

Interactive comment on “Ice nucleation in sulfuric acid/organic aerosols: implications for cirrus cloud formation” by M. R. Beaver et al.

M. R. Beaver et al.

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The authors would like to thank anonymous referee #1 for the thoughtful comments. We have addressed the authors concerns point-by-point below:

Specific Responses:

1. Page 2062, line 9. “there is much less data available for ice nucleation from other inorganic and organic species”. Many studies on ammonium sulfate have been carried out previously, so would change this statement to reflect this fact.

It is true that approximately equal amounts of ice nucleation work have been done on sulfuric acid and ammonium sulfate aerosols. Therefore, page 2061, line 5 has been changed to read: “Several laboratory studies, using a variety of techniques, have established homogeneous ice nucleation conditions for aqueous sulfuric acid and am-

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monium sulfate aerosols over the troposphericly relevant concentration range (0-50 wt%) (Bertram et al., 1996; Bertram et al., 2000; Hung et al., 2002; Koop et al., 1998; Chen et al., 2000; Cziczo and Abbatt, 2001; Prenni et al., 2001b)."

Bertram, A.K., Koop, T., Molina, L.T., and Molina, M.T.: Ice formation in (NH₄)₂SO₄-H₂O Particles, *J. Phys. Chem. A.*, 104, 584-588, 2000.

2. Page 2064, line 20. "Although some infrared absorption cross-sections were available in the literature, infrared absorption cross sections were separately determined for all compounds in the present study and used to calculate partial pressures." Later the authors state, "Cross-sections could not be determined experimentally for 2-nonanone or decanal due to vapor pressure limitations." Are these two statements consistent with each other?

The authors agree that the inability to determine the infrared absorption cross-sections for 2-nonanone and decanal should be explained in the initial statement, and the word "all" should be removed. Therefore, the authors have changed the sentence beginning page 2064, line 20 to read: "Although some infrared absorption cross-sections were available in the literature, infrared absorption cross-sections were separately determined for most compounds in the present study and used to calculate partial pressures. Due to vapor pressure limitations, cross-sections could not be determined for 2-nonanone and decanal."

3. Page 2064, line 15. "This conditioning tube served to maintain the sulfate to water ratio of the aerosols and to pre-cool the aerosols." How does this work? When the temperature decreases the sulfuric acid particles should take up water, and thus the sulfate to water ratio should change? Why does the concentration of the sulfuric acid solutions stay at 15 % when the temperature decreases? Please include more details here. Also other experimental details such as the aerosol concentration (number of particles/cm³) and the size of the aerosol particles would be beneficial.

The aerosols were produced via atomization from a 30 wt% H₂SO₄ solution (page

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2063, line 9) then pre-conditioned using a sulfuric acid bath, which added water to the particles. Then, with the water vapor of the ice inside the conditioning tube, the particles reached the final 15 wt% sulfuric acid concentration. So, the particles did take up some water when cooled in the conditioning tube. The absolute particle concentration and size distribution was not measured due to the acidic nature of the particles. However, it should correspond to that produced with a TSI Model 3076 atomizer. Page 2064, line 15 has been changed read, “This conditioning tube served to set and maintain the sulfate to water ratio...”.

4. Related to the above, on page 2066, line 9, the authors state: “all experiments were conducted using 15 wt% sulfuric acid composition as the precursor aqueous sulfuric acid aerosols”. The concentration of the sulfuric acid aerosol was also 15 wt % in the observation region? Correct?

Yes, the aerosols were 15wt% sulfuric acid in the observation region as well.

5. Did the authors determined the sulfate to water ratio (from the spectrum) in the presence of organics or only before the organics were added.

The authors determined the sulfate to water ratio both before and after the addition of organics. Page 2065, line 3. “The water to sulfate ratio was conserved both before and after organic compound addition.” It has been clarified to read: “The FTIR spectral calibrations were used to verify the water to sulfate ratio remained constant after the addition of the organic compounds.

6. Page 2071, Equations 1 and 2. In the literature these equations are used to predict how the freezing point and melting point of solutions vary from pure water. Are the authors also trying to do the same thing here? What “m” is used in Equation 2? Please expand or delete this section. I am not sure of the point of this section.

The purpose of this section is to quantitatively describe our results with the empirical relationships given in Eqs. (1) and (2) since the Koop et al. (2000) water activity can not

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be used to describe these results. An attempt to make the purpose of this paragraph and the use of these equations clearer has been made.

