

Interactive comment on “Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component” by A. K. Bertram et al.

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Listed below are our responses to the comments from reviewers 1 and 2. The reviewers' comments are in quotes. We thank the referees for carefully reading our

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manuscript and for their helpful comments.

Both referees had comments regarding the location of information. Referee #1 recommended that parts of the experimental descriptions and Figures S1 and S2 be moved from the supplementary information section into the main article. Referee #2 suggested that Figure 5 might be placed in the supplementary information section, whereas Table S2 should go into the main manuscript.

Since there was no clear consensus on what information should be moved we would prefer to leave the information in the current locations to maintain a concise article, unless the editor or the referees object.

Referee #1:

"The experiments done in this study, as well as the parameterizations derived using the data, correspond to a certain temperature range. Furthermore, RH of phase transitions are at least weak functions of temperature. In most captions of the tables and figures, a statement on the temperature would therefore be appropriate. For what temperature range are the parameterizations considered applicable?"

Parameterizations were developed from data recorded at temperatures ranging from 290 to 298 K. Over this temperature range, ERH and DRH values for ammonium sulfate do not strongly depend on temperature [2, 6]. Initial work with 1,2,6-trihydroxyhexane and ammonium sulfate mixtures also suggest that SRH does not strongly depend on temperature over this narrow temperature range. This information will be added to figure captions and table information, as well as other appropriate locations in the text. Thank you for the advice.

"Abstract, first sentence: In Section 3 it is mentioned that the authors distinguish between HOA- and OOA-like organics. Therefore it should be mentioned in the abstract that only oxygen-containing organic compounds are considered in this study, e.g., by writing "oxygenated organic material" in the second line."

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As suggested we will add the word "oxygenated" to the second line of the abstract.

"Abstract, lines 7-9: This sentence could be written better using a more precise wording. Currently the first part for example reads: "These transitions include liquid-liquid phase separation (SRH),...", however, I guess "SRH" does not literally mean "liquid-liquid phase separation", rather it means the RH where liquid-liquid phase separation is present – or better: its upper RH limit (onset). Hence, I recommend writing this sentence differently in order to distinguish between the processes and the RH they are observed or related to."

We will modify the wording in the abstract to address this comment and make it more clear what is meant by SRH, ERH, and DRH.

"Abstract, lines 14, 15: "..., ERH within 5 % for 86 % of the measurements, and DRH within 5 % for 95 % of the measurements." I guess here it is meant "within 5 % RH". Without the "RH", the meaning could be different."

We will add "RH" to this sentence to make the meaning clear.

"p. 17765, l. 11: "The morphology is an organic coating surrounding an aqueous ammonium sulfate core,...". Is this morphology found to be the same for all experiments at all org:sulf ratios? This should be made clear."

For some systems we have also observed several sulfate rich inclusions with diameters on the order of a few micrometers within an organic rich phase. We will add this information to the revised manuscript.

"p. 17766, l. 2: "ERH has greater sensitivity than DRH to increases in org:sulf". This statement can be misleading. For high O:C and high org:sulf in a single mixed phase, the DRH of ammonium sulfate is expected to also span quite a large range of RH (from ~80 % RH down to very low RH at org:sulf > 10)."

We will remove this sentence to avoid confusion.

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"p. 17766, l. 7: "Salting out is described by Setchenov equation...". As the Setchenov equation is not the definition of salting-out nor a perfect description, a better wording is: "Salting out may be described by the Setchenov equation..." On line 11: ", S0 is the solubility without the salt,...". The solubility in what?"

We will change the wording on p. 17766, L.7 to "Salting out may be described by the Setchenov equation" as suggested. Also, we will add "solubility in water" to make this section clear.

"p. 17767, l. 18: "to be consistent with the ERH of pure ammonium sulfate." The ERH at what temperature and from what references? Contrary to the DRH of pure ammonium sulfate, the ERH is not a thermodynamically fixed function of temperature only."

