

# ***Interactive comment on “Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation” by A. Zuend and J. H. Seinfeld***

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The authors would like to thank Referee #3 for the careful review of the manuscript and valuable comments. We address the reviewer’s comments in our point-by-point response given below. We will incorporate corresponding changes and clarifications in a revised version of the manuscript.

## **Comments**

**Referee #3:** 1)Page 2217, line 7-8. “hence there is no aqueous electrolyte phase C1118

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present and corresponding model computations were carried out for the ammonium sulfate-free 15-component alpha-pinene SOA and water system at 40% RH and 298K." I could be wrong, but I assume that the solid ammonium sulfate seed will come into equilibrium with whatever aqueous phase is present. In this case, solid ammonium sulphate will be in equilibrium with an aqueous phase containing water, ammonium and sulfate ions and organics. Could the presence of dissolved ammonium and sulfate ions influence the partitioning? The authors should either indicate why the arguments above are incorrect or alternatively discuss why the presence of dissolved ammonium and sulphate ions is not important in this case.

**Author's response:** This is a good point that we will further discuss in the revised manuscript. In the presence of a liquid mixture consisting of water and organic components, a solid ammonium sulfate seed will come into equilibrium with the solution. In case of the system of this study, at 298 K and 40 % RH, this equilibrium is almost completely on the side of crystalline ammonium sulfate. Hence, the amount of dissolved ammonium and sulfate ions is marginal and their effects on the partitioning of water and the organic compounds is negligible. To substantiate this point, and to justify our approach of using an electrolyte-free aqueous organic system for comparison with the chamber experiments, we refer to a computation of the full (equil. case) phase diagram of the 16-component system in RH vs. water-free composition space, provided at the end of this document (Fig. B1).

The phase diagram is calculated using a fixed molar ratio between the different organic compounds in the liquid phase, based on the PM phase composition data from the equilibrium case gas-particle partitioning calculations; conditions:  $T = 298$  K, 80 % RH, moderate SOA loading,  $\lambda = 10$  %. Assuming a fixed ratio of organic compound abundances to allow the calculation of this phase diagram is supported by Fig. 4b, which shows that the relative abundance of PM-phase organic species does change only slightly over the RH range considered. Following the solubility limit curve of ammonium sulfate in the solution, shown by the pink, dash-dotted curve in Fig. B1, indicates that the solubility at 40 % RH is vanishingly small. Figure B1 shows also

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clearly that a binary aqueous electrolyte phase (without organics) cannot exist, i.e. is unstable, at 40 % RH, since the deliquescence RH of ammonium sulfate in the binary aqueous solution is at  $\sim 80$  % RH.

**Manuscript revision:** Page 2217, line 6 - 10: The sentence

“The chamber experiments use dry ammonium sulfate seed particles at 40 % RH and 298 K (see Table 1 for experimental conditions), hence, there is no aqueous electrolyte phase present and corresponding model computations were carried out for the ammonium sulfate-free 15-component  $\alpha$ -pinene SOA + water system at 40 % RH and 298 K.”

is replaced by: “The chamber experiments use dry ammonium sulfate seed particles at 40 % RH and 298 K (see Table 1 for experimental conditions). In the presence of a liquid mixture consisting of water and organic components, a solid ammonium sulfate seed will come into equilibrium with the solution. At 298 K and 40 % RH, this equilibrium is almost completely on the side of crystalline ammonium sulfate. The ammonium sulfate solubility limit, the pink curve in the calculated phase diagram shown in Fig. B1 and discussed in Appendix B, indicates that it is justified to neglect the dissolution of the crystalline ammonium sulfate seed. Therefore, model computations corresponding to the chamber experiments were carried out for the ammonium sulfate-free 15-component  $\alpha$ -pinene SOA + water system at 40 % RH and 298 K.”

Page 2236: A new section “Appendix B” will be added in the revised manuscript, including Fig. B1. Appendix B will provides a short description of relevant features of the calculated phase diagram.

**Referee #3:** 2)Page 2220, line 5. I agree with Referee #1 that it should be made clear that the chamber experiments are mainly a test for the MCM-EVAPORATION models, not the MCM-EVAPORATION-AIOMFAC combination since in the comparison a salt-free case was assumed.

