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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.

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Anonymous Referee 1

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: p. 4440; l. 14-19: Do both sentences refer to literature studies? It reads as if the scatter mostly occurs for particles < 150 nm.**

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

Introduction

2. **Comment: 1st and 2nd paragraph: I suggest to carefully reword these very general statements. As they are, they give a misleading picture of aerosol effects on climate**

Response: The sentences describing the aerosol effects on climate have been rewritten so that they are less ambiguous.

a. **Comment: p. 4440; l. 25/26: this sentence implies that aerosols may enhance the greenhouse effect and not counteract it. Clarify that the aerosol effect has the opposite sign in terms of radiation effects.**

Response: This sentence has been clarified.

b. **Comment: p. 4441; l.4: There are many studies that show that aerosol composition is not the most influential parameter in determining their (direct and indirect) effects on radiation.**

Response: We are aware of the studies that show a relative lack of sensitivity of climate effects on aerosol composition (although this lack of sensitivity may be a regional phenomenon). The sentence has been rewritten as:
"The high uncertainties are due to the currently inadequate representation of the complex interactions of aerosols with climate due to their intrinsically complex composition, morphology, and size distributions."

c. **Comment: p. 4441; l. 9-11: Dynamic processes (meteorology), and not aerosol type and composition, determine type of clouds and extent of cloud cover.**

Response: The sentence has been removed and the second paragraph of the introduction has been rewritten as:
"Atmospheric aerosol particles influence global climate by direct and indirect processes. The direct process of aerosol climate-forcing involves the absorption, reflection, and scattering of incoming solar radiation by atmospheric aerosols. The indirect

ACPD

8, S2669–S2678, 2008

Interactive Comment

process involves atmospheric particles serving as cloud condensation nuclei (CCN) on which water vapor condenses to form cloud droplets. CCN activity depends on the shape, size, structure, and composition of the aerosol particles. An aspect of CCN activity is the subject of this work."

3. **Comment: p. 4442: Since you refer so many times to the Standard Koehler theory, you should move Appendix A into the main text. In this way, you will be able to shorten the text and avoid repetition. E.g., in l. 11, it would be easier to follow if you mention in the main text where the surface tension data were published.**

Response: As suggested by the referee, the relevant parts of the theory section of the Appendix have been moved to what is now Section 2 of this paper.

Experimental

4. **Comment: p. 4442, l. 28: Specify "wider range of conditions." Wider range of particles sizes, RH, mass fractions,...?**

Response: We have modified the text to read:
"Toward these ends, we studied the CCN activity of adipic acid aerosol over a significantly wider range of conditions (particle diameter, particle phase, and particle coatings) than has been previously encompassed in any single study."

5. **Comment: p. 4444, l. 4: I believe that the accuracy is 2% of (e.g.) 3.2% (?). Clarify.**

Response: This statement has been modified to read:
"The instrument is capable of generating nearly constant values of supersaturation between 0.07% and 3.7%. The stated accuracy of these supersaturation values is $\pm$ 2%."

6. **Comment: p. 4445, l.1-8: In my opinion, this list of the experiments is redundant since you describe them in the following section in detail anyway.**

ACPD

8, S2669–S2678, 2008

Response: We understand the referee's perspective; still, we feel that this short list provides a clarifying entry into the next section. Accordingly, we have kept this list in the text.

7. **Comment: p. 4445, l. 10: The meaning of this sentence is not clear. Remove.**

Response: The sentence has been clarified by re-writing it as follows:
"The methods of generating particles for the 6 studies listed in Section 3.2 are described below."

8. **Comment: p. 4446, l. 16: In what sense can these particles be considered as single-component particles? Is their behavior the same as pure adipic acid (Sc, crit. diameter) or do they just show a uniform behavior, i.e. no stepwise dissolution of the less soluble compound?**

Response: An additional 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.

9. **Comment: p. 4447, l. 20: Figure 3 could be removed or at least moved into the Appendix. Just a statement that the calibration of the instrument showed similar results compared to literature would seems sufficient here.**

Response: It should be noted that this is not a calibration figure. Rather, this figure illustrates the procedure to determine the critical supersaturation for any species (sulfate or adipic acid or anything else). This point was not made clearly in the text and has now been clarified.

