Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-19-AC1, 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.

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Received and published: 3 May 2019

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 #1 (Reviewer comments in black text)

The paper "Liquid-liquid phase separation in secondary organic aerosol particles pro-

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duced from α-pinene ozonolysis and α-pinene photo-oxidation with/without ammonia" by Ham et al. characterizes the presence or absence of LLPS at high relative humidities under certain experimental conditions, as expressed in the title. The data are compelling and the writing is clear. This study builds directly on the corresponding author's prior work in this area. These systems are expected to impact the formation of CCN, and as a result, are relevant to the audience of Atmospheric Chemistry and Physics. My one main concern about the paper is that the conclusions are too far reaching. In particular, the authors relate their findings to the O:C ratio needed for LLPS without measuring the O:C ratio for their systems.

Major comments

[1] How much does the O:C vary for oxidation in different chambers or flow reactors under the same reactant concentrations? I am skeptical that conclusions about O:C and LLPS can be reached in this paper because there is no direct measure of the O:C of the aerosol particles. How relevant is it to have aerosol particles just composed of secondary organic material with no other species?

[A1] Thank you for the comment. It is difficult to answer since there is no reference showing O:C ranges for SOA generated from α-pinene photooxidation under the same reactant concentrations using different chambers or flow reactors. Lambe et al. (2015) compared the O:C ranges of SOA particles produced from α-pinene photooxidation using different chambers and flow reactors (Fig. 2a in Lambe et al., 2015) although the experimental conditions were not exactly same. The O:C varies in the range of 0.3 - 1.0 depending on experimental conditions and chambers/reactors. In our study, we chose the O:C ranges (0.4 - 0.9) in the literature that were the closest to our experimental condition.

As shown in Fig. 6 in the manuscript, there appears to be a relationship between the occurrence of LLPS and the O:C of the SOA particles. This behavior was also observed in bulk solutions containing two organics and water (Ganbavale et al., 2015). We will

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add sentences below in the revised manuscript (pg. 10, lines: 1-6.). An additional study on O:C limit for occurrence and absence of LLPS of organic aerosol particles will come up very soon. However, as the three referees pointed out that the O:C conclusion for LLPS is too strong at this stage, we will put down the values in the abstract.

"Similar to the results of LLPS in the SOA particles with O:C ratio, bulk solutions containing two organics and water also showed the miscibility gap (Ganbavale et al., 2015). For example, bulk solutions of two organics with a low O:C and water (e.g. a mixture of 1-butanol, 1-propanol, and water) formed two liquid phases (Ganbavale et al., 2015). However, bulk solutions of two organics with a high O:C and water (e.g. a mixture of ethanol, acetic acid, and water) formed a single liquid phase."

As mentioned in Introduction section (pg. 2, lines: 4-5), it has been found that SOA particles comprise from 20 to 80 % of ultrafine aerosol particles depending on the location (Zhang et al., 2007; Jimenez et al., 2009).

References:

Ganbavale, G., Zuend, A., Marcolli, C., and Peter, T.: Improved AIOMFAC model parameterisation of the temperature dependence of activity coefficients for aqueous organic mixtures, Atmos. Chem. Phys., 15, 447-493, 10.5194/acp-15-447-2015, 2015.

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Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, Artn L13801Doi 10.1029/2007gl029979, 2007.

Minor comments:

[2] pg 3, line 2: You could add Rastak et al. 2017, Hodas et al. 2016, Altaf et al. 2018 here as well.

[A2] Thank you. These references will be included in the revised manuscript.

[3] pg 3 line 12: Really, too few systems have been studied so far to define these boundaries in comparison to the number of systems explored for LLPS in the presence of inorganic salts.

[A3] We agree the referee's comment that only a few systems have been studied on the effect of O:C for occurrence of LLPS in organic aerosols compared to studies for LLPS in the presence of inorganic salts. To address the referee's comment, we will add

this point to the revised manuscript in Introduction (pg. 3, lines: 18-19).

“Since still a few systems have been studied so far, more studies are needed to confirm the effect of O:C for LLPS in organic particles.”

[4] pg 4 line 14: I don’t understand these two different timescales. Do these correspond to different residence times in the flow cell? Only one number is given for residence time.

