Response to anonymous referee #3

The referee's comments are italicized and our responses are in plain text

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. 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.

The authors would first like to thank anonymous referee #3 for their insightful comments that have improved the clarity of this manuscript.

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).

The authors agree that this statement is misleading and have changed it to read: "The results of these experiments are shown in Fig. 10. At temperatures ≥ 220 K, the C6/C10 and C6/C10/AS systems have similar flow behavior to pure C6 and C6/AS. Furthermore, their ice nucleation behavior is qualitatively similar. Here, the pure organic system tends to be a poor IN; however, it is important to note that the pure organic mixture nucleates ice below the Koop homogeneous nucleation line and, therefore, the particles are likely acting as heterogeneous IN."

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?

The authors agree that the ice nucleation data points for the pure organic mixture from 220 to 230 K are surprising results. Using the same analysis found in the new Fig. 8, we are able to conclude that the pure organic mixtures particles are able to flow and stretch with the growing ice particle. To affirm that these particles were indeed inducing ice formation below the homogeneous freezing line we conducted a minimum of six ice nucleation experiments on three independent samples for these data points rather than the usual three experiments on two independent samples. Analysis of the ice nuclei were also conducted to confirm that solid impurities, capable of acting as immersion mode ice nuclei, were not present visually or spectrally. Although it is beyond the scope of this paper to ascertain the mechanism behind these surprising results, the authors postulate that these particles may have the flow behavior of a liquid, but are still sufficiently viscous to provide a surface template for heterogeneous ice nucleation. To support this postulation, the viscosity of the pure organic mixture at the temperature and relative humidity of the ice nucleation event has been calculated using Equation 1. For the 220, 225, and 230 K experiments, ice formation was noted at approximately 79.8, 80.2, and 85.3% relative humidity with respect to water, respectively; this corresponds to estimated viscosities of $5.2\text{x}10^3$, $1.5\text{x}10^3$, and $1.2\text{x}10^2$ Pa s, respectively. These viscosities roughly correlate to those of peanut butter to ketchup and are considered low-viscosity semi-solids (Koop et al., 2011). While these calculations provide only a rough estimation of these particles' viscosity, they affirm that the pure organic mixture at these temperatures and relative humidities could be viscous enough to provide a surface for heterogeneous ice nucleation.

As suggested by the referee, we have highlighted these results in section 3.3 and added the above discussion in section 3.4.

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 temperature 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.

The authors agree that the manuscript would benefit from an additional experimental procedure diagram. This has been added as Figure 2 (see below).

Additional text has also been added to Sections 2.3 and 2.4 to guide the reader through this figure.

Technical Corrections/Minor Comments:

P. 30952, line 14. "cycohexanol" should be "cyclohexanol".

Changed

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."

This line was changed to "complex organic-sulfate particles studied by Song et al. (2012), consisting of three separate dicarboxylic acids, 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.

Deleted

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

Deleted

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- 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)."

This sentence was changed and the Virtanen et al. (2010) reference added to manuscript

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

Added

P. 30957, line 8. Isn't it just water being evaporated? Why do you say "water mixture"?

Deleted the word "mixture"

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

Changed

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.

Changed

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."

Changed

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

Changed

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

Changed

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

This was changed to "this is still in accordance …"

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

The new Fig. 5 caption now reads "Two-dimensional Raman spectral map of a phase-separated, effloresced C6/AS particle at 298 K. The sulfate-containing region is shown as a color map where warmer colors refer to a higher intensity of the SO_4^{2-} peak (972 cm^{-1}). The organiccontaining region has undergone a similar analysis using the C-H peak (2900 cm^{-1}); however, this map has been grey-scaled for clarity. As shown, the particle is fully coated laterally."

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.

The images shown in the new Fig. 8, 9, 11, and 12 were all taken at 215 K. This temperature has been added to the appropriate figure captions.