**Author’s response:** This point has been further clarified; see the response to Referee #1.

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**Referee #3:** 3) Throughout the document the authors assume that the equilibrium case (benchmark) has the highest level of accuracy. See for example Table 2, column 3 and Page 2228, line 18-19, “while the benchmark equilibrium case achieves the highest level of accuracy, it requires also the largest computational efforts.” In some of the previous papers using the AIOMFAC model it was pointed out that there can be considerable uncertainty when predicting liquid-liquid phase separation with AIOMFAC. For example, Zuend, Marcolli et al. [ACP, 2011] stated “there are some liquid-liquid equilibrium data sets that reveal larger deviations compared to AIOMFAC computations”. Some discussion on the accuracy of the model for predicting liquid-liquid phase separation seems appropriate here. Perhaps on page 2211, line 23.

**Author’s response:** We will clarify the meaning of “accuracy” in the text. In the context of computational aspects of the gas-particle partitioning calculations (Section 4.4 and Table 2), “accuracy” refers to the ability of a calculation case to correctly describe the thermodynamic partitioning and phase separation solution, as compared to the benchmark equil. calculation case, the case with the least number of assumptions involved in the solution of the partitioning problem. With respect to the physically “true” solution, we furthermore make the idealized assumption that the equil. modeling case describes the physical reality best (but not perfectly). Of course, neither AIOMFAC nor the other models involved are perfect representations of reality and there are uncertainties involved in group-contribution predictions of activity coefficients as well as vapor pressures. However, since we use AIOMFAC for the calculation of activity coefficients in all calculation cases, and since the equil. case is not affected by additional constraints, such as the assumption of a complete organic/electrolyte phase separation, we believe that this is a reasonable choice for the meaning of “accuracy” in the manuscript. In the absence of detailed and accurate measurements of the gas-particle partitioning and LLPS behavior of the  $\alpha$ -pinene ozonolysis SOA + AS system covering the RH range modeled, there is no other way to judge the correctness of the model results.

**Manuscript revision:** Page 2211, line 23: We add the following statements:

“‘Accuracy’ of a modeling case is here judged on the basis of the assumption that the equil. case provides the best estimate for the physically “true” solution, since, in comparison to the simplified cases, the equil. case is least affected by additional assumptions and constraints. All of the models involved in the gas-particle partitioning and phase separation computations are subject to uncertainties. The degree of correctness of the coupled MCM-EVAPORATION-AIOMFAC model is tested and discussed in the comparison of the model results to chamber data (Section 4.1), which is mainly a test for MCM v3.1 and EVAPORATION. In the absence of detailed and accurate measurements of the gas-particle partitioning and LLPS behavior of the full  $\alpha$ -pinene ozonolysis SOA + ammonium sulfate system, covering the RH range modeled, a direct comparison to the physically correct solution is not possible. Uncertainties related to the group-contribution prediction of activity coefficients with AIOMFAC, and related to that, the prediction of LLPS, are discussed by Zuend et al. (2011) and Song et al. (2012).”

Page 2249, Table 2: We add a footnote referring to the column header “Accuracy”:

“Accuracy of a modeling case is here judged relative to the equil. case. It is assumed that the equil. case provides the best estimate for the physically “true” solution of the gas-particle partitioning problem, since, in comparison to the simplified cases, the equil. case is least affected by additional assumptions and constraints. However, deviations from the actual solution may still be significant.”

**Referee #3:** 4)The work of Song, Marcolli, et al. [ACP, 2012] showed that liquid-liquid phase separation is predicted at an O:C of 0.8 with the AIOMFAC model, but not observed in experiments with an O:C of 0.8 using dicarboxylic acids. From this, is it fair to conclude that AIOMFAC over predicts liquid-liquid phase separation? Is it possible that the combined models (MCM, EVAPORATION, and AIOMFAC) are also over predicting liquid-liquid phase separation for ammonium sulfate combined with alpha-pinene SOA? Please discuss.

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**Author's response:** The article by Song et al. (2012) shows that AIOMFAC may over-predict the onset RH of a liquid-liquid phase separation with dicarboxylic acids in the presence of ammonium sulfate. However, it is also shown that for lower O:C ratios ( $\sim 0.57$ ), the model results agree better with observations from droplet experiments. Hence, at the even lower average O:C of the  $\alpha$ -pinene SOA (O:C =  $\sim 0.5$ ), the discrepancy between modeled and actual LLPS onset RH may be small (if this trend holds). Jumping to a general conclusion, such as "AIOMFAC over-predicts LLPS" is not fair to make from these findings, because AIOMFAC does not only describe mixtures with organic acids and ammonium sulfate. The AIOMFAC model parameterization by Zuend et al. (2011) shows that the extent of a LLPS may be over-predicted in some systems, but under-predicted in case of other systems. Furthermore, the  $\alpha$ -pinene SOA products include many other functional groups besides the carboxyl and alkyl groups involved in the study of Song et al. (2012). So, it is possible that the onset RH of LLPS is over-predicted in the  $\alpha$ -pinene SOA case, but this cannot be concluded with certainty.

