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Atmospheric
Chemistry
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Discussions

Interactive comment on "Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles" *by* M. Song et al.

Anonymous Referee #2

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This manuscript describes observations of liquid-liquid phase separations in multicomponent droplets containing mixtures of dicarboyxlic 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

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publication, the authors should be given the opportunity to consider the following minor comments and any revisions they consider appropriate.

- 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?

- 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 AIMOFAC 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 15 because of their low aqueous solubility.”

- 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?

- 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?

- 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.

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

- 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.

- 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 susbtrate/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?

- Figure 10, page 29193: Why is the apparent diameter still so large when the Raman

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is measured at a 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29141, 2011.