Response to anonymous referee #1

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

General Comments

This manuscript describes laboratory experiments of phase separation, deliquescence, efflorescence, and ice nucleation by generated aerosol particles composed of ammonium sulfate mixed with alcohols. Experiments were performed in an environmental cell, and optical and Raman microscopy were used for particle analysis. The manuscript is clear, concise, well written, and describes an interesting set of experiments. The experimental procedure is particularly well suited to studying particle nucleation and phase behavior, and the authors were creative in teasing out relevant details. The growth of organic coating around the expanding ice, and the particle morphology analysis in section 3.2 are particularly noteworthy. Relevant results from recent literature were used widely and appropriately and to great benefit. The results are highly valuable to the ever-expanding research effort to understand ice nucleating and phase behavior of realistic aerosol mixtures at cold temperatures. Overall, this high quality work should be published in ACP without major revisions. The authors should address the minor comments listed below.

The authors would first like to thank referee #1 for their insightful comments that have improved the clarity of this manuscript.

The manuscript would benefit from a simple schematic diagram of the experimental procedure. Start from the impacted wet aerosol as placed inside the cell and list all temperature & RH adjustment steps with labels describing the step. One diagram for the deliquescence/efflorescence experiments, one for the ice nucleation experiments. Could be added to Figure 1.

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.

p. 30959 l. 17 and p. 30960 l. 11. Specify if the three repetitive experiments were performed using different particles.

The authors agree that it is important to emphasize that more than one set of particles were used. These lines now read “at least three experiments were performed at each temperature on at least two independent sets of particles.”

Section 2.4. As written, the experimental procedure is essentially the same as for the deliquescence procedure. The key difference is the lower temperature for the ice nucleation

experiments. Make this clear. It is interesting that the ice nucleation experiments require that the particle will freeze before it deliquesces under those conditions.

The authors acknowledge that the similarity between the deliquescence and ice nucleation experiments provides interesting information about the mode of nucleation. The following sentence has been added to section 2.4: “This experimental procedure is essentially the same as the deliquescence experiment, but at lower temperatures; thus, in these experiments, depositional nucleation is only possible before deliquescence occurs.”

p. 30964 l. 21. It is surprising that the pure organic mixtures, presumably liquid, seem to act as heterogeneous IN. Can the authors propose an explanation for this? Perhaps the pure C10 organic would act as a heterogeneous IN? The authors might choose to highlight this result in section 5.

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 5.2×10^3, 1.5×10^3, and 1.2×10^2 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.

Section 4. Add a sentence or two discussing any possible size effects. Particles in the experiment have factors of 100’s to 1000’s more volume than a typical accumulation mode aerosol particle. One obvious difference is the coating thickness in the LLPS particles and thus the diffusion time for water. Might phase separation be affected?

The authors acknowledge that possible size effects, especially those regarding the thickness of the organic coatings and the diffusion time for water should be discussed. The following sentences have been added to Section 4: “It should be noted, however, that the particles used in this study are larger than potential ice nuclei expected to be found in the upper troposphere (Froyd et al., 2009); in fact, particles used in this experiment have volumes a factor of hundreds to thousands larger than a typical accumulation mode particle. This could induce a size effect, especially with regard to the diffusion of water to the particle core. Since water diffusion times will be longer for thicker organic coatings/larger particles, the particles used in this study could exhibit glassy behavior at warmer temperatures than smaller particles typically found in the upper troposphere.”

p.30968 l. 23. Written in this context, it is important to note that Jensen assumed that organic coatings or mixtures did not inhibit ammonium sulfate efflorescence, ie, ERH = 35%.

The authors acknowledge this an important point to clarify to the reader. This sentence now reads “Finally, modeling work from Jensen et al. (2010) have shown that deliquesced ammonium sulfate particles that detrain from deep convective updrafts in the cold tropical tropopause layer can undergo efflorescence and be dry 20-80% of their lifetime; however, it is important to note that these results only hold if the organic coatings or mixtures do not inhibit efflorescence.”

Fig 2. The organic-to-sulfate ratio at the particle core seems to have increased significantly upon efflorescence. Is this a real effect?

This is not a real effect as the organic-to-sulfate ratio of the particle in Fig. 3 is constant. The authors postulate that in Fig. 3c, the Raman laser is probing the aqueous sulfate core with a thin organic layer on top; however in Fig. 3e, the laser is probing a smaller sulfate core because the ammonium sulfate has effloresced, and, therefore, a relatively thicker organic shell.

