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Interactive comment on "Observations and implications of liquid–liquid phase separation at high relative humidities in secondary organic material produced by α-pinene ozonolysis without inorganic salts" *by* L. Renbaum-Wolff et al.

Anonymous Referee #2

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This manuscript describes observations of the interactions between atmospheric water and organic mixtures containing species formed in alpha-pinene ozonolysis, probed with optical microscopy. The interpretation of the observations is supported by thermodynamic calculations. The topic is interesting and within the scope of ACP. However, I have a number of questions and concerns, some of which are relatively major, that need to be satisfactorily clarified before the manuscript can be considered for publication in ACP. Especially the description of the thermodynamic modeling and theoretical interpretation of the results needs to be substantially improved.

General / major comments:

1. Representativeness of the results needs to be discussed in more detail.

The authors need to elaborate on the representativeness of the sample as compared with atmospheric SOA in terms of e.g. the distributions of solubilities and volatilities of the compounds forming the mixture as well as the size of the investigated particles (which is rather large as compared with what one would expect for atmospheric SOA). Furthermore, the authors need to comment on the representativeness of the gas-phase composition at different stages of the experiment as compared with the real atmosphere.

2. The interpretation of the results and the thermodynamic calculations need to be explained more rigorously.

The authors seem to be observing the formation of an organic surface phase whose formation is preceeded by complete dissolution of the organics and mixing of the aqueous phase formed. On the rising branch of the Dp vs. RH curve (Fig. 1A), one starts with an organic-dominated phase (with potentially some water adsorbed within the organic matrix) at low relative humidities, and as the humidity is increased, heterogeneous nucleation of an aqueous phase with dissolved organics takes place around 96.0 % RH, leading to a complete dissolution of the organics between 96 and 99.9% RH. And, through mixing of the aqueous droplet, re-alignation of the organic species close to the droplet surface, which is here termed as liquid-liquid phase separation.

On the decreasing branch of the RH curve, on the other hand, the interpretation of the observed behavior is less clear – in their schematic the authors seem to imply a phase transition between 95.2 and 95.0 % RH, but it seems to be a rather bold conclusion to draw just based on the images provided. The authors need to elaborate more on the justification of their interpretation of the images, based on quantitative thermodynamic arguments or at least clarify what are the marked differences between the images corresponding to 95.2 and 95.0 % RH. The same naturally holds for the interpretation of the images in Fig. 2b (which evidence actually implies that a phase transition occurs 95.4 and 95.1 % RH?).

It is well known that many organic molecules tend to populate the air-particle interface due to their hydrophobic functional groups. If the formation of a surface phase is indeed the case, I suspect the authors need to consider surface tension modifications in their thermodynamic calculations to truly predict the phase separation observed at the high relative humidities. All in all, does the thermodynamic model predict the presence of two liquid phases and what compounds do they consist of? This information should be provided.

3. In general more details are needed on the results of the thermodynamic calculations with AIOMFAC, the hygrosopic growth factor and the CCN activation (see also point 5 below). Do you expect the surface tension to be that of water, looking at the images presented in Figs. 1-2? Which phases did the model predict at different RHs as compared with the experimental data given in Figs. 1-2? Did the model support the interpration of the data in Figs. 1-2 (following the schematics), i.e. what was predicted to happen between 95-96% RH? Did the model predict the differences between increasing and decreasing RH? If yes, what are the theoretical grounds for this behavior?

4. The authors use the term ”spinodal decomposition” as the process explaining the proposed liquid-liquid phase separation at high relatively humidities. Correct me if I am wrong but the term simply refers to barrierless nucleation within the liquid (in this case it would be the aqueous) phase. The authors need to provide theoretical arguments to clarify why they would expect this phenomenon to happen more readily at higher relatively humidities for the studied systems. Furthermore, the authors need to provide a brief theoretical summary of what spinodal decomposition means in terms of the energetics of the system.

5. The authors are discussing a system with apparently several phase transitions happening over the RH ranges probed (?). It is stated that the thermodynamic model can

predict the observed liquid-liquid phase separation at high RHs. However, in Fig. 3 and the associated discussion it is only vaguely stated that below about 95% the particles are in ”liquid or semisolid” phase ”depending on RH”. What do the authors mean by this? Is this reproduced by the thermodynamic model? How does the physical phase of the expected homogeneous phase depend on RH and what controls it – when would be expect a liquid and when and semi-solid phase? More detailed discussion on this is needed.

6. In the abstract the authors state that ”the presence of LLPS at high RHs can explain inconsistencies between measured CCN properties of SOM particles and hygroscopic growth measured below water saturation”. It is unclear how LLPS per se can explain such differences. Please clarify (based on the more detailed explanation of the theoretical calculations).

Technical / minor comments:

7. P. 7, lines 17-18. The interpretation of the figures is unclear. What do the authors mean by the ”volume ratio of the outer phase to the inner phase”? How are the ”outer” and the ”inner” phase exactly defined from the images?

8. It would be useful to be able to directly compare the RHs to each other on the increasing and decreasing RH branches of Figs. 1 and 2. Now images collected at different RHs as presented in the same column, which makes the direct comparison difficult.

9. P. 8, lines 8-9. What do the authors mean by ”the amount of phase separation increases as the RH decreased”. Please quantify.

10. P. 10, lines 21-29: This section seems unneccessary and speculative without any theoretical or experimental new results to back up the statements.

11. Figure 5A: The LLPS seems to disappear from the model predictions at 500 nm droplet size. What happens there? Is this theoretically sound?

12. Figure 5B: The decreasing trend of the hygrosopicity parameter with increasing RH at sub-saturated conditions is interesting. What is the thermodynamic explanation for this behavior?

13. The authors need to go carefully through the manuscript for typos and inconsistencies. The manuscript seems to have been put together in a hurry and consequently the presentation quality can probably be improved with one more round of careful editing by the authors.

14. The experimental methodology needs to be briefly specified in the abstract.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 33379, 2015.