[A4] These are OH exposures that correspond to the atmospheric aging time of 0.5 day and 2.5 day as shown in Table 1. Atmospheric aging time was determined using OH radical concentration in the flow reactor, atmospheric OH radical concentration (1.5 $\times$ 10ˆ6 molecules cmˆ-3), and residence time in the flow reactor (3.63 min). OH concentrations in the flow reactor were calculated using first order photochemical decay of toluene with OH radical (Babar et al., 2017). The concentration of OH radicals was estimated from the photochemical corrosion of toluene because toluene is well known for its OH reaction rate 5.48 $\times$ 10ˆ-12 molecules cmˆ-3 sˆ-1 with insignificant reaction rate with O3 (Atkinson and Aschmann, 1989). This will be included in Sect. 2.1 in the revised manuscript.

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 $\pm$ 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.

[5] pg 4: How similar are the concentrations of α-pinene and ammonia to atmospheric concentrations?

[A5] α-pinene and ammonia concentrations have been measured in the range of $\sim$10

- 600 ppt (Kim et al., 2005; Jaars et al., 2018) and 0.3 - 120 ppb (Carmichael et al., 2003; Meng et al., 2011; Artíñano et al., 2018; Song et al., 2018; Kumar et al., 2019), respectively, in different environments (i.e. forest and polluted regions). Compared to the concentrations of α-pinene and ammonia in the atmosphere, much higher concentrations of the α-pinene and ammonia were used in this study due to the experimental constraints for SOA generation. Further studies are needed to confirm LLPS in SOA particles produced more atmospherically relevant the VOC mass concentrations. We will address this point in Summary Sect. (pg. 11 lines: 18-20).

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Kim, K., Kim, J., and Lim, J.: Comparison of anthropogenic and natural VOC concentrations in the forest ambient air, J. Kor. Soc. Environ. Anal., 8(3), 132-136, 2005. Kumar,

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Song, L., Liu, X., Skiba, U., Zhu, B., Zhang, X., Liu, M., Twigg, M., Shen, J., Dore, A., Reis, S., Coyle, M., Zhang, W., Levy, P. and Fowler, D.: Ambient concentrations and deposition rates of selected reactive nitrogen species and their contribution to PM2.5 aerosols at three locations with contrasting land use in southwest China, Environ. Pollut., 233(2), 1164–1176, doi:10.1016/j.envpol.2017.10.002, 2018.

[6] pg 4: How much O3 is expected to be converted to OH? What is the concentration of O3 in the flow reactor? What are the expected rate coefficients for α-pinene oxidation with OH vs. O3?

[A6] In case of α-pinene photooxidation at 10% RH corresponding to the atmospheric aging time of 0.5 d and 2.5 d, residual O3 concentrations in the flow reactor were approximately 1300 ppb and 3600 ppb, respectively, as already mentioned in the main text of the manuscript (pg. 4, lines 18-22). In case of α-pinene photooxidation at the atmospheric aging time of 0.5 d and 2.5 d, the OH-reaction rates were 6 and 12 times higher than O3-reaction rates, respectively. The detailed method of SOA particle generation was described previously by Babar et al. (2017).

Reference:

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.

[7] pg 6, line 12: I don't understand how the written sentences leads to this subset of references on LLPS. Be more specific about the "consistent results" that this paper has in common with those cited.

[A7] The references will be relocated in the revised manuscript to make this point clear (pg. 6 lines: 21-26).

"Moreover, previous studies using surface tension (Jasper, 1972), spreading coefficient (Kwamena et al., 2010; Reid et al., 2011), Raman spectroscopy (Song et al., 2013; Gorkowski et al., 2016; Gorkowski et al., 2017), atomic force microscopy (Zhang et al., 2018), and scanning electron microscopy (O'Brien et al., 2015) showed consistent results with regard to the morphology of the particles consisting of organic and inorganic salts"

[8] pg 6, line 18: Is the mass concentration at SOA provided for a specific RH?

[A8] These are dry SOA mass concentrations at 60% RH measured by SMPS. We will give more information in Experimental Sect. (pg. 4, line 28 – pg. 5, lines 1-4).

"A diffusion dryer loaded with silica gel was used at the upstream of Scanning Mobility Particle Sizer (SMPS+C, Grimm, Germany) for the measurement of dry SOA mass concentrations. After dilution, the mass concentrations of the SOA particles were measured to range between ~480 μg·m-3 and ~880 μg·m-3 using the SMPS for different experimental conditions as presented in Tables 1 and 2."

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