Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-14-AC1, 2016

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Relative humidity-dependent viscosity of secondary organic material from toluene photo-oxidation and possible implications for organic particulate matter over megacities" *by* M. Song et al.

M. Song et al.

mijung.song@jbnu.ac.kr

Received and published: 7 May 2016

The manuscript describes measurements of the viscosity of secondary organic aerosol (SOA) samples derived from the oxidation of the anthropogenic precursor toluene using poke-flow and bead mobility techniques. The results are compared with previous measurements for the system derived from impactor measurements and uptake measurements of ammonia, and contrasted with previous measurements for SOA derived from typical biogenic precursors. The manuscript is concisely and clearly written, and the arguments presented are largely substantiated by the data reported. I have only a few minor comments suggesting possible revisions before the manuscript can be accepted for publication.

[1] My most significant comment is on the interpretation of the viscosities at low RH (below 20 %) and the conclusions the authors draw from these measurements. On page 12 of the manuscript, the authors state "Hence, the number of cases classified as having particles not well-mixed based on the viscosity data presented here and the Stokes-Einstein relationship should be considered as an upper limit." Earlier in the manuscript the authors highlight that the viscosity measurements made at such low RHs are only lower limits, with fluid flow and the recovery in particle shape in the poke flow measurements requiring longer time than could be reasonably measured. Therefore, categorically stating that the diffusional mixing times at these low RHs provide an "upper limit" of the equilibration timescale seems to neglect that the viscosities could be orders of magnitude higher than the authors are assuming. Indeed, the authors state in the abstract that the diffusion constant is LOWER than _3 × 10ËĘ-17 cm2 s-1 for RH < 17%. So, although I would agree that the trend in viscosities from measurements at higher RHs would suggest that their conclusions about the limitations of slow mass transport being irrelevant for most geographical locations are probably reasonable, the data do not actually categorically prove this. Because of this I think the authors should add this caveat to their interpretation of the atmospheric relevance, both in the abstract and in the discussion/conclusions.

[A1] To address the referee's comment, we have done the following.

1. Added the following statement to the abstract, "As a starting point for understanding the mixing times of large organic molecules in organic particulate matter over cities, we applied the mixing times determined for toluene-derived SOM particles to the world's top 15 most populous megacities."

2. Added the following to Section 5: "Due to these caveats, the analysis below should be consider as a starting point for understanding the mixing times of large organic

molecules in organic particulate matter over megacities. Additional studies are needed to explore the implications of the caveats discussed above.”

3. Removed the statement “Hence, the number of cases classified as having particles not well-mixed based on the viscosity data presented here and the Stokes-Einstein relationship should be considered as an upper limit”.

[2] Equilibration time before measurements are made, top of page 7: The authors state "These times are sufficient for the particles to equilibrate with the surrounding water vapor based on recent measurements of diffusion coefficients of water within SOM (Price et al., 2015)." The measurements the authors refer to are for alpha-pinene SOM. Thus, the timescale they must leave toluene SOA to equilibrate does not necessarily follow from this reference. A comment should be included by the authors on this.

[A2] This is a good point. To address the referee’s comment, we have now added the following text in Section 2.3. “These times should be sufficient for the particles to equilibrate with the surrounding water vapor based on recent measurements of diffusion coefficients of water within the water-soluble component of -pinene-derived SOM (Price et al., 2015). For example, the time to equilibrate with the surrounding of water vapor was calculated to be 25.3 min at 10 % RH based on diffusion coefficients of water within the water-soluble component of -pinene-derived SOM (Price et al., 2015). These diffusion coefficients should be applicable to SOM derived from toluene studied here, since both SOM have similar viscosities as a function of RH (compare Fig. 2 in Renbaum-Wolff et al. (2013a) with Fig. 5 below).”

[3] Uncertainties, top of page 9: The authors state "The uncertainty in the viscosity of approximately two orders of magnitude arises from the uncertainties in the physical parameters used in the simulations." The authors should say more explicitly what these uncertainties are.

[A3] To address the referee’s comments we have modified this sentence to the following: “The uncertainty in the viscosity of approximately two orders of magnitude

arises from the uncertainties in the physical parameters used in the simulations (i.e. slip length, surface tension, density and contact angle). Of these parameters, the slip length contributed the most to the uncertainty in the viscosity.”

[4] The authors present their new measurements of inferred diffusion constants from Stokes Einstein as being consistent with previous measurements, for example those of Li. Li et al. report diffusion constants of 10ËȨ-17.5 m2 s-1 at 35-45 % RH. Given Stokes Einstein should fail to a similar degree for ammonia and water, it would suggest to me that the diffusion constants for semi-volatile organic molecules would be considerably lower than this at 35-45 % RH and even lower at RHs below 20 %. This is consistent I believe with the authors conclusions. However, they frequently switch between quoting diffusion constants in units of m2 s-1 and cm2 s-1, making it very confusing for the reader and difficult to verify the claims without very careful consideration. The authors should use one unit throughout.

[A4] We now use the same unit (cm2 s-1) through the manuscript. Also it should be kept in mind that in Li et al. it was assumed that the overall rate of reaction was limited by the rate at which carboxylic acids diffused to the surface region of the particle, not the rate of diffusion of ammonia in the particles. The relevant section of the current manuscript has been modified to make this clear. The modified text is included below: “Li et al. (2015) previously estimated the diffusion coefficient of carboxylic acids within toluene-derived SOM from measurements of reactive uptake of NH3. They estimated a diffusion coefficient for carboxylic acids of 10-13.5±0.5 cm2ÂůsâĂŚ1 for RHs between 35 and 45% using SOM mass concentrations of 44 to 125 μg mâĂŚ3. If a hydrodynamic radius of 0.1 - 1.5 nm is assumed for the carboxylic acids (Li et al., 2015), viscosity of 1 104 – 2 106 PaÂůs is calculated using the Stokes-Einstein equation (blue box in Fig. 5), consistent with our measurements.”

[5] On page 10, the authors state: "However, the Stokes-Einstein relationship should give reasonable estimations of diffusion rates for large organic molecules for conditions not close to the glass transition temperature of the matrix". This is further supported

by a recent study and review of recent data provided by Reid and coworkers on the effective volatility of a semi-volatile organic component from organic aerosol of varying viscosity (Chem. Sci., 2016, 7, 1298-1308, DOI: 10.1039/C5SC03223G). Referring to this paper could support further the argument.

[A5] Thank you for the reference. It has been added to the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-14, 2016.