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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.

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We thank the reviewer 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 #3

This work investigate the liquid-liquid phase separation of α-pinene derived SOA from

both ozonolysis and photo-oxidation in the presence or absence of ammonia gas. This work shows that only reaction products originated from ozonolysis of α-pinene undergo phase separation at a very high humidity. The authors suggest that bulk elemental composition (e.g. O/C ratio) could be a good proxy for determining the phase separation of α-pinene derived SOA formed from ozonolysis and photo-oxidation. This work provide valuable data which allow us to better understand the phase state and morphology of ambient SOA. I have a few comments for the authors' consideration.

Major comments:

[1] Abstract, "LLPS occurred when the O:C ratio was less than ~0.44 and LLPS did not occur when the O:C ratio was greater than ~0.40. When LLPS was observed". Since the elemental ratios of the SOAs have not been measured in this work, it may not be appropriate to put down the O/C ratios in the abstract.

[A1] We agree the referee's suggestion. We will remove the value from the Abstract as suggested.

[2] Experiment section, my major comments are how the high gas-phase concentration of α-pinene, ozone, OH, ammonia and aerosol mass loading used in this study affect the molecular composition of the SOAs, which would ultimately govern the phase separation of the aerosols. The authors should give more discussion on these aspects.

[A2] For the case of α-pinene ozonolysis and photooxidation, high gas phase concentration of α-pinene elevates SOA mass loadings and yield by the condensation of low volatile species into particle phase (Cocker et al., 2001; Na et al., 2007; Saathoff et al., 2008; Wang et al., 2014). It has been reported that this did not significantly affect the molecular compositions (Shilling et al., 2008; Shilling et al., 2009; Bertram et al., 2011; Chen et al., 2011; Zuend and Seinfeld, 2012). For instance, Shilling et al. (2009) and Zuend and Seinfeld (2012) showed that the O:C in α-pinene SOA did not depend significantly on mass loadings. Table S1 will be updated with the references in the revised manuscript.

References:

Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., and Zorn, S. R.: Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component, Atmos. Chem. Phys., 11, 10995-11006, 10.5194/acp-11-10995-2011, 2011.

Chen, Q., Liu, Y., Donahue, N. M., Shilling, J. E., and Martin, S. T.: Particle-Phase Chemistry of Secondary Organic Material: Modeled Compared to Measured O:C and H:C Elemental Ratios Provide Constraints, Environ. Sci. Technol., 45, 4763–4770, doi:10.1021/es104398s, 2011.

Cocker, D. R., Flagan, R. C. and Seinfeld, J. H.: State-of-the-Art Chamber Facility for Studying Atmospheric Aerosol Chemistry, Environ. Sci. Technol., 35(12), 2594–2601, doi:10.1021/es0019169, 2001.

Na, K., Song, C., Switzer, C., and Cocker, D. R.: Effect of ammonia on secondary organic aerosol formation from alpha-Pinene ozonolysis in dry and humid conditions, Environ. Sci. Technol., 41, 6096-6102, 10.1021/es061956y, 2007.

Saathoff, H., Naumann, K.-H., M€, O., Jonsson, Å.M., Hallquist, M., Kiendler-Scharr, A., Mentel, T.F., Tillmann, R., Schurath, U.: Temperature dependence of yields of secondary organic aerosols from the ozonolysis of a-pinene and limonene. Atmos. Chem. Phys. Discuss. 8, 15595e15664. http://dx.doi.org/10.5194/acpd-8-15595-2008, 2008.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., McKinney, K. A., and Martin, S. T.: Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of α-pinene, Atmos. Chem. Phys., 8, 2073–2088, doi:10.5194/acp-8-2073-2008, 2008.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D., Jimenez, J. L., Martin, S. T.: Loading-dependent elemental composition of α-pinene SOA particles, Atmos. Chem. Phys., 9, 771-782, 10.5194/acp-9-771-2009, 2009.

Wang, X., Liu, T., Bernard, F., Ding, X., Wen, S., Zhang, Y., Zhang, Z., He, Q., Lü, S., Chen, J., Saunders, S., Yu, J.: Design and characterization of a smog chamber for studying gas-phase chemical mechanisms and aerosol formation. Atmos. Meas. Tech. 7, 301e313. http://dx.doi.org/10.5194/amt-7-301-2014, 2014.

[3] Page 5, line 13, "During a humidity cycle, RH was reduced from ∼100% to 0%, and then, it was increased to ∼100% at a rate of 0.5–1.0% RH minˆ-1 if LLPS was not observed. If LLPS was observed, the RH was reduced from ∼100% to ∼5–10% lower than the RH at which the two liquid phases merged into one phase, followed by an increase to ∼100% RH at a rate of 0.1–0.5% RH minˆ-1." Could the authors elaborate how they could confirm an equilibrium state could be achieved for all systems under these RH increasing or decreasing rate?

[A3] This is a good point. At the beginning of LLPS experiments, the SOA particles were equilibrated at ∼100% RH for 60 min. Then, a humidity cycle was performed at a rate of 0.1–0.5 % RH minˆ-1 for occurrence of LLPS and at a rate of 0.5–1.0 % RH minˆ-1 for absence of LLPS. We did not observe a dependence of LLPS and non-LLPS on the RH ramp rate. This point will be included in the revised manuscript (pg. 5, lines 22-26).

