

Response to Reviewers:

Thanks for the reviewer's comments on our manuscript entitled "Observations on hygroscopic growth and phase transitions of mixed 1, 2, 6-hexanetriol/(NH₄)₂SO₄ particles: Investigation of liquid-liquid phase separation (LLPS) dynamic process and mechanism and secondary LLPS". The manuscript has been revised according to the reviewer's suggestions. The responses to the comments are given point-to-point below.

Major comment:

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

Author reply: The Raman spectra acquired at the same position under the same RH have the almost identical intensity ratios. For the secondary LLPS, first, the LLPS in the mixed phase is related to the salting out effect, i.e., the decrease in the solubility of organics in an aqueous salt solution. The correlation of the solubility of organics, S , and the concentration of the salt, C_s , can be expressed by the Setchenov equation: $S/S_0 = k_s C_s$, where S_0 is the solubility of organics in water without the salt, k_s is the Setchenov constant. Second, there were a small amount of 1, 2, 6-hexanetriol present in the inner sulfate-rich phase. The concentration of AS in the inner phase would increase significantly with decreasing RH after LLPS, resulting in the formation of more concentrated AS inclusions in the inner phase due to the salting out effect. Finally, according to the phase rule, the degree of freedom of the mixed system is zero in the case of coexistence of the three liquid phases during secondary LLPS. In the phase diagram of three pairs of partially miscible systems, the concentration of the three phases cannot be changed when the three phases coexist, but the relative content of the three phases can be changed according to the position of the system points in the phase diagram. Thus, we

conclude that the mixed system is in an equilibrium state during the secondary LLPS.

Minor comments:

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

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

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

Author reply: Thanks for the reviewer's suggestion. We have adopted the reviewer's advice and revised the caption.

Page 4 Line 119-120: slowly -> gradually, rapidly-> abruptly. Changes of GF values with RH are thermodynamic processes, rather than kinetic processes.

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