

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.

Received and published: 20 June 2006

The authors would like to thank anonymous referee #2 for the thoughtful comments. We have addressed the authors concerns point-by-point below:

Specific Responses:

1. The most significant shortcoming in this manuscript is that there are no error bars presented in any figure. A number of uncertainties are mentioned in the text but it is not clear what the result is on the figures and thus the data interpretation. For example: A) The uncertainty in temperature is 0.6 deg C; the difference in freezing point for 15wt % H₂SO₄ versus similar experiments is about 1 deg C. This should be reflected in Figures 4 - 8. B) The uncertainty in H₂SO₄ wt% is 2%, please add to the figures. C) See point 6 regarding the uncertainty in Mie calculation; this should set error bars in

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Figure 3.

The authors have added error bars to figures as asked.

2. A description of the work of Koop et al. (2000) is made. This is discussed throughout the manuscript until the statement on page 2072 ' ˇ Ea direct comparison to Koop et al. (2000) ˇE is not possible in this case' due to the lack of water activity data for the mixed organic/sulfuric acid aerosols. It is clear that this is true but two questions results: A) Why are there references throughout the text to water activity if this comparison can not ultimately be made with these data? B) More importantly, Figure 8, which is arguably the central figure of this paper, compares all data to the freezing point of 15wt% sulfuric acid. This should only be done if the water activity of all points is the same otherwise there is no reason to assume the freezing temperature would be the same. One can imagine this is a reasonable comparison in cases where only small amounts of organic is in solution but it is clear that this comparison is essentially meaningless in cases where significant organic is involved (i.e., the shorter chain organics which exhibit significant uptake); it would be analogous to putting a point for 50wt% H₂SO₄ on the plot. It should be made clear in the text and the figure caption what the limitations of this comparison are.

A) The Koop et al. (2000) theory for homogeneous ice nucleation is mentioned in the introduction and discussion of the paper as it is currently the theory used to predict homogeneous ice nucleation temperatures. It is the theory that similar experiments have aimed to use to interpret their results. Therefore, it is highly relevant to this research. However, due to the nature of the experiments described in this paper, a rigorous analysis using Koop et al. (2000) methodology was not possible. However, we do use the theory qualitatively to explain the results seen for the smaller organic molecules like propanal and acetone.

B) The authors agree with this reviewer's point, and have added clarification to the text (page 2073, line 5) and caption for figure 8. The water activity of these data is likely

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constant except for the soluble short chain organics like acetone and propanal.

3. It would be useful to put both the calculated and NIST data in Table 1 and then the differences between them. There is reference to solubility data for organics on page 2070 for bulk data and from this experiment. These should both be shown in Table 2 along with differences.

As mentioned in the text page 2064, line 4, literature values for infrared absorption cross-sections are only available for acetone and propanal, but these two values have been added to Table 1. The calculation mentioned on page 2070, line 20, was only applicable for propanal, the only organic compound we experimentally observed reaching the solubility limit. And, as the text says, it was at a lower temperature, so therefore, the authors will refrain from including this value in the table, but leave it in the text. The result from this calculation has also been shown in the units of g/L in the text on page 2070, line 19 (230g/L) for easier comparison.

4. Are the lines in Figures 3, 5, 6 and 7 fits to the data or from some theory? This should be explained in the figure captions or the lines should be removed.

The authors agree this information should be included. Figure 3: The curves shown are non-linear fits to the data. This has been added to the caption. Figures 5 and 6: Because partial pressure and molality (molarity) are linearly related (Henry's law), and because molality and freezing temperature are linearly related (Eqns. 1 and 2), we have theoretical grounds to expect a linear relationship between partial pressure and freezing temperature. Therefore in figure 5, we have retained the linear fit to the partial pressures of 0.15 torr and below, and have removed the fit to the higher partial pressure data. Figure 7: From equations 1 and 2 we expect a linear relationship between freezing temperature and molality, therefore a linear fit to the data is shown in the figure. Therefore, this information has been added to the figure captions where applicable.

5. The attribution of homogeneous or heterogeneous freezing appears to be inferred

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based on a difference from the freezing point of 15wt% H₂SO₄ (Figure 8). The authors' group has used FTIR to observe phase changes (e.g., efflorescence) in past publications. Thus I wonder if it is not possible to show if a second phase (i.e., a pure organic) is present? Figures 5 and 6 are consistent with the formation of a second phase and no second phase, respectively, but it would seem the authors should see this formation in the FTIR spectra. Is this the case?

It is not possible in these experiments to determine if a pure organic phase exists on the sulfuric acid particles, since FTIR is not a surface specific technique in this configuration. In past work examining organic coatings (palmitic acid) on inorganic particles from this group (Garland et al, 2005), the existence of the organic phase was verified using TEM. This technique was appropriate and useful in those studies at room temperature, and with an organic of very low volatility, therefore, not very helpful in the work in this manuscript.

Garland, R. M., Wise, M. E., Beaver, M. R., DeWitt, H. L., Aiken, A. C., Jimenez, J. L. and Tolbert, M. A.: Impact of palmitic acid coating on the water uptake and loss of ammonium sulfate particles, *Atmos. Chem. and Phys.*, 5, 1951-1961, 2005.