“During a humidity cycle, RH was reduced from ∼100% to ∼5–10% lower than the RH at which the two liquid phases merged into one phase, followed by an increase to ∼100% RH at a rate of 0.1–0.5% RH minˆ-1. If LLPS was not observed, RH was reduced from ∼100% to 0%, and then, it was increased to ∼100% at a rate of 0.5–1.0% RH minˆ-1. We did not observe a dependence of LLPS on the humidity ramp rate.”

[4] Page 6, line 17, As shown Table 1, the phase separation was observed at very high RH. Could the authors explain why this happens for the investigated systems? Also, in

addition to the comments on the O/C ratios, could the authors explain why the phase separation does not occur for the SOAs generated from photooxidation of α-pinene (e.g. from a molecular insight or perspective)?

[A4] As RH increases, water molecules would increase in the particle leaving organic molecules which are less hydrophilic resulting in phase separation in the SOA particles. Previous studies showed that a number of water-soluble organic compounds such as carboxylic acids were identified in the SOA particles produced from α-pinene photooxidation (Reinning et al., 2008; Eddingsaas et al., 2012).

References:

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Chan, M., Schilling, K. A., Chhabra, P. S., Seinfeld, J. H., and Wennberg, P. O.: alpha-pinene photooxidation under controlled chemical conditions - Part 2: SOA yield and composition in low- and high-NOx environments, Atmos. Chem. Phys., 12, 7413-7427, 10.5194/acp-12-7413-2012, 2012.

Reinnig, M.C., Müller, L., Warnke, J., Hoffmann, T.: Characterization of selected organic compound classes in secondary organic aerosol from biogenic VOCs by HPLC/MSn, Anal. Bioanal. Chem., 391, 171–182, https://doi.org/10.1007/s00216-008-1964-5, 2008.

[5] Page 9, line 16, "The range of O:C ratio corresponding to the absence of LLPS is wider than that reported by a previous work (Song et al., 2017). The difference could be attributed to the fact that the SOA particles were generated from different types of VOCs." Could the authors elaborate this point a more?

[A5] Thank you for the comment. To make this point clearer, we will modify the sentences in Sect. 3.4 (pg. 9, lines 27-30).

“However, LLPS did not occur when the average O:C ratio was between 0.45 and 1.30 in this study. Using a new type of SOA particle generated from α-pinene photooxidation, we suggest that the absence of LLPS is wider than that reported by a previous work (0.52 - 1.30) (Song et al., 2017).

Reference:

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.

[6] Page 10, line 19, "Moreover, LLPS occurred in the SOA particles at high RH (as high as âĹij100%), implying that these results can provide additional information toward the CCN properties of organic particles." Could the authors elaborate what addition information could be gained from the results of this work? How this information would help us to better understand the CCN properties of the particles?

[A6] We fully agree the referee’s suggestion. We will address LLPS occurrence and related CCN properties in the revised manuscript (pg. 11 lines: 6-13).

“The two phases consisting of an organic-rich shell and water-rich core were observed at RH as high as $\sim$100% in all cases. Recent studies of Rastak et al. (2017) and Liu et al. (2018) showed from laboratory study and modeling results that the presence of LLPS in organic particles at $\sim$100% RH can lead to lower surface tension, and finally a lower kinetic barrier to CCN activation. Our result can also give an additional insight into attempting more accurate predictions of the CCN properties of organic particles (Petters et al. 2006; Hodas et al. 2016; Renbaum-Wolff et al., 2016; Ovadnevaite et al., 2017; Rastak et al., 2017; Liu et al., 2018).”

References:

Hodas, N., Zuend, A., Schilling, K., Berkemeier, T., Shiraiwa, M., Flagan, R. C., and Seinfeld, J. H.: Discontinuities in hygroscopic growth below and above water saturation for laboratory surrogates of oligomers in organic atmospheric aerosols, Atmos. Chem. Phys., 16, 12767-12792, 10.5194/acp-16-12767-2016, 2016.

Liu, P. F., Song, M., Zhao, T. N., Gunthe, S. S., Ham, S. H., He, Y. P., Qin, Y. M., Gong,

Z. H., Amorim, J. C., Bertram, A. K., and Martin, S. T.: Resolving the mechanisms of hygroscopic growth and cloud condensation nuclei activity for organic particulate matter, Nat. Commun., 9, ARTN 4076 10.1038/s41467-018-06622-2, 2018.

Ovadnevaite, J., Zuend, A., Laaksonen, A., Sanchez, K. J., Roberts, G., Ceburnis, D., Decesari, S., Rinaldi, M., Hodas, N., Facchini, M. C., Seinfeld, J. H., and Dowd, C. O.: Surface tension prevails over solute effect in organic-influenced cloud droplet activation, Nature, 546, 637-641, 10.1038/nature22806, 2017.

Petters, M. D., Kreidenweis, S. M., Snider, J. R., Koehler, K. A., Wang, Q., Prenni, A. J., and Demott, P. J.: Cloud droplet activation of polymerized organic aerosol, Tellus. B., 58, 196-205, 10.1111/j.1600-0889, 2006.

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.

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