Another important aspect to note is that calculated phase diagrams, especially of multicomponent systems (> ternary), represented in a 2-D plot, such as those shown in Song et al. (2012) and Fig. B1 here, do not say anything about the relative size (volume) of two coexisting phases. The relative phase sizes will depend on (1) the "starting point" in the overall phase composition space and (2) whether all or only a few species partition between coexisting phases. A phase separation may well be present in a droplet experiment, but the minor phase may constitute only a thin layer on the droplet, potentially below the detection limit of the experimental setup. In such a case, the 2-D representation of the phase diagram may look the same as in the case when both coexisting liquid phases have a similar volume. Thus, in certain cases a model prediction of LLPS may be quite correct, but not confirmed by a droplet experiment.

**Referee #3:** 5) In the conclusions the authors make several broad statements about SOA. Although these broad statements are likely correct they are not categorically

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proven in the current manuscript. For example, the authors have not proven that all SOA completely phase separate at O:C ratios lower than 0.5. The authors should re-phrase some of these conclusions slightly to indicate that these are reasonable speculations based on the conclusions from the current manuscript and also previous research.

**Author's response:** We agree with the Referee and will rephrase some of the more general statements. In Section 5 (page 2230, line 27ff.), we discuss several reasons for why our calculations allow some statements in a more general sense.

**Manuscript revision:** Page 2232, line 19 - 20: Fragment “reproduce SOA mass yields” replaced by: “reproduce  $\alpha$ -pinene SOA mass yields”.

Page 2233, line 4 - 5: Sentence rephrased: “Assuming ideal mixing in organic-inorganic particles may lead to highly overpredicted organic PM mass (> 200% at 95% RH in the  $\alpha$ -pinene SOA system).”

Page 2233, line 6 -8: We modify the statement (as given in the response to Referee #1):

“Based on the computational results for the aqueous  $\alpha$ -pinene + ammonium sulfate SOA system and the group-contribution concept of our model, it is highly probable that SOA of moderate or lower average O : C ratio will cause LLPS in the presence of aqueous inorganic ions. Given the abundance of organic aerosol of moderate or lower average O : C in the troposphere (e.g., Aiken et al., 2008; Ng et al., 2010), it is reasonable to assume that such phase separations are a prevalent feature of atmospheric aerosols over a wide range of RH, aerosol loading, and temperature.”

Page 2233, line 14: we include “likely”: “... WSOC will likely partition ...”.

Page 2233, line 17 - 18: Sentence rephrased: “For O : C ratios lower than  $\sim 0.5$ , the results from the  $\alpha$ -pinene SOA system calculations suggest that it is justified to assume a complete organic/electrolyte phase separation up to high RH.”

Page 2233, line 20: we include “where applicable”: “Partitioning schemes based on complete organic/electrolyte phase separation, where applicable (see point above), ...”.

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**Referee #3:** 6)Page 2218, line 4-7. Would the model results agree more closely with the lower yields of other experiments if the dimer concentrations were set to zero.

**Author's response:** The agreement would be slightly better, since the modeled yield curve would shift, more or less in a parallel fashion, to slightly lower values. But: by setting the dimerization parameter to zero, the modeled yield is still in much better agreement with the data of the higher experimental yields than with the lower experimental yields reported in the literature.

**Referee #3:** 7)Page 2223 line 1-3. Please add a reference to support the comment.

**Author's response:** We provide references in the revised manuscript: Koop et al. (2011) and Lienhard et al. (2012).

**Referee #3:** 8)Page 2232, line 23-25. This bullet is confusing.

**Author's response:** Sentences rephrased:

**Manuscript revision:** Page 2232, line 22 - 25: Revised statement:

“The modeling results suggest that ignoring non-ideality by assuming ideal mixing (activity coefficients of unity) in salt-free “organics + water” mixtures, may lead to only small deviations at lower RH (40 % RH in the studied case). However, assuming ideality at higher RH (> 60 %), will very likely lead to significant overprediction of SOA mass and total PM mass. This is clearly the case when the actual organic mixture is only moderately hygroscopic, i.e., typically the case for organic mixtures of lower O : C ratios.”

