We thank the referees for carefully reading our manuscript and for their helpful comments! Listed below are our responses to the comments from the referees of our manuscript. 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]*). Author's responses are offset in blue below each referee statement with matching numbers (e.g. *[A1]*).

Response to Referee #2

Summary: In this work, the authors provide new valuable experimental data related to the liquid-liquid phase separation (LLPS) of aqueous droplets containing single or two components found in the ozonolysis α-pinene- and β-caryophyllene. The findings of works (e.g. relationship between LLPS and O/C) give us greater insights into the phase state of atmospheric aerosols under different environments, which largely govern many important atmospheric processes such as water uptake and CCN activities. I support the publication of this work and have some comments/suggestions for the authors' consideration.

Comments

[1] In the introduction, the authors should provide more information why these classes of compounds are selected for this study. What are the atmospheric significances and abundances of these selected species? What the knowledge gap related to LLPS would like to be filled by investigating these compounds?

[A1] Thank you for the comment. α-pinene and β-caryophyllene are the most abundant types of monoterpene ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) in the atmosphere, respectively (Guenther, 1995; Pathak et al., 2007; Henrot et al., 2017). However, the studies of LLPS and morphologies for α-pinene and β-caryophyllene oxidation products are still rare. Compared to previous studies on LLPS in organic particles, we investigated atmospherically relevant SOA products and showed that increased complexity of particulate organic species widen the range of O:C ratios over which LLPS will occur, improving our understanding of the LLPS behavior and providing better constrain of the O:C range required for LLPS. To address the referee's comment, we will add the following to the introduction of the revised manuscript (Sect. 1).

"α-pinene and β-caryophyllene are the most abundant types of monoterpene ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) in the atmosphere, respectively (Guenther, 1995; Sakulyanontvittaya et al. 2008; Henrot et al., 2017). However, the studies of LLPS and morphologies for α-pinene and β-caryophyllene oxidation products are still rare. Our results can provide additional insight into the O:C range required for LLPS in organic particles free of inorganic salts. Moreover, our results can provide that the chemical complexity of organic particles effects on LLPS. These observations should improve our understanding of LLPS behavior and provide more accurate constrained the value of the O:C ratio for LLPS. The results from these studies should also improve the understanding and modelling of CCN activity of SOA free of inorganic salts.”

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Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M., Milford, J. and Guenther, A.: Monoterpene and sesquiterpene emission estimates for the United States, Environ. Sci. Technol., 42(5), 1623–1629, doi:10.1021/es702274e, 2008.

[2] Page 3, Line 78, “Seven of the products from the ozonolysis of α-pinene and β-caryophyllene were synthesized. The detailed synthesis methods for these species are described in Bé et al. (2017).” Please provide the purity of these synthesized chemicals used in this study.

[A2] All synthesized compounds were > 95 % for purity. We will add this information to the revised manuscript (Sect.2.1).

[3] Page 5, Line 113, “At the beginning of LLPS experiments, organic particles inside the flow-cell were equilibrated at ~100% RH for 15–20 min.”. When the experiment ran at ~ 100% RH, does the condensation of water vapor on the surface of hydrophobic substrate and flow-cell affect the LLPS measurements?

[A3] At ~100 % RH, we observed water vapour condensation on the hydrophobic substrate, but the water vapor was evaporated and organic droplets were left on the substrate when the relative humidity was decreased to ~99-95%.

[4] Page 5, Line 119, “Organic particles were selected in the diameter range of 30–100 µm, which was required for LLPS experiments.” Could these results be applicable to submicron sized aqueous droplets?

[A4] Please see response to *[A6]* for the Reviewer #1. In this study, supermicrometer-sized particles (30-100 µm) were used since this is an optimum size to reach good quality images using the optical microscope equipped with a long working distance objective. We did not observe a size dependence for the LLPS within the size ranges studied. So far, there is no study investigated size effects for LLPS in organic particles free of inorganic salts. However, using organic/inorganic aerosol particles, Krieger et al. (2012) and You et al. (2014) reported that the separation relative humidity is not significantly depended on the micrometer-sized particles. Altaf et al. (2016), and Altaf and Freedman (2017) showed that LLPS

was independent of size down to ~50 nm when a slow drying rate was used. Further studies are needed to explore LLPS behaviour with submicron sized particles. This information will be added to the revised manuscript.

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Altaf, M. B., Zuend, A. and Freedman, M. A.: Role of nucleation mechanism on the size dependent morphology of organic aerosol, Chem. Commun., 52(59), 9220–9223, doi:10.1039/c6cc03826c, 2016.

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Krieger, U. K., Marcolli, C. and Reid, J. P.: Exploring the complexity of aerosol particle properties and processes using single particle techniques, Chem. Soc. Rev., 41(19), 6631–6662, doi:10.1039/C2CS35082C, 2012.

You, Y., Smith, M. L., Song, M., Martin, S. T. and Bertram, A. K.: Liquid-liquid phase separation in atmospherically relevant particles consisting of organic species and inorganic salts, Int. Rev. Phys. Chem., 33(1), 43–77, doi:10.1080/0144235X.2014.890786, 2014.

