Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-19-AC2, 2019

Atmospheric Chemistry and Physics Discussions

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.

Suhan Ham et al.

mijung.song@jbnu.ac.kr

Received and published: 3 May 2019

We thank the reviewers for carefully reading our manuscript and for their very helpful suggestions! For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. [1]). Authors' responses are below each referee statement with matching numbers (e.g. [A1]).

Response to Referee #2

This manuscript studied the liquid-liquid phase separation criteria of α-pinene derived

Printer-friendly version

Discussion paper

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 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 pinene ozonolysis ranges from 0.42–0.44 as per Li et al. (2015), whereas that for SOA particles derived 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 flow tube.

[A1] Thank you for the comment. The referee suggested to narrow down the O:C regions for the non-LLPS due to O:C overlapping. However, we would like to keep it with the ranges at this stage because 1) the O:C ranges (0.4 - 0.9) were from literature (Lambe et al., 2015, exposure time: 0.2 – 17 days) that was the closest to our experimental condition (not our direct measurement), and 2) previous studies have also showed O:C region overlapping for LLPS and non-LLPS (Renbaum-Wolff et al., 2016;

Rastak et al., 2017; Song et al., 2017). An additional study on O:C limit for occurrence and absence of LLPS of organic aerosol particles will come up very soon.

References:

Lambe, A. T., Chhabra, P. S., Onasch, T. B., Brune, W. H., Hunter, J. F., Kroll, J. H., Cummings, M. J., Brogan, J. F., Parmar, Y., Worsnop, D. R., Kolb, C. E., and Davidovits, P.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol chemical composition and yield, Atmos. Chem. Phys., 15, 3063-3075, 10.5194/acp-15-3063-2015, 2015.

Rastak, N., Pajunoja, A., Navarro, J. C. A., Ma, J., Song, M., Partridge, D. G., Kirkevag, A., Leong, Y., Hu, W. W., Taylor, N. F., Lambe, A., Cerully, K., Bougiatioti, A., Liu, P., Krejci, R., Petaja, T., Percival, C., Davidovits, P., Worsnop, D. R., Ekman, A. M. L., Nenes, A., Martin, S., Jimenez, J. L., Collins, D. R., Topping, D. O., Bertram, A. K., Zuend, A., Virtanen, A., and Riipinen, I.: Microphysical explanation of the RH-dependent water affinity of biogenic organic aerosol and its importance for climate, Geophys. Res. Lett., 44, 5167-5177, 2017.

Renbaum-wolff, L., Song, M., Marcolli, C., Zhang, Y., and Liu, P. F.: Observations and implications of liquid – liquid phase separation at high relative humidities in secondary organic material produced by α -pinene ozonolysis without inorganic salts, Atmos. Chem. Phys., 16, 7969-7979, 10.5194/acp-16-7969-2016, 2016.

Song, M., Liu, P. F., Martin, S. T., and Bertram, A. K.: Liquid-liquid phase separation in particles containing secondary organic material free of inorganic salts, Atmos. Chem. Phys., 17, 11261-11271, 2017.

[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 val-

ues 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-chemphys.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.

[A2] Thank you for the comment. We fully agree the Reviewer's comment. As the three Reviewers suggested, we will add more references for O:C ratio of SOA particles produced by α-pinene ozonolysis and α-pinene photo-oxidation using flow reactors or flow tube reactors under similar reactant concentrations in the revised manuscript (Table S1).

[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.

[A3] Thank you for the suggestion! To make it clearer, we will include sentences in Summary Sect (pg. 11, lines 8-10).

"LLPS occurred in the SOA particles produced by α-pinene ozonolysis while no LLPS was observed in the SOA particles produced by α-pinene photo-oxidation. In addition, the occurrence of LLPS did not depend on the presence and absence of NH3."

[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?

[A4] In previous studies of Song et al. (2012) and You et al. (2013), they showed no relationship with H:C for occurrence of LLPS in particles containing organic and inorganic salts.

References:

Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation in aerosol particles: Dependence on O:C, organic functionalities, and compositional complexity, Geophys. Res. Lett., 39, 1-5, 10.1029/2012GL052807, 2012.

You, Y., Renbaum-Wolff, L., and Bertram, A. K.: Liquid-liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride, Atmos. Chem. Phys., 13, 11723-11734, 10.5194/acp-13-11723-2013, 2013.

[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.

[A5] As suggested, Tables 1 and 2 will be updated in the revised manuscript to include geometric mean diameter and mass concentration of particles for each experimental condition.

