

Thank you for reviewing our paper. The comments were certainly very useful in revising the manuscript and we tried to answer your questions and concerns to the best of our ability. Note that throughout this response, the original comments are highlighted in red and our responses follow in black.

Response to Anonymous Referee #1

General comments

The authors mention the size effect on phase separation in the investigated systems based on the results of Veghte et al. (2013). However, the chemical compositions of the model systems (polyols) in this study are different from those of Veghte et al. (2013) (acids). At present time, there is no evidence of size effect on phase separation in aerosol particles consisting of polyols and ammonium sulfate so the current model system results should not directly be compared to other studies to draw a conclusion on the size effect on phase separation. Therefore, the authors should provide more experimental data to make clearer statements of the size effect on phase separation of polyol/ammonium sulfate particles.

We have strongly considered changing the model systems in this work to suit the comparison with the Veghte et al. work. The Veghte et al. (2013) paper examines acid/ammonium sulfate systems. However, our personal communication with Miriam Freedman indicates that their experiments on 1,2,6-hexanetriol/ammonium sulfate system showed that those particles are always core-shell regardless of size and weight fraction. At the time of the communication, the paper with those results has still been in prep and we were asked to cite as personal communication. To our knowledge, the paper has not been published yet. In the manuscript, we have tried to clarify the source of this communication better. The reason to stay with 1,2,6-hexanetriol and other polyol systems instead of carboxylic acids is that acids have absorption bands that overlap with liquid water absorption bands of interest in this paper. We have added this clarification to text: "Note that the polyols used in these experiments do not show very strong absorption bands. The C-H and O-H stretches are obscured by water features. Carboxylic acids, on the other hand, were found to have many strong features in the 900-1700 cm^{-1} region, which overlapped with water features of interest in this work."

In addition, the authors could specify the particle size range for the occurrence of phase separation in the manuscript.

Note that this comment was mentioned by both reviewers. To this end, we now include size distributions representative for all of our experiments in figure 1. The two distributions show particles produced from a solution of ammonium sulfate only and 1:1 ammonium sulfate/1,2,6-hexanetriol mixture.

Temperature during the experiments needs to be stated. It should be mentioned how the temperature was controlled during the spectroscopic experiments.

We have clarified in text that those experiments were done at room temperature: “All experiments described here were carried out at room temperature ($23^{\circ}\text{C} \pm 2^{\circ}\text{C}$).”

Specific comments

Abstract: The abstract focuses too much on introducing the topic (half of the abstract). Please describe more what the new findings and the summary of the presented work are.

Change made: Introductory material was removed. The last sentence of the abstract was rewritten to read: “Some results of this study tend to be in agreement with previous microscopy experiments, but others, such as phase separation properties of 1,2,6-hexanetriol, do not agree with previous work. Because the particles studied in this experiment are of a smaller size than those used in microscopy studies, the discrepancies found could be a size-related effect.”

The structure of the introduction is at some point hard to follow. For example, the authors describe literature work and suddenly introduce the model systems of this study in page 6542, line 12-13 and page 6541 line 4-5. I would suggest the authors to make a paragraph in the end of the introduction to introduce the model systems, motivation, objectives, and outline of this study.

Restructuring suggestions were incorporated into the manuscript. Instances where the manuscript discusses the methods and model systems of this study were moved to the end.

6542, line 2-5: Please rewrite this sentence. Phase separated particles can show core-shell morphology or partially engulfed morphology (Kwamena et al., 2010; Reid et al., 2011; Krieger et al., 2012; Song et al., 2013). In addition, even though liquid-liquid phase separation occurs in a mixed particle, some fractions of organic can be found in inorganic phase (Krieger et al., 2012; Ciobanu et al., 2009; Song et al., 2012; You et al., 2014).

Change made. The sentence now reads: “Phase separation occurs when the organic fraction of the aerosol does not fully mix with the aqueous inorganic fraction. This results in a particle whose core is predominantly aqueous inorganic and outer shell is predominantly organic. Partially-engulfed morphologies are also possible (Song et al., 2013; Veghte et al., 2013).”

6542, line 14-22: This paragraph describes the mechanism of liquid-liquid phase separation. However, it seems that this is unnecessary because the current work does not show any processes or mechanisms of liquid-liquid phase separation.

We have decided to keep the material describing the mechanisms. This text is important motivation for the D₂O work even though phase separation had no effect on the D₂O uptake from gaseous phase.

6540, line 10-18: Please distinguish the references properly by clearly separating those discussing phase transition of single particle and those discussing phase transition of particles on a substrate.

