

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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The paper presents a laboratory study of SOA particles produced during nucleation and condensational growth of products formed in the ozonolysis of alpa-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

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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:

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"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

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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

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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 be-

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haviour. 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 on 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.

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