Atmos. Chem. Phys. Discuss., 6, S7208–S7222, 2007
www.atmos-chem-phys-discuss.net/6/S7208/2007/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Cloud condensation nucleus (CCN) behavior of organic aerosol particles generated by atomization of water and methanol solutions" *by* T. A. Rissman et al.

T. A. Rissman et al.

Received and published: 13 March 2007

Response to Anonymous Referee and Short Comments on Manuscript acpd-6-13251

The authors greatly appreciate the comments of the reviewers and feel that their insights have been very valuable and have enhanced the paper. We present our paper and experimental observations to highlight the discrepancies in the different studies and bring about discussion about sources of discrepancies that result from different experimental designs (particle formation under different conditions, etc). Unfortunately, due to time constraints, we are only able to point out these issues and hope that future studies will be more aware of these issues and will report their experimental conditions and setup more clearly. We are pleased that our paper sparked so much interest

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

and has lead to many ideas for future studies, including those that the reviewers have suggested.

While responding to these and other comments, we have determined that we are unable to "correct" the experimental data for malonic and glutaric acid and are unable to present the CCN results for these compounds. The discussion for these two compounds remains in the paper, but we no longer present activation diameters for these two compounds because we do not feel that we are able to determine them with sufficient scientific certainty.

Author Responses to Referee Comments "Review" from Anonymous Referee #1 Received and published: 25 January 2007

1) Methanol was chosen as an atomization solvent because it is more volatile than water and for organic solubility considerations. Past CCN studies have indicated that organic particles formed by atomization from aqueous solutions can be difficult to dry completely, resulting in particles that may contain residual water. For this reason, we wanted to look at particles formed from atomization from a solvent other than water. Methanol was chosen mainly because it is more volatile than water and would be expected to evaporate more easily and more quickly from droplets formed from atomization. We considered looking at other solvents, as well, but the scope of the paper became too large, so we focused on the differences between particles formed from atomization from water and methanol solutions.

We clarified our choice of methanol in Section 3.5.1, which begins on page 13264, by changing paragraph 2 of that section to read:

"Organic particles were generated from both methanol and water solutions for the experiments presented here. The hypothesis is that particles created from atomization of methanol solutions are easier to dry because methanol is more volatile than water and, therefore, would evaporate from the atomized droplets more easily and more quickly. Nevertheless, residual methanol left in the particles after drying could also affect apparent CCN activation. If a compound is more soluble in methanol than water, the presence of a small amount of methanol could facilitate the dissolution of the particle, which would facilitate condensation of water. A heater was placed after the atomizer for some experiments in an attempt to facilitate the evaporation of the atomization solvents from the particles. The heater was controlled at 40°C when used, but the sample stream cooled to 25°C before entering the CCN instrument."

2) We do believe that the morphological characteristics of the solid particles formed from evaporation of atomized droplets (or from any process for that matter) could affect the CCN measurements. Hori et al. (2003) addressed this:

"In addition, morphology of the solid particles might be another important factor to be taken into account when the particles exhibit crystallization and also a highly non-spherical shape, because a solubility enhancement effect might occur."

It was not our intention to assert that the effect of shape factor on DMA measurements were the only, or even most important, effect that particle morphology has on CCN activity. However, in laboratory CCN activation experiments, the first correction that should be made with respect to the shape factor of particles is in the DMA measurements. We have revised Section 3.5.3 to read:

"The shape and morphology of the aerosol particles are important to size selection in the DMA. Non-spherical particles, such as NaCl, are not properly sized in DMAs because charging efficiency and electrical mobility depend on particle morphology, mass, and cross-section (Hori et al., 2003), and a shape factor is often employed to correct for this error (Hinds, 1999). Also, observed CCN activity could be affected directly by particle morphology. Hori et al. (2004) state that solubility enhancement effects could occur when particles are non-spherical or exhibit crystallization. Different compounds could form particles of varied morphology, and particles of the same compound could have different shapes caused by differences in aerosol generation. It is possible that organic particles generated from atomization of methanol could exhibit morphology different than those generated from water solutions. Shape differences could also be caused by the temperature at which the particles are dried, since the particles would form at different drying rates. Thus, the addition of the heater after the atomizer could cause differences in morphology, and subsequently in the apparent CCN activity of the compound, from improper size selection in the DMA.”

