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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C" *by* Mijung Song et al.

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Summary: The paper investigates the liquid-liquid phase separation (LLPS) in organic particles. LLPS was observed when the O:C ratios of the particles were $\leq$ 0.44 for single organic species and $\leq$ 0.58 for mixtures containing two organic compounds. Most of the LLPS can be observed at RH close to 100%. The authors demonstrate that the LLPS may have important implications on the CCN properties of organic particles. The manuscript is well written, and the results are clearly presented. I would like to recommend this manuscript to be published in Atmos. Chem. Phys. If my following concerns are fully addressed.

Concern. [10] 1. Page 4, Line 8. The dimensions of the particles were measured around 30-80 μm. Depending on the particle generation methods, sizes of the particles used in the LLPS studies in the literature vary from 1 to 80 micrometers. 80 micrometer used in this study is at the higher end. Does particle size affect the results of LLPS?

[A10] The resolution of the microscope used in the current experiments was roughly 1 micrometer. From experience, detection of LLPS with our microscope setup is the clearest when the size of the particles are roughly 30 - 80 ïA■m, although smaller sizes are possible with optical microscopy. We did not observe a size dependence for the LLPS, although only a narrow range of sizes were investigated. This information will be added to Sect. 3.1 of the revised manuscript.

[11] 2. Page 5, Line 29. a. Have the authors tried nonanedioic acid (C9H16O4) and tetradecanedioic acid (C14H26O4)? These are the isomers of suberic acid monomethyl ester and diethyl sebacate with the same O:C ratio. One may expect different results with these isomers. For example, due to the stronger polarity and hydrogen bonding of acids as compared to esters, the acid compounds may have stronger interactions with water molecules, leading to higher SRHs. Or no LLPS may be observed. These effects may actually be helpful to explain why the authors did not observe LLPS with poly (propylene glycol) and PEG-400. Can you comment on whether/how the intermolecular interactions between organic compounds and water affect LLPS?

[A11] Thank you for the comment. Nonanedioic acid and tetradecanedioic acid are solid at room temperature. In our studies we only used liquid organics species to ensure the mixtures were homogeneous prior to nebulization. Regarding intermolecular interactions, see response to comment [8] above.

[12] b. In contrast to the experiments with organic + ammonium sulfate conducted in the same group (e.g., Bertram et al.1 and You et al.2), no LLPS was observed in this study using the same organic compounds (i.e., polyethylene glycol, PEG-400, and diethyl-L-tartrate). I wonder if the authors have any explanation regarding the different

observations between these two studies.

[A12] The difference observations between the two studies is likely due to salting out by ammonium sulfate (Marcolli and Krieger, 2006). We are currently working on a manuscript that will focus on this point. Marcolli, C., and Krieger, U. K.: Phase changes during hygroscopic cycles of mixed organic/inorganic model systems of tropospheric aerosols, J Phys Chem A, 110, 1881-1893, Doi 10.1021/Jp0556759, 2006.

[13] 3. Page 6, Line 2 and Table 3 What is the molar/mass ratio between the two organic compounds in the mixtures in Table 1? Is it 1:1? Have you tried any other mixing ratios? When nebulizing the mixture, how can the authors be sure that the composition of individual particle was the same as its original mixture?

[A13]All experiments for two organic species were conducted with the mass ratio of 1:1. This information will be added to the Sect. 2.2 of the revised manuscript. All organic species used in this study are liquid at room temperature. Based on visual observations, the mixtures of two liquid organics were one phase prior to nebulizing as described in Sect. 2.2, hence a change on composition of the individual particles was not expected due to nebulizing the mixture. This information will be added to the revised manuscript.

[14] 4. Page 6, Line. a. It is interesting that adding PEG-400 which itself did not give LLPS, expanded the LLPS RH range of other compounds. Does it simply due to the change of O:C ratio? If not, please explain it in more detail.

[A14] In addition to the average O:C, the spread in O:C values within an organic particle and the types of organic functional groups are likely also important. The manuscript will be modified to make these points clear (Sections 3.1).

[15] b. For polypropylene glycerol/PEG-400, no LLPS was observed in the single organic species scenarios. But mixing them together yielded LLPS with a low SRH ($\sim$75%). Have the authors tried any other mixtures of the following: diethyl sebacate,

glyceryl tributyrate and suberic acid monomethyl ester? I wonder if the SRH and LLPS RH range will also change? Can you comment on this?

[A15]We are not sure if we completely understand the referee's comments. The following binary mixtures related to the referee's comments were studied: diethyl sebacate + glyceryl tributyrate, diethyl sebacate + suberic acid monomethyl ester, and glyceryl tributyrate + suberic acid monomethyl ester (see Table 3). Is the referee suggesting we try ternary mixtures? We have not tried any ternary mixtures.

[16] 5. Page 8, Line 7. SOM is a bulk mixture. Why the results of SOM are similar to those from single organic components (i.e., LLPS occurred with O:C ratio $\leq$ 0.44; narrower LLPS RH range was observed)? Is it just a coincidence? It seems that O:C ratio solely cannot fully explain the results. Can the authors comment on this?

[A16] First, the uncertainty of O:C of the SOM mixtures are large and thus we cannot determine based on our results if the SOM results are in better agreement with the studies using one organic species or two organic species. Second, we agree that the O:C ratio cannot solely explain the results. The manuscript will be revised to try and make this point clearer (Section 3.3).

Minor comments [17] 1. Page 4, Line 10: "deposing". Should it be "depositing"?

[A17] We will correct "deposing" to "depositing" in the revised manuscript.

[18] 2. Page 17, Table 1: For diethyl-L-tartrate, I don't think there are ether group and carboxylic acid group.

[A18] Thank you for the correction. Diethyl-L-tartrate is alcohol and ester group. We will correct it in Table 1 of the revised manuscript.

Reference (1) Bertram, A. K.; Martin, S. T.; Hanna, S. J.; Smith, M. L.; Bodsworth, A.; Chen, Q.; Kuwata, M.; Liu, A.; You, Y.; Zorn, S. R. Predicting the relative humidities of liquidliquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio

of the particle and the oxygen-to-carbon elemental ratio of the organic component. Atmos. Chem. Phys. 2011, 11 (21), 10995–11006. (2) You, Y.; Renbaum-Wolff, L.; Bertram, A. K. Liquid-liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride. Atmos. Chem. Phys. 2013, 13 (23), 11723–11734.

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