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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

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Received and published: 18 December 2014

David Topping Editor of Atmospheric Chemistry and Physics University of Manchester,
Centre for Atmospheric Science

Dear David,

Listed below are our responses to the comments from reviewer 1 and 2. The reviewer's comments are in bold type and our responses are in normal text. We thank the referees

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for carefully reading our manuscript and for excellent comments.

Sincerely, Allan Bertram Professor of Chemistry University of British Columbia

Referee #1

Major comments: 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.

Response: To address the referee's comments, in the Introduction of the revised manuscript we have added a discussion on why there is reason to believe that the two parameters studied may influence LLPS. Specifically we have added the following text:

“Molecular weight of the organic molecules is of interest because viscosity of organic-inorganic salt mixtures can depend roughly on the molecular weight of the organic species, and at high molecular weights, liquid-liquid phase separation may become kinetically inhibited in highly viscous solutions. The effect of molecular weight of the organic material on the occurrence of liquid-liquid phase separation in mixed organic-inorganic salt particles has not been explored. Temperature is of interest since temperature ranges from approximately 220 to 300 K in the troposphere, and temperature can influence the thermodynamics and kinetics of liquid-liquid phase separation. As an example of the effect of temperature on the thermodynamics of liquid-liquid phase transitions consider the binary mixture of water and butanol. At room temperature the binary mixture is partially immiscible. But as the temperature increases the region of immiscibility decreases until the upper critical solution temperature is reached. At

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higher temperatures the binary mixture is completely miscible. Certain mixtures can also have lower critical solution temperatures due to an increase in hydrogen bonding as the solution temperature decreases (Levine, 2009). Temperature may also influence the kinetics of liquid-liquid phase transitions. Some mixtures of organic species and inorganic salts can become highly viscous at lower temperatures and low relative humidities (Tong et al., 2011; Zobrist et al., 2008; Koop et al., 2011; Zobrist et al., 2011; Murray, 2008; Mikhailov et al., 2009; Saukko et al., 2012). At these low temperatures and relative humidities, liquid-liquid phase separation may be kinetically inhibited due to diffusion limitations. Only two studies have investigated liquid-liquid phase separation in mixed organic-inorganic salt particles at temperatures below 290 K.”

Why do large MW and low temperatures have so little effect on liquid-liquid phase separation in the data collected?

Response: A possible reason that a stronger dependence on temperature was not observed in the studies with organic-ammonium sulfate particles may be because for the systems studied the particles either didn't undergo liquid-liquid phase separation or the SRH was relatively high (> 65% RH). For the cases where liquid-liquid phase separation did not occur, an increase in viscosity from a decrease in temperature is not expected to change the results. For cases where the SRH was relatively high (> 65% RH), the water content in the particles was also likely high. Since water is a plasticizer, high water contents can lead to low viscosities and high diffusion rates. In this case, unless the temperature is very low, liquid-liquid phase separation is not expected to be kinetically inhibited. To address the referee's comment, we have added this discussion to the revised manuscript. See Section 3.2 in the revised manuscript.

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?

Response: To fully answer this question, one would need to know the viscosities as

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a function of relative humidity and temperature for the systems studied. To our knowledge, this information is not available for many of the systems we studied. To at least partially address the referee's comments, we have added to the revised manuscript the glass transition temperatures of the organic compounds studies when available. See Tables 1 and 2 in the revised manuscript.

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?

Response: Song et al. 2012b showed that in the range of $0.56 < O/C < 0.8$ the SRH can depend on the type of organic functional groups. Hence, a possible reason for the divergent behavior of organic compounds in the zone of $0.57 < O/C < 0.83$ is organic functional groups. To address the referee's comments, in the revised manuscript we have pointed out that measurements have also illustrated that the type of functional groups can influence the relative humidity required for liquid-liquid phase separation when the O:C of the organic material is in the range of approximately 0.5 to 0.8.

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?

Response: The ranges will depend slightly on which organic molecules are studied. Hence, there is some uncertainty in the O/C "borders". To address the referee's comments we have added this information to the revised manuscript. See Section 3.1.

p. 23350 line 10: While it may be true that SRH is "not a strong function of temperature," many of the organic compounds show trends that appear to be statistically significant

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in Figures 4 and 5. Further analysis to determine the level of significance of these trends would be appropriate.

Response: To determine the level of significance of the temperature dependent trends, we carried out a linear regression analysis. In short, 5 out of the 12 systems studied had a high correlation coefficient ($r \geq 0.94$) and low p-value (≤ 0.06). In the revised manuscript, this information has been added to Section 3.2 and the linear regression analysis has been included in the Supplementary Material.

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.

Response: This is a good point. In the revised manuscript we have also stated that particles that do not undergo liquid-liquid phase separation are also common. See Section 3.2 and Section 4.

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

Response: As suggested, we have added a column of functional groups to Table 1.

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?

Response: To address the referee’s comments the Sigmoidal-Boltzmann fit has been removed from the revised manuscript.

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.

Response: We have split the references into two groups, as suggested.