If the particles created were hollow, instead of solid, spheres, the DMA measurements would not be affected - the selected size would still correspond to the physical size, unless the particles were to collapse at some point in the system. The CCN activity would be affected, however, in that the amount of solute present would be lower for a hollow sphere than for a solid one. This effect would be difficult to assess in a CCN activation laboratory study because even particle imaging methods may not indicate whether a particle is hollow or not. Also, the degree of hollowness would be critical because a thicker shelled hollow sphere would contain more solute than a thinner shelled sphere. This issue would be more suitable for study in an activation model with comparisons to laboratory studies.

We would have liked to have run more in-depth filter studies on the particles that were formed during the atomization and drying process to determine their morphological characteristics. To do this, we would have tried to look at the particle shapes formed at each size using TEM or SEM methods. The purpose of this paper was to discuss possible sources for discrepancies in the CCN activity of organic particles caused by different laboratory conditions. Further filter studies were determined to be outside the scope of the paper and are being considered for future studies. We hope this paper will also encourage other investigators to consider these morphological issues more in-depth in future studies.

The ADDEM does not include considerations of particle morphology at this time, and a study of the effect of particle morphology is outside the scope of this paper, considering the purpose of the paper that was stated above. To include restructuring within ADDEM would be very difficult, and it is an effect that can be elucidated from devi-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ations between modeled and measured hygroscopic growth from HTDMA work. For example, Mikhailov et al (2004) found restructuring effects upon drying out aerosol particles composed of proteinaceous material that could not be predicted. The same holds for various studies of soot particles. However, good agreement has been found between HTDMA measurements and ADDEM model predictions for the organics used in this study. Unfortunately, this isn't published in extensive detail, apart from Topping et al. (2005a, b), in which oxalic acid is studied. Because of the flexibility of the ADDEM, good agreement was found between measured and predicted growth when the dry oxalic acid particle was assumed to be in the hydrated form rather than the anhydrous. This was also found by Prenni et al (2001). So, these effects con be included to some extent but ADDEM results need to be compared with lab measurements before altering the thermodynamics. Of course, one other example is sea salt, which forms a cube like structures upon drying. This requires a shape "correction" factor within model predictions for comparison with experimental results.

3) We do not believe that it is necessary to develop or identify an organic standard for CCN instrument calibrations. The calibration salts are chosen because, as stated in the manuscript,

"The activation of inorganic salts, such as ammonium sulfate ((NH4)2SO4), ammonium bisulfate (NH4HSO4), and sodium chloride (NaCl), is well understood, for which measurements and predictions agree closely."

Because we are able to predict the CCN behavior of NaCl, (NH4)2SO4, and NH4HSO4 using traditional Köhler Theory, we use these salts as calibration standards to determine the operating supersaturation of each column of the CCN instrument at a chosen temperature gradient. Measurement of the activation curves of these salts at the chosen temperature gradient of the CCN instrument allows us to define the operating supersaturation of the instrument at that temperature gradient in the manner described in the manuscript. We do this so that we can report our data as functions of supersaturations and not temperature gradient settings.

The fact that our calibrations for all three salts fall within 20% of each other when the activation curves are expressed as functions of critical supersaturation rather than dry diameter shows that our instrument is fairly stable at a given temperature gradient.

To develop or recommend an organic compound as a calibration standard, we would need to understand and be able to predict its CCN activation behavior. We are not confident enough in organic CCN closure for any one compound to be able to recommend such a compound and do not feel that it is necessary. The use of inorganic salts as calibration standards is done is such a way that the results are applicable to all compound classes, not just inorganic salts.

4) The literature results are presented to illustrate the discrepancies between studies and to emphasize the large range of experimentally determined activation diameters. We do not attempt to explain the reasons for these discrepancies but believe that they result from differences in experimental setup. Even in presenting our experimental results, we do not mean to imply that the experimental uncertainty was larger in any other studies. We are careful not to state this because we do not necessarily believe it to be so. For this reason, we opt not to spend a lot of time investigating the differences in experimental setup or conditions. In most cases, we would not be able to determine these differences from reading the papers based on past studies. Instead, we present our paper and results to highlight the discrepancies in the different studies and bring about discussion about possible sources of discrepancies that result from different experimental designs.

5) The actual reason for adding the heater to our experimental setup was not to ascertain the effects of heating the particles on CCN behavior. As stated on page 13265:

“A heater was placed after the atomizer for some experiments in an attempt to facilitate the evaporation of the atomization solvents from the particles.”

We expected that the presence of the heater would help the solvent evaporate from the atomized droplets and result in completely dry particles. However, the heater results only brought up more questions.

