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Interactive comment on "Effects of molecular weight and temperature on liquid–liquid phase separation in particles containing organic species and ammonium sulfate" *by* Y. You and A. K. Bertram

Anonymous Referee #1

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General comments

This manuscript describes a consistent set of experiments that clearly show that liquid-liquid phase separation between aqueous and organic phases in aerosol particles does not depend measurably on the molecular weight of the organic compound present, but rather on the O/C ratio, as shown in previous work published by the Bertram group. The experiments show only subtle effects of temperature: declines in SRH of less than 10% are observed as temperatures are reduced from 290 to 244 K, a trend which the

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authors describe as insignificant. The work raises several interesting questions that, unfortunately, the manuscript hardly addresses. For this reason, I would like to see significant revisions to the manuscript, as described below.

The paper is framed as a negative result, but the authors could increase its impact (or at least its interest level) by providing a better justification for the study in the introduction. This justification eventually comes in the last paragraph of the discussion: the presence of large molecular weight organics are thought to contribute to increases in particle viscosity, which could eventually make liquid-liquid phase separation kinetically difficult. Particles are more likely to become highly viscous at low temperatures, hence the need to see if large MW organics can affect liquid-liquid phase separation, especially at low temperatures. Given this justification, the authors could then try to answer the questions that their results will raise in the minds of readers: Why do large MW and low temperatures have so little effect on liquid-liquid phase separation in the data collected? Are the systems studied likely to become viscous at or above the temperatures and SRH levels used, or only below? Most critically, have the authors tested the effects of high viscosity on liquid-liquid phase separation using these chemical systems, or not? Finally, what are the most likely reasons for the divergent behavior of organic compounds in the “maybe” zone of 0.57 < O/C < 0.83, where some compounds cause liquid-liquid phase separation, and others don’t?

Other comments

p. 23350 line 1: In the intro, the “frequently observed” liquid-liquid phase separation range is stated as O/C = 0.5 to 0.8 based on earlier studies. This data shows that the range is now 0.57 to 0.8 (and two pages earlier, 0.57 to 0.83). Here, the manuscript states that these ranges are consistent with each other, but they seem to be creeping upward. Are these differences significant, or is there some uncertainty in the O/C “borders” of liquid-liquid phase separation behavior that need to be acknowledged?

p. 23350 line 10: While it may be true that SRH is “not a strong function of temperature,”

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many of the organic compounds show trends that appear to be statistically significant in Figures 4 and 5. Further analysis to determine the level of significance of these trends would be appropriate.

p. 23350 line 18: The O/C range of atmospheric particles also overlaps the range where liquid-liquid phase separation is frequently observed, and part of the range where it is never observed. So while the statement that "liquid-liquid phase separation is common in atmospheric particles" must be true, to be fair one could also state that particles that do not undergo liquid-liquid phase separation are also common.

Table 1: It would be helpful to add a column listing the functional groups present in these materials, like in Table 2.

Figure 3: I find the Sigmoidal– Boltzmann fit to be unsatisfying for the data with O/C ratios between 0.57 and 1. How can a continuous function fit what is essentially a discontinuous data set?

Technical corrections

p. 23343 line 26 – p. 23344 line 7: Rhetorical question: Can there be too many references? Perhaps these nine lines of references could be split into two groups – references about efflorescence and deliquesce and those about liquid-liquid phase separation.

p. 23344 line 15: This is a strange statement. Mixing in an organic compound can modify the deliquescence and efflorescence relative humidities of an inorganic aerosol component, but liquid-liquid phase separation reverses that modification and makes the particle effloresce and deliquesce at nearly the same RH as pure inorganic aerosol particles. Perhaps a statement using the term "mitigate" instead of "modify" would be clearer.

p. 23344 line 23: This paragraph repeatedly uses the phrase "studies have shown. . ."

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