6. Given point 5 the sentence in the Implications and Conclusions ' ˇ E by a homogeneous mechanism ˇ E via a heterogeneous mechanism ˇ E' would seem to be too definitive a statement. Please change the wording throughout the paper to make it clear that heterogeneous/homogeneous mechanisms are inferred, not directly observed.

We agree that it should always be clear in the text that homogeneous vs. heterogeneous ice nucleation is inferred from our results. Wording has been changed when we feel this was not clear, specifically on page 2060, line 12; page 2075, line 7 and line 24.

7. Section 2.2 describes the use of Mie scattering to obtain the organic content. If I understand correctly the aerosol size change between just sulfuric acid and acid and

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organic aerosol is differenced and this is attributed to the amount of organic uptake. This section should be expanded as this is an interesting method to obtain organic uptake but it is not clear how accurate these data are. Specifically: A) What is the variability in the produced sulfuric acid aerosol? Typical atomizers have an output that is variable in both radius and total number. Is this uncertainty larger or smaller than the observed uptake? B) What is the uncertainty in the Mie scattering fit? Mie fits are not normally single valued; several choices of r and GSD normally return good fits. What is the range in suitable fit choices and how does this relate to the observed uptake?

A) The variability in the diameter of the produced sulfuric acid aerosol, before the addition of organic, determined by examining the Mie scattering fits is 5.0%. This variability has been added to the scattering analysis results section. This variability is much less than the diameter increase seen due to the incorporation of organic compounds except for at the lowest partial pressure exposures, 0.075 torr for both acetone and propanal where the diameter increase is only about 5.0%.

B) Yes, the Mie scattering analysis program is very sensitive to the choice of GSD as described in the text on page 2067, beginning line 11. To reiterate, since the absolute particle diameter did in fact depend on the choice of GSD, only relative differences in particle diameter were used to calculate particle organic content.

8. On page 2068 the term ‘a similar diameter increase was observed $\&\#711$; E’ for ammonium sulfate as for sulfuric acid. It is then assumed that the uptake of organics is the same for neutral and acidic species. Please state the observed increase ratios as it pertains to the uncertainty in this measurement. For how many of the organic species was this experiment performed?

This measurement was only performed for one organic species, hexanal. Therefore uncertainty measurements are not possible, and the word qualitatively has been added to the sentence.

9. On page 2072 reference is made to the use of λ as a model for supercooling

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of aerosols (equation 1). The original work using this sensitivity parameter is by Rasmussen, for example Rasmussen, D. H., and A. P. MacKenzie. *Water Structure at the Water Polymer Interface*, New York, Plenum, 1972; Prenni et al. (see following points) and Demott are only recent users of this concept.

A reference to the original use of lambda (Rasmussen and MacKenzie, 1972) has been added for completeness.

10. Lambda is not defined as the authors use it here. Lambda is the factor by which the melting point depression at a given concentration is multiplied by to obtain the observed freezing points after subtraction of the supercooling of pure water supercooling. Observations give the typical values between 1.4 and 2.2 that are referenced using this concept. Thus a lambda equal to unity is a constant depression of the melting line by the amount that pure water supercools (≈ 38 deg C) NOT an ‘absence of supercooling’.

The authors believe a change in wording will clarify what we meant by the definition of lambda, making us in agreement with the reviewer. Therefore, the sentence on page 2071, line 15, has been changed to read, “The parameter lambda is the ratio of the depression of the ice nucleation temperatures of solute-containing droplets to bulk solute-containing solutions each relative to pure water (i.e., lambda would be equal to unity in the absence of increased supercooling effects over those of water).”

11. It is not clear what the source of equation 2 is. K_f is referenced as the freezing point depression constant for ‘15wt% H₂SO₄’ and then 1.86 deg C m⁻¹ is the value for ‘water’. Is m the molality? Is this a fit to this data? I should note that after looking at Prenni et al. (2001a) I can find neither equation and Demott (2002) only has equation 1 so what is the source?

Equation 1 can be found on p 3042, eqn 2 of Prenni et al. 2001b. Our original manuscript mistakenly referenced Prenni et al., 2001a, therefore this typo has been changed in the submitted manuscript.

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And Equation 2 is simply the empirical equation for bulk freezing point depression as related to solution concentration, therefore not derived from a fit to our data. K_f is the experimentally determined value for water. It has been clarified in the revised manuscript that m is indeed molality. We have added a reference to a physical chemistry book (Atkins, 1997) for this equation.

12. Is it known that pure externally mixed organic particles are not formed in the experiment (i.e., in addition to organic vapor partitioning to the sulfuric acid aerosol)? If the impurity level in the organics is up to 5% is it known what the impurities are? Could they be a species that promotes ice nucleation in the longer chain organics?

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. Also, these spectra were identical to reference gas phase spectra. These points have been added to the text on page 2067, line 2.

Impurities in the commercially available organics are not known, nor were they determined in these experiments. However, the method used to introduce the organics to the sulfuric acid aerosols would not allow the introduction of a significant contaminant with a lower vapor pressure than the compound of interest, which is what would likely be required to induce the nucleation at the warmer temperatures observed with the longer chain organics.

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

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