

Professor Annele Virtanen
Co-Editor of Atmospheric Chemistry and Physics

Dear Annele,

Listed below are our responses to the comments from the reviewers of our manuscript. For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. *[I]*). Authors' responses are in red below each referee statement with matching numbers (e.g. *[AI]*). We thank the reviewers for carefully reading our manuscript and for their very helpful suggestions!

Sincerely,
Allan Bertram
Professor of Chemistry
University of British Columbia

Anonymous Referee #1

The paper presents a laboratory study of SOA particles produced during nucleation and condensational growth of products formed in the ozonolysis of alpha-pinene in the absence of inorganic material. Using an optical microscope to determine the phases present on single-stage impactor-sampled SOA particles of 5 to 80 microns diameter during RH adjustment, the authors draw inferences about the influence of LLPS and the impact on inferring CCN behaviour from sub-saturated hygroscopicity measurements. The manuscript addresses areas of current importance and interest in atmospheric science, and is thereby clearly in the scope of ACP. The findings are of potential importance and reinforce some of the findings from previous investigations. I believe the material may ultimately be publishable, but have a number of reservations about recommending publication as it currently stands. Perhaps the authors can alleviate these concerns by addressing some of the following points.

[1] Sample collection: The authors use two techniques for sample collection. In both, the authors take appropriate care to prevent continued reaction and partitioning by removal of excess reactants. The first technique electrostatically collects submicron particles on siliconised glass, activates them by cooling and subsequently deactivates them to 98% by warming to evaporate water. These droplet residuals were between 5 and 30 micron diameter. The second technique collected and coagulated material into 10 to 80 micron diameter particles on hydrophobically coated glass slide impactor substrates with no cooling (activation) - warming (deactivation) cycle. As I understand it, in the first technique, the collected material has had its gas vapour phase components removed

prior to being subjected to a cooling and warming cycle. Can the authors clarify how they ensured that condensed components did not evaporate by partitioning to the vapour phase which is heavily depleted below its equilibrium concentration of all condensed components? This could occur in both the cooling and warming parts of the cycle, but especially in the warming. Secondly, the activation cycle leads to the components being present in the droplets which act as aqueous "chemical reactors". Can the authors comment on how they ensured that the same components were present in the droplet residuals as in the initially collected submicron particles? In the second technique, the first of the problems outlined above may be evident. Again, the authors might like to comment on how they ensured that components did not evaporate during sampling, thereby changing the composition of the condensed material.

[A1] The referee raises the issue of possible sampling artifacts. This is a good question, and to address the referee's comments we have added a new paragraph to Section 2.1.1. The new paragraph is listed below:

"This hygroscopic cycling of method 1 did introduce the possibility for aqueous phase reactions to occur (e.g., simulating cloud water reactions) that might not be present under subsaturated conditions (e.g., aerosol water only). Furthermore, during the RH cycle some of the secondary organic material may have evaporated from the particles. However, the similarities in the results for two collection methods (see Table 1) suggest that neither of these possible processes, if present, changed the chemical composition enough to influence LLPS. Also prior to collection with both methods excess gas phase components were removed with a carbon filter. During this process some of the more volatile material in the SOM may have evaporated. If some evaporation of higher volatility species occurred, the SOM would likely be more similar to the chemical composition of SOM particles in the atmosphere, which are formed at lower particle mass concentrations compared to in the current laboratory experiments."

[2] Methodology for the determination of phases: The observations by optical microscope of the phase separation appears reasonable. However, in the description of the methodology, there is no mention about how the saturation ratio of the organic vapours was controlled. I guess it should be assumed that the vapour phase remained stripped of all reactants. Can the authors comment on how they ensured that there was no evaporation of the components which must have very significant vapour pressures? Having been collected at loadings between 75 microgram/m³ and 11 mg/m³, the saturation concentrations ("C*") range over 3 orders of magnitude (each far greater than those in atmospheric samples). Indeed, if they did not show very significant evaporation during the experiment, this should be explained. One explanation might be that there was significant condensed phase reaction of components after collection, lowering the vapour pressures

of all components. If this is the case, would the authors like to comment on the atmospheric relevance and applicability of their thermodynamic modelling using MCM components?

[A2] Here the referee is raising the issue of SOM evaporation during experiments to determine the phase state. This is also a good point. In the revised manuscript we have added a paragraph to Section 2.1.2 to address this point. The new paragraph is added below:

“During the experiments used to determine SOM phase state the concentration of organic vapours in the flow cell was not controlled. Hence, some of the more volatile material in the SOM may have evaporated during these experiments. However, no visible change in the particle volume occurred during these experiments, suggesting evaporative loss was minimal. The SOM particle mass concentrations used when generating the SOM were similar to those used in Grayson et al. 2015, and the sample preparation methods were identical to those used in Grayson et al. 2015, who showed no visible volume change of the droplets over time periods of greater than 44 hours. It is possible that condensed phase reactions may have occurred that lowered the vapor pressure of the SOM.”