Change made. Those sentences now read: “Other measurement techniques that have been used to investigate aerosol phase changes include single particle levitation coupled with spectroscopy (Raman, Mie resonance, micro-FTIR) as well as different types of microscopy on a substrate (Liu et al., 2008; Zhao et al., 2008; Parsons et al., 2006; Bertram et al., 2011). Many microscopy techniques require depositing particles on a hydrophobic slide, which represents a possible surface for heterogeneous phase transition (Liu et al., 2008; Bertram et al., 2011). Levitation techniques, such as electrodynamic balance, acoustic suspension and light pressure suspension coupled with spectroscopy are well suited for studying condensation and freezing events on single particles but not the properties of a multi-particle flow (Zhao et al., 2008; Parsons et al., 2006).”

6541, line 18-22: Please check the references. Not all references discussed malonic acid. In addition, do the authors refer to Ciobanu et al. “2010” for the nucleation of ammonium sulfate?

Change made. This material does not refer to malonic acid specifically anymore: “Crystalline ammonium sulfate has been shown to be a poor nucleus for subsequent heterogeneous nucleation of organics, which may serve to explain why certain organics suppress ERH of ammonium sulfate (Ciobanu et al., 2009; Parsons et al., 2006; Smith et al., 2011; Braban and Abbatt, 2004).” Additionally, we have checked the citations and believe they are correct.

6542, line 25: Are all references showing the evidence for liquid-liquid phase separation using microscopy and EDB? Please cite only references where liquid-liquid phase separation was observed

Change made. One of the references was removed (additionally, separated by technique): “The evidence for liquid-liquid phase separation comes almost solely from microscopy (Bertram et al., 2011; You et al., 2013; Ciobanu et al., 2009) and EDB studies (Marcolli and Krieger, 2006).”

6543, line 16-18: It would be useful to mention the investigated ratios of ammonium sulfate and organics.

Change made: “All pure organics were produced from 10 wt% solutions but the ratio of ammonium sulfate and organics in the ternary solutions was variable (1:1, 1:2, and 1:3 organic/(NH₄)₂SO₄).”

6544, line 11: What type of salts have the authors used for the humidity calibration?

Change made. This was clarified: "The humidity sensor, with $\pm 1\%$ quoted error, was verified using saturated solutions of salts with various deliquescence points, such as ammonium sulfate, sodium chloride, potassium chloride."

6545, Fig 3: It is difficult to follow the sentences together with the figure. Please add shaded areas in the figure to discriminate the different bands.

Change made: we have added shaded bands over the IR features of interest and labeled them more clearly.

6546, line 7-9: Please add references for the signatures.

Change made: "Gas-phase lines at $2600\text{-}2800\text{ cm}^{-1}$ correspond to D_2O and DOH (Cziczo et al., 1997). The broad absorption at 2500 cm^{-1} corresponds to condensed-phase DOH that forms when vapor phase D_2O exchanges with liquid water in the aerosol droplets (Cziczo et al., 1997)."

6547, Fig 5: The DRH of ammonium sulfate seems to be between 75-80 %, which is the DRH range that the authors should state in the manuscript (not 80%). In addition, it is difficult to capture the DRH from Figure 5 (eg. 1,4-butanediol/ammonium sulfate for 1:1). Marcolli and Krieger (2006) showed the DRH $\sim 80\%$ in the mixture of 1,4-butanediol/ammonium sulfate. Please compare and discuss this result with literature results.

Change made: "For pure ammonium sulfate, efflorescence was observed at 35% - 40% RH and deliquescence at 75% - 80%, consistent with the literature (Cziczo et al., 1997)." And later: "Using quantification of the HOH bend area, the deliquescence point was in the range of 75% - 80%. This follows results of Marcolli and Krieger (2006), who showed DRH between 78% - 80.1% for 1:1 mixtures of 1,4-butanediol and $(\text{NH}_4)_2\text{SO}_4$." Shaded bands showing the ranges for transitions were also added to all the figures.

6547, line 8-13: The authors observed DRH of $\sim 40\%$ for 1:3 glycerol/ammonium sulfate solution. However, literature studies showed that mixed glycerol/ammonium sulfate particles of similar organic/inorganic ratio have a higher DRH. Do the authors have explanations of the discrepancy?

Change made: "Studies that used microscopy and EDB methods found higher DRH for the 1:1 $(\text{NH}_4)_2\text{SO}_4$ /glycerol system (72%-75%) (Marcolli and Krieger, 2006; Parsons et al., 2004). Different sizes of particles studied by those techniques could be a reason for the discrepancy."

6548, line 18-22: In many other places, the authors mention size effect on phase transitions of aerosol particles. The specific size range from which the authors can discriminate small and large particles from their measurements in comparison to those of Veghte et al. (2013) should be stated.