Results and Discussion

10. **Comment: 1st paragraph: The whole paragraph is just a copy of previous text; refer to experiments 1-6 (without repeating the list again). Move the impor-**

ACPD

8, S2669–S2678, 2008

tant parts of Appendix A here and discuss them in view of your results within the main text.

Response: The paragraph has been rewritten. The key parts of Appendix A have been moved to Section 2 in accord with the referee's suggestion. See response to Comment 8.

11. **Comment: p. 4449; l. 16/17: How do you quantify the effect on CCN activity? What do the 10% refer to? Supersaturation or critical size,...?**

Response: As stated previously, we have moved the theoretical discussion referred to in this comment into a new Section 2. Section 2 clarifies the 10% issue as is discussed in Comment 8.

12. **Comment: p. 4450; l. 3: Again, what does wide range refer to?**

Response: This issue has been clarified by re-writing the first sentence as:
"In this set of experiments, we conducted CCN activation studies with adipic acid particles generated by atomization of adipic acid solutions over a range of particle diameters (dm) from 30 nm to 300nm."

13. **Comment: p. 4450; l. 22/23: Is the surface tension for the particles really calculated? It seems that the upper value is the one for water. Is the lower value the one you obtain for concentrated adipic acid solutions? How likely is it that a particle is composed of such a solution close to its activation?**

Response: This issue is discussed in the Theory Section (2.2). The surface tension for adipic acid particles of diameter greater than 40 nm is calculated to be in the range between 0.060 J/m2 and 0.072 J/m2 at activation using the Szyszkowski-Langmuir equation (Henning et al. 2005). The lower surface tension value corresponds to the most concentrated adipic acid solution at CCN activation (for a 40nm particle).

14. **Comment: p. 4452; l. 9: Replace 'the'; by 'that' (...possible factors that may affect...)**

ACPD

8, S2669–S2678, 2008

Response: Correction made.

15. **Comment: p. 4452; l. 16-20: What are likely shape factors for adipic acid? What is the extent to which a "likely shape factor" could move the lines in Figure 5.**

Response: The shape factor generated by homogenous nucleation was measured in this study to be less than 1.2 (dynamic shape factor chi = 1 for spheres). As discussed in the text, due to experimental limitations, we were not able to obtain reliable shape factors for adipic acid generated by atomization. In the text, dealing with this issue, we suggest factors that may displace the Sc lines in the figure.

16. **Comment: p. 4453; l. 13: What do you mean by "eliminate impurities"?**

Response: As discussed in the text, our experiments indicate that adipic acid particles generated by atomization of solutions are contaminated, most likely by ammonia. Generating adipic acid via evaporation/condensation of the substance is not prone to the impurities that may be associated with wet atomization from an aqueous solution (Dinar et al., 2007). This issue has been clarified in the text.

17. **Comment: p. 4453; l.13-17: Can you combine these sentences?**

Response: This has been done.

18. **Comment: p. 4453; l. 18: Clarify what you mean by "the CCN activity is determined within 10% by adipic acid."**

Response: This has been clarified in Comment 8.

19. **Comment: p. 4454; l. 26: Add ’nm’ (181 nm).**

Response: Done.

20. **Comment: p. 4455; l. 18 ff. The explanation of why the large soot particles behave so differently as compared to the smaller ones does not seem really**

ACPD

8, S2669–S2678, 2008

Interactive Comment

satisfying to me. Is there any experimental evidence (from other studies and/or systems) that indeed the coating is different on small vs. large particles? I do not understand the statement: the Sc measurements for the larger soot cores are displaced to the right. It seems to me in Fig. 8 that they are not displaced to the right but rather to a higher supersaturation. Thus, they activate at an even higher supersaturation than a wettable particle.

Response: Responding first to the second part of this comment, we note that the referee is correct; the data for the larger soot cores are displaced towards higher Sc. This is a more appropriate way of describing the displacement than was done in our previous text. The displacement is now described accordingly. Returning to the referee's first point in the comment; we do not have a verifiable explanation for the observation related to the CCN activation of large soot cores. Our explanation in the text is a speculation. In the revised manuscript, we make this clearer by stating at the beginning:
"At this time we do not have a verifiable explanation for this observation. We suggest a possible reason for this difference between the CCN behavior of the larger and smaller coated soot particles."