[6] The particles generated from the flow tube should be submicron, however the authors described the size collected on the substrate was 1-5 um. 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.?

[A6] In this study, the SOA particles during generation were collected on a hydrophobic substrate at the outlet of the flow tube reactor. During the particle collection time, the SOA particles might coagulate on the substrate resulting in larger particles consisting of up to ~5 μm. To make it clearer, an optical image of the SOA particles on a hydrophobic substrate at the outlet of the flow tube reactor will be included in Supplement (Fig. S1). For the LLPS experiments, supermicron particles consisting of 20 - 80 μm in diameter are required since the microscope is equipped with a long working distance objective and a flow-cell. In order to obtain the appropriate particle sizes for the LLPS experiments, the SOA particles collected on the substrate at the outlet of the flow tube reactor underwent a process of growth and coagulation at $\sim$100 % RH. The detailed method of producing supermicron particles was described previously in Renabum-Wolff et al. (2016) and Song et al. (2015). In our study, we did not observe a dependence of LLPS on the particle size across the studied range. Ault et al. (2013) also showed that LLPS occurred in sea spray aerosol particles consisting of 0.3 – 2 μm. We will include this reference in Introduction Sect (pg. 2, line 23).

References:

Ault, A. P., Guasco, T. L., Ryder, O. S., Baltrusaitis, J., Cuadra-Rodriguez, L. A., Collins, D. B., Ruppel, M. J., Prather, K. A., Bertram, T. H., Grassia, V. H.: Inside versus Outside: Ion Redistribution in HNO3 Reacted Sea Spray Aerosol Particles as Determined by Single Particle Analysis, J. Am. Chem. Soc., 135(39), 14528-14531, 2013.

Renbaum-Wolff, L., Song, M., Marcolli, C., Zhang, Y., and Liu, P. F.: Observations and implications of liquid – liquid phase separation at high relative humidities in secondary organic material produced by α -pinene ozonolysis without inorganic salts, Atmos. Chem. Phys., 16, 7969-7979, 10.5194/acp-16-7969-2016, 2016.

Song, M., Liu, P. F., Hanna, S. J., Li, Y. J., Martin, S. T., and Bertram, A. K.: Relative humidity-dependent viscosities of isoprene-derived secondary organic material and atmospheric implications for isoprene-dominant forests, Atmos. Chem. Phys., 15, 5145-5159, 10.5194/acp-15-5145-2015, 2015.

Minor comments:

[7] 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+/- 2.3% and 95.4+/- 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%.

[A7] As stated in Sect. 2.2 (pg. 6, line: 5), the uncertainty of the RH after calibration was ±2.0%. The uncertainties of the separation relative humidity (SRH) upon moistening and the merging relative humidity (MRH) upon drying indicate the 2σ from several humidity cycles for one sample and from the uncertainty of the calibration as stated in Table 1 and 2. To make this point clearer, we will add sentences in Sect. 3.1 in the revised manuscript (pg. 6, line 30 - pg. 7, line 2).

[8] 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 a-pinene vapor (1000 ppb) affect the calculation of the OH concentration?

[A8] As suggested, we will add the information of the OH concentrations and the method in the revised manuscript (pg: 4, lines: 13-18):

“In the flow reactor, OH concentrations were determined from the photochemical decay of toluene because toluene is well known for its OH reaction rate. The OH reaction rate constant (kOH) of toluene is 5.48 × 10-12 molecules cm-3 s-1 with insignificant reaction rate with O3 (Atkinson and Aschmann, 1989). OH concentrations were calculated by varying O3 and RH from 2000 ppb to 8000 ppb and 10% to 60%, respectively. OH concentrations were calculated by first order decay of toluene by reaction with OH radicals (Babar et al., 2017)”

References:

Atkinson, R. and Aschmann, S. M.: Rate constants for the gas-phase reactions of the OH radical with a series of aromatic hydrocarbons at 296 ± 2 K, Int. J. Chem. Kinet., 21(5), 355–365, doi:10.1002/kin.550210506, 1989.

Babar, Z. B., Park, J.-H., and Lim, H.-J.: Influence of NH3 on secondary organic aerosols from the ozonolysis and photooxidation of α-pinene in a flow reactor, Atmos. Environ., 164, 71-84, 10.1016/j.atmosenv.2017.05.034, 2017.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-19, 2019.

Printer-friendly version

Discussion paper