Reply to comments on "In−situ observation for RH−dependent mixing states of submicron particles containing organic surfactants and inorganic salts" by Xiong et al.

Reply to Anonymous Referee #2

This manuscript reports an experimental study on humidity-dependent mixing states of submicron particles that contain both organic surfactants and inorganic salts. The topic is thus clearly suitable for Atmospheric Chemistry and Physics. The work covers a wide range of compositions and conditions that are potentially relevant for a range of questions on the physics and chemistry of atmospheric aerosol particles such as the impact of liquid−liquid phase separation. The chosen laboratory proxies are dicarboxylic acids, organosulfates and organosulfonates which are some of the important organic constituents in secondary organic aerosols. However, atmospheric aerosols are not as simple as the binary chemical systems studied here and given there is no model interpretation of the experimental data presented, comments on atmospheric implications have very limited applicability which is a clear weakness of the work as it is presented currently. It would thus be important to identify in the manuscript how this wider applicability could be achieved. Nevertheless, the experimental results are quite novel (incl. direct observation of Ostwald ripening, some interesting O:C dependencies and surfactant shell effects) and well described, so that they could motivate modellers to feed these results into their models to enhance the understanding of the mixing states of atmospheric aerosols and/or motivate further experimental studies on other size ranges and with complementary methods to

overcome some of the shortcomings of the experimental work presented here. This additional work should be motivated better with a much stronger atmospheric implications section outlining the groundwork needed to establish how the gap between the lab proxies used here and atmospheric interpretation could be bridged. Once this is added, the manuscript is likely to be suitable for publication in Atmospheric Chemistry and Physics.

This study follows experimentally the mixing states of submicron particles containing inorganic salt and organic surfactants with varying organic volume fractions during humidity cycling using Environmental Scanning Electron Microscopy (ESEM); the ESEM data presented are useful and well described overall. Particle sizes studied are in an atmospheric relevant range (aerodynamic "size" – diameter I presume- of 0.7−1 μm), although the size range is very limited; another potential limitation are surface effects as the particles are not floating as e.g. possible with frequently used levitation methods – this should at least be considered and the potential implications need to be discussed (e.g. contrasting the work presented with results from levitation studies or other methods that have different limitations in terms of spatial or temporal scales).

Response:

We truly appreciate the constructive comments and suggestions raised by the reviewer. Those comments are valuable and very helpful for improving our paper. 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.

Major comments:

1) Short exposure times are mentioned to avoid beam damage – have the authors tested

for beam damage (e.g. by moving sampling location/contrasting short vs long exposures etc.)? How was it established that 5 µs avoids beam damage and that the results are not affected by artefacts from beam damage (I can see no indication that this would be the case from the data presented, but a discussion of this potential issue is needed; the authors reference a paper (O'Brien et al, 2015) that has developed this technique, but this earlier paper does not specify 5 µs – just fast scans- so it needs to be clarified how this time limit was derived)?

Response: In fact, for a selected focusing area, relatively slow scan rate could diminish the beam exposure thus possible damage for focused particles (Ott et al., 2021), especially for long time observation in our experiment. As demonstrated in supplemental information of O'brien et al. (2015), a line scanning rate of 1 to 10 µs different fields of view for images recording was used, in order to minimize the beam damage. Therefore, taking this in consideration, we set our line scanning rate 3 to 5 µs, which was within the range used in O'brien et al. (2015) through the whole experiment.

Revision/addition:

1) L128: "images were recorded with line scanning rates of 3−5 µs to minimize the possible beam damage (Supporting information, O'brien et al., 2015)"

2) It is unclear how many experiments were performed and how reproducible results were – this is particularly important when considering the point above about beam damage; this needs to be clarified before publication to confirm suitable rigour of the experimental approach (there are a few error bars in Figs 6 and 7, but not in other plots, so this is something that needs to be addressed/clarified)

You should contrast the applied experimental methods to other approaches (e.g. in a table) and briefly comment on advantages and shortcomings of your chosen approach; also include a discussion of the size range relevant in the atmosphere compared to the one you have studied (and generally accessible with experimental methods)

Response: Thank you for the advice.

1) Each image in our study contained at least 5 particles (or droplets) to ensure the ESEM reproducibility and decrease the uncertainty. We have added the error bar in Figure 1 in the manuscript. In addition, we have reproduced some of the experiment for validation, e.g., in the RH decreasing period, and the results showed good reproducibility (Fig. R1 below).
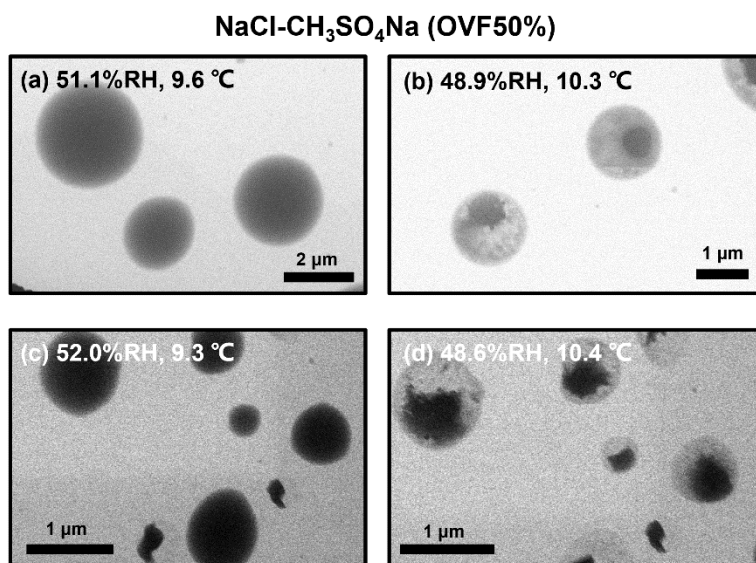
Figure R1. ESEM images of solid phase state of NaCl−CH₃SO₄Na with 50% OVF in two repeated experiments (Experiment 1: a and b, Experiment 2: c and d). Solid Phase separated RH showed good consistency.

2) We have added the description and contrast in the main text as suggested.

Revision/addition:

1) **SI**: Fig. R1 was added in the SI (Fig. S1).

2) **Line 128**: "The varying range of RH value between two consecutive pictures were mostly 0.2~0.4%RH (very narrow), in order to capture the possible quick transitions of mixing states. Each image in our study contained at least 5 particles (or droplets) to ensure the ESEM reproducibility and decrease the uncertainty. In addition, we have repeated some of the experiment (e.g., in the RH decreasing period) for reproducibility validation, and the results showed good consistence (Fig. S1)"

3) **Line 106**: "Optical microscopy (Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013), microfluidic device (Roy et al., 2020), Cryo-TEM (Veghte et al., 2014; Freedman, 2020; Ott and Freedman, 2021; Ott et al., 2021; Zhang et al., 2022), ESEM (O'brien et al., 2015), optical tweezer (Stewart et al., 2015; Tong et al., 2022)and F-AFT (Fluorescence aerosol flow tube) (Ohno et al., 2021; Ohno et al., 2023) were reported methods for detecting aerosol mixing state in the literature. Optical microscopy and microfluidic device were commonly used direct method for substrate-supported droplets but was limited by size range (at least dozens of micrometers). Optical tweezer and F-AFT could investigated LLPS in a levitated micrometer and sub-micrometer droplet, respectively, but are indirect way, although no distinct differences when comparing to substrate-supported droplets (Ohno et al., 2023). Cryo-TEM and ESEM could detect mixing state in sub-micrometer scale but damage caused by electron beam may exist (depend on chemistry and beam parameters settings). Ott et al. (2021) give some useful suggestions in minimize the damage, e.g., decreasing exposure dose and time to particles."

3) The atmospheric implications section is very limited given this is an atmospheric science journal – it is important to bring this experimental study into context with other experimental studies covering the range of atmospheric conditions experimentally accessible, then consider relevant model studies of atmospheric aerosols and how they link to the results presented here and finally also consider if there are links that can be made to field work findings (which may or may not be possible); this should also expand into a more specific consideration of future studies to bridge the gaps between the currently studied proxy systems and the processes actually occurring in the atmosphere – an appreciation of the shortcomings of the proxies will help to understand differences and also motivate other groups to use their techniques to address the remaining challenges.

Response: Thanks for suggestion. We have improved our atmospheric implication.

Revision/addition:

Implication section: Dicarboxylic acids, organosulfates, and organosulfonates are important surface−active organic constituents in secondary organic aerosol. Few studies comprehensively studied their mixing state upon fluctuating RH cycling, which is a simulate of real atmospheric condition. In this work, we concluded that mixing state affected interactions of inorganic salt with water. Since common assumptions in chemical transport models (including ISORROPIA-II (Fountoukis and Nenes, 2007), EQSAM (Metzger et al., 2002a; Metzger et al., 2002b), and MOSAIC (Zaveri et al., 2008)) are that water uptake is determined separately by the inorganic compounds and organics (i.e., the effect of mixing state was ignored) (Myhre et al., 2007; Nandy et al., 2021), thereby our results implied further effect of

mixing states on estimations of aerosol hygroscopicity (e.g., growth factor), optical properties, and radiative forcing.

During dehydration, we investigated phase−separated before and after efflorescence for inorganic salts−organic surfactant particles. Compared with homogeneous particles, phase−separated particles could decrease trace gas uptake (You et al., 2012), resulting in reduction of the formation of secondary organic aerosols (SOAs) (Zhang et al., 2018). In addition, organic phase was enriched in "outer shell", which can potentially alter aerosol water activity and lower aerosol surface tension, hence affecting aerosol−cloud interactions because water uptake of organic matter in current models (e.g. MPMPO (Griffin et al., 2003) and SOA treat-ment in CMAQ v5.2 (Pye et al., 2017)) is estimated by highly parameterized relationships assuming ideal solutions, e.g., using the kappa hygroscopicity parameter with water surface tension (Petters and Kreidenweis, 2007; Nandy et al., 2021).