The atomized droplets entered the heated section directly after the atomizer. The exact flow rate of the droplets from the atomizer is not known, but the heated section was approximately 12” long with a tube diameter of ij”. The tubing after the heater was insulated to avoid cooling of the sample stream before being introduced to the driers. In the driers and afterwards, the particles were allowed to return to room temperature before measurement in the DACAD and CCNC3, since calibrations were run at room temperature.

It is possible that changing the heating temperature, heating duration, and/or heating rate could affect the resulting particle morphology and the resulting DMA size selection and measured CCN activity. A detailed study of the effects of temperature, heating duration and/or heating rate is beyond the scope of this paper. We agree that a future study that looks at how different drying rates affect particle morphology is warranted and would be greatly beneficial to the community.

6) We would hypothesize that the particle morphology effects would depend on compound chemical properties, such as, perhaps, melting point, density, crystallization properties, etc, and also on the concentration of the atomization solution. It would be beyond the scope of the paper to do an in-depth study of these differences.

The morphology differences may not have been observed for all the organic species because we only looked at one heater temperature and one solute concentration. A certain particle morphology may exist over a range of temperatures (or solute concentrations) and then change for another range of temperatures (or concentrations). It may be possible that the particle morphology is the same for organic compound A from 25°C to 40°C, while organic compound B exhibits two different particle morphologies at these temperatures.

Iskandar et al. (2003) discusses the morphology of nanoparticles created by an ultrasonic nebulizer as a function of “the sol size in the droplet, the droplet size, the viscosity of droplet, the drying temperature, the gas flow rate, and the addition of surfactant". They found that these are all crucial parameters that all affect the morphology of the resulting particles. The viscosity and surface tension of the droplet could be affected by the presence of an organic, regardless of the atomization solvent, and could result in different results for different organic compounds.

We have modified Section 3.5.3 to include this information.

7) The particles leaving the first DMA were truly monodisperse in terms of their mobility. However, we can not be sure that all particles of a given mobility were also uniform in their morphology and/or composition.

The statement that these particles may have trapped solvent which was subsequently released was a hypothesis that would have explained the multipeaked behavior of these compounds. There was no way of proving whether this was actually the case with the setup and resources that were available. Eslamian and Ashgriz (2007) discuss the trapping of solvents in particles greater than 4 μm after air mist atomization. No references were found to discuss the solvent trapping abilities of malonic and glutaric acids, specifically.

After careful consideration of these multipeaks, we have determined that they could be the result of the combined effects of a number of size-altering processes, including the presence of doubly charged particles, collapsed particles, and solvent trapping. While responding to these and other comments, we have determined that we are unable to "correct" the experimental data for malonic and glutaric acid and are unable to present the CCN results for these compounds. The discussion for these two compounds remains in the paper, but we no longer present activation diameters for these two compounds because we do not feel that we are able to determine them with sufficient scientific certainty.

8) It is possible that esterification products form in the methanol solution experiments without the heater as well but probably not to the extent it does in the heater ex-

periments. We can't know this for sure because no filter data was collected for the methanol/no heating experiment. It is actually the methanol/no heating results that fall within the ADDEM calculations. ADDEM currently does not consider reactions within the liquid phase, apart from inorganic dissociation and solid formation. A caution to readers was added to state that the agreement between ADDEM and the results of the methanol/no heating experiments could be coincidental.

We can not be sure about the hygroscopicity esterification products of glutaric and malonic acids. The comment made in the paper was intended as a statement about the possibility that this could be true and that it would explain the results. To be sure, we would need to run a glutaric or malonic acid standard on the LC/ESI-MS and compare the results to their respective ester-derivative products. However, after further consideration of the malonic acid and glutaric acid data, we have decided that we cannot present the CCN data for these compounds with any scientific certainty. The results for malonic and glutaric acids have been removed from the paper.

9) The difference in the activation diameters between the water/heater and water/no heater experiments is not that different than experimental error. However, particle morphology could explain either of these observations. Also, as stated in the paper, adipic acid is more soluble in methanol than in water, and we expect more of the methanol solvent to be removed from the particles when the heater is present. So, we hypothesize that some methanol solvent may remain on the particles when the heater is not present and may facilitate the condensation of water onto the adipic acid particles and subsequent droplet activation.