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.

Response: We have revised this sentence to improve clarity. The revised sentence is listed below:

“Liquid-liquid phase separation can also influence the deliquescence and efflorescence relative humidity in mixed organic-inorganic salt particles (Bertram et al., 2011; Smith et al., 2012; Song et al., 2013).”

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

Response: We have revised this paragraph to reduce the redundancy. The revised paragraph is listed below:

“Recent work has investigated different parameters that influence liquid-liquid phase separation in particles containing mixtures of organic species and inorganic salts (You et al., 2014). Understanding the parameters that affect these transitions is necessary for predicting these phase transitions in atmospheric particles. Studies have shown that O:C is an important parameter for predicting liquid-liquid phase separation in these particles, with this phase transition always observed for O:C less than 0.5, frequently observed for O:C values between 0.5 and 0.8, and never observed for O:C values greater than 0.8 (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013). Measurements have also illustrated that the type of functional groups can also influence the relative humidity required for liquid-liquid phase separation when the O:C of the

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organic material is in the range of approximately 0.5 to 0.8 (Song et al., 2012b). On the other hand, the occurrence of liquid-liquid phase separation is not a strong function of the OIR or the number of organic species (Marcolli and Krieger, 2006; Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012a, b; Schill and Tolbert, 2013). In addition, the occurrence of liquid-liquid phase separation may not be a strong function of the type of inorganic salt for $O:C \geq 0.8$ and ≤ 0.5 , but, in the range of 0.5 to 0.8, the occurrence of liquid-liquid phase separation can depend on the salt type (You et al. 2013).”

Referee #2 Major comments:

The authors present experimental data focusing on liquid-liquid phase separation (LLPS) in aqueous solution droplets for a set of organics mixed with ammonium sulfate. Specifically, they look at the effect of molecular mass of the organic compound and temperature on the onset relative humidity (SRH) of LLPS. The find negligible influences for both parameters for the systems they studied. The paper is well written and the conclusions are clearly supported by the experimental data. However, what is missing is a discussion why there is reason to believe that the two parameters studied (molecular mass and temperature) should influence LLPS at all.

Response: To address the referee’s comments in the Introduction of the revised manuscript we have added a discussion on why there is reason to believe that the two parameters studied may influence LLPS. For more details see response to Referee #1.

The last paragraph before the conclusion section seems to indicate that the authors think of kinetic limitations to LLPS. The argument being that higher molecular mass organics exhibit high viscosity at lower temperature and hence diffusion may kinetically inhibit LLPS on atmospherically relevant timescales. Of course, if this is the argument the authors have in mind, they should look for a system with high molecular mass but even more important low SRH, because viscosity (and diffusivity) depends strongly on water content in the droplet. From their previous studies (You et al., 2013) a system

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with low water content at the onset of LLPS is α ,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate (SRH = 38 %).

Response: Studies of LLPS in α ,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium bisulfate is a great idea. To address the referee's comments we have gone back and studied this system. The results from this system are included in the revised manuscript and plotted in a new figure (Figure 6). Thank you for the great suggestion!

It is not quite clear to me why they choose the systems they studied (specifically, the type of salt and the specific OIR).

Response: In the revised manuscript we have more clearly state why we choose the systems we studied. Listed below information included in the revised manuscript that explains why we choose the systems we studied.

“Particles consisting of ammonium sulfate mixed with one of twenty organic species were studied (see Table 2) at 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K, as well as 290 ± 1 K for a few of these particle types. For these studies, we chose the same particle types previously studied by You et al. (2013) at 290 ± 1 K. These particle types cover a wide range of O:C values and included functional groups found in atmospheric particles. Also, ammonium sulfate is one of the most common inorganic salts found in the atmosphere. In addition to picking the particles types previously studied by You et al. (2013), we also studied two additional organic species mixed with ammonium sulfate. These two organic species were raffinose and poly(ethylene glycol) diacrylate. These two species were chosen since they had relatively high molecular weights. An OIR value of 2.0 ± 0.1 was used in all the studies, consistent with You et al. (2013). The glass transition temperatures of the organic species studied cover the range of at least 192 K to 396 K.”

And

“Particles containing ammonium sulfate mixed with one of ten organic species were

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studied at 290 ± 1 K (see Table 1). Most of previous laboratory studies of liquid-liquid phase separation in particles containing organic species mixed with ammonium sulfate used organic species with molecular weight less than 200 Da (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013). To complement these previous studies, in the current study we investigated particles containing ammonium sulfate and organic species with molecular weight ranging from 180 to 1153 Da (see Table 1). The specific organic species selected for these studies (Table 1) also had a relatively wide range of O:C values. The glass transition temperatures of the organics studied covered at least the range of 223 K to 412 K (see Table 1). In all the studies, the organic-to-inorganic mass ratio (OIR) was 2.0 ± 0.1 . This value was chosen so that the current studies could be compared with the previous studies by You et al. (2013), who also used an OIR = 2.0 ± 0.1 . In addition, this OIR value is in the range of OIR values observed in many field studies (Zhang et al., 2007; Jimenez et al., 2009).”

