

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.

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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

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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.

[A1] For the representativeness of the samples as compared with atmospheric SOA see response #4 to Referee # 1. Regarding the size of the investigated particles, we have added additional simulations of the hygroscopic growth factors of 100 nm particles to address the referee's comments. See Section 3.2 and Panel B of Figure 4. The new text added to Section 3.2 is reproduced below.

"Shown in Panel B of Fig. 4 are the simulated hygroscopic growth factors of a 100 nm dry particle for the three different SOM mixtures (SOM-high, SOM-low, SOM-ox) and again assuming a surface tension of water. This figure illustrates that LLPS can shift to $\text{RH} > 100\%$ in small particles due to the Kelvin effect. In 100 nm particles, the SOM took up little water at $\text{RH} < 100\%$, and LLPS is predicted above 100 % RH. "

[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 preceded 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

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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-alignment 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?).

[A2] To address the referee's comments we have added three additional movies (Movies S2-S4) to the Supplement. Movie S2 will correspond to Figure 1B, Movie S3 will correspond to Figure 2A and Movie S4 will correspond to Figure 2B. These movies show much clearer the phase behavior with decreasing and increasing RH.

[3] 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.

[A3] To address the referee's comments regarding surface tension, we have added additional simulations of Kohler curves and hygroscopicity parameters using a surface tension of 40 mN m⁻¹ which is consistent with the surface tension of aqueous mixtures of pinonic acid, pinic acid, and pinonaldehyde (see Section 4.1 and Figure 6). Below is the new text added to Section 4.1.

"Shown in Panel A of Fig. 6 are simulated Köhler curves for SOM particles with dry diameters of 100 nm and using the surface tension of 40 mN m⁻¹, which is consistent with the surface tension of aqueous mixtures of pinonic acid, pinic acid, and pinonaldehyde. Panel A of Fig. 6 illustrates that a lower surface tension has a large effect on the first maximum in the Kohler curve and also lowers the barrier of the second maximum. During the activation process, the surface tension is expected to increase as the phase state changes from organic-rich to water-rich, but this process is not modelled here. Additional studies are needed to fully understand the effect of varying surface tension on the resulting Kohler curves."

[4] In general more details are needed on the results of the thermodynamic calculations with AIOMFAC, the hygroscopic 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 interpretation 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?

[A4] Most of these comments are now addressed in the responses to other questions. For example, see the response to the previous question and the response to Referee #1, Question #3. Regarding the difference between increasing and decreasing RH, the thermodynamic model cannot predict differences between increasing and decreasing RH because it calculates thermodynamic equilibrium. The important finding is that LLPS is indeed predicted by the thermodynamic calculations.

[5] 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

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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.

[A5] To address the referee's comments we added a brief discussion of what spinodal decomposition means in terms of the energetics of the system (Sect. 3.1). In addition in the revised manuscript we discussed why it is reasonable to expect LLPS to occur at high relative humidites. Below is the added paragraph on the latter topic.

"The behavior observed here for SOM is consistent with bulk thermodynamics. Consider, for example, a mixture of a relatively hydrophobic organic with a less hydrophobic organic, such as a mixture containing equal mole ratios of heptanol and propanol. Under dry conditions this mixture exists as a single phase. As water is added to the system, the mixture exists as a single (organic-rich) phase until the water content is approximately 0.3 mole fraction. At this point, the mixture separates into an organic-rich phase and a water-rich phase. As water is further added to the system, the two phases co-exist until a large amount of water has been added, at which point all the organic material dissolves into the water-rich phase. The formation of two phases is due to the non-ideality of the mixture. I.e. if the mixture was ideal, LLPS would not occur. Examples of other organic mixtures that exhibit this type of behavior include mixtures of hexanol and acetic acid and mixtures of octanol and acetone. For a long list of organic mixtures that undergo liquid-liquid phase separation when mixed with water, see Table 1 in Ganbavale et al. (2015)"

[6] 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

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of the expected homogeneous phase depend on RH and what controls it – when would we expect a liquid and when a semi-solid phase? More detailed discussion on this is needed.

[A6] Thank you for pointing this out. The thermodynamic model does not calculate viscosities. We were classifying the phase as “liquid or semisolid” based on previous measurements in our group as well as other groups. To avoid confusion, we will remove the discussion of semisolid from the manuscript as well as from Fig. 3.

[7] 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).

[A7] This section of the abstract has been re-written for clarity.

Technical / minor comments:

[8]. 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?

[A8] The interpretation has been rewritten to try and improve the clarity.

[9] 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 are presented in the same column, which makes the direct comparison difficult.

[A9] We appreciate the comment and agree that directly comparing the images would provide clarity in some senses; however, as the purpose of Fig. 1-2 is to show the onset and disappearance of LLPS and not to compare the images at similar RH, and because reversing the direction of Figs. 1b and 2b may make it appear at first glance

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2016

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as if the RH is increasing, we have opted to leave the figure as-is. However, to address the comment by the reviewer, the corresponding movies have been added to the Supplemental Information. These movies provide insight into LLPS during RH cycling. We have also changed the color scheme in Figs. 1 and 2 to improve clarity.

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

[A10] This sentence was rewritten for clarity.

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

[A11] To address the referee's comments we have removed this section from the revised manuscript.

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

[A12] The disappearance of LLPS at 500 nm is consistent with our theoretical understanding. At 500 nm size, the particle has now taken up a large amount of water and even the more hydrophobic organic material can completely dissolve, resulting in a single aqueous phase.

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

[A13] The decrease in the hygroscopicity parameter is explained by the solution non-ideality. This has been clarified in the manuscript.

[14] 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

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by the authors.

[A14] We have gone through the manuscript a few additional times, and we hope that now all the typos and inconsistencies are removed.

[15] The experimental methodology needs to be briefly specified in the abstract.

[A15] To address the referee's comments in the revised abstract the experimental methodology has been briefly specified.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/15/C13463/2016/acpd-15-C13463-2016-supplement.zip>

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

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2016

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