

Daniel Knopf
Co-Editor of Atmospheric Chemistry and Physics

Dear Daniel,

We appreciate your carefully reading and giving us valuable comments. Listed below are our responses to your comments in blue. The manuscript has been revised, accordingly (in blue).

Besides the referees' comments, during the revision, we found our small mistakes of 1) optical observation for efflorescence behavior of sucrose/AS particles with an organic-to-inorganic mixing ratio of 1:1 (Fig. 3c), and 2) production of a sucrose calibration line (Fig. S1) (details are below). These errors have been corrected throughout the manuscript and these changes does not impact the findings and conclusions of this work. We apologize the confusion which we did not elaborate the reason of these changes carefully.

Thank you for handling this manuscript.

With kindest regards,
Mijung Song
Professor of Earth and Environmental Sciences
Jeonbuk National University

Regarding Referee #1: This comment refers to the multiphase nature of the sucrose/AS/H₂O particles with OIR = 1:4. I believe, the referee is looking for the response you are giving starting with "Regarding the sucrose.....". The referee would like the acknowledgment in the manuscript that the multiphase nature of the particle could not be resolved. Most of the text could be included in the manuscript to communicate this to the reader.

→ Thank you for the comment and suggestion. The following text has been added to Section 3.2 (lines: 249-252) of the revised manuscript.

"At the RH, the particle was observed containing multiphase nature from the optical image (Fig. 3d). While the presence of a crystalline AS phase is likely (compare Figs. 3a and 3d), it is unclear whether the remaining liquid forms a more structured gel state or an amorphous viscous semisolid or solid state. This ternary system may therefore be of interest for future studies employing other probing techniques and phase

composition analysis.”

You added a new statement beginning on line 231 without elaborating in the author response.

- ➔ Thank you for the comment. Regarding the new statement on line 232, when we rechecked our optical images during the revision, we found that the particles with an OIR = 1:1 looked like effloresced at about 28% RH as shown in Fig. 3c but it was not accurately observed optically. Most of the particles with an OIR = 1:1 showed such a morphology. Therefore, we added the new statement as: “At the close RH where particles cracked, the particles crystallized or effloresced although it was not accurately observed optically (Fig. 3c).”

This is bit confusing. In previous sentence, you state particles cracked at 27% RH and refer to Fig. 1d. Then in this new sentence, you state particles effloresce at 28% but this was not well observed and refer to Fig. 3c. The connection you are making here is not clear. This is followed by discussion of Tong et al. data. This feels like a jump. Maybe make clear that you refer back to Fig. 4. There is a typo (“give RH”). Please improve this section

- ➔ To make it better connection and make it clearer, we have modified the paragraph to the following (lines: 229-240):

“In particles consisting of sucrose/AS/H₂O particles with an OIR = 1:1, the mean viscosity varied from $\sim 5 \times 10^{-2}$ to $\sim 1 \times 10^2$ Pa·s from $\sim 70\%$ to $\sim 34\%$ RH (yellow symbols in Fig. 4). At $\sim 30\%$ RH, we could not determine the viscosity using the poke-and-flow technique because the droplets were supersaturated with respect to AS upon dehydration. The particles cracked by poking at $\sim 27\%$ RH (Fig. 1d), so the lower limit of the viscosity of the particle was estimated as $\sim 1 \times 10^8$ Pa·s (Fig. 4). At the close RH where particles cracked, the particles crystallized or effloresced although it was not accurately observed optically (Fig. 3c). The viscosities of sucrose/AS/H₂O particles for an OIR = 1:1 using an optical tweezer are also included in Fig. 4 (Tong et al., 2022). Results showed that viscosities for sucrose/AS droplet from this study and Tong et al. (2022) are consistent within ~ 1 order of magnitude at given RH. The viscosity deviations at given RH when comparing the two series of measurements may come

from uncertainties associated with the different techniques, temperature ranges, and mode of RH changes (i.e. decreasing or increasing RH). From the RH-dependent viscosities, our result showed that sucrose/AS/H₂O particles with an OIR = 1:1 existed as liquid for RH > ~34%, semisolid for ~34 % < RH < ~27%, and semisolid or solid for RH < ~27% (Fig. 4).”

Regarding Referee #2, first comment: Your definition of physical state is correct. I believe, the confusion is the following: a liquid-liquid phase separated aerosol particle has a "total" particle physical state of liquid. A particle with a solid and liquid phase, what is its physical state? Multiphase. This comes also back to referee #1's comment: the identification of the physical states of the various phases inside the particle. In the case above, the AS is solid, but the remaining solution may be solid, may be not. In either case, if you poke the particle, it will still shatter. Does this mean the particle is overall solid? Can you state that the physical state of this particle is solid? I believe, these are the main issues of both referees. I feel like referee #2 wants a clear definition of these concepts in the introduction.

→ You are right! We defined the physical state of “total” aerosol particle in this study. To avoid the confusion, we have revised and added the sentences for the physical states of aerosol particles in the introduction as below:

Line: 43-45

“Physical states (i.e. liquid, semi-solid, and solid) of aerosol particles can be determined from their dynamic viscosities; a viscosity of less than 10² Pa·s indicates a liquid state, a viscosity between 10² and 10¹² Pa·s indicates a semi-solid state, and a viscosity of greater than 10¹² Pa·s indicates a solid state (Zobrist et al., 2008; Koop et al., 2011; Kulmala et al., 2011).”