To address the referee's comment, this sentence will be changed to the following: "At an org:sulf value of 0.1, the DRH was fixed to 80% RH to be consistent with thermodynamic calculations for pure ammonium sulfate, [1] and ERH was fixed to 35% RH to be consistent with ERH values for pure ammonium sulfate determined with the optical microscope technique.[4]"

"p. 17768, l. 1: "... DRH of three-component organic-ammonium sulfate particles". The term "three-component" can be misleading in this context, as I guess the authors do not mean ternary mixtures of only three individual components (substances)."

To make this clearer, "three-component organic-ammonium sulphate particles" will be changed to "three-component particles (i.e. particles containing one organic plus ammonium sulfate and water)."

"p. 17782, Table 2: What is the applicable temperature range of the expressions? The parameterizations for ERH at low and high O:C ratios should be spaced more apart vertically for better distinction. Now it looks like the lower equality summarizes the upper expression, which is of course not the intention. Same issue in case of the DRH

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expressions."

The applicable temperature range will be added to the table description. The formatting will also be adjusted to address the referee's comment.

"p. 17763, l. 6: "and they dominant relative to...". Check wording."

"p. 17764, l. 1: "... water/methanol mixture was than evaporated..."; "than" should be "then"."

"p. 17767, l. 10: "a decreases". Spelling."

These mistakes will be corrected in the final version.

Referee #2:

Specific comments

"Page 17764, line 13: what type of RH sensor was used? What is its accuracy and precision?"

The relative humidity of the gas was determined using a chilled mirror sensor (General Eastern). The uncertainty in measuring the relative humidity of the carrier gas was 0.3%, and the uncertainty in the reported SRH, ERH, and DRH-values were 2.5%, 2.8%, and 2.5%, respectively, based on the reproducibility of the data. This discussion will be added to the manuscript.

"Page 17766, line 21: The formulation should be improved. It should be added that this statement refers to Fig. S2."

A reference to Figure S2 will be added.

"Pages 17767 and 17768, discussion of "reduced chi squared": Considering Fig. 5a, the large "reduced chi squared" values arise from cases where the parameterization wrongly predicts liquid-liquid phase separation. In those cases, the experimental SRH is set to 0 %, leading to large contributions to "reduced chi squared". Therefore, it

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might be interesting to calculate a second "reduced chi squared" that excludes the cases where no liquid-liquid phase separation was observed."

When we exclude the cases where no liquid-liquid phase separation was observed the reduced χ^2 value is 62.15. We will add this information to the document.

"Page 17771, line 10: point (2) is difficult to understand. It should be explicitly stated what O:C and org:sulf range should be covered."

We will add the O:C and org:sulf range to be explicit.

"Caption to Table 1: "We also excluded any ERH results where it could not be shown that ammonium sulfate was the first solid to crystallise in the three-component particles": How do you show that ammonium sulfate is the first component that crystallizes?"

We excluded ERH results if the ERH data increased with an increase in the org:sulf ratio. In this case, efflorescence most likely was due to crystallization of the organic material (a process that likely doesn't occur under most atmospheric conditions).[3] We will modify the description of Table 1 to make this clear.

"Table 1: ERH values of polyethylene glycol-400 / ammonium sulfate values are given in more detail in "Ciobanu et al., J. Phys. Chem. A 2010, 114, 9486–9495"."

Ciobanu et al. JPC, 2010, measured ERH values for two compositions of polyethylene glycol (PEG) mixed with ammonium sulphate. For a 1:1 ratio of PEG to ammonium sulphate, they observed ERH values ranging from 26.8 to 33.9%. For an 8:1 ratio of PEG to ammonium sulfate they observed ERH values ranging from 24.3 to 29.3%. We will incorporate the median values for these ranges into our data set and update our reference list. Thank you for the reference.

"Figure 1: The contrast of the droplets in panel (b) should be improved."