Change made: "As described in the Experimental section, the constant output atomizer used in this work produces a polydisperse particle distribution across a wide size range shown in Figure 1." We hope that this is now clear by addition of the size distribution in figure 1.

Section 3.2: It would be useful for readability of the manuscript to compile a table of the result summary discussed in the text (SRH, ERH, DRH and gas-phase exchange). Please add all results with different organic to ammonium sulfate ratio investigated in this study and available in the literature. It should be given what N/A stands for.

SRH, ERH and DRH values are now shown in table 1. We have also added the results of the D₂O exchange experiments to the table. N/A was clarified in the table.

6551, line 10: which theory are the authors referring to?

Change made. The text has now been clarified: "The (NH₄)₂SO₄/1,2,6-hexanetriol mixture behaved like the (NH₄)₂SO₄/glycerol mixture: ERH and DRH were inhibited as would be the case for a non-phase separated aerosol."

Figure 5 and 6: Please modify the legend (eg. hydration and dehydration) since all the data points do not indicate deliquescence and efflorescence. The authors could use shaded area to indicate the RH range where those processes take place.

Changes made. The legends have been modified and the shaded bands were added to the figures.

Response to Anonymous Referee #3

General comments

Several conclusions are drawn in relation to particle size, but the size distribution of the particles used are not shown. Size selected experiments would have formed a stronger basis for making such conclusions.

In order to address the general comment about including the size distribution of particles used in this experiment, we have now included size distributions in figure 1. There are two size distributions, one for ammonium sulfate only and one for a 1:1 solution of ammonium sulfate and 1,2,6-hexanetriol. Size-selected experiments were not possible at this time, as we could not get high enough concentration of monodisperse particles for the FTIR signal to be adequate. They will become a part of our future work on this topic.

Specific comments

Page 6539: “. . .Are overwhelmingly faster in the aqueous phase – that in which other phases ? – should be explained.

Change made: “For example, reactions of nitric acid with sea salt aerosols (SSA) are faster in the aqueous than in gaseous phase (Liu et al., 2008; Tolocka et al., 2004)”

The references given on how organics alter CCN properties are rather old, a lot of work has been done on this topic since 2001. More recent references should be provided.

Change made. Two recent references added: “Additionally, there is evidence that organic aerosols can be efficient CCN, but also that the nature of the organic can alter the CCN properties (Clegg et al., 2001; Cruz and Pandis, 1998, 2000; Lambe et al., 2011; King et al., 2012).”

Page 6540: The discussion of previous work and methods is mixed with methods from this work. It is not clear from the description what the different techniques mentioned do. Which ones require deposition on slides, which ones not, which ones can have a continuous flow, which ones not, what are the sizes studied in the different techniques ?. I would suggest a table summarizing these characteristics.

The introduction has been restructured to address the issues with clarity and separate the discussion of previous work and methods. Additionally, we clarify what techniques have been used to obtain the results in table 1.

Page 6541 A lot of theories and equations are mentioned but not explained. E.g. what is the consequence of the salting out mentioned, what does it mean for the

systems studied by the authors? Is the Setchenow equation important here – then it should be written as an equation

Change made. After the reviewer's comment, we realized that the Setchenow equation and the salting out effect are not applicable.

Page 6542: The authors could refer to Table 2 already in the introduction.

Change made. The introduction now refers to: "The organic compounds used here are diols and triols, such as glycerol, 1,4-butanediol and 1,2,6-hexanetriol. Refer to table 1 for the O:C ratios of these compounds and comparison to literature-reported hygroscopic and phase-separation properties." Note that the table order has been changed to reflect this.

Some of the text on O:C ratio was already mentioned on page 6541.