And

“In addition to studying particles consisting of ammonium sulfate mixed with one of twenty organic species, we also studied particles containing ammonium bisulfate mixed with α ,4-dihydroxy-3-methoxybenzeneacetic acid at temperatures of 244 ± 1 K, 263 ± 1 K, and 278 ± 1 K. This system was studied since it has a low SRH-value (38%) at 290 ± 1 K and hence has relatively low water content at the onset of liquid-liquid phase separation.”

And how about thermodynamic reasons for an influence of molecular mass and/or temperature on LLPS? Why I do not see any immediate reason for molecular mass influencing miscibility of ternary mixtures of organic, water and salt, temperature could be a very significant parameter. It is well known that binary aqueous organics exhibiting a miscibility gap show an upper critical solution point which is the highest temperature at which two phases coexist because of the temperature dependence of the entropy of mixing. (This point may be not accessible experimentally because its temperature is higher than the boiling temperature of the mixture.) Some aqueous systems show in

addition a lower critical solution temperature, because of the temperature dependence of the hydrogen bonding network of the organic compound in water. To be specific, for example polypropylene glycol (425) - one of the systems studied in the paper – show a lower critical solution temperature of about 50_C (Malcom and Rowlinson, 1957), i.e. it is miscible at room temperature at any ratio with water, while at higher temperatures two phases coexist in equilibrium. The results reported in the manuscript indicate that at an organic to inorganic ratio (OIR) of 2 (as chosen by the authors) the miscibility gap is extended very significantly to lower temperatures. Here the authors could have studied the system at higher OIR ratios and still observe LLPS if it occurred because the volume ratio of the two phases would be significant at intermediate RH even for low salt concentrations. Does a lower critical solution temperature still exist for small to moderate salt concentrations? Of course, this would mean a strong dependence on SRH with temperature as well. The authors may argue that high OIR is not atmospherically relevant, but extending (or at least discussing) the more basic physical chemistry aspects would make it more interesting and relevant at least in my view.

Response: Thank you for the feedback. To address the referee's comments in the Introduction we have added thermodynamic reasons for an influence of temperature on LLPS. See discussion above. In addition we have added the following text to the Results and Discussion:

“Based on our results, particles containing poly(propylene glycol) and ammonium sulfate had SRH values ranging from 87.7 to 94.1% as the temperature ranged from 244 to 290 K. Solutions of water and poly(propylene glycol) show a lower critical solution temperature of approximately 50 oC. A comparison between this result and our current results indicate that the lower critical solution temperature is decreased significantly when ammonium sulfate is added to mixtures of poly(propylene glycol) and water.”

Minor comments: In the introduction you state that the occurrence of LLPS is not a strong function of the type of the inorganic salt. However, in You et al. (2013) you show that the type of salt becomes significant for an O:C ratio between 0.5 and 0.8 which

may be quite significant in an atmospheric context.

Response: Thank you for this comment. To address the referee's comment, the statement that the referee referred to has been modified to the following in the revised manuscript:

“In addition, the occurrence of liquid-liquid phase separation may not be a strong function of the type of inorganic salt for $O:C \geq 0.8$ and ≤ 0.5 . However, in the range of 0.5 to 0.8, the occurrence of liquid-liquid phase separation can depend on the salt type.”

In section 2.1 you state that the RH sensor was calibrated using the deliquescence humidity of ammonium sulfate. It is not absolutely clear to me, but I assume the sensor is at room temperature? Does your calibration mean that you use one calibration point only? Could you please describe your calibration and your estimate of RH accuracy in more detail?

Response: The hygrometer was calibrated prior to experiments at each temperature (244 ± 1 K, 263 ± 1 K, 278 ± 1 K, and 290 ± 1 K) by measuring the deliquescence relative humidity (DRH) of ammonium sulfate particles, and comparing the measured DRH value to the DRH valued predicted with Extended Aerosol Inorganic Model (E-AIM model) (Clegg et al. 1998). The uncertainty (2σ) of the hygrometer was ± 2.5 % RH after calibration, based on reproducibility of the DRH measurements. This information has been added to the revised manuscript in Section 2.1.

Of the twelve systems which show LLPS, most of those exhibiting a significant trend in temperature show a decrease in SRH with decreasing temperature. Could you please comment on this? It may be expected if there would be a closed loop miscibility gap of which you probe the lower temperature part?

Response: As mentioned above, to determine the level of significance of the temperature dependent trends, we carried out a linear regression analysis. In short, 5 out of the 12 systems studied had a high correlation coefficient ($r \geq 0.94$) and low p-value

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(≤ 0.06). In the revised manuscript, this information has been added in Section 3.2, and the linear regression analysis has been added to the Supplementary Material. In addition, we have point out that a decrease in SRH with a decrease in temperature may be expected if there is a closed loop miscibility gap and the measurements are probing the lower temperature region of the closed loop.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 23341, 2014.

ACPD

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