We have tried several ways to improve the contrast between the droplets and the background shown in Figure 1. However, we were not able to improve this figure.

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"Figure 3: at what RH have the Raman spectra been measured? What is the light spot in the middle of the droplet, the illuminating laser?"

For the Raman experiments the particles were exposed to room air and, hence, the relative humidity was not controlled. We will add this information to the experimental section and figure caption. The light spot in the middle of the droplet is an optical effect from the white light source used to take the optical images. It is not due to the illuminating laser.

"Figure 4: Panels (b) and (c) might be improved when additional contour lines for ERH between 30 – 35 % and DRH between 75 – 80 % would be added."

In the final version of the manuscript we will add additional contours.

Supplementary material:

"Lines 345 – 355: The procedure to adjust the measured ERH to the parameterization is not justified. The values in the Tables and Figures should be the measured values without any corrections for particle size. The parameterization should be adjusted to describe ERH of submicrometer particles, not the other way round."

This is a good point. In the final version of the manuscript the values in the tables and figures will be the measured values. When comparing the ERH parameterization to the 1×3TDMA, we will adjust the parameterizations to take into account the different particle size and observation time as suggested.

"Table S1: This Table is almost the same as Table 1 of the main manuscript. These two tables might be merged to one Table in the main manuscript."

Table 1 already contains a lot of information, and Table S1 is useful as a simple summary of the new organic systems explored. With Table S1 a reader doesn't have to sort through Table 1 to find out what new chemicals have been studied. Unless the Referee or Editor strongly objects, we would like to keep both tables.

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"Table S2: Some cells in the columns "ERH" and "DRH" are empty. Does this mean that no ERH (down to 2 %) and no DRH was observed or that the cycle was stopped at a higher RH?"

The blanks for DRH indicated that this transition was not measured (i.e. the cycle was stopped before the DRH was reached). For ERH, some cells were left blank because the organic likely crystallized in the experiments before ammonium sulphate. In the final version of the manuscript we will include this information for clarity. Thank you for the comment.

"Table S3: this table would be much more informative if columns with the SRH values were added."

For all the compositions reported in Table S3, we did not observe liquid-liquid separation, and hence, there are no SRH values to report. This is stated in the caption for Table S3.

"Table S5: are the ERH values in this Table shifted by 4.2 %?"

No. In the final version, the ERH data in the tables will not be shifted by 4.2% to address an earlier comment by the referee.

"Table S6: DRH and ERH values for each individual data point should be given in an additional column."

Data collection and analysis for the SGP data set are described in Martin et al. [5] In that study, the occurrence of deliquescence and efflorescence was reported by demonstration of the irreversible nature of hygroscopic growth. The data were not analyzed in the way necessary to provide DRH and ERH values for each individual data point in Table S6. Although this analysis is in principle possible, certain factors and uncertainties would need to be taken into account, and this research analysis is beyond the scope of the present report. Therefore, for each individual data point we have information on whether or not the particles effloresced or deliquesced. In addition for a broad time

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window, we know the range for DRH and ERH (77-79% and 30-26%, respectively). This discussion will be added to Table S6.

References:

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3. Marcolli, C., B.P. Luo, and T. Peter, Mixing of the organic aerosol fractions: Liquids as the thermodynamically stable phases. *Journal of Physical Chemistry A*, 2004. 108(12): p. 2216-2224.
4. Parsons, M.T., D.A. Knopf, and A.K. Bertram, Deliquescence and crystallization of ammonium sulfate particles internally mixed with water-soluble organic compounds. *Journal of Physical Chemistry A*, 2004. 108(52): p. 11600-11608.
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6. Bodsworth, A., B. Zobrist, and A.K. Bertram, Inhibition of efflorescence in mixed organic-inorganic particles at temperatures less than 250 K. *Phys. Chem. Chem. Phys.*, 2010. 12(38): p. 12259-12266.

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