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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles" *by* M. Song et al.

Anonymous Referee #1

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This manuscript investigates liquid-liquid phase separation in particles containing ammonium sulphate, water and dicarboxylic acids. These particles are used as proxies for atmospheric particles containing inorganic salts, organics, and water. Since the number of studies on liquid-liquid phase separation of atmospherically relevant particles is rather limited, these studies are timely and important. Previous work on the subject mainly focused on particles containing one organic species. This study improves on these previous studies by investigating particles containing three organic species. Included in this manuscript is information on the relative humidities at which liquid-liquid phase separation occurs, information on the mechanism of phase separation, and information on particle morphology after phase separation. The authors have also in-

cluded thermodynamic calculations to better understand the studied phase transitions. In short, the manuscript is rich with new information and insight, and I strongly recommend it for publication. Listed below are several comments that should be addressed adequately before publication.

Comments:

1. Page 29146, line 5-12. Here I think the authors are implying (likely inadvertently) that crystallization of the organic substance may have occurred in previous studies. This is a minor comment, but I would not criticize some of the previous studies since often care was taken to pick systems where the organics didn't crystallize (for example Ciobanu et al. 2009). I would argue things differently. Studies on more complex organic mixtures are needed since atmospheric aerosols are more complex.

2. Page 29150, line 15 to 20. At this point it was not clear why calculations were necessary on both 5-component systems and 3-component systems. It may be useful to the reader to add this information at this point in the manuscript.

3. Page 29157, line 25-30; Page 29158, line 1-5; and Figure 5. The authors suggest that the needles are composed of crystalline ammonium sulphate. These needles appear to grow out of the organic rich phase. Is it possible that the needles consist of crystalline organic material? Also, in these experiments, did nucleation start in an aqueous AS inclusion?

4. Page 29158, line 24-26. In the experiments where LLPS was not observed, is it possible that LLPS occurred, but the phase separation was not detected with the optical technique? For example, could AS inclusions spread out at the bottom of the droplet and not be detected?

5. Page 29160, line 29. Would it be clearer and still accurate to say that spinodal curves were calculated for 3-component particles rather than 5-component particles due to the computation expense of calculating spinodal curves for 5-component particles.

6. Page 29162, line 15. Smaller than what?

7. Page 29163, line 14-25. I don't completely understand this section. The authors state "we do not have a regular LLPS in this composition range but a more structured phase with a fixed stoichiometry". Later on they state "leading to a different mixture composition and a LLPS in a relatively narrow AS mass fraction range, partly overlapping with the coexistence curve at higher AS mass fractions". The two statements above sound inconsistent. Are they referring to a crystalline phase? It would be good to add some references to show that this type of behaviour has been observed before.

8. Page 29165, line 29. I assume "wt %" should be "wt % AS"?

9. Page 29167, line 25-27. "Figure 11 gives the position of the organic components of alcohol and polyol/AS/water and carboxylic and dicarboxylic acid/AS/water system from literature (see table 2)." Table 2 also includes ethers, esters and aromatics. Does Figure 11 include data for these functional groups as well, or have they been excluded from the figure?

10. Page 29169, line 24-26 (as well as other places in the manuscript). The authors conclude from their studies that a core-shell structure and partially engulfed configuration might very likely be present in the troposphere. Can the authors rule out that the hydrophobic surface doesn't affect/change the morphology of the particles in their experiments? In other words, if someone repeated these studies with suspended particles, would the authors expect the same result? This should be discussed in the manuscript.

11. Page 29159, line 26. "... spinodal decomposition occurs barrier-free at the border to the unstable region." Do the authors mean that when spinodal decomposition occurs at the border to the unstable region, it occurs without a kinetic barrier? Maybe rewrite this sentence to improve clarity.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29141, 2011.