Atmos. Chem. Phys. Discuss., 12, C9410–C9413, 2012
www.atmos-chem-phys-discuss.net/12/C9410/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on “State transformations and ice nucleation in glassy or (semi-)solid amorphous organic aerosol” *by* K. J. Baustian et al.

Anonymous Referee #2

Received and published: 15 November 2012

General comments

In the work on hand, three compounds considered surrogates for secondary atmospheric aerosol (SOA) are investigated experimentally upon their behavior toward water uptake and ice nucleation under atmospherically relevant conditions. Furthermore, mixtures of these organics with ammonium sulfate are described to increase significance of the conclusions for actual chemical compositions in the tropical tropopause layer (TTL). Therefore, the submitted manuscript is clearly within the scope of ACP and the title clearly reflects its contents.

The combination of optical microscopy, raman spectroscopy and application of the

CARMA model provides a very complete consideration of the topic and all employed methods can be followed reasonably well. The data presented in this study leads to nice quantitative conclusions for the relevance of heterogeneous ice nucleation on glassy aerosols in atmospheric conditions, which are substantial enough for publication. As not indicated otherwise in the specific comments, the paper is well written in a clear and concise fashion. I therefore recommend the paper for publication, but have a few points of critique that need to be addressed.

Besides some minor points (see specific comments), my main points of critique are the lack of consideration of diffusional limitations to the deliquescence process and the very indirect way of inferring glass transition values. In this manuscript, water uptake is assumed to occur simultaneously with glass transition and used to build up the glass transition parameterization. This might be misleading in several ways which should at least be indicated in the paper: As mentioned in l. 5-11 on page 27346, the uptake of water depends on the actual humidification rate (and furthermore on other parameters such as particle size) so that the reported water uptake onset should be considered as an upper limit for the water uptake onset under full equilibration conditions (infinitely slow change in RH). Especially at very low temperatures, this might (in part) explain why values measured by Zobrist et al. (2008), consistently lie at lower temperatures. Tg values in Zobrist et al. (2008) were determined calorimetrically, thus following the thermodynamic definition of a glass! The thermodynamic and kinetic definitions of the glass state are not the same and it is furthermore still unclear how the permeation speed of water behaves as function of the viscosity of the organic matrix. For both reasons, it is doubtful that water uptake onset and glass transition of the organic matrix coincide in a deliquescence experiment. I would suggest working out the differences in both methods of Tg determination a bit more and you may want to point out what assumptions go into your proposed values for Tg.
To correctly discuss Fig. 1 it might be helpful to plot the "state diagram" in T vs. water activity (aw) space to omit the problem of non-equilibrium aerosol particles or alternatively point out that the particle has to be in full humidification equilibrium to adopt the

state suggested by the state diagram.

Specific comments

p. 27336, l. 16ff - This sentence implies that Debenedetti and Stillinger (2001) treated glassy solids in the context of atmospheric aerosol, which is not the case.

p. 27337, l. 8 - What do you mean with “natural” aerosol particles?

p. 27340, l.20 - It is not clear to the reader what feature in the C-H-stretch signal at 2900-3100 cm^{-1} can lead to distinction of glassy and crystalline organics. It is neither obvious from Fig. 2, nor is it used for distinction later in the text.

p. 27344, l. 18f - Please indicate again how exactly liquid water was observed here, I guess raman spectroscopy?

p. 27344, l. 21ff - If the glass transition values at 0 % and 100 % RH have been weighted differently than the other experimental values in the polynomial fit, please indicate this. Glass transition values normally follow a Gordon-Taylor relationship (see e.g. Zobrist et al. (2008), Koop et al. (2011)), have you tried to do the fitting following this approach? This could be helpful for the comparability of your study to existing studies.

p. 27345, l. 1 - Please make more clear that this only the case after full equilibration with the surrounding air, which must not be the case at humidification rates of 0.1 % RH/min, especially at very low temperatures due to diffusion limitations. It would be correct in any case if the state diagram would be T vs. aw.

p. 27346, l. 19 - Where do you find this value in Wang et al. (2012)? They found rather ≈85 % RH or ≈115 % RHice.

p. 27348, l. 17ff - Wang et al. find heterogeneous nucleation onsets of Sice > 1.35. This is a significant deviation to the values in this study (Sice=1.2-1.4) that I find worth mentioning.

p. 27348, l. 28ff - In this sentence it is hard to understand what exactly can be explained by competition between water uptake and ice nucleation. Please reformulate. Does competition occur between particles or for every individual particle? You could also mention the possibility of a potential immersion freezing here.

p. 27349, l. 6 - Which paper is meant here, Wang et al. still? Please make this clearer.

p. 27349, l. 8f - What exactly is similar in the ice habit? This would be worth mentioning if it can be explained in 1-2 sentences.

p. 27351, l.10 - Liquid and amorphous don't exclude another. What you mean is "either liquid or (semi-) solid amorphous".

Fig. 1 - Why does the experimental trajectory bend off? This is not explained in the text.

Fig. 2 - The exact onset cannot be determined from the diagrams. I'd suggest adding figures with spectral subtraction data as supplementary material.

Technical corrections

p. 27339, l. 13 - Consider writing "glass transition curve (Tg, blue)" for consistency inside the sentence.

p. 27346, l. 19 - Here it should be "onsets" instead of "onset".

p. 27343, l. 15 - I find "dramatic" too strong here.

Table A1 - Denotation "A1" is usually used for tables in the appendix, consider changing it to "1". First column: Consider using substance(s) instead of substance.

Figs. 3 to 5 - Right panels contain a lot of blank space, consider changing y-axis range to Sice=0.8 - 1.8.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 27333, 2012.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper