

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.

Anonymous Referee #1

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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.

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- 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 $\sim 3 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ for $\text{RH} < 17\%$. 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.

- 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.

- 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.

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- 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 $10^{-17.5} \text{ m}^2 \text{ s}^{-1}$ 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 $\text{m}^2 \text{ s}^{-1}$ and $\text{cm}^2 \text{ s}^{-1}$, making it very confusing for the reader and difficult to verify the claims without very careful consideration. The authors should use one unit throughout.

- 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.

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