

Response to Reviewer 2 (Reviewer comments in black text):

This manuscript describes observations of liquid-liquid phase separations in multicomponent droplets containing mixtures of dicarboxylic acids of varying carbon chain length with ammonium sulfate. The measurements are shown to compare well with predictions from the AIOMFAC model, an invaluable step forward in validating the model when the paucity of data on liquid-liquid phase separations is considered. Given the atmospheric relevance of the organic O:C ratios and mass fractions studied, the prevalence of dicarboxylic acids, and the relative humidity (RH) range explored, this is an extremely important body of work and should be published in Atmospheric Chemistry and Physics. The work is extremely rigorous and impressive and exactly what is needed in this area of research. The paper is very well written and clearly organised. Before publication, the authors should be given the opportunity to consider the following minor comments and any revisions they consider appropriate.

We acknowledge reviewer 2 for the useful comments and suggestions. The detailed responses as well as their location in the revised manuscript are indicated.

- A limited range of RH gradients is explored. Given that the authors suggest that the organic phase may become very viscous and impervious to water transport, should measurements be repeated over slower changes in RH?

We performed the experiment with different particles and also repeated with different rates between 0.1-0.3 % RH min⁻¹. With our setup, we are restricted in the range of RH rates that we can explore. For lower rates, the experiments require much longer time scales of observations. We could have performed efflorescence experiments at a lower rate, however, this was not the main focus of this study.

- The authors chose to use 5-component droplets containing 3 organic acids of the same O:C ratio to suppress crystallization. They suggest that this does not alter the expected hygroscopic behaviour/phase separation RHs. While I agree that this is true if the group additivity approach used by AIOMFAC is accepted, to what extent is this generally valid? Given this argument it seems as though the two sentences on page 29151 are inconsistent: “Instead of using one dicarboxylic acid, three acids of equal carbon number are mixed together in mixtures C5–C7 to better mimic the complexity of real aerosol compositions and to avoid early crystallization of one component during humidity cycles. For the same reason, the straight chain C6 and C7 dicarboxylic acids (adipic and pimelic acid) were excluded from the mixtures because of their low aqueous solubility.”

One of our intentions of mixing components was indeed organic crystallization suppression. However, we nevertheless observed crystallization of some organic components in the mixtures triggered by the crystallization of AS. Hence, the mixtures of three dicarboxylic acids stay liquid in much of the RH range on a dehydration cycle, at least down to the RH of efflorescence of AS. This is not generally the case when only one dicarboxylic acid is used, especially straight-chain dicarboxylic acids like adipic and pimelic acid tend to crystallize at much higher RH when they are the only organic component in aqueous solutions. In atmospheric aerosols, hundreds organic components have been found in the organic fraction, efficiently suppressing crystallization even at low RH. To make this clearer in the revised manuscript, we change/add the following statements in Section 3.1:

“Instead of using one dicarboxylic acid, three acids of equal carbon number are mixed together in mixtures C5 – C7 to better mimic the effect of a complex mixture of compounds in the organic fraction of real aerosols, in which crystallization of organic components during humidity cycles is effectively suppressed due to the many components, as discussed in Marcolli et al. (2004). In this context, the straight chain C6 and C7 dicarboxylic acids (adipic and pimelic acid) were excluded from the mixtures because of their low aqueous solubility and related limited crystallization suppression of these dicarboxylic acids when the organic fraction is only represented by three compounds.”

- Page 29153. I do not understand the phrase: “: : aqueous outer phase that was confirmed to consist of organics (see Sect. 3.3) was sucked into the crystalline inner phase within a few seconds ($t = 139.3$ min) most probably because of capillary forces (Sjogren et al., 2007).” Do the authors mean that the two phase system transitions to a 1 phase system? Do they mean that inorganic crystals are just immersed within the organic phase?

The inner phase (aqueous ammonium sulfate) in the C7/AS/H₂O particle effloresced while the outer phase still remained in the liquid state at 41.4 % RH (Fig. 2c). Within duration of 0.3 min, the (aqueous) organic outer phase shrank toward the crystallized inner phase. This behavior could result from capillary forces due to the polycrystalline nature of the effloresced AS phase (veins between crystalline needles). It does not imply a phase transition to a one phase system. We have revised the manuscript to make this clearer.

- Page 29154: The authors discuss the assignment of the various Raman bands but no mention is made of the Raman signature from the ammonium ion. How does this complicate the assignment of the C-H and O-H stretching regions?

We mention now the position of the NH_4^+ band in the revised manuscript. The NH_4^+ band does not interfere with the C-H stretching band, however, it introduces an ambiguity whether the weak signal above 3000 cm^{-1} at low RH is due to water or a feature of AS.

- In an organic rich aqueous volume, presumably there can be some partitioning of ammonium forming the ammonium salt of the deprotonated acid. This would suggest some equilibrium partitioning between ammonium in this phase and in the gas phase.