We added a paragraph to Section 4.4.3 to discuss this:

"The heater/no heater trends are opposite for adipic acid particles created from aqueous and methanol solutions. With water as the activation solvent, the activation diameters of the adipic acid particles with the heater in place are smaller than those without the heater, but the difference in the activation diameters is not much greater than that expected from experimental error. However for adipic acid particles created from a methanol solution, the observed activation diameters are greater when the heater is in place. These observations could be a result of differing particle morphology caused by the different solvents and/or the presence of the heater, as discussed. Also, the methanol solvent is expected to be more completely removed from the adipic acid particles when the heater is present. So, some methanol solvent may remain on the particles when the heater is not present and may facilitate the condensation of water onto the adipic acid particles and subsequent droplet activation."

Author Responses to Referee Comments "CCN behavior of organic particles" from Anonymous Referee #2 Received and published: 12 February 2007

1) shape factor of NaCl particles: what about hollow spheres?

NaCl is used as a calibration salt to test whether the instrument is operating consistently at a certain temperature gradient. Since the NaCl calibration curves matched up well with the calibration curves of (NH4)2SO4 and NH4HSO4 when using the size-dependent shape factor, we feel that further study of the morphology of the NaCl particles and shape factor corrections is beyond the scope of this paper.

2) Why should the solvent itself affect the morphology of the particles? Different time scales for drying could also be an issue.

The solvent itself could affect the drying time of the particles, depending on the volatility and solute solubility differences between the solvents. We also feel that different time scales for drying are an issue, as we stated in the following (Section 3.5.3, page 13266):

"Shape differences could aso be caused by the temperature at which the particles are dried, since the particles would form at different drying rates. Thus, the addition of the heater after the atomizer could cause differences in morphology, and subsequently in the apparent CCN activity of the compound, from improper size selection in the DMA."

We changed Section 3.5.3 to better emphasize that drying rate has a large effect on

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

particle morphology and that the drying rate could varying for different solvents. Other considerations for particle morphology are also discussed more in depth now. Section 3.5.3 now reads:

"The shape and morphology of the aerosol particles are important to size selection in the DMA, which is central to the CCN experiments and determination of the activation diameters. Non-spherical particles, such as NaCl, are not properly sized in DMAs because charging efficiency and electrical mobility depend on particle morphology, mass, and cross-section (Hori et al., 2003), and a shape factor is often employed to correct for this error (Hinds, 1999). Also, observed CCN activity could be affected directly by particle morphology. Hori et al. (2004) state that solubility enhancement effects could occur when particles are non-spherical or exhibit crystallization, which would, in turn, affect the apparent CCN behavior of the particles. Different compounds could form particles of varied morphology, and particles of the same compound could exhibit different shapes, depending on differences in aerosol generation. A certain particle morphology for a certain organic species may exist over a range of temperatures and then change for another range of temperatures. Iskandar et al. (2003) discusses the morphology of nanoparticles created by an ultrasonic nebulizer as a function of "the sol size in the droplet, the droplet size, the viscosity of droplet, the drying temperature, the gas flow rate, and the addition of surfactant" and found that these are crucial parameters that affect the morphology of the resulting particles. The viscosity and surface tension of the droplet could be affected by the presence of an organic, regardless of the atomization solvent, and could result in different results for different organic compounds. Organic particles generated from atomization of methanol could exhibit morphology different than those generated from water solutions because of differences in the drying rate, depending on solvent volatility and solute solubility differences, as well as other properties. Shape differences could also be caused by the temperature at which the particles are dried, since the particles would form at different drying rates. Thus, the addition of the heater after the atomizer could cause differences in morphology, and subsequently in the apparent CCN activity of the compound, from improper size selection in the DMA.”

3) Figures. the figures are very hard to read in the print version. The font size in Figure 6 is much too small.

We will work with the editors to make sure that this is taken care of in the final version of the paper. Figure 6 is supposed to show up as a landscape figure, which would increase the font sizes.

4) In several figure captions the term "aerosol" was used synonymous to "particles".

Thank you for pointing this out. The figure captions for Figures 1, 2, and 4 have been changed. We also changed “aerosol” to “aerosol particle” in lines 15, 22, and 25 of page 13264, line 24 of page 13266, and line 13 of page 13274.

Author Response to Short Comment “General Comment” from Christopher Cappa C. Cappa christopher.cappa@noaa.gov Received and published: 10 February 2007

1) The reason that we added the heater was explained in the text, on page 13270, line 22:

“In an attempt to vaporize as much solvent as possible from the atomized organic particles, a heater was added after the atomizer but before the driers for experiments with adipic acid, malonic acid, and glutaric acid atomized from both water and aqueous solutions.”

The point of the heater was to drive the solvent into the vapor phase to allow it to be more easily removed by the driers. We did not place the heater after the drier for any experiments, but agree that the different results could be observed. However, for the purposes of these experiments, it made more sense to drive the solvent off the particles before the driers to attempt to dry the particles as much as possible. Also, heating the particles after the driers may not have allowed the particles to cool to room temperature before entering the other instruments. This, too, would affect the CCN results, since it is more difficult to condense water on warm particles than on cooler particles.

2) Further experiments concerning the esterification reactions are beyond the scope of this paper, but should be addressed in future work. In the paper, we simply speculate that this size dependence because it would explain the results. We have added a statement to Section 4.4.3 to further explain this:

“Even though it appears that esterification reactions might occur to a larger extent in smaller particles, further investigation is warranted. Size resolved composition measurements should be made to validate this possible effect and until such measurements are made, the size-dependence of esterification reactions will remain an unproven hypothesis.”

3) We didn’t conduct chemical analysis on the non-heated methanol experiments. A more detailed study of the esterification reaction is beyond the scope of this paper and should be addressed in further work. We present our preliminary, incomplete study to highlight the possibility and guide future work.

From Section 4.4.3:

“For example, at 250 nm, AR is about 0.82. This could imply that 82% of the particles is adipic acid and 18% are ester derivatives of adipic acid that are not CCN-active at 250 nm at the operating supersaturations of the CCN instrument. As dry diameter decreases, the degree of esterification could be increasing.”

We are careful not to state that this is fact. It is speculation that requires further investigation. To clarify this, we added the following to this section.

“Even though it appears that esterification reactions are size-dependent, further investigation is warranted. Size-resolved composition measurements should be made to validate this possible effect and, until such measurements are made, the size-dependence of esterification reactions remains an unproven hypothesis that could provide an explanation for the observations of this study.”

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

There remains the possibility that a dimethylated ester (or some other neutral ester product) is present, which would remain unionized in the mass spectrometer and not be detected because there is no free acid group available for ionization in ESI negative mode. Due to time constraints, we were unable to collect additional filter studies of monodisperse aerosol of multiple sizes. As an example, an increase in the LC/MS peak areas for ester peaks for 150 nm particles would be observed over those for 250 nm particles, if this effect exists.

4) We do not necessarily believe that morphological changes and solvent removal are the only reasons for the change in CCN activity for particles atomized from aqueous solution. These seem to be the most probable causes for the differences, but we can not prove that they are the only causes. Unfortunately, we did not have equipment or time available to look at the morphology of the particles more closely. We agree with the reviewer's suggestions for future work that could help determine the exact causes of these differences. We present the differences that we observed, propose possible reasons for those differences, and hope that future work will better address these aspects of particle state at the time of activation.

5) The statement that these particles may have trapped solvent which was subsequently released was a hypothesis that would have explained the multipeaked behavior of these compounds. There was no way of proving whether this was actually the case with the setup and resources that were available.

After careful consideration of these multipeaks, we have determined that they could be the result of the combined effects of a number of size-altering processes, including the presence of doubly charged particles, collapsed particles, and solvent trapping. While responding to these and other comments, we have determined that we are unable to "correct" the experimental data for malonic and glutaric acid and are unable to present the CCN results for these compounds. The discussion for these two compounds remains in the paper, but we no longer present activation diameters for these two compounds because we do not feel that we are able to determine them with sufficient scientific certainty.

References

Eslamian, M. and N. Ashgriz, Effect of Atomization Method on the Morphology of Spray-Generated Particles, J. Eng. Mat. Tech., 129, 130-142, doi:10.1115/1.2400270, 2007.

Iskandar, F., Gradon, L., and Okuyama, K.: Control of the morphology of nanostructured particles prepared by the spray drying of an nanoparticle sol, J. Coll. Inter. Sci., 265, 296-303, doi:10.1016/S0021-9797(03)00519-8, 2003

Mikhailov, E., Vlasenko, S., Niessner, R., and Pöschl, U.: Interaction of aerosol particles composed of protein and salts with water vapor: hygroscopic growth and microstructural rearrangement, Atmos. Chem. Phys., 4, 323-350, 2004.

Topping, D. O., McFiggans, G. B., and Coe, H.: A curved multi-component aerosol hygroscopicity model framework: Part 1 - Inorganic compounds, Atmos. Chem. Phys., 5, 1205 - 1222, 2005a.

Topping, D. O., McFiggans, G. B., and Coe, H.: A curved multi-component aerosol hygroscoplicity model framework: Part 2 - Including organic compounds, Atmos. Chem. Phys., 5, 1223 - 1242, 2005b.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 13251, 2006.