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Discussions

Interactive comment on "Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C" *by* Mijung Song et al.

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Summary: I have reviewed the paper "Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C" by M. Song et al. which was submitted to Atmospheric Chemistry and Physics Discussions. This paper builds nicely on the group's previous work, which showed that aerosol particles composed of secondary organic material can undergo liquid-liquid phase separation (LLPS) at high relative humidities. This phenomenon has been proposed to be important in the formation of CCN. This paper takes a more fundamental approach, showing that LLPS is found for much simpler systems consisting of 1-2 organic species.

The paper is well written and concise, and its points are straightforward. It will make a good contribution to ACP after revisions.

Concerns. [1] My two major comments are that 1) I do not think that the authors can be so definitive about the O:C ratio needed for phase separation since they have used a limited number of systems and see exceptions to the ratio they state. and 2) the authors miss an opportunity to hypothesize about the fundamental chemistry that underlies the phenomenon that they observe.

[A1]To address the referee's comments we will 1) make it clearer in the revised manuscript that the average O:C is not the only parameter needed to predict LLPS (Abstract and page 6 line 7 – 8) and 2) include some discussion on the possible fundamental chemistry that underlies the phenomenon (page 8, line 15 - 28). Specifically, the following text will be added to the manuscript.

"Figure 5 also suggests that the average O:C is an important factor (although not the only factor) in determining the occurrence of LLPS in organic particles. For particles containing one organic species, LLPS was observed when the O:C was $\leq$ 0.44 (but not in all cases); for particles containing two organic species, LLPS was observed when the O:C was $\leq$ 0.58 (but not in all cases); and for particles containing SOM, LLPS was observed when the O:C was âĽš0.44. In Fig. 5, the O:C range founded in ambient organic aerosols is also shown (Zhang et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009; Heald et al., 2010; Ng et al., 2010). Based on this range and the range over which LLPS was observed in one-component organic particles, two-component organic particles, and SOM particles, LLPS is likely a common feature of organic aerosols in the atmosphere. In addition to the average O:C and the types of functional groups, the spread in the O:C values of the organic molecules with the same particles is likely important for LLPS. Additional studies are needed to isolate the effect of average O:C, functional groups, and spread in O:C values on LLPS in organic particles."

[2] Table 1: It would be helpful to have the molecular structure of these species listed as well. Please also include solubility.

[A2] As suggested, we will add molecular structure and solubility to Table 1 of the revised manuscript.

[3] Table 3: It would be helpful to know the mass fractions of the compounds in the mixture rather than having to back calculate based on the O:C ratio.

[A3]All experiments for two organic species were conducted with the mass ratio of 1:1. This information will be added to Sect. 2.2 of the revised manuscript.

[4] pg 5 line 5: Can you comment on the “stems” that seem to connect the inclusions to the edge of the particles in Figs. 1b and 1c? I assume these are an optical artifact.

[A4]Yes, it is an optical artifact in Figs. 1b and 1c. In the revised manuscript this will be mentioned in the figure caption for clarity.

[5] pg 5 line 8: How do you know that the organic-rich phase is the outer phase? Are you basing this on surface tensions or was it measured? I have the same question for pg 6 lines 10 and 15.

[A5]We assume that the core of the particle is water-rich because the size of the core decreases and eventually disappears as the RH decreases. The surface tension of water and the surface tensions of organics are consistent with this assumption (Jasper, 1972). To address the referee’s comment, we will add this information to the revised manuscript (Sect 3.1).

Jasper, J. J.: The surface tension of pure liquid compounds, J. Phys. And Chem. Ref. Data, vol 1, 841-1009, Doi: http://dx.doi.org/10.1063/1.3253106, 1972.

[6] pg 5 line 14: Ciobanu et al. 2009 make a distinction between nucleation and growth from the edge of the particle vs. nucleation and growth that originates in the interior of the particle. It looks like Movies S4 and S6 show nucleation and growth that originates

at the edge, and in Movie S5, the growth originates from the interior of the particle. If this result is consistent across many particles, it is worth pointing out to the reader.

[A6]Thank you for the comment. Nucleation and growth begun from the edge of the particles of diethyl sebacate (Movie S4) and suberic monomethyl ester (Movie S6) while nucleation started from the interior of the particles of glyceryl tributyrate (Movie S5). Such process was observed in all particles. This information will be added to the Sect. 3.1 of the revised manuscript.

[7] pg 5 line 22: Was there any size dependence to the range of LLPS values that is observed across a number of particles?

[A7]We did not observe a dependence of LLPS on the particle size, although only a small range of sizes were explored. This information will be added to the Sect. 3.1 of the revised manuscript.

[8] pg 5 line 30: I don’t think you can draw any conclusion about the O:C ratios at which LLPS is observed based on Table 2 because some systems phase separate and others do not at O:C < 0.44 and there are not a lot of systems studied. Can you make any conclusions based on the functional groups?

[A8]To address the referee’s comment, we will modify the sentence on page 6 line 7 - 8 to the following: “Table 2 also illustrates that LLPS can occur (but not always) in organic particles containing one organic species when the O:C ratio is ≤ 0.44.” In addition, we will also add the following discussion: “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), since different functional groups lead to different strengths of intermolecular forces with water.” The following reference will also be added: “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, Geophysical Research Letters, 39, 10.1029/2012gl052807, 2012.”

[9] Movie S7 was not included in the zip file I downloaded. Movies S8-S12 were not readable by Quicktime (even though they have the same file extension as the other to these solutions, would the same phenomenon be observed or would ammonium sulfate increase the solubility of these compounds at high RH (salting in behavior)?

[A9]For the issue of the movies, we will check with Copernicus Publication regarding readability and will add movie S7. Regarding LLPS process when ammonium sulfate is added, the presence of ammonium sulfate would likely enhance LLPS process due to salting out effect (Marcolli and Krieger, 2006) but further studies are needed to verify this point. Marcolli, C., and Krieger, U. K.: Phase changes during hygroscopic cycles of mixed organic/inorganic model systems of tropospheric aerosols, J Phys Chem A, 110, 1881-1893, Doi 10.1021/Jp0556759, 2006.

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