Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-421-RC1, 2018

Atmospheric Chemistry and Physics
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.

Anonymous Referee #1

Received and published: 29 May 2018

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. 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.

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

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.

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.

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.

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.

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

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?

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 movies).

pg 6 line 23: Optical microscopy may not provide the best observation of the spinodal decomposition mechanism. Phase diagrams indicate that the binodal and spinodal meet at a single point for systems like PEG 400/ammonium sulfate/water. If the system has the exact composition that is needed to go through this critical point, the system will undergo LLPS by spinodal decomposition. At other compositions, it depends on the activation energy. Since you have hypothesized that the activation barrier is low based on the fact that the mixing and separation RH are the same or very similar, nucleation and growth is more likely. Ciobanu et al. 2009 report that they observe spinodal decomposition for a large range of systems, but Altaf et al. Chem Comm 2016, 52, 9220 shows for the same system that only one composition has no activation barrier (i.e. undergoes spinodal decomposition).

pg 7 line 14: PEG 400 mixed with diethyl sebacate or glyceryl tributyrate needs further explanation. Why are the ranges so large and the lower value of LLPS so low?

pg 7 line 29: Please acknowledge that the first two sentences are based on very small numbers of compounds.

pg 8 lines 4-9: Based on the fact that small numbers of compounds were used and there are exceptions in this range, the determining O:C ratios can be hypothesized, but should not be stated as definitively as in this paragraph.

Based on some of my comments above, the title to the paper is a bit strong, as I do not think the average O:C at which phase separation occurs can be concluded from this study, only hypothesized.

The authors miss an opportunity to comment on the fundamental chemistry that drives the behavior they observe. It seems odd that we can make solutions of these compounds, and yet they phase separate in droplets as more water is added to the system. Why don't they stay dissolved? On a similar note, if you added ammonium sulfate

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)?

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