## References

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  - Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 26912712, doi:10.5194/acp-12-2691-2012, 2012.
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### Caption to Fig. B1 (see below)

(B1). Computed phase diagram of the 16-component system “ $\alpha$ -pinene SOA products + water + ammonium sulfate (AS)” in the liquid PM, based on the method of Zuend et al. (2010). Conditions:  $T = 298$  K, fixed molar ratio of relative organic compound abundances as derived from equil. case gas-particle partitioning calculation at 80% RH and moderate SOA loading ( $\lambda = 10\%$ ). Shown is a point-by-point mapping of the 16-dimensional phase composition space to a 2-D representation: water activity vs. mass fraction of AS in the “dry” (on water-free basis) mixture of organics + AS,  $mf_a(\text{AS})$ . The color-axis shows the Gibbs energy difference between a forced

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one-phase (non-ideal) calculation and the equilibrium state calculation, showing LLPS up to high water activity, i.e., high RH.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2199, 2012.

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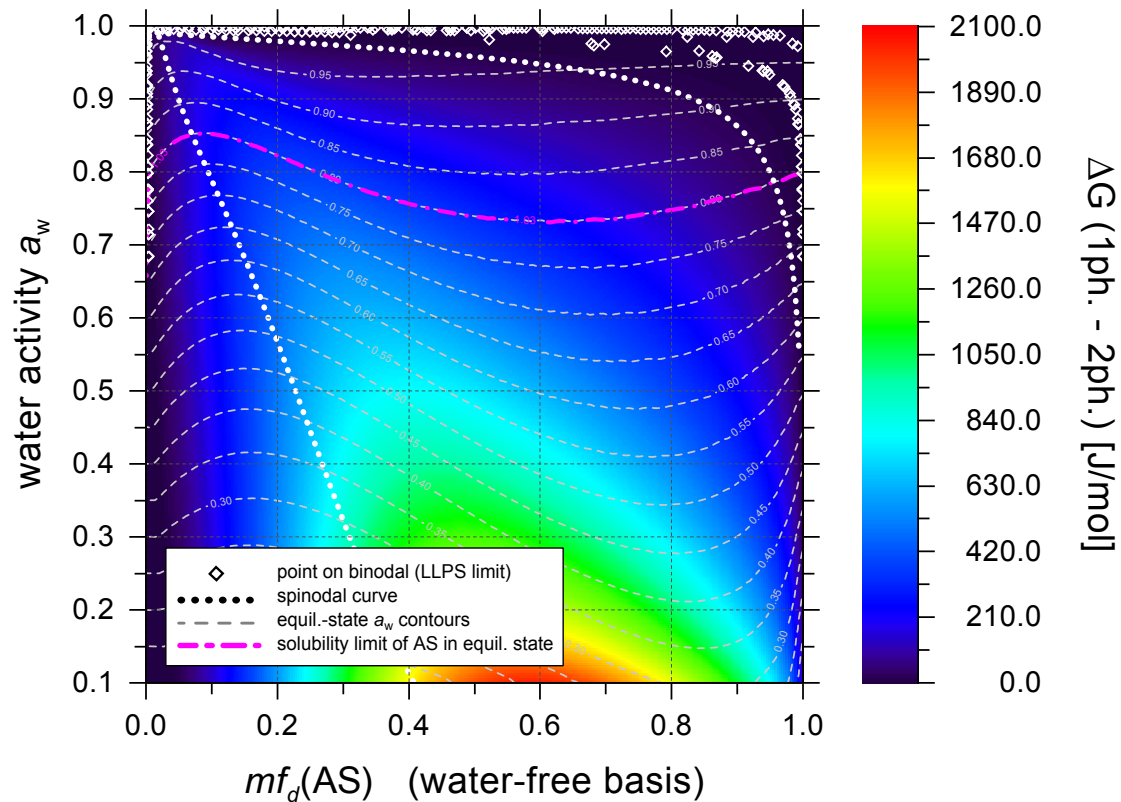
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**Fig. 1.** (B1). Caption: see complete figure caption given above (previous page).

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