Technical Corrections

p. 30958 l. 26. Use of schlieren here. . .? (“diffused into each other. . .”).

The authors acknowledge that this sentence was worded confusingly and now reads “Initial phase separation occurred in the form of schlieren (Ciobanu et al., 2009), which coalesce to form AS inclusions that diffuse into each other to eventually form two distinct phases.”

Fig 4 caption. Mention that this is an effloresced particle. The ‘warmer colors’ description is not well applied to the grayscale shading.

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 organic-containing 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.”

p. 30967 l. 26. Specify Aerodyne AMS.

Changed

p.30969 l. 11. Wording. “This is accord. . .”

Changed to “this is still in accordance …”

FIGURES

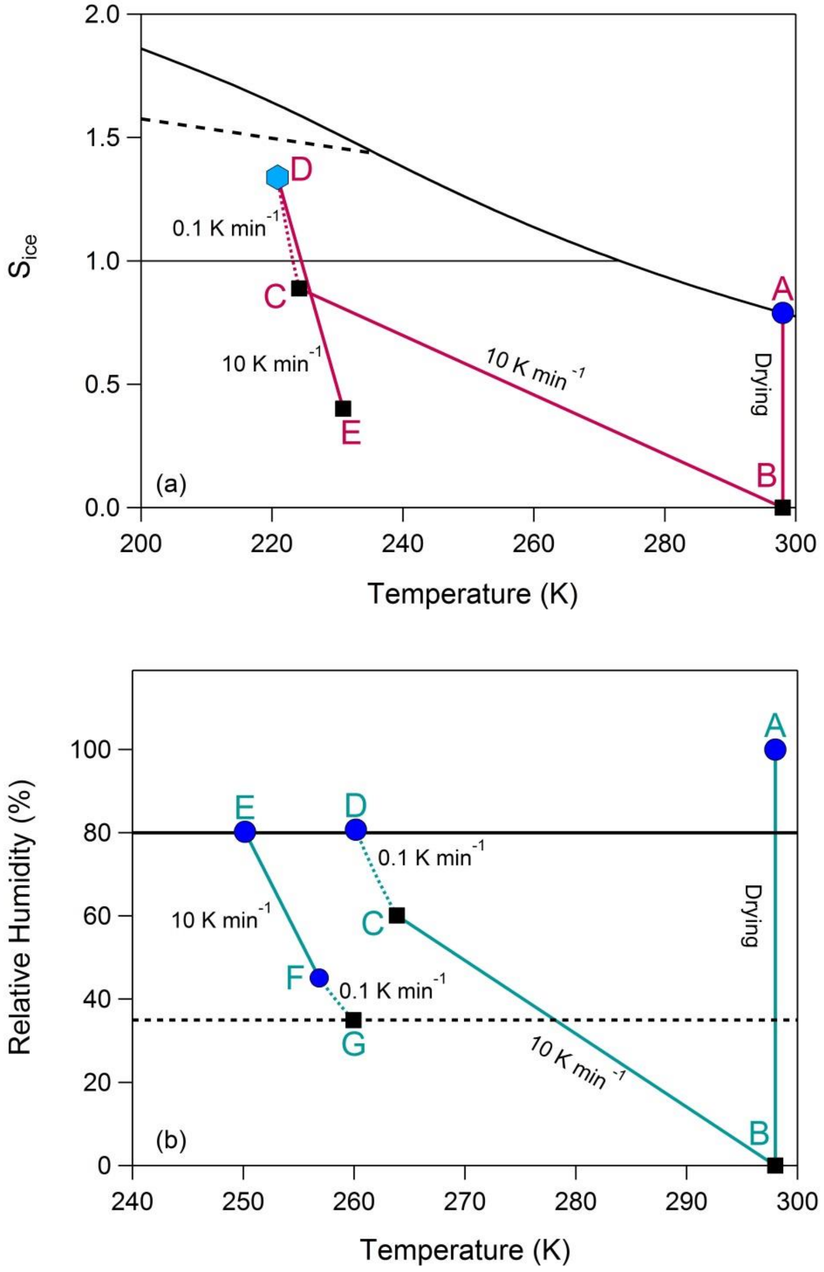

Figure 2. Experimental trajectories for (a) deliquescence/efflorescence and (b) ice nucleation shown in relative humidity and ice saturation ratio (S_{ice}) space, respectively. Each trajectory line has been labeled with an experimental heating/cooling rate. The solid and dashed black lines in Figure 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

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