

Referee #2

Summary:

In this study the authors investigate liquid-liquid phase separation (LLPS) and viscosity of secondary organic aerosol (SOA) formed in photooxidation of diesel fuel vapors. Such multi-precursors studies on SOA are needed to understand atmospheric SOA and the topic fits well in the scope of Atmospheric Chemistry and Physics. The study is based on experimental observations of LLPS and viscosity and comparison to viscosity parameterizations. Overall the study seem carefully conducted. The manuscript is in most parts clear and carefully written, although I have listed below few points which should be considered before the manuscript is accepted for publication.

Major comment:

[1] While the authors have overall resented the results carefully considering uncertainties and they discuss some caveats of the technique on page 12 L4-10, one aspect of the experimental technique has been neglected in the discussion of the results. The particles where collected on the glass slides and then conditioned for up to an hour for desired RH. During the conditioning (and the viscosity/LLPS measurements), the particles were surrounded by gas phase free of organics and this should cause some of the organics to evaporate. Therefore, the composition of the particles during viscosity or LLPS measurements would not have been the same as for it was when the particles were suspended in the chamber. This issue should be mentioned and the resulting uncertainty or systematic error in viscosities should be discussed in the text.

[A1] This is a similar comment as Referee #1. Please see the answer [A1].

Minor comments:

[2] P7 L1-8: Why are different values of coefficient k_{GT} used?

[A2] Based on previous studies, k_{GT} of 1 is applied for organic-organic mixtures and k_{GT} of 2.5 is applied for organic-water mixtures. We will clarify this point in the revised manuscript in Sect. 2.4.

[3] P7 L13-20: Is the predicted viscosity sensitive for the assumed viscosity of 10^{-5} at very high temperature and the assumed value of $D_f = 10$? Why did the authors chose $D_f = 10$ which they state is a lower limit from a previous study? Was the viscosity parameterization tuned to match the measured values in this study by selecting these specific values?

[A3] The viscosity of 10^{-5} Pa s at a very high temperature is well established in the glass community (Angell, 1991; Angell, 2002). In these equations, D_f is the fragility parameter and T_0 is the Vogel temperature. In our calculations, we fixed D_f to be 10 because a previous study that showed D_f approaches 10 when the molar mass of the organic compounds exceed ~ 200 g

mol⁻¹ (DeRieux et al., 2018) and because many of the detected compounds in diesel SOA have molar masses > 200 g mol⁻¹. Even though the Df value does affect predicted viscosity (see Fig. 5b in DeRieux et al., 2018), Df is not as critical as other parameters such as the glass transition temperature or hygroscopicity. We will clarify this point in the revised manuscript in Sect. 2.4.

References:

Angell, C. A.: Relaxation in liquids, Polymers and plastic crystals - Strong fragile patterns and problems, *J. Non-Cryst. Solids*, 131, 13-31, [https://doi.10.1016/0022-3093\(91\)90266-9](https://doi.10.1016/0022-3093(91)90266-9), 1991.

Angell, C. A.: Liquid fragility and the glass transition in water and aqueous solutions, *Chem. Rev.*, 102, 2627-2649, UNSP CR000689Q 10.1021/cr000689q, 2002.

DeRieux, W. S., Li, Y., Lin, P., Laskin, J., Laskin, A., Bertram, A. K., Nizkorodov, S. A., and Shiraiwa, M.: Predicting the glass transition temperature and viscosity of secondary organic material using molecular composition, *Atmos. Chem. Phys.*, 18, 6331-6351, 10.5194/acp-18-6331-2018, 2018.

[4] P8 L6-7: “two liquid phases may still have been present in the particles, but not in the focus of the microscope” Meaning of this sentence was not clear, probably since the authors have not explained how these optical measurements were actually done.