Conclusions:

21. **Comment: p. 4456; l. 14: This bullet point should be modified. According to your study, at least some of the scatter can be explained based on the generation of the particles.**

Response: The bullet point has been modified to read:
"2. A solvent-independent method for generating pure organic particles (via homogeneous nucleation) was used for this study and found to provide results that were more reproducible than those obtained in our experiments as well as previously published experiments with particles produced by atomizing solutions. The homogeneously nucleated particles were measured to be nearly spherical (chi = 1.2). These results suggest that the observed scatter in the published literature for the CCN activity of

ACPD

8, S2669–S2678, 2008

adipic acid particles may be related to either the impurities in the solvents used or the inadvertent formation of non-spherical particles."

22. **Comment: p. 4456; l. 24/25: Clarify what is meant by an effective diameter that is smaller than particle diameter.**

Response: The bullet point has been re-written to read:
"4. An adipic acid coating on hydrophobic CCN inactive soot particle yields a CCN active particle at atmospherically relevant supersaturations. For relatively small soot cores (dcore = 88 nm and 102 nm), the CCN activity of the coated particles approaches the deliquescence line of adipic acid. This suggests that for coated soot particles in this range of diameters, the total size of the particle determines CCN activation and the soot core acts as a scaffold for the deposition of adipic acid vapor. It appears that the CCN activation of larger coated soot cores occurs at higher supersaturations than is predicted by the deliquescence curve. It is hypothesized that larger soot particles are only partially coated with adipic acid, causing the mixed particles to be chemical composition dependent, and not total particle size dependent as observed for small soot core sizes."

Appendix A

23. **Comment: You can shorten major parts of this text and should incorporate it in the main text in order to have a better flow of the whole discussion**

Response: We have responded to this comment, as discussed in the response to Comment 8.

24. **Comment: p. 4459; l. 15: Why is this approximation only valid for particles > 30 nm?**

Response: The simplified expression is a result of truncating the expansion of the Taylor series for the exponential. As stated by Laaksonen et al. (1998), this approximation provides reasonable accuracy for particles >30 nm.

ACPD

8, S2669–S2678, 2008

Interactive Comment

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25. **Comment: p. 4459; l. 20: On p. 4457, you define Kelvin and Raoult term as expressions that include dp.**

Response: The referee is correct; we were inconsistent in referring to the Kelvin and Raoult terms. This was corrected by stating:
"In Eq. (A1), the aw/dp term represents the Kelvin effect while the bs/dp3 term represents the Raoult effect."

26. **Comment: p. 4460; l. 11-24: How relevant is this discussion for the experiments performed here? What case does the adipic acid/ammonium sulfate mixture represent?**

Response: It is relevant in the sense that modified Köhler theory was developed and used in the literature to describe the CCN activation of internally mixed particles. Since we investigate the CCN activity of adipic acid/ammonium sulfate, we believed that we should address modified Köhler theory. For the particle diameters and compositions studied, modified Köhler theory predicts the same Sc value as standard Köhler theory. To address this comment, we have decided to remove the section that discusses modified Köhler theory in detail and instead replace it with a paragraph that states that modified Köhler theory predicts the same Sc value as standard Köhler theory.

27. **Comment: p. 4461; l. 17: This equation is just a simplified form of equation A1, i.e. it includes the assumption that the mole ratio of water is 1.**

Response: The two equations are not quite the same. The surface tensions used are different. This is clarified in the text by stating:
"We note that the surface tension used in Eq. (4) is that of a saturated solution whereas in Eq. (1), the solution need not be saturated."

Figures

28. **Comment: Figure 5: Is this figure necessary? It does not include any additional result or information as compared to Figures 1 and 4.**

ACPD
8, S2669–S2678, 2008

Response: This is the one figure that displays the results obtained in our study together with the results obtained from other studies. For this reason, we believe the figure needs to be included in the manuscript.

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

ACPD

8, S2669–S2678, 2008

Interactive Comment