FIGURES

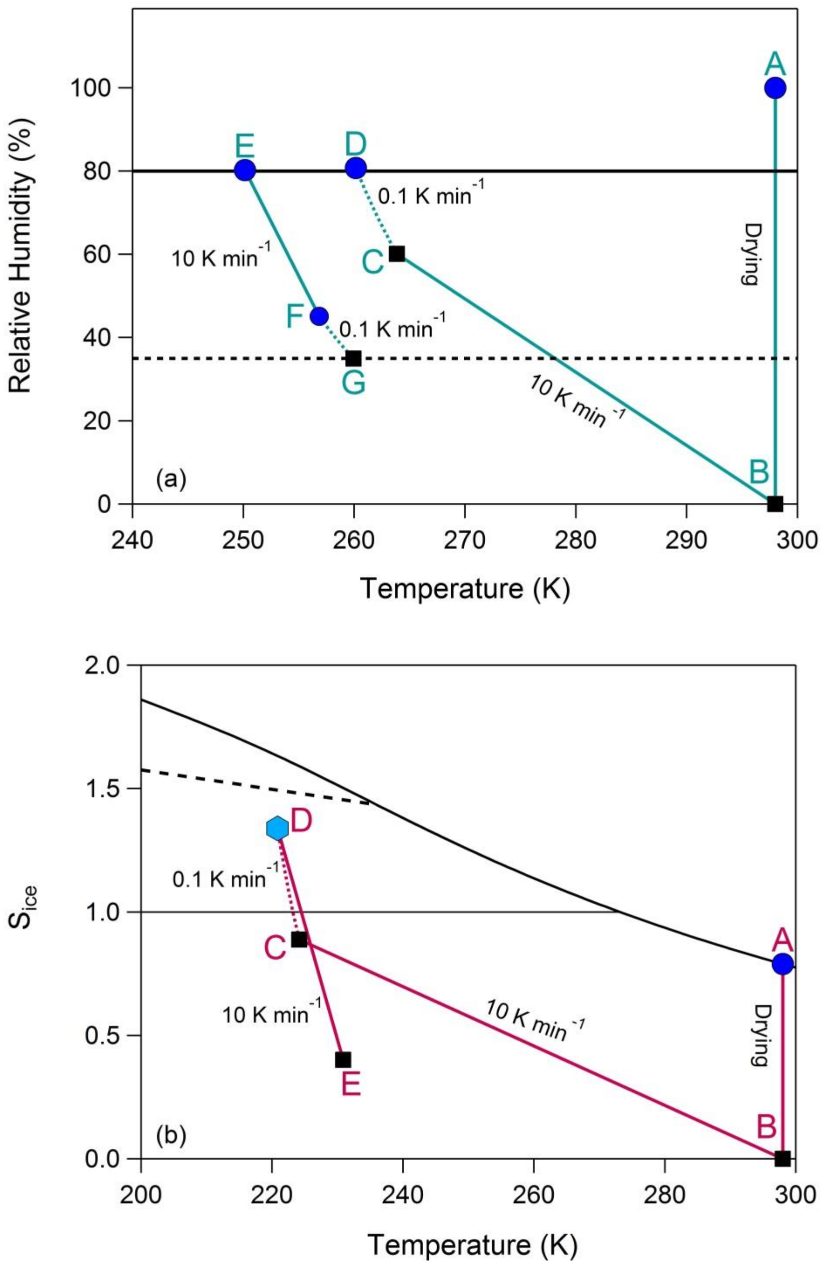

Figure 2. Experimental trajectories for (a) deliquescence/efflorescence and (b) ice nucleation shown in relative humidity and ice saturation ratio (S_{ice}) space, respectively. Each trajectory line has been labeled with an experimental heating/cooling rate. The solid and dashed black lines in Figure 2a correspond to the deliquescence and efflorescence RH of ammonium sulfate, respectively. The thick solid, dashed, and thin solid black lines in Figure 2b correspond to water saturation, the S_{ice} values for homogenous nucleation of an aqueous droplet, and ice saturation, respectively. The capital letters in the panels indicate points that are of special interest; see text for details.

REFERENCES

Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Physical Chemistry Chemical Physics, 13, 19238-19255, 10.1039/c1cp22617g, 2011.

Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmospheric Chemistry and Physics, 12, 2691-2712, 10.5194/acp-12-2691-2012, 2012.

Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirila, P., Leskinen, J., Makela, J. M., Holopainen, J. K., Poeschl, U., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: An amorphous solid state of biogenic secondary organic aerosol particles, Nature, 467, 824-827, 10.1038/nature09455, 2010.