

1 **Response to Reviewers:**

2 Thanks for the reviewer's comments on our manuscript entitled "Observations on hygroscopic
3 growth and phase transitions of mixed 1, 2, 6-hexanetriol/(NH₄)₂SO₄ particles: Investigation of
4 liquid-liquid phase separation (LLPS) dynamic process and mechanism and secondary LLPS".
5 The reviewers' comments are helpful for improving the quality of our work. The responses to the
6 comments and the revisions in manuscript are given point-to-point below.

7
8 **Reviewer #1:**

9 1. Line 37: Mixed organic-sulfate particles can be regarded as model systems for troposphere
10 aerosols? I think it is an inappropriate expression. The 1, 2, 6-hexanetriol/AS may be a model
11 system for mixed aerosols that undergo LLPS, but it isn't a model system for atmospheric
12 aerosols.

13 **Author reply:** Thanks for the reviewer's suggestion. The sentence "Thus, mixed
14 organic-sulfate particles can be regarded as model systems for troposphere aerosols to explore
15 their hygroscopic growth and phase transitions." is revised to "Thus, mixed organic-AS
16 particles can be regarded as model organic-inorganic mixed systems and have been previously
17 chosen in numerous laboratory studies." in lines 37 and 38 in the revised manuscript.
18 Meanwhile, the sentence "1, 2, 6-hexanetriol is chosen as a model organic species with O:C
19 < 0.7. Mixed 1, 2, 6-hexanetriol / (NH₄)₂SO₄ particles can be regarded as a model system for
20 troposphere aerosols undergoing LLPS during the RH fluctuation." is added in lines 65-67 in
21 the revised manuscript.

22 2. The authors suggested that the formation of brighter aqueous phase in the center of inner AS
23 solution phase indicated the occurrence of secondary LLPS. How did the authors determine
24 that this phenomenon come from secondary LLPS, not the optical effect?

25 **Author reply:** Thanks for the reviewer's suggestion. As mentioned in the text, the bright
26 globe in the center and the dark ring at the edge were owing to the optical effect of light
27 scattering when the particle existed in homogenous mixed phase. However, the optical effect
28 could not cause any visual errors during the phase transitions, in other words, the dynamic
29 processes of LLPS and secondary LLPS were not affected by the optical effect. Besides, the

- 30 secondary LLPS processes could be clearly distinguished by the movies in the Supplement.
- 31 3. In Fig. 3, b2 represented the intensity ratio of stretching vibration bands of crystalline SO_4^{2-} to
32 C-H, which differed with other intensity ratios, please indicate this in the caption.
- 33 **Author reply:** Thanks for the reviewer's suggestion. We have added the sentence "Note that
34 the value of b2 in (c) represents the intensity ratio of stretching vibration bands of crystalline
35 SO_4^{2-} to C-H." in the caption of Fig. 3.
- 36 4. Line 192: What does the "morphological changes upon crystallization" refer to? How can the
37 authors conclude that aqueous 1, 2, 6-hexanetriol will enter into the veins of the AS crystal
38 and then is enclosed by a crystalline AS crust?
- 39 **Author reply:** As shown in Fig. S4, the morphology of the OIR = 1:4 particle became more
40 irregular and darker as the RH decreased. This indicated that the crystal growth continued at
41 lower RH after efflorescence. Thus, we conclude that aqueous 1, 2, 6-hexanetriol enters into
42 the veins of the AS crystal and then is enclosed by a crystalline AS crust. More importantly,
43 the particle size remained constant until 84.0% RH, differing from the particles with the other
44 OIRs.
- 45 5. Line 212: The secondary LLPS occurred at ~77.9% RH, almost the same RH as the
46 appearance of LLPS, for the OIR = 1:4 particle with the highest sulfate fraction. Thus,
47 whether the sulfate fraction can determine the RH at which the secondary LLPS occurs?
- 48 **Author reply:** The secondary LLPS occurred at ~68.6%, 69.0%, and 77.9% RH for OIR =
49 1:1, 1:2 and 1:4 particles, respectively. Moreover, no secondary LLPS was observed for OIR
50 = 2:1 and 4:1 particles. It is clear that the higher sulfate fraction tended to cause the
51 occurrence of secondary LLPS, but the relationship between the sulfate fraction and the RH at
52 which secondary LLPS occurs remains unclear and needs to be further investigated.
- 53 6. Line 245: The measured SRH in this work was slightly higher than the measurement results
54 (~71.0% RH) by Bertram et al. (2011). Please discuss some of the sources of this discrepancy.
- 55 **Author reply:** Indeed, the measured SRH values in our work were around 75.0%, slightly
56 higher than the measurement results of 71.0% RH by Bertram et al. There are several possible
57 sources of this discrepancy: First, the particle size employed in our work (55-80 μm) was
58 larger than that in Bertram's work (10-30 μm); second, in both cases, the uncertainty in the
59 measured SRH was 2.5% RH; finally, the rate of RH changes was 0.06-0.07% RH s^{-1} in our

60 work, higher than that of 0.4-0.6 % RH per minute in Bertram's work, probably causing
61 higher measured SRH values in our work.

