

Reply to comments on “Influence of acidity on liquid-liquid phase transitions of mixed SOA proxy-inorganic aerosol droplets” by Yueling Chen et al.

Reply to Anonymous Referee #1

1) I have read the revised version of this manuscript and the authors have answered the majority of my questions. I have some further questions and suggestions based on the response to review, which I have included below.

Response: We truly appreciate the constructive comments and suggestions raised by the referee. Those comments are valuable and very helpful for improving our paper, with important guiding significance to our studies. Below we provide a point-by-point response to individual comment. The responses are shown in brown and bold fonts, and the added/rewritten parts are presented in blue and bold fonts.

Specific Comments:

1) **Reviewer 1 #11 Methods section:** Please clarify which systems have added H₂SO₄ and which systems have added NaOH. This is important for comparison to Losey et al. 2016 and 2018.

Response: “For the 3-MGA/AS system, either SA or NaOH was utilized, while for the HEXT/AS and HEXD/AS systems, only SA was used.”

New Question: Is this true for all samples, i.e. did all samples of 3-MGA/AS have either sulfuric acid or sodium hydroxide, did all samples of HEXT/AS and HEXD/AS have added sulfuric acid?

Response: It is true for all system. But in each system, there is a sample where no acid or base was added. We have revised the statement in the manuscript:

“The pH of the 3-MGA/AS solution without the addition of an acid or base was 2.70. For solutions with a lower pH (1.19 and 0.48), SA was added, while NaOH was added to solutions with a higher pH (3.70, 5.21, and 6.53) to adjust their pH levels.”

“The pH of the HEXT/AS solution without the addition of any acid was 5.11, and SA was utilized to adjust the pH to lower levels (3.14, 2.02 and 0.92).”

“For HEXD/AS (O:C=0.33) system, the pH of the HEXD/AS solution without the addition of any acid was 5.01, and SA was used to adjust the pH to lower levels (3.13, 2.71, 2.03 and 1.39).”

2) Reviewer 1 #12 Paragraph beginning at line 186 Comment 1: Is it possible to calibrate the AOT to the DRH or ERH values of known salts to give confidence in the obtained SRH and MRH values?

Response: Measuring the DRH or ERH values of known salts using AOT is challenging. AOT is unable to capture salt droplets at low humidity because, under such conditions, the droplets become too small to be effectively trapped by the AOT. Meanwhile, the shape of the droplet particle becomes irregular due to deliquescence, which results in more difficulty in particle capture. The size range of AOT to capture droplets stably is typically between 6 μm and 20 μm in diameter (Rafferty et al., 2023).

3) Reviewer 1 #13 paragraph beginning at line 186 Comment 2: As the pH decreases, ammonium sulfate becomes ammonium bisulfate. The salting out ability of sulfate vs. bisulfate should be different. This is the argument made in Losey et al. 2018.

Response: “With a decrease in pH, ammonium sulfate transforms into ammonium bisulfate. Predicted by the Hofmeister series, ammonium bisulfate exhibits a weaker salting out effect compared to ammonium sulfate and thus hinders the ability of organic matter to precipitate out of the solution (Losey et al., 2018).”

New Comment: The Hofmeister series only lists sulfate and not bisulfate, so more accurate wording would be: “With a decrease in pH, ammonium sulfate transforms into ammonium bisulfate. Our results are consistent with the hypothesis that ammonium bisulfate exhibits a weaker salting out effect compared to ammonium sulfate and thus hinders the ability of organic matter to precipitate out of the solution (Losey et al., 2018).”

Response: Thanks for the advice, we have revised the manuscript accordingly.

4) **Reviewer 1 #14 paragraph beginning at line 186 Comment 3:** This manuscript reports that MRH differs from SRH for all pH values except 5.21. Losey et al. 2016 finds that MRH differs from SRH only at pH 5.17 and 6.45. MRH is the same as SRH at all other values of pH used in Losey et al. 2016 and 2018. Why is a difference observed between these two papers? Also, if MRH differs from SRH, one would expect a higher value (just as DRH>ERH because of the activation barrier required for ERH), but this is not the case for pH 6.53. What is the author’s explanation of this result?

Response: Thank you for pointing this out. In principle, The MRH is higher than SRH, because the SRH process has an activation barrier while the MRH process does not, and lower RH is needed for the aerosol droplet to overcome the activation barrier to form two phases. The MRH is high in both articles across all pH values. Therefore, we hypothesize that the difference in MRH is associated with the discrepancy in SRH, which could be attributed to the distinct ambient conditions experienced by the droplets. The

laser levitation, resulting in a spherical morphology, while the optical microscopy involves substrate deposition, leading to a morphology resembling a spherical crown (Tong et al., 2022), as we discussed previously.

For pH 6.53, we have conducted the parallel experiment. The SRH at this pH is higher than the MRH, and the values are relatively close to each other. We do not have a specific explanation for this phenomenon, but we suspect that it might potentially be attributed to experimental error.

New Comment: It would be helpful to future readers to add to add some text to the manuscript regarding the SRH and MRH values at pH 6.53, as MRH should occur at higher RH values than SRH.

Response: Thanks for the advice, we have added some text to the manuscript regarding the SRH and MRH values at pH 6.53:

“The SRH was higher than the MRH at pH 6.53, which was abnormal because a lower SRH is commonly expected due to the activation barrier. We do not have a specific explanation for this phenomenon, while it should be noted that the observed values were relatively close to each other, indicating that the higher SRH at pH 6.53 might potentially be attributed to experimental error.”

5) **Reviewer 1 #17 paragraph beginning at line 209:** I agree with most of this response with the exception of the line (this is in the response statement as well as the edits to the manuscript): “The concentration of HEXT in this work (50 g/L) is higher than concentration (2.5 wt%, about 26 g/L) of Losey et al. (2018). This difference may facilitate the precipitation of organic matter from the inorganic salts in our work.” This reasoning ignores the fact that these systems both in the optical microscope and the AOT

will equilibrate to the surrounding RH, so the initial concentration of the solution is not generally the same as the concentration in the experimental droplet after equilibration.

Response: Thanks for the suggestion, we have deleted this statement in the manuscript.

Reference

Rafferty, A., Vennes, B., Bain, A., and Preston, T. C.: Optical trapping and light scattering in atmospheric aerosol science, *Physical Chemistry Chemical Physics*, 25, 7066-7089, 10.1039/D2CP05301B, 2023.