ammonium sulfate core (by diffusion) and produces a wet adipic acid particle. An added discussion in the Theory section (Section 2.5) has been added to provide a validation for this method of generating 'wet' adipic acid particles. In brief, the Sc of these sulfate-adipic acid particles (when the mass fraction of adipic acid >85%) is within 10% of the Sc of a pure wet adipic acid particle of equivalent diameter. This theoretical calculation is confirmed experimentally in Section 4.2.4.

Results and Discussion

3. Comment: Page 4448 Line 6 Define dva and dm.

Response: This is now done in the new Section 2.6.

4. Comment: Page 4450 For all Results and Discussion sections In the text, it might help to include a quick summary of your results, i.e. by giving a range of measured experimental values for the reader.

ACPD

8, S2679–S2687, 2008

Interactive Comment

Response: Table 1 has been added to Section 3.3 and shows all the particle types studied, their method of generation, and their diameter range. Figures 7, 9, 10, and 11 are the clearest summary of the experimental results.

5. Comment: Line 15 Could you make the following sentence more specific? "The data are the results for each point of at least 3 independent measurements performed over a period of 3 days." What does "results" mean? Is it an average of the data from three different experiments? Also, what does "each point" mean? Does "each point" refer to each diameter or each supersaturation?

Response: Each point refers to each dry particle diameter produced. This has been clarified by stating: "The critical supersaturation values in the figure are the average of at least three measurements for each dry particle diameter (the standard deviation is indicated by the error bars). Measurements were conducted over a period of several days to ensure reproducibility."

6. Comment: Page 4451 Lines 2 through 11 Could you comment on the relevance of these particle sizes in the atmosphere? Are they realistic sizes for particles found in the atmosphere? If so, under what conditions? Under what conditions would other sizes be more prevalent?

Response: As shown, the adipic acid particle sizes studied ranged from dm 70 -150 nm for 'wet' particles. The adipic acid particle sizes studied for dry particles ranged from dm 88 -250 nm. Particles in these diameter ranges activate at supersaturations typically encountered in the atmosphere.

7. Comment: Can you make the following sentence more specific and/or explain this limitation in the experimental discussion? "(This size was the smallest for which we were able to obtain accurate results.)" What is meant by "accurate results" Do you mean your results were inconsistent at smaller sizes? Why? Could the particles be less spherical at smaller sizes than at larger sizes or could the particle morphology be less consistent at small sizes, as a result of the particle

ACPD

8, S2679–S2687, 2008

generation method?

Response: The issues stated above were clarified by stating in the revised text: "We could not obtain data for particles smaller than dm = 88 nm because to produce such small particles with our homogenous nucleation apparatus, we had to reduce the adipic acid vapor pressure to a point where the number of particles produced was too small to perform the CCN experiments."

8. Comment: You may be omitting very important information by ignoring or throwing out the experiments that gave less "accurate results". Those experiments might give some insight into the activation process of adipic acid, if you dig deeper and find out why those experiments were "inaccurate" or "inconsistent." It seems that what you have observed at these smaller sizes is what has been observed in past experiments.

Response: As the above response shows, we did not ignore or throw out experimental data. Rather, we could not obtain an adequate number of particles to perform the CCN experiments.

9. Comment: Lines 12 through 17 (last paragraph) What mechanisms or chemical characteristics would result in non-spherical particle generation by homogeneous nucleation?

Response: Homogenous nucleation produces solid adipic acid particles. We may expect such particles to be compact. As we state, within estimated accuracy, the particles appear to be spherical (i.e. dynamic shape factors < 1.2). The homogenous nucleation process is essentially a crystallization process where adipic acid self-aggregates. One can imagine such self-aggregation producing spatially asymmetric configurations, but we have no indication that such is the case.

10. Comment: Why is the uncertainty in dva measurements as high as $\pm$ 15%? How was this uncertainty determined? Is the instrument calibrated (is dva mea-

ACPD

8, S2679–S2687, 2008

Interactive Comment

sured by the AMS or DMA)? I would suggest adding some instrument calibration discussion in the experimental discussion rather than the appendix, so that these issues are discussed up front and not as side bars.

Response: The sources of the dm and dva values are explicitly described in the text by stating: "The mobility diameter (dm) is measured by the DMA apparatus and the vacuum aerodynamic diameter (dva) is measured by the AMS." The 15% uncertainty in the dva measurement is due to the uncertainty in measuring t0 (the time at which an aerosol particle passes through the chopper in the AMS). This starting point is used to measure the particle velocity, which, in turn, is used to calculate dva.

11. Comment: You use the bulk density for the calculation of the dynamic shape factors. Could you comment on whether this is a good assumption for particles formed by homogeneous nucleation? How would your calculations change if you used a particle density instead of a bulk density?

Response: This issue is addressed to the best of our ability by the following statement which is now included in the text: "The use of bulk density in Eq. (5) assumes that the particle does not contain internal voids. This seems to be a reasonable assumption of particles that are formed by vapor condensation."

12. Comment: Page 4453 Section 3.2.3 Would you expect the wet adipic acid particles to be spherical (because they have taken up water)?

Response: The 'wet' adipic acid particles described in this section are created by dry vapor deposition of adipic acid on an ammonium sulfate core. Since atomized ammonium sulfate particles are close to spherical, it is possible that this spherical 'seed' will promote spherical deposition of adipic acid onto the surface. Since measurements for homogenously nucleated adipic acid are consistent with a spherical configuration, it is likely that dry vapor deposition will also produce spherical particles on a spherical 'seed' of ammonium sulfate.