[3] Modelling representativeness: LLE and water uptake calculations were based on components modelled by the MCM at two yields, the highest of which was 3 times lower than the lowest concentration in the current experiments and 523 times lower than the highest. Three observations: i) it is widely known that the MCM is incapable of producing sufficient SOA mass, the predicted compounds being too high in vapour pressure for them to be reliable predictors of the components in the condensed phase, ii) it has been widely reported that the early formation of heavily oxygenated molecules of extremely low vapour pressure contributes to a significant fraction of the SOA forming products in alpha-pinene ozonolysis. Their formation is not included in the MCM and iii) obviously partitioning of components is heavily dependent on condensed phase mass. Why were components used that partitioned under conditions so wildly different from the experiments (and surely the SOM-ox is going in exactly the wrong direction, with less oxidised, higher volatility components dominating condensed mass in such high concentration experiments)? Can the authors comment on how well the components in table 2 can be expected to represent LLE in their experiments and critically evaluate the calculated properties in table 3? I would have thought that there can be little confidence in these predictions.

[A3] This is a good point. To address the referee's comment we have added information to the revised manuscript in Section 2.2 that discusses the representativeness of the modelling studies. The new text is copied below.

“...The average oxygen-to-carbon (O:C) elemental ratios used in the thermodynamic modelling studies are similar to those measured in environmental chambers (e.g. see Chhabra et al. (2011) and references therein).

The oxidation products and their mole fractions used in the thermodynamic modelling studies were used to 1) improve our understanding of the phase state of multicomponent organic mixtures such as those generated during SOM formation from α -pinene ozonolysis and 2) to explore the possible implications of liquid-liquid phase separation in multicomponent organic mixtures such as SOM. However, the oxidation products and their mole fractions were not intended to reproduce the laboratory conditions used here or atmospheric SOM. ”

[4] Atmospheric relevance of components and conclusions about implications: It is stated that alpha-Pinene was chosen for the precursor gas for SOA because it is an important contributor to organic particle mass concentrations in the atmosphere. This is undoubtedly true. However, the concentrations of alpha-Pinene and ozone are both extremely high. The reasons for conducting work under such elevated concentrations in a flow reactor are well understood. However, for the purposes of the current study, there are a number of questions that should be addressed before attempts to discuss the atmospheric relevance of the findings. These relates to all the points outlined above. In the flow tube studies at such high concentrations, the extent to which the oxidation products (at the highest 4 or 5 concentrations, components with C* of hundreds, thousands and even 10000s of microgrammes/m³!) have managed to condense to approach their equilibrium concentrations is not clear. In any case, the high concentrations will lead to partitioning of components that would not be present in the atmosphere under any reasonable condition and will be much lower in O:C and C number than in atmospheric SOA. This will undoubtedly lead to different LLPS behaviour. I don't disagree that LLPS may be responsible for discrepancies in low and high RH hygroscopic growth, but quantitative conclusions as presented in section 4 based on the current laboratory and modelling studies seem to stretch the possibilities. In discussing the implications of their results, the authors should comment n the likely relative magnitude of the influence of the partitioning of components and of LLPS given the differences between their experimental conditions and those in the atmosphere. In making this comment, they should refer to their answers to the points raised in this review. A band in figure 3 showing the concentration range of measured atmospheric biogenic SOA would be helpful to focus the mind.

[A4] To address the referee's comments, we have added a discussion in Section 3.1 that points out the difference between atmospheric mass loadings and mass loadings used in the current experiments. In addition a band showing the concentration range of measured atmospheric biogenic SOA has been added to Figure 3. The new discussion added to the manuscript to address the referees comment is listed below:

“Figure 3 and Table 1 also show that within uncertainties of the measurements, there is no effect of the SOM particle mass concentrations in the flow tube reactor on the lowest RH at which two liquid phases were observed for the range of 75 to 11,000 $\mu\text{g m}^{-3}$. Also included in Figure 3 are

typical SOM particle mass concentrations measured over boreal forests, where α -pinene is an important contributor to SOM (Cavalli et al., 2006). Since the SOM particle mass concentrations used in our experiments when generating the SOM were lower than typically observed in the atmosphere, additional studies are needed to confirm LLPS in SOM produced using atmospherically relevant particle mass concentrations.”

Experimental results: I think the observations of phase separation are robust and contrast well with the previous literature that reported LLPS in the presence of inorganics. These data are consistent, robust and of significance and should ultimately be published.

Anonymous Referee #2

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.

[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 $RH > 100\%$ in small particles due to the Kelvin effect. In 100 nm particles, the SOM took up little water at $RH < 100\%$, 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 D_p 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-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 Köhler 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 Köhler 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 relative 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 relative 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 humidities. 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 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 as 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 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 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.