62 7. The sulfates are ubiquitous in atmospheric aerosols, but the concentration of 1, 2,
63 6-hexanetriol is limited. Why did the authors choose the 1, 2, 6-hexanetriol/AS as the research
64 system?

65 **Author reply:** In Bertram's work, LLPS in mixed sulfate-organic particles commonly
66 occurred when the O:C < 0.7, while for O:C > 0.7, no LLPS was observed. Based on this, the
67 1, 2, 6-hexanetriol can act as a model organic matter with O:C < 0.7 and mixed 1, 2,
68 6-hexanetriol/AS represents a model system for mixed organic-inorganic aerosols which
69 would undergo LLPS upon the RH fluctuation. Thus, we choose the 1, 2, 6-hexanetriol/AS
70 system to investigate the LLPS dynamic process and mechanism of mixed aerosols.

71

72 **Reviewer #2:**

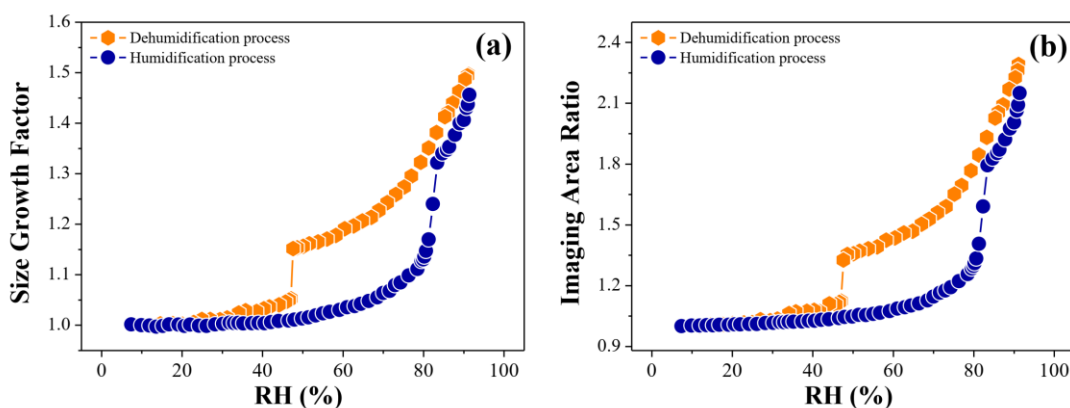
73 1. Line 65: I suggest authors to give a brief introduction about the atmospheric significance of 1,
74 2, 6-hexanetriol, the organic species investigated in this work. Has it ever been detected in
75 ambient aerosols? Or it was selected as a model species according to the O:C ratio, similar to
76 Bertram et al., (2011)? This should be clarified in Introduction.

77 **Author reply:** Thanks for the reviewer's suggestion. The organic species in the mixed
78 atmospheric aerosols consists of 1000s of different molecules, with only about 10% identified
79 (Hallquist et al., 2009). In the present work, the 1, 2, 6-hexanetriol could act as a model
80 organic species with O:C < 0.7. Thus, the 1, 2, 6-hexanetriol/AS mixed system represents a
81 model system for mixed organic-inorganic aerosols undergoing LLPS. We have added the
82 sentence "1, 2, 6-hexanetriol is chosen as a model organic species with O:C < 0.7. Mixed 1,
83 2, 6-hexanetriol / $(\text{NH}_4)_2\text{SO}_4$ particles can be regarded as a model system for troposphere
84 aerosols undergoing LLPS during the RH fluctuation." in the Introduction.

85 2. Line 100: Why not calculate GF using the image areas of particle at different RH and that of
86 dry particle? How to estimate the diameter for the irregular or non-spherical particles in the
87 software, especially for particles in effloresced state? The deviation between these two
88 approximation methods should be estimated in this section. In addition, have the imaging

89 pixel been calibrated in your measurement?