[5] Page 5, Line 125, “Out of the eleven different types of one-component organic particles studied, eight underwent LLPS during humidity cycles (Table S1).” Could the authors comment how the chemical structure of the investigated compounds determine the occurrence of LLPS?

[A5] Thank you for the comment. As shown in Fig. 3b, the value of the $LLPS_{lower}$ tends to decrease as the O:C ratio increases. However, organic functional groups could also be an important parameter for LLPS that still need to be studied. To address the referee’s comments, the discussion will be added to the revised manuscript (Sect. 4).

“In addition to the O:C ratio, the types of organic functional groups present in the molecules are also likely important for LLPS (Song et al., 2012b) because different functional groups lead to different strengths of intermolecular interactions with water. Further studies are needed to elucidate the effect of functional groups on the occurrence of LLPS in organic particles.”

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, L19801, doi:10.1029/2012GL052807, 2012b.

[6] Page 5, Line 133, “Particles of β-caryophyllonic acid and β-nocaryophyllonic acid had a partially engulfed morphology after LLPS (Fig. 1b, d and Movies S2, S4) (Kwamena et al., 2010; Reid et al., 135 2011; Song et al., 2013) while the others particles had a core-shell morphology after LLPS.” Could the

authors comment how the chemical structure of the investigated compounds determine the morphology of the organic particles after LLPS?

[A6] Please see response to *[A1]* for the Reviewer #1. To address referee’s comment, we will add the discussion (Sect. 4).

[7] Page 6, Line 164, “For comparison purposes, also included in Fig. 4 is the miscibility boundary of organic compounds based on the BAT model (Gorkowski et al., 2019).” Could the authors elaborate whether the BAT model can predict the RH at which LLPS occurs for the investigated compounds? Could the authors comment how the functional groups of the investigated compounds determine the occurrence of LLPS?

[A7] To address comments from Referee 3, we will remove the comparison between our research and the BAT model (Fig. 4). In terms of functional groups, organic functional groups present in the molecules are also likely important for LLPS (Song et al., 2012b) because different functional groups lead to different strengths of intermolecular interactions with water. Further studies are needed elucidate the effect of functional groups on LLPS in organic particles.

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, L19801, doi:10.1029/2012GL052807, 2012b.

[8] Page 7, Line 192, “In contrast, in experiments with particles containing ozonolysis products mixed with pyruvic acid, phase separation began with the growth of a second phase at the surface of the particle as the RH increased (Figs. 6c, d and Movies S22, 23).” Can the authors elaborate or explain this observation? What are the causes or mechanisms?

[A8] We will re-write the sentence for clarity. “In contrast, in experiments with particles containing ozonolysis products mixed with pyruvic acid, the mechanism for LLPS of the particles was likely nucleation and growth based on the appearance of nucleation from the interior of the particles as the RH increased (Figs. 5c, d and Movies S22, 23 in the revised manuscript). Nucleation and growth mechanism is a phase transition which has to be overcome an energy barrier to form stable nuclei of the second phase within a liquid droplet (Shelby, 1995; Papon et al., 1999; Ciobanu et al., 2009; Song et al., 2012a).”

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Papon, P.; Leblond, J.; Meijer, P. H. E. The Physics of Phase Transitions: Concepts and Applications, Springer, 1999.

Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U. and Peter, T.: Liquid-liquid phase separation in mixed organic/inorganic aerosol particles, J. Phys. Chem. A, 113(41), 10966–10978, doi:10.1021/jp905054d, 2009.

Song, M., Marcolli, C., Krieger, U. K., Zuend, A. and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 2691–2712, doi:10.5194/acp-12-2691-2012, 2012a.

[9] Atmospheric implications: can the authors further elaborate how different morphologies of the organic particles after LLPS affect atmospheric processes?

[A9] Thank you for the comment! In addition to the CCN properties on LLPS, we will add the following discussion of heterogeneous reaction on LLPS to address the referee's comments.

"LLPS in aerosol particles has an impact on heterogeneous reactions (Folkers et al. 2003; Anttila et al. 2006; Cosman and Bertram, 2008; Cosman et al. 2008; McNeill et al., 2008; Lam et al., 2019) and CCN (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). The reactive uptake of gas-phase oxidants can differ depending on the number of phases present in the particles (Folkers et al. 2003; Anttila et al. 2006; Cosman and Bertram, 2008; Cosman et al. 2008; McNeill et al., 2008; Lam et al., 2019). For example, the effective OH uptake coefficient of 3-methylglutaric acid/ammonium sulfate particle decreased with a factor of ~2.4 than the particle of 3-methylglutaric acid (Lam et al., 2019)."

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Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N_2O_5, J. Phys. Chem. A., 110, 10435– 10443, doi:10.1021/Jp062403c, 2006.

Cosman, L. M. and Bertram, A. K.: Reactive uptake of N_2O_5 on aqueous H_2SO_4 solutions coated with 1-component and 2-component monolayers, J. Phys. Chem. A., 112, 4625–4635, doi:10.1021/Jp8005469, 2008.

Cosman, L. M., Knopf, D. A. and Bertram, A. K.: N_2O_5 reactive uptake on aqueous sulfuric acid solutions coated with branched and straight-chain insoluble organic surfactants, J. Phys. Chem. A, 112(11), 2386–2396, doi:10.1021/jp710685r, 2008.

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