Lines: 83-84

“Next, we determined the physical states (i.e. liquid, semi-solid, and solid) of the particles as a function of RH based on the viscosity-value of the binary and ternary mixtures. In this study, we defined the physical states of the total aerosol particles.”

I do not see any changes in revised abstract with regard to the referee's initial comment

(definitions of viscosity/phase/particle physical state). The referee suggests mentioning the particle physical state as well, i.e., which particle systems are entirely liquid or solid or multiphase in nature.

→ To address the editor's comment, we have revised the abstract as following:

“Herein, we quantified viscosities at 293 ± 1 K upon dehydration for the binary systems, sucrose/H₂O and ammonium sulfate (AS)/H₂O, and the ternary systems, sucrose/AS/H₂O for organic-to-inorganic dry mass ratios (OIRs) = 4:1, 1:1, and 1:4 using bead-mobility and poke-and-flow techniques. Based on the viscosity-value of the aerosol particles, we defined the physical states of the total aerosol particles studied in this work. For binary systems, the viscosity of sucrose/H₂O particles gradually increased from $\sim 4 \times 10^{-1}$ to $> \sim 1 \times 10^8$ Pa·s when the relative humidity (RH) decreased from $\sim 81\%$ to $\sim 24\%$ ranging from liquid to semisolid or solid state, which agrees with previous studies. The viscosity of AS/H₂O particles remained in the liquid state ($< 10^2$ Pa·s) for $\text{RH} > \sim 50\%$, while for $\text{RH} \leq \sim 50\%$, the particles showed a viscosity of $> \sim 1 \times 10^{12}$ Pa·s, corresponding to a solid state. In case of the ternary systems, the viscosity of organic-rich particles (OIR = 4:1) gradually increased from $\sim 1 \times 10^{-1}$ to $\sim 1 \times 10^8$ Pa·s for a RH decrease from $\sim 81\%$ to $\sim 18\%$, similar to the binary sucrose/H₂O particles. This indicates that the sucrose/AS/H₂O particles ranges from liquid to semisolid or solid across the RH. In the ternary particles for OIR = 1:1, the viscosities ranged from less than $\sim 1 \times 10^2$ for $\text{RH} > 34\%$ to $> \sim 1 \times 10^8$ Pa·s at $\sim 27\%$ RH. The viscosities correspond to liquid for $\text{RH} > \sim 34\%$, semisolid for $\sim 34\% < \text{RH} < \sim 27\%$, and semisolid or solid for $\text{RH} < \sim 27\%$. Compared to the organic-rich particles, in the inorganic-rich particles (OIR = 1:4), drastic enhancement in viscosity was observed as RH decreased; the viscosity increased by approximately 8 orders of magnitude during a decrease in RH from 43% to 25% resulting in liquid to semisolid or solid in the RH range. Overall, all particles studied in this work were observed to exist as a liquid, semi-solid or solid depending on the RH.”

Looking at abstract revision, some sentences changed, and experimentally derived parameters changed as well (also in main text) without explanation in the authors' response. Do these parameter changes impact the findings or conclusions of this work? Please elaborate.

→ During our final check on the revision, we found a mistake on the production of a sucrose calibration line using bead-mobility technique which was used with formal data in our group. Thus, we have replaced the calibration curve of sucrose using corrected data that were produced from Rani Jeong (the first author of this manuscript) from her experiments (corrected Fig. S1 is below). This modification has changed slightly the viscosity-value and corresponding RH obtained from the bead-mobility experiments, but this is more accurate and it is not significantly affect the results.

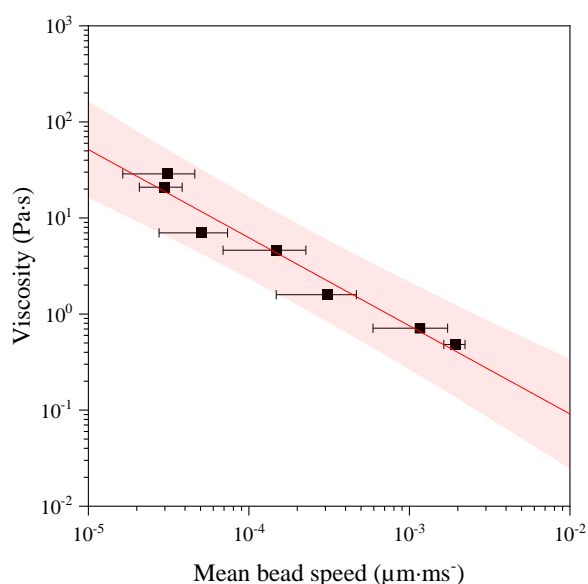


Figure S1: Calibration curve showing mean bead speeds as function of viscosities of sucrose/H₂O particles at different relative humidity (RH) values. The red curve is produced by a linear fit to the measurements, which yields the equation: $bead\ speeds = 7.35 \times 10^{-4} \times (viscosity, \eta)^{-1.09}$. The pink shaded envelope indicates 95% prediction bands of fitting to the data in this study. The error in mean bead speed (x-axis) is a standardization of 3-5 beads in one or two particles at given RH.