In the experimental system described here, any partitioning of ammonia between the gas and condensed phases is most likely irreversible with evolution of the ammonia into the gas phase leading to depletion of ammonium in the particle over time. Can the AIOMFAC model represent this gas phase partitioning? Indeed, the organic acids will be lost over some time-frame. It would be helpful if the authors described the relative importance of this gas-particle partitioning of the organic and ammonia components.

AIOMFAC does not treat the dissociation of the dicarboxylic acids and the formation of ammonia from the ammonium ion. The experiments are carried out under a constant $\text{H}_2\text{O}/\text{N}_2$ flow. We therefore do not have an equilibrium gas/particle partitioning. For micrometer-sized particles, evaporation of C5 – C7 dicarboxylic acids is not strong enough to be relevant on the timescales of our experiments. Therefore, there is no need that the phase equilibria calculations include gas-particle partitioning.

- The first appearance of mf_d is on page 29156. This quantity needs to be defined.

We do this now in the revised manuscript (page 29150, line 22 which is the first appearance of $\text{mf}_d(\text{AS})$).

- Page 29159: Using the Raman peak heights to judge phase composition seems to be fraught with problems. It seems unlikely that the Raman signature comes from just one single phase given the expected morphologies (eg. Figure 10) – see also my comments on depth resolution below. Although this can provide a qualitative guide, it seems unlikely to allow compositional determination as suggested. I think the authors should be more cautious in suggesting that it might.

The Raman analysis in this paper should not be considered as quantitative determination of the phase composition but as a tool to identify the phases and the location of the inclusions. The black symbols in Figure 6a indeed reflect the AS/C6 ratio in the one liquid phase state because the corresponding spectra were measured at 85 % RH when only one liquid phase was present. Figure 6a should be considered as an illustration of the anomalous behavior of the C6/AS/ H_2O system with no constant phase composition of the organic-rich phase. This result is very clear because the AS/C6 ratio of the organic-rich phase varies by a factor of 3, which is definitely larger than the experimental uncertainty.

- Figure 7, page 29190: The images in panel (c) are used to suggest that the phase separation arises from different mechanisms and leads to different morphologies in the C6 and C7 cases. It is not clear if the apparent core-shell structure in these images is truly reflective of core-shell or just arises from a 3-phase boundary induced phase separation at the meeting of the droplet with the substrate. Similarly, Figure 10 suggests that the substrate/inorganic rich phase and substrate/organic rich phase interactions are quite key in governing the morphologies observed. It would be helpful if the authors described in a little more detail any impact they feel the substrate may have on the phase separation mechanism and morphology. For example, presumably, when an inclusion settles onto the substrate, it is fairly immobile due to the adhesional energy.

Can this prevent the inclusions sampling the full range of morphologies, such as the inclusion in Figure 10 moving towards the droplet edge?

The reviewer raises here several interesting points that deserve further investigations. However, we think that the body of evidence that we present here does not allow additional conclusions. Any further discussion would be too speculative. We intend to address this topic in a further study where we directly compare experiments performed with the Raman microscope with electrodynamic balance experiments and calculations of morphologies based on measured values of surface and interfacial tensions of the systems under investigated systems. We state this now in the conclusions of the revised manuscript.

- Figure 10, page 29193: Why is the apparent diameter still so large when the Raman is measured at height of 32 microns? It would be helpful to show the ‘measured’ diameter at much larger height to confirm that it goes to ‘zero’. This suggests that the spatial extent of the volume sampled by the confocal Raman signature is much deeper than suggested by making measurements at a 6-7 microns resolution. Given this, how confident are the authors in their interpretation of the depth profile reported in 10(b)? It is not clear why this Raman peak intensity ratio remains larger than the outer value.

The apparent diameter is still so large at 32 microns because the droplet is out of focus and blurred. The measured diameter does not go to zero because the droplet becomes more and more blurred until it “disappears”. We do not want to imply that our depth resolution is 6 -7 microns by using this step size. We cannot use the full capabilities of confocal Raman microscopy because we need to work with a long working distance objective to focus on the droplet in the cell. Moreover, we are not scanning through a flat coating but a curved droplet with a curved inclusion. This in addition leads to stray light and will reduce the depth resolution. We did not perform an experiment to accurately determine the depth resolution of our setup, but we assume that the main signal might come from a section of 6 – 7 microns,

however, with large tails to lower and higher depths. This is confirmed by the finding that the Raman signal is still visible at 15 microns above the droplet (see Fig. 10b). The depth profile shows very clearly that the highest AS/C6 ratios appear close to the substrate. This was the case for all investigated droplets and evidence enough to conclude that the AS inclusions are at the bottom of the droplets. We do not think that our depth resolution is good enough to deduce the contact angle of the AS inclusion to the substrate from the depth profile. The difference between the Raman peak intensity ratio of the outer phase and the signal measured above the particle might be within experimental error. Again, the aim of this Raman analysis was not an accurate quantification of phase composition but the identification of the phases and the location of the inclusions.