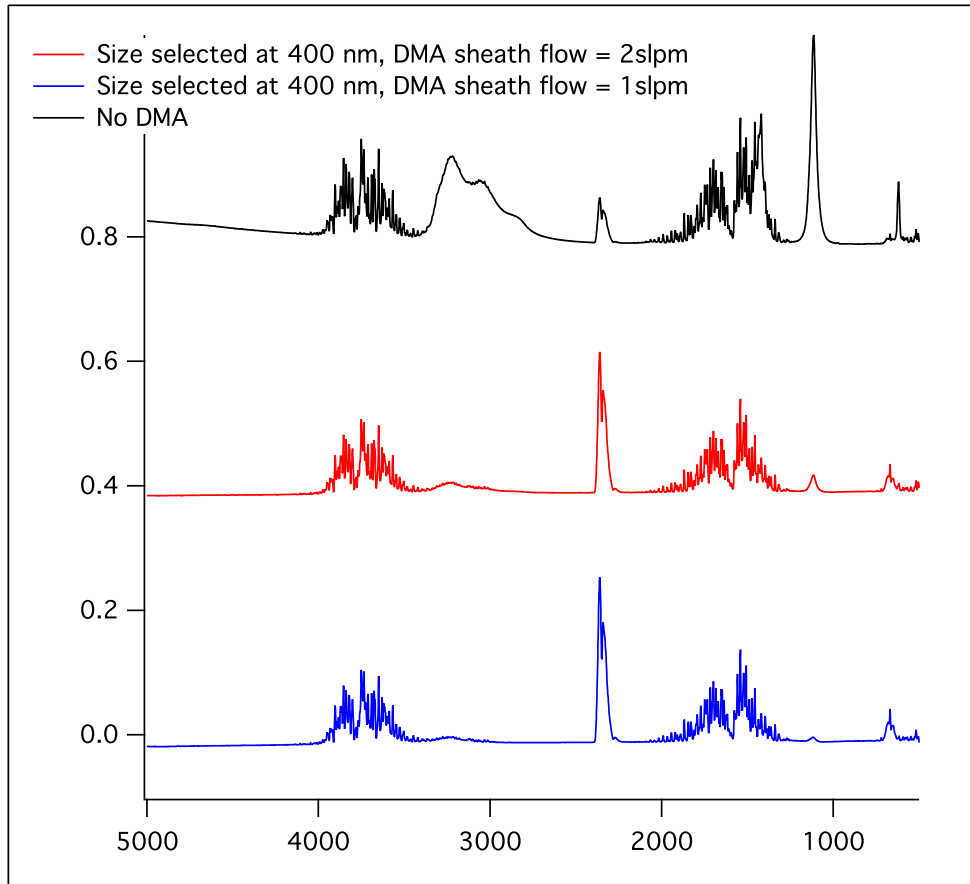
The introduction was restructured to avoid repetition issues. Previous results and the methods of this study are now separated.

Experimental: The authors state that the atomizer aerosol output was centered around 120 nm determined with a DMA. Size is highlighted as a very important parameter in the discussion and thus more information on particle size should be given. Where was this measured, before or after drying? It must have been measured with a system containing also a neutralizer and a CPC – not only a DMA? What was the width of the size distribution? How many particles per cc? Was the size of super-micrometer sized particles measured?

The authors should show one or more of the measured size distributions in a Figure. Did it vary with the presence of organics in the atomizer bottle?

Some of the speculations in the discussion and conclusion section could be confirmed or vice versa if the authors did some size –selected experiments.

A size distribution of particles used in this experiment was now added in figure 1. This includes both a size distribution for ammonium sulfate only particles and particles made out of a 1:1 solution of ammonium sulfate and 1,2,6-hexanetriol. We have also provided more information about the particle size in the experimental section. We have tried to vary out those experiments on aerosol particles that were size selected with a DMA. The results are shown in the figure below. Size selecting, even near the peak of the size distribution and with a high DMA sheath flow, results in an FTIR signal that is attenuated more than 10-fold and is not enough to do experiments of the kind that were described in this paper. Size-selected experiments will require a redesign on the FTIR beam path. It might be a part of our future work on this topic.



It is said that the flow tube used was of glass in the majority of experiments – what was the material in the rest of the experiments? Why were different materials used?

The remark about glass flow tube for majority of experiments was removed: it was, in fact, the same for all experiments shown in this paper.

It says throughout the text that for pure ammonium sulfate the efflorescence observed in this work was 35 % and the deliquescence was ~80 %. This is not what the figures show as far as I can see – they show efflorescence around 40% and deliquescence below 80 % - more like 75% ?. Both should perhaps rather be reported as intervals that takes account of the uncertainties – when is the amount of condensed water significantly different from zero (in terms of uncertainties) and likewise for efflorescence. In some figures the efflorescence band is below the deliquescence band – why – this tells something about uncertainties?

We are now stating ranges of DRH and ERH for experiments where such transitions are unclear. We have also added shaded bands in figures to show the ranges for the transitions.

Page 6547: For the mixed particles containing 1,4 butanediol the authors state: “Our results indicate some inhibition of ERH due to the presence of organics”. This I

cannot see from Figure 5 - within the order of magnitude uncertainties indicated by the bars on the data point to the left it seems to me that there is no difference between the efflorescence points between the mixed and pure ammonium sulfate particles ?

Change made. This was removed and the manuscript no longer makes this claim.

It says that efflorescence is completely suppressed in e.g. panel d of Figure 7 – I do not quite understand how that is observed from the figure. What are the definitions of “complete suppression” of deliquescence and efflorescence points respectively? How is that defined in terms of change in water content per change in RH? (and taking into account uncertainties)

By “suppressed” efflorescence, we are in fact referring to lack of a sharp transition in water uptake. The particles still uptake water, but the transition is now spread uniformly over a large range of relative humidities. We have clarified the language to reflect this: “In the 1:2 glycerol/ $(\text{NH}_4)_2\text{SO}_4$ and 1:1 glycerol/ $(\text{NH}_4)_2\text{SO}_4$ solutions there is no evidence of a sharp efflorescence point and, consequently, a sharp deliquescence point cannot be observed.”

Page 6548: The study by Veghte et al. (2013) should be explained briefly in the introduction since several conclusions in the manuscript are based on results from this study.

Change made. The introduction now includes: “Veghte et al. (2013) found that for $(\text{NH}_4)_2\text{SO}_4$ /succinic acid system, no phase separation occurred below 170 nm and for $(\text{NH}_4)_2\text{SO}_4$ /pimelic acid system, no phase separation occurred below 270 nm. Additionally, there are special compounds, such as 1,2,6-hexanetriol that retain the core-shell morphology independent of particles size (Miriam Freedman, personal communication, 2014).”

It says that the size- distribution spanned from sub 200 nanometer size to super micrometer diameter as described in the experimental section – this was not described in the experimental section . . . it is a very broad interval – if the center was at 120 nm I would assume there were very few micrometer sized particles ? again it would be very useful for the reader to see the size distribution of the particles studied.

The size distribution is now shown in figure 1 and some of the language regarding the size of the particles used in this experiment is cleaned up and clarified.

Page 6549: “exposing particles to an increasing flow of D2O” – should be rephrased – does this mean increasing concentrations of D2O in the gas phase?”

Change made: “Using this methodology, the possible uptake of water by ternary aerosol was investigated by exposing particles to increasing concentrations of D₂O in the gas phase.”

“Assuming a relative constant aerosol content” – how good is this assumption – how much did the size and number concentration of particles vary during an experiment?

This experiment used a buffer volume to homogenize the atomizer output. In addition, big changes to aerosol concentration can be seen in the FTIR spectra and effort was made to take data only when the aerosol concentration was somewhat constant. The text was changed to reflect this: “The flow was then passed into a 9 L glass volume, which allowed for a ~1 minute interaction time between vapor and particles, and to buffer any particle production variability before moving into the flow tube in order to reduce the small scale flux.”

Page 6550: the background for the conclusions regarding rapid phase separation and no limitation of mass accommodation must be better explained. “on this time scale” – it is not clear what the time scale was – and would any effects be expected from theory on such a time scale?

Change made. This section now reads: “Shorter residence time experiments were also performed. For these measurements the 9 L mixing volume was removed to reduce the time during which phase separation could occur, before mixing with D₂O, to seconds. There was no evidence of exchange stopping at the shorter residence time. This reinforces that phase separation happens on fast timescales, less than a second, which is expected because the diffusion of water is fast. However, organics can decrease mass accommodation of water, possibly having an influence on fast time scales (Allan Bertram, personal communication, 2013). No evidence for such an effect was found.”

Conclusions: Several of the issues above should be addressed also in the way that the conclusion is formulated. What was the reason that size-selected experiments were not performed – do I understand the last sentence in the conclusion right that this is currently not possible because there are too few particles to get enough intensity in the IR-spectra for the size-intervals that can be selected with a DMA?

Size-selected experiments could not be performed at this time because of the intensity issue in the FTIR signal. They will be a part of our future work on this topic. Please see comments above.

Table 2: Results from this study should be in separate lines. The table could be extended to also include details about the method used (parameters important e.g. size of particles studied).

Note that this is now table 1. It has been extended and details on the methods used to obtain cited results have been added.

Abstract: The first part is mostly like an introduction. The abstract could be rewritten and focus on the methods and results of this work.

“the results of this work tend to be in agreement with previous microscopy experiments, with several key differences which possibly reveal a size-dependent effect on phase separation in organic/inorganic aerosol particles” . This statement I find confusing and suggest that it is rephrased.

Changes to the abstract were made: the abstract was shortened, some of the introductory material was removed and the last sentence was cleaned up to say: “Some results of this study tend to be in agreement with previous microscopy experiments, but others, such as phase separation properties of 1,2,6-hexanetriol, do not agree with previous work. Because the particles studied in this experiment are of a smaller size than those used in microscopy studies, the discrepancies found could be a size-related effect.”