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 #3

Summary: In this manuscript, authors investigated the liquid-liquid phase separation (LLPS) as a function of average O:C ratio in organic particles free of inorganic species containing one component and binary mixture of α-pinene and β-caryophyllene-derived ozonolysis products and commercially available organic species. Compared to previous studies on this topic, this work used 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. I am supportive of the publication of this manuscript on Atmospheric Chemistry and Physics with the following comments/suggestions for the authors to consider in their revision.

[1] Specific Comments: 1) Lines 163-171 and Figure 4: As indicated in the Gorkowski et al. (2019), the BAT model was intended for use to represent thermodynamics for with only bulk O:C information rather than a specific single organic system. It is not clear how the BAT model result was generated here. Is it simply a reproduction of the Figure 2 in the original paper (Gorkowski et al., 2019)? If it is, the comparison here doesn't seem to be fair. Or some modifications were made to tailor the model to the organic species studied in this work? If this is the case, could author include a section in the SI to describe the parameters and assumptions chosen when using that BAT model to generate the result shown in Figure 4? Either way, the discussion on Figure 4 doesn't seem to be sufficient. Could the author elaborate more on what implications one could draw from the discrepancies between the BAT model and observations? Especially if the model wasn't used in a system it was designed for the comparison here was potentially misleading. Given the complex composition and matrix effect within the ambient aerosols, it might be more appropriate to compare the observation vs. model comparison for the two component particles compared to one component particles.

[A1] For the miscibility gap in Fig 4 in the manuscript, we used the miscibility line from Fig. 2a and SI in Gorkowski et al. (2019). As stated by the referee and the authors of the BAT model, the point of the BAT model is to represent the bulk O:C and molar mass dependences for mixtures, and the BAT model may not represent well the thermodynamics of a single organic system. Nevertheless, we thought that it was interesting that the BAT model was reasonably consistent with our measurements. The referee

suggests that this comparison may be unfair, and their criticism is reasonable. As a result, to address the referee's comments, we will remove the comparison between our results and the BAT model (Fig. 4) in the revised manuscript.

The referee also suggested that a comparison between the two component particles and the BAT model may be more appropriate. This is true, except if the O:C values of the two organic components vary greatly. In this case, the low O:C component in the mixture can remain immiscible and the high O:C component can remain miscible for a wide range of RH values. Unless we misunderstand, the BAT model was not developed to describe this type of situation. To avoid additional concerns that we are using the BAT model outside the conditions intended, we would prefer not to compare the results for the two component particles with the BAT model.

[3] Figure 3b showed that several points of $LLPS_{lower}$ RH were significantly lower than what the Sigmoid-Boltzmann fit would predict. It is obvious that O:C ratio is not a single determinant for LLPS. Authors should comment on possible explanations (relevant properties of the organic species, functional groups, spread in O:C values, etc.) for the variations of $LLPS_{lower}$ for two component organic particles.

[A3] As the referee commented, three data of the $LLPS_{lower}$ of one mixture of polyethylene glycol-400/ β-caryophyllene aldehyde from this study and two mixtures of polyethylene glycol-400/diethyl sebacate and polyethylene glycol-400/glyceryl tributyrate from Song et al. (2018) were lower than what the Sigmoid-Boltzmann fit. We will add the discussion to address the comment (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.

Song, M., Ham, S., Andrews, R. J., You, Y. and Bertram, A. K.: Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C, Atmos. Chem. Phys., doi:10.5194/acp-18-12075-2018, 2018.

Minor Comments:

[4] On lines 132-133 β-caryophyllinic acid was discussed while the labeling on Figure 1e as well as in the caption was β-noncaryophyllininc acid.

[A4] Thank you for the correction. We will correct the Figure 1 in the manuscript.

[5] It is hard to read the black texts of RH on top of the dark optical images. I would suggest either changing the color of the texts or not overlaying the labels and the images.

[A5] As suggested, we will revise the color and font size of the Figures 1, 2, 5, and 6.

[6] Authors are recommended to double check the manuscript for grammatical errors. For example, on line 199, “When LLPS was observe” should be “When LLPS was observed”.

[A6] Thank you for the correction. We will correct them!