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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous ice nucleation on phase-separated organic-sulfate particles: effect of liquid vs. glassy coatings" *by* G. P. Schill and M. A. Tolbert

Anonymous Referee #3

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General Comments:

This manuscript describes the ice nucleation activity of phase-separated ammonium sulfate-organic polyol particles. Low temperature deliquescence and efflorescence transitions were investigated and phase separation of the organic and ammonium sulfate phases was confirmed using microscopy images and Raman spectra. Liquid organic and semi-solid organic coatings were studied. The phase of the organic coating was found to affect the nucleation mechanism, but, interestingly, the IN activities of particles having both liquid organic and semi-solid organic coatings were similar to that of pure ammonium sulfate.

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Interactive Discussion
Discussion Paper

Overall, the methods and results presented in this manuscript are clearly described and scientifically sound. The topic of ice nucleation on or in phase-separated organic-inorganic particles is timely and of scientific interest to the ACP readership. Thus, I recommend the manuscript be published in ACP with only a few comments and minor corrections to be addressed.

Specific Comments:

1. On page 30964, lines 17+, I found the statement "At temperatures > 220 K, the C6/C10 and C6/C10/AS systems behave similarly to pure C6 and C6/AS" to be slightly misleading. There are some qualitative similarities among pure C6/C10 and C/6, such as the observation that the pure organic particles are poor IN compared to the organic mixed with AS. However, there are also significant differences: The IN activities of pure C6/C10 and C6 particles do not agree quantitatively (as far as I can tell from Figures 6 and 9), and the authors attribute different mechanisms of ice nucleation to each system (homogeneous freezing in C6 particles, heterogeneous nucleation in C6/C10 particles).

2. Page 30964, lines 20-21. As a follow on to comment 1, if water is able to diffuse through the C6/C10 coating and nucleate on the AS core at T > 220 K in the mixed C6/C10/AS particles, is heterogeneous nucleation really expected on the pure C6/C10 surface at T > 220 K? Were any images collected of ice nucleation on the surface of the pure organic C6/C10 at T > 220 K that could support the occurrence of heterogeneous nucleation? Alternatively, is it possible that C6/C10 is more solid-like in pure form (and hence more likely to act as a heterogeneous nucleus) than when present as a coating on ammonium sulfate, possibly because small amounts of ammonium sulfate and water were mixed into the organic material in the C6/C10/AS particle?

3. I suggest a few clarifications in experimental sections 2.3 and 2.4 to aid in the reader's understanding of the experimental procedures:

a. It would be easier to follow the experimental procedure if the cycles of RH and tem-

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perature that a particle experienced throughout the experiment were explicitly summarized, perhaps in a table or figure.

b. On page 30960, when the ice is sublimed by increasing T by 10 K, is the water vapor control also cut off? Consider including the temperature and RH for this step in the experimental summary table or figure suggested above.

c. What specific dew points were used? Consider including this information also in the experimental summary table or figure suggested above.

Technical Corrections/Minor Comments:

P. 30952, line 14. “cycohexanol” should be “cyclohexanol”.

P. 30954, lines 11+. The statement that “complex organic-sulfate particles consisting of three separate dicarboxylic acids will always phase separate” is too strong. I suggest modifying the statement to something like the following: “complex organic-sulfate particles consisting of three separate dicarboxylic acids are also very likely to phase separate” or “complex organic-sulfate particles consisting of three separate dicarboxylic acids studied by Song et al. (2012) always phase separated, as long as their combined O:C ratio was <0.7.”

P. 30955, line 2. I suggest deleting the word “bare” in this sentence. It is confusing, as the authors refer to the ammonium sulfate as coated in the same sentence. The subsequent sentence is sufficient to explain that the coating was partial and so ice nucleation occurred on an uncoated, or bare, ammonium sulfate surface.

P. 30955, line 6. I suggest deleting the word “liquid” in this sentence because the manuscript examines both liquid and glassy organic coatings.

P. 30955, lines 10+. Recent literature implies that secondary organic material is an amorphous solid, especially at low RH (e.g., Virtanen et al. 2010 and Saukko et al. 2012). Therefore I suggest modifying the statement beginning on line 10 (sentence beginning “Real organic aerosol. . .”) such that it reflects the recent literature. For ex-

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ample, “Real organic aerosol will most likely be composed of thousands to hundreds of thousands of species (Goldstein and Galbally, 2007), and be in a liquid or solid amorphous, not crystalline state (Marcolli et al., 2004, Virtanen et al., 2010).”

P. 30956, line 17. Add unit “K” to (Tg =193.5±1.3).

P. 30957, line 8. Isn’t it just water being evaporated? Why do you say “water mixture”?

P. 30961, line 11. Suggest changing “simple component” to “binary”.

P. 30961, line 13. Change “little temperature dependence” to “no temperature dependence within error” if the SRH values at 245 K and 273 K are really consistent.

P. 30962, line 24. Is the 2:1 organic-to-sulfate mass ratio used to calculate VAS/Vtotal really an assumption (i.e., isn’t it the composition of the bulk solution and deposited droplets)? If accurate, change statement to: “We then calculated the experimental ratio VAS/Vtotal using the 2:1 organic-to-sulfate mass ratio of the bulk solution.”

P. 30962, line 28. Change “are” to “is” as follows: “and is inconsistent with both configurations.”

P. 30967, line 24. Typo: “Smith et al. (2011)” should be “(Smith et al., 2011).”

P. 30969, line 9. Typo: “This is accord with previous work on ice nucleation on simple organic glasses.”

Figure 4 caption. Instead of using cool-to-warm scale for gray, perhaps use a more descriptive wording such as dark-to-light?

Figure 7, 8, 10, 11 captions: I may have missed it, but at what temperatures were the images shown in Figures 7, 8, 10, 11 taken? I would suggest listing the temperature in either the caption or as an inset in the figures.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 30951, 2012.