7. Page 2072, line 5. “Because the partial pressure of the organics is measured and the aerosol molarity is determined using the Mie scattering analysis, it is possible to carry out a Henry’s law analysis to determine the solubilities.” For the Henry’s law measurements, did the authors measure the partial pressure of the gas in equilibrium with the particles at low temperatures? This is the measurement needed for a Henry’s law analysis, so I assume this is what was measured, but it was unclear from the manuscript.

The partial pressure of organic was not measured in equilibrium with the particles at low temperature. Spectral interferences prohibited this. So, in fact, the partial pressure organic was measured at low temperatures in the absence of aerosol. However, a quick calculation, assuming maximum coverage of the particles, was performed to ensure that the addition of particles did not change the partial pressure of organic. Briefly, for 0.5 torr propanal (2×10^{16} molecules/cm³); $N_d = 1 \times 10^5$ particles/cm³; $D_p(\text{before}) = 300 \text{ nm}$; $D_p(\text{after}) = 900 \text{ nm}$; percent org = 96%; 3.1×10^{14} molecules/cm³ needed to coat all the particles to become mostly organic, and there are 2×10^{16} molecules/cm³ available in the gas phase. Therefore, no change in partial pressure results from the addition of particles. The following sentence has been added on page 2063, line 19 to clarify this in the manuscript. “Based on a calculation involving aerosol concentration, aerosol growth, and partial pressure of organic, the partial pressure in the absence of and in the presence of aerosols should be the same, and was used as such throughout this study.”

8. Page 2072, line 24. I don’t think the results demonstrate a depression of the water activity.

The (and water activity) from page 2072, line 24 has been removed.

9. Page 2073, line 23. For the longer chained organics, which have a low solubility,

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could the organics homogeneously nucleate to form pure organic particles in the flow system?

Yes, the authors wondered this as well while conducting these experiments, therefore, the authors have added the following to the text to address the experiments done to ensure organic particles did not form via homogeneous nucleation. “To determine if a distribution of pure organic particles was present in these experiments, investigative experiments were performed where the organic compounds were flowed through the low temperature flow tubes in the absence of sulfuric acid aerosols, and FTIR spectra were collected. Under these conditions, the IR spectra indicated no nucleation of organic particles, i.e. no Mie scattering was observed in the 5000 to 3500 cm^{-1} region. These spectra were also identical to reference gas phase spectra.”

10. Page 2067, line 5. “The difference in aqueous sulfuric acid aerosol mean diameters, before and after organic addition was converted to an aerosol volume change, which also allowed the calculating of organic aerosol molarity ($M = \text{moles solute/L of solution}$).” Please give more details on how volume change was converted into M (e.g. what assumptions were used?).

To clarify this calculation, the section has been rewritten to include all details involved in the calculation. It now reads as follows: “The results from this scattering analysis were used to determine aerosol organic molality ($m = \text{moles solute/kg of solution}$). The difference in aqueous sulfuric acid aerosol mean diameters, before and after organic addition, was converted to an aerosol volume change. The increase in aerosol diameter was assumed to be due only to the incorporation of organic into the aerosol. This volume increase, along with the molecular weight of the organic compound, was used to calculate moles of organic, in order to calculate organic aerosol molality. Then, the total aerosol volume with an estimate of aerosol density based on sulfuric acid, water, and the organic compound densities, were combined with moles of organic to calculate the aerosol organic molarity ($M = \text{moles solute/L of solution}$).

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11. Page 2068, line 14. “To determine if the organic uptake was due to acid-catalyzed chemistry, control experiments were performed with aqueous ammonium sulfate (approximately 30 wt %). Why did the authors use 30 wt % rather than some other composition?”

30 wt% ammonium sulfate aerosols were arbitrarily chosen for these investigative experiments.

12. Figure 8. It would be good to have error bars in Figure 8, to better appreciate the significance of the results.

Error bars have been added.

13. The final question is related to the implications for this research to cirrus clouds. The authors show that at some concentration a solubility limit will be reached and a second organic phase will begin to form on the aqueous aerosol, and this second phase can lead to heterogeneous freezing. However, in the atmosphere will this solubility limit be reached? Marcolli et al.¹ suggested that in most cases a second organic phase will not form because the solubility limit of one specific organic molecule will not be reached. The authors should address this point. (1) Marcolli, C. et al. *J. Phys. Chem. A* 2004, 108, 2216.

A reference to the Marcolli et al., 2004 paper has been added, along with an additional sentence in the implications section. “However, if no reaction transforms the shorter carbon chain organic compounds to larger organic compounds, the solubility limit will likely not be reached for the shorter carbon chain, highly soluble organic species in the atmosphere.”

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 6, 2059, 2006.

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