Our results provide comprehensive information of mixing states between inorganic salts and organic surfactant in nanoscale perspective, which could help the establish of incorporation atmospheric modeling, to improve predictions on indirect effects of aerosol−climate interactions. We should note that in the atmosphere most particles are smaller (e.g., 0.1 to 0.3 μm) than sample particles and the chemical characteristics of ambient aerosol are not as simple as binary chemical systems in the current study. Therefore. the water kinetic inhibition should be further investigated for smaller particles containing more complex systems in the future.

4) Data should -if at all possible- be made available or added in the supplement (which is

very light at the moment) rather than requiring a request to the corresponding author especially since this is a purely experimental study that will need modellers to engage to allow a meaningful atmospheric interpretation.

Response: We have uploaded the corresponding data to an open access website.

Revision/addition:

L348: *Data availability*. **The experiment data are available at ZENODO (https://doi.org/10.5281/zenodo.8079001).**

Minor comments:

5) Some of the figures lack clarity, e.g. need explanation of the color coding of the symbols, meaning of the shapes of the symbols used; also all scale bars should be labelled consistently, diagrams to the right of Figs 1 and 2 need further explanation and Fig. 5 needs to more clearly distinguish visually between data reported here and those from literature.

Response: We have added the explanation to make it clearer as suggested.

Revision/addition:

Figure 1: "ESEM images of (a−d) pure NaCl and (e−h) NaCl−C$_2$H$_5$SO$_4$Na (70% OVF) with different RH. Blue and green arrows indicate the inorganic phase and organic phase, respectively. The RH value that NaCl core fully dissolved (DRH) for NaCl−organic surfactant systems with different OVF (i). Grey area in (i) covers DRH range of NaCl in the literature obtained from Peng et al. (2022). Red line indicates the measured average DRH of pure NaCl (80.9 ± 0.1%). Scale bars in (a-h) were 1 μm."

Figure 2: "ESEM images of (a−d) pure AS and (e−h) AS−C$_2$H$_5$SO$_4$Na (50% OVF) with different RH. Blue and green arrows indicate the inorganic phase and organic

phase, respectively. The RH value that AS core fully dissolved (DRH) for AS−organic surfactant systems with different OVF (i). Grey area in (i) covers DRH range of AS in the literature obtained from Peng et al. (2022). Red line indicates the measured average DRH of pure AS (82.1 ± 0.6%). Scale bars in (a-h) were 1 μm."

Figure 5: "Van Krevelen Diagram for the mixed inorganic−surfactants particles in the current study (symbols in red, orange and cyan): (a) NaCl−surfactant and (b) AS−surfactant systems. Solid symbols indicate that LLPS was observed for particles with at least one OVF, while hollow symbols indicate that LLPS was not observed for particles with all OVFs. Symbols in grey in (a) and (b) were results obtained from Bertram et al. (2011), You et al. (2013) and You and Bertram (2015). Yellow-hatched region (O:C < 0.43) means that LLPS observed in all investigated systems, while grey-hatched region (O:C > 0.8) means no LLPS detected in any of the investigated systems."

6) While mostly clear, the manuscript should be proof-read carefully to correct grammar/improve language/sentence structure in a few places (examples include lines 59, 133, 145 or 146)

Response: Thanks for suggestion. We have carefully revised the incorrectness through the manuscript.

Revision/addition:

1) Line 58: "which is consistent with inorganic salting out efficiencies."

2) Line 152: "… form a new phase (Altaf and Freedman, 2017; Altaf et al., 2018; Freedman, 2020; Ott and Freedman, 2021). According to Freedman (2020), morphology of most systems were found size dependence, where large particles

were phase-separated and small particles were homogeneous. Furthermore, all systems (e.g, AS–PA and AS–succinic acid systems) with dry diameters larger than 0.7 µm were observed phase-separated no matter the occurrence of size dependence (Altaf and Freedman, 2017). Freedman (2020) expected that phase-separation could be attributed by nucleation and growth, therefore larger particles tended to be phase-separated morphology, as was observed in the present study. In another study, Ohno et al. (2021) also found that LLPS occurred at lower RH in smaller droplet (70 – 190 nm) than in larger droplet (260 – 370 nm)."

3) Line 168: "According to the above-mentioned studies, DRH of pure AS and NaCl displayed weak dependence on size (> 100 nm) and temperature, and we therefore concluded that surfactant shell inhibits water diffusion exposing to inorganic cores, resulting in delays of deliquescence of inorganic cores."

Reference

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