[A4] To address this question, the following information on how the optical measurements were done will be included in the revised manuscript in Sect. 2.2:

“SOA was collected on hydrophobic glass slides by impaction, resulting in SOA particles on the hydrophobic glass slides with diameters > 10 μm and a spherical cap geometry. LLPS was detected using an optical microscope (Zeiss Epiplan 10X/0.20 HD) coupled to a flow-cell with temperature and RH control (Parsons et al., 2004; Pant et al., 2006; Song et al., 2012b). During the experiments, a constant flow (1.5 L min⁻¹) of humidified N₂ gas was maintained within the flow-cell and measured with a dew point hygrometer (General Eastern M4/E4 Dew Point Monitor, Canada). The temperature within the flow-cell was maintained at 290 ± 1 K and measured with a thermocouple (OMEGA, Canada). At the beginning of the experiments, the SOA particles were equilibrated at around 100 % RH for at least 15 min. At this point, the focus of the microscope was adjusted so the focal plane of the microscope corresponded to the top or interior of several SOA particles. Due to the different sizes of the SOA particles on the hydrophobic glass slides, the focal plane of the microscope corresponded to the top of some SOA particles and the middle of some SOA particles while some smaller particles were not in the focal plane (leading to blurry images). Next, the RH was reduced at a rate of 0.5% RH min⁻¹ until a value close to 0% was reached. While the RH was decreased, images of the particles were acquired every 10 sec with a CCD camera connected to the microscope. From the images, the number of phases (e.g. one phase or two phases) present in the particles were determined. Typically the focus of the microscope was not adjusted as the RH was reduced. As the RH was reduced, the size of the SOA particles decreased due to the loss of water, and some SOA particles that were in focus at high RH values became out of focus at low RH values.”

[5] What is the difference between the particles a-c in Fig. 1 and particles a-c in Fig. S2? Where all of these particles generated under same conditions?

[A5] Figs. 1 and S2 show six different particles generated with the same conditions. This information will be added to the revised manuscript (Sect. 3.1).

[6] It seems that there is LLPS at 70 % RH in particles in Fig. 1, but in particles shown in Fig. S2 there is no LLPS always even at 82% RH. What causes this? Fig. S2 c shows LLPS at 4.7 % RH but not at the higher RH of 50.2%. This raises a question about the reliability of these results and such issues should be explained in the manuscript.

[A6] This confusion is mainly from us not illustrating well the morphology of the particles in Figs. 1 and S2. In the original manuscript, the illustrations suggested that there is no LLPS in Fig. 1c, 5.7%; Fig. S2b, 82.6%; Fig. S2b, 74.1%; Fig S2b, 52.0%; and Fig. S2c, 50.2%. After closer inspection, the images corresponding to these illustrations do have heterogeneity (i.e. non-uniformity) that suggests the presence of a small amount of a second phase. In the revised manuscript, we will adjust the illustrations in Figs. 1 and S2 and corresponding text to make this point clear.

In addition, the poor quality of the images in Fig. S2a make it impossible to determine if there is LLPS in this particle at $\leq 70.9\%$; the images are extremely blurry and the particle is outside the focal plane at RH values $\leq 70.9\%$. As a result, we will remove Fig. S2a from the revised manuscript. Sorry for the confusion we created by include these poor quality images.

Technical comments:

[7] P12 L18: “the presence of an organic-rich outer phase at high RH values can lower the barrier to cloud droplet formation” Barrier of what? Please rephrase.

[A7] This sentence will be changed to the following: “... since the presence of an organic-rich outer phase at high RH values can lower the supersaturation with respect to water required for cloud droplet formation.”

[8] Fig. 3b: Please revise the legend regarding Song et al. results. Currently the legend advises that Song et al. results would be shown with a green solid line. As such line is not present in the figure, I assume these results are the ones shown by the green error bars.

[A8] The line corresponding to Song et al. will be changed to a circle and a circle will be added to the data for clarity.

[9] Fig. 4: The times written on top of the figures do not show well. Please consider writing them with another color.

[A9] As suggested, we will change the color to white in Fig. 4.

[10] Fig. S1: “Mass Dp” and “particle Dp” were confusing in labels. The “Mass Dp” refers also to the diameter of particles. E.g. “Mass Dp” and “Number Dp” would be more clear and consistent names.

[A10] Thank you for the suggestion. We will change the names to Mass Dp and Number Dp as suggested.