

Interactive comment on “Liquid-liquid phase separation in secondary organic aerosol particles produced from α -pinene ozonolysis and α -pinene photo-oxidation with/without ammonia” by Suhan Ham et al.

Anonymous Referee #2

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This manuscript studied the liquid liquid phase separation criteria of alpha-pinene derived SOA from both ozonolysis and photo-oxidation pathways with and without the exposure of ammonia gas. The results show that only the ozonolysis pathway could generate LLPS at high relative humidity, regardless of ammonia exposure or not. The manuscript is an extension of the author's previous work and the results are interesting. However, the lack of direct measurements of the chemical composition of the SOA makes it more difficult and less convincing to justify the conclusions that the authors made. I suggest the authors either include more evidence or modify the conclusions

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based on existing evidence before publishing the manuscript. I outline some comments below for the manuscript.

Major comments:

1. The author stated that “The O:C ratio for the SOA particles derived from α -pinene ozonolysis ranges from 0.42–0.44 as per Li et al. (2015), whereas that for SOA particles derived 10 from α -pinene photo-oxidation is 0.40–0.90 according to Lambe et al. (2015).” And then the author makes the conclusion that “LLPS occurred when the average O:C ratio was between 0.34 and 0.44. However, LLPS did not occur when the average O:C ratio was between 0.40 and 1.30.” Please note that the regions of O:C ratios between the LLPS and non-LLPS are overlapping, which makes the conclusion confusing. The author should try to narrow down the O:C ratio for the non-LLPS regions. I recall that the paper by Lambe et al. 2015 shows the O:C ratio based on different OH exposure times. So maybe the authors can compare the OH exposure time in this study with that of the Lambe et al. to obtain a more precise O:C value for photo-oxidation of a-pinene in the the flow tube.

2. Since there is no direct measurement of the chemical composition of the SOA generated from this study, the authors should include more research results to back up the O:C ratios for a-pinene SOA under ozonolysis and photo-oxidation. For instance, Shilling, et al 2009 (<http://www.atmos-chem-phys.net/9/771/2009/>) shows the O:C values of ozonolysis SOA are 0.3-0.45; Zhang et al 2015 (<https://doi.org/10.5194/acp-15-7819-2015>, 2015.) used flow tube studies which is similar to the authors' setup, and shows the O:C values are 0.42-0.45; Chen et al. (www.atmos-chem-phys.net/13/5017/2013) used PAM and shows the photo-oxidation SOA has O:C values of 0.6-0.9, all of which are different from the literature values the authors provided in the manuscript. More of these past literatures data need to be included to provide a more convincing conclusion of the O:C values of a-pinene SOA since no actual measurement was made during the experiment.

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3. The authors' results seem to imply that whether or not adding ammonia, it would not change the LLPS within the range of the error bars within the reaction timescale of this experiment. However, this result was not included in the conclusion part. The author should state this result more clearly.

4. The author states that O:C values have an influence on the LLPS. How about H:C values? Did any literature suggest that H:C values can alter the LLPS as well?

5. The experimental conditions were not very clear and detailed. Table 1 needs to include more information such as the mode diameter of the particles generated under each situation and the mass concentrations of the particles.

6. The particles generated from the flow tube should be submicron, however the authors described the size collected on the substrate was 1-5 μm . Why would be such difference between the particles suspended and on the substrate? I suppose it was due to impaction of the plate. How would this morphology change affect the LLPS process? Have you compared with size values from past AFM and SEM studies performed by Andrew Ault et al.?

Minor comment:

1. The author states that the error bar of the relative humidity control system is 2%, however the results show that the LLPS occurs at 95.8 \pm 2.3% and 95.4 \pm 2.9%. Since the system has an intrinsic error of 2%, the error bar of the final results should not be down to one decimal point. The results should round up and end at 96% and 95%.

2. The author should specify more in detail how the OH concentrations were calculated. Was it using the rate constant from Eqns 1 and 2? How would the high concentration of α -pinene vapor (1000 ppb) affect the calculation of the OH concentration?

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