ACPD

8, S2679–S2687, 2008

Interactive Comment

13. Comment: In some studies, it has been found that even a small amount of ammonium sulfate can enhance CCN activation of organic compounds. Here, you state that activation is not affected by the presence of ammonium sulfate if it is present in a mass percentage less than 15%, based on calculations in Appendix A1. Is this consistent with past experimental studies? If not, could you discuss why? Could the presence of water have an effect on the CCN activation of these particles?

Response: As stated in response to Comment 2, both theory and experimental results show that the critical supersaturation of the sulfate-adipic acid particles is within 10% of the Sc of a pure wet adipic acid particle of equivalent diameter when the mass fraction of adipic acid >85%. That is to say that a small amount (<15% by mass) of ammonium sulfate in the adipic acid enhances the CCN activation by <10% compared with theoretical predictions from the Koehler equation. It is worth noting, however, that this small amount of ammonium sulfate does in fact affect the adipic acid particles significantly. Without the ammonium sulfate, dry adipic acid particles less than 150 nm mobility diameter do NOT follow the Köhler predictions, but rather a deliquescence curve with much higher Sc than the predicted Köhler values. Thus, small amounts of soluble inorganic material do affect slightly soluble organic particles (i.e. the organic particles pick up water due to the inorganic contaminant and act like metastable organic solution droplets rather than dry organic particles). However, the observed effect results in a measured Sc (i.e. critical supersaturation) that is very close to the predicted Köhler values for adipic acid (Köhler theory does NOT account for cases, such as adipic acid, where the deliquescence transition is greater than 100% RH).

14. Comment: Page 4454 Section 3.3 Could you discuss in a bit more detail the difference in the 'wet' adipic acid studies and the coating studies? Is it simply the amount of ammonium sulfate present and/or adipic acid coating thickness?

Response: In the coating studies shown in Figure 10, it is observed that the CCN activity of the sulfate - adipic acid particle depends on the mass fraction of adipic acid.

ACPD

8, S2679–S2687, 2008

Interactive Comment

As the mass fraction increases, the CCN activity approaches that of pure adipic acid as predicted by Köhler theory. The experimental points in Figure 9 are the points shown in Figure 10 where the mass fraction of adipic acid >85%.

15. Comment: It might be helpful to discuss how dTc and Sc are related, as well as instrument calibrations, in the experimental section instead of in an appendix.

Response: The relationship between dTc and Sc is included in the Experimental Section 3.4. The operation of the CCNC apparatus has been previously described in the literature (Roberts and Nenes 2005). Since it is not part of our experimental work, we prefer to give an overview of the instrument calibration in the Appendix where it does not divert attention from the main points of our work.

Appendix A2

16. Comment: Be specific and differentiate between calculated Sc and experimentally determined Sc. For example, the point of this section may be misunderstood when the statement "Sdel<Sc" is made. Earlier in the paper, Sc is defined as the experimentally determined critical supersaturation.

Response: In the revised manuscript, we have moved the key parts of the Theory Section into the main portion of the text as Section 2. The theory section has now been changed to clarify the difference between calculated Sc and experimentally measured Sc. The former is designated Sc,calculated.

Technical Corrections

17. Comment: Page 4440 Line 26 I suggest adding the word ’is’ between the words ’but’ and ’much.’

Response: Done.

18. Comment: Page 4441 Line 3 I suggest adding the word ’atmospheric’ between the words ’of’ and ’aerosol.’ Line 13 I suggest adding some reference to

ACPD

8, S2679–S2687, 2008

Interactive Comment

the fact that these compounds influence CCN activity when they are presence in atmospheric aerosol particles (not just gas phase).

Response: These sentences have revised in updated manuscript.

19. Comment: Page 4442 Line 22 The Rissman et al. (2007) citation should be moved to be immediately after the word "preparation"

Response: Done.

20. Comment: Page 4443 Line 1 The word 'then' should be replaced with the word 'than.'

Response: Done.

21. Comment: Page 4444 Line 17 I suggest placing parentheses (or commas) around 'S' and 'dT.'

Response: Done.

22. Comment: Page 4449 Lines 5 through 19 I suggest moving item (c) up in the paragraph, so that it is included right after item (b). Then, go into the discussion of standard Köhler theory, etc. It's confusing to have item (c) pop up in the middle of the paragraph. In previous lists, similar to this one, numbers were used instead of letters for the listings. I suggest using consistent formatting throughout. Also, check punctuation on all such lists.

Response: The paragraph has been re-written to be clearer. The consistency and punctuation of lists throughout the paper has been checked and corrected if needed.

23. Comment: Page 4452 Line 1 Should this section be numbered?

Response: Yes. It has been numbered.

Line 21 The word 'atomizing-generated' should be 'atomization-generated.'

Response: Done.

ACPD
8, S2679–S2687, 2008

24. Comment: Page 4456 Line 1 I suggest adding the word ’an’ between the words ’with’ and ’effective.’

Response: Done.

25. Comment: Use ACP guidelines for reference format in the figure annotations (Figures 1 and 5). Also, italicize symbols in the figure annotations and axes labels (Figures 1, 3-8, A1-4,and B1-2). "

Response: Done.

Figure 7 ’Wettable’ is misspelled in the annotation (’wettalble’).

Response: Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4439, 2008.

ACPD

8, S2679–S2687, 2008

Interactive Comment