90 **Author reply:** Thanks for the reviewer’s suggestion. The hygroscopic growth of aerosol
91 particles is generally expressed as mass growth factors, i.e., the mass of particles at a given
92 RH divided by the mass of dry particles (Ma et al., 2019), or size growth factors, i.e., the
93 diameter of particles at a given RH divided by the diameter of dry particles. In the present
94 work, the size growth factors of mixed particles were determined by the optical images with
95 an image analysing software to explore the hygroscopic behaviours of mixed particles, similar
96 to the treatment of Sun et al. (2018). Indeed, the size of particles after efflorescence was
97 estimated approximatively in the software, but the error of growth factors caused by such the
98 approximation was negligible compared with the large GF values of homogeneous aqueous
99 droplets. The ratio of image area of the OIR = 1:1 particle at different RH to that of the
100 effloresced particle is determined by the same software, as shown in Fig. R1. It is clear that
101 the image area ratio and the size growth factors show similar trends regarding the hygroscopic
102 behaviours of the OIR = 1:1 particle. In addition, we have calibrated the imaging pixel with a
103 fixed pixel and size ratio ($1 \mu\text{m} = 10.667 \text{ pix}$).



104

105 Figure R1: Size growth factors (a) and imaging area ratio (b) of mixed 1, 2, 6-hexanetriol/AS particles with
106 OIR = 1:1 during the RH cycle.

107 3. Line 149-150: “the continuous water release would cause a gradual increase in sulfate
108 concentration in the inner phase, which ultimately results in the occurrence of secondary
109 LLPS.”. What cause the secondary LLPS? Why was it not observed in the study of Bertram et
110 al. (2011)?

111 **Author reply:** First of all, the phase separation in the mixed particles can be attributed to the

112 salting out effect, i.e., the decrease in the solubility of organics in an aqueous salt solution.
113 The correlation of the solubility of organics, S , and the concentration of the salt, C_s , can be
114 expressed by the Setchenov equation (Lee, 1997): $\ln S/S_0 = k_s C_s$, where S_0 is the solubility of
115 organics in water without the salt, k_s is the Setchenov constant. Second, as confirmed by our
116 Raman spectra in the present work, there were a small amount of AS and 1, 2, 6-hexanetriol
117 present in organic-rich and sulfate-rich phases, respectively. Thus, as RH decreased after
118 LLPS, the concentration of AS in the inner phase increased significantly and the solubility of
119 organics decreased, resulting in the formation of more concentrated AS inclusions in the inner
120 phase due to the salting out effect, similar to the occurrence of LLPS. In the study of Bertram
121 et al. (2011), the size of observed particles was around 10-30 μm , while that was 55-80 μm in
122 our work. We speculate that the secondary LLPS may not be clearly observed in the case of
123 smaller particle size.

124 4. Line 178 and 179: I suggest to first introduce the result of mixed particles with OIR=1:4,
125 followed by that of OIR=1:2. Also suggest for Line 200, Figure 4, 5 and 8 and related
126 statements in main text, in an order with increasing molar fraction of organics.

127 **Author reply:** Thanks for the reviewer's suggestion. We have adopted reviewer's advice and
128 revised our manuscript accordingly.

129 5. Line 192-194: Please provide appropriate references to support the argument.

130 **Author reply:** Thanks for the reviewer's suggestion. We have adopted the reviewer's advice
131 in the revised manuscript.

132 6. Line 240: When compared the phase transition RH with different OIR, I suggest to summarize
133 the DRH, ERH and SRH values in a table in the revised manuscript for clear presentation. Of
134 course, the DRH and ERH of AS, the results for the same systems investigated in previous
135 study, i.e., Bertram et al. (2011), should also be included for comparison.

136 **Author reply:** Thanks for the reviewer's suggestion. We have adopted the reviewer's advice.
137 The Table S1 summarized the DRH, ERH and SRH of mixed particles with different OIRs has
138 been placed in the Supplement.

139 7. Line 250 and Figure 8: Please clearly mention the temporal changes of LLPS dynamic process,
140 not including secondary LLPS in the revised manuscript.

141 **Author reply:** Thanks for the reviewer's suggestion. We have adopted the reviewer's advice
142 and added the sentence "not including secondary LLPS" in line 271 in the revised
143 manuscript.

144 8. Figure 3(c): Please add the error bars.

145 **Author reply:** Thanks for the reviewer's suggestion. We have adopted the reviewer's advice
146 and revised our manuscript accordingly.

147

148 Reference:

149 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J.,
150 Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y.,
151 Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.
152 F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The
153 formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos.*
154 *Chem. Phys.*, 9, 5155-5236, 2009.

155 Lee, L. L.: A molecular theory of Setchenov's salting-out principle and applications in mixed-solvent
156 electrolyte solutions, *Fluid Phase Equilib.*, 131, 67-82, 1997.

157 Ma, S. S., Yang, W., Zheng, C. M., Pang, S. F., and Zhang, Y. H.: Subsecond measurements on aerosols:
158 From hygroscopic growth factors to efflorescence kinetics, *Atmos. Environ.*, 210, 177-185, 2019.

159 Sun, J. X., Liu, L., Xu, L., Wang, Y. Y., Wu, Z. J., Hu, M., Shi, Z. B., Li, Y. J., Zhang, X. Y., Chen, J.
160 M., and Li, W. J.: Key role of nitrate in phase transitions of urban particles: Implications of important
161 reactive surfaces for secondary aerosol formation, *J. Geophys. Res.-Atmos.*, 123, 1234-1243, 2018.

162

163 Reviewer #3:

164 Major comment:

165 The authors claimed that more concentrated AS inclusions form inside the inner sulfate rich
166 core, and this is defined as a secondary LLPS. Optical images indeed indicate heterogeneity in
167 the inner core. The Raman spectra showing different sulfate/organic ratios in Fig 3, however,
168 were actually taken from different RH values. I am not fully convinced that these Raman
169 spectra indicate a secondary LLPS within the inner core. Do Raman spectra within the inner
170 core measured at the same RH show different intensity ratios? What is the thermodynamics
171 explanation of the proposed secondary LLPS? Is the secondary LLPS an equilibrium state or a
172 transitional state?

173 **Author reply:** The Raman spectra acquired at the same position under the same RH have the
174 almost identical intensity ratios. For the secondary LLPS, first, the LLPS in the mixed phase is

175 related to the salting out effect, i.e., the decrease in the solubility of organics in an aqueous salt
176 solution. The correlation of the solubility of organics, S , and the concentration of the salt, C_s ,
177 can be expressed by the Setchenov equation: $S/S_0 = k_s C_s$, where S_0 is the solubility of
178 organics in water without the salt, k_s is the Setchenov constant. Second, there were a small
179 amount of 1, 2, 6-hexanetriol present in the inner sulfate-rich phase. The concentration of AS
180 in the inner phase would increase significantly with decreasing RH after LLPS, resulting in the
181 formation of more concentrated AS inclusions in the inner phase due to the salting out effect.
182 Finally, according to the phase rule, the degree of freedom of the mixed system is zero in the
183 case of coexistence of the three liquid phases during secondary LLPS. In the phase diagram of
184 three pairs of partially miscible systems, the concentration of the three phases cannot be
185 changed when the three phases coexist, but the relative content of the three phases can be
186 changed according to the position of the system points in the phase diagram. Thus, we
187 conclude that the mixed system is in an equilibrium state during the secondary LLPS. The
188 sentences “Based on the phase rule, the degree of freedom of the mixed system is zero in the
189 case of coexistence of the three liquid phases during secondary LLPS. In the phase diagram of
190 three pairs of partially miscible systems, the concentration of the three phases cannot be
191 changed when the three phases coexist, but the relative content of the three phases can be
192 changed according to the position of the system points in the phase diagram.” have been added
193 in lines 153-156 in the revised manuscript.

194 Minor comments:

195 Introduction: it might be worth to mention that LLPS can also occur for organic mixtures, such
196 as in secondary organic aerosol (e.g., <https://acp.copernicus.org/articles/16/7969/2016/>
197 <https://acp.copernicus.org/articles/17/11261/2017/>;[https://www.nature.com/articles/s41467-018-](https://www.nature.com/articles/s41467-018-06622-2)
198 [-06622-2](https://www.nature.com/articles/s41467-018-06622-2))

199 **Author reply:** Thanks for the reviewer’s suggestion. We have adopted the reviewer’s advice
200 and revised our manuscript accordingly. The sentence “Recent studies also show that LLPS
201 can occur in mixed organic systems without inorganic salts, causing more hydrophilic and less
202 hydrophilic phases under high RH conditions (Renbaum-Wolff et al., 2016; Song et al., 2017;
203 Liu et al., 2018).” is added in lines 41-43 in the revised manuscript.

204 2 state in the caption that LLPS and secondary LLPS are measured during the dehumidification

205 **Author reply:** Thanks for the reviewer's suggestion. We have adopted the reviewer's advice

206 and revised the caption of the manuscript.

207 Page 4 Line 119-120: slowly -> gradually, rapidly-> abruptly. Changes of GF values with RH

208 are thermodynamic processes, rather than kinetic processes.

209 **Author reply:** Thanks for the reviewer's suggestion. We have adopted the reviewer's advice

210 and revised our manuscript accordingly. In line 121, the work "slowly" is revised to

211 "gradually". In lines 122 and 226, the work "rapidly" is revised to "abruptly".