

Interactive comment on “Viscosity of erythritol and erythritol-water particles as a function of water activity: new results and an intercomparison of techniques for measuring the viscosity of particles” by Yangxi Chu et al.

Anonymous Referee #2

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A new method for determining the viscosity of bulk solutions using rectangular area fluorescence recovery after photobleaching (rFRAP) is presented. This is a useful and relatively simple way to determine viscosity, which has been a major topic regarding the viscosity of organic atmospheric aerosol particles. We do need more and more reliable techniques to determine viscosity (and really diffusivity), so this is a valuable contribution to the atmospheric chemistry community. The authors focus on erythritol as it is a proxy for polyalcohols that form from the hydrolysis of IEPOX (an isoprene oxidation product) in the atmosphere, and due to a large disagreement in its viscosity previously

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reported using very different techniques (bead mobility, and optical tweezers). I appreciate their honesty in re-evaluating their prior optical tweezers experiments and acknowledging unrecognized issues in the viscosity measurements under dry conditions due to limited time resolution of the measured signal. I recommend the manuscript for publication in AMT, but would like to see the following questions and comments addressed first to further improve the clarity and quality of the manuscript.

I do agree with the other referee that it is really important to clarify that it is diffusivity and not viscosity that is the key property that governs all the important processes they discuss such as vapor uptake, evaporation, reactive uptake, etc. Viscosity and diffusivity are related, but the relationship breaks down in highly viscous systems, as the authors discuss. Please discuss the key role of diffusivity instead of focusing on viscosity.

The concept of photobleaching needs a more thorough explanation, since it is key to this technique, and very new to the atmospheric science community. It appears to be an irreversible process? This is important to explain. If the fluorophore can regenerate that would require a different approach using this technique, since the fluorescent recovery is entirely attributed to diffusional transport of new fluorophores into the optical volume. Regeneration of the fluorophore does not seem to be the case however. So what is it that causes the photobleaching? Photolysis at this long laser wavelength seems unlikely, unless there is extensive vibrational overtone excitement taking place (unlikely). Does the laser produce a reactant that reacts with the fluorophore? Even if the mechanism isn't entirely understood more explanation of the photobleaching process is required.

Line 204-206: Related to this, the concept of "reversible photobleaching" needs to be explained. Do you have any direct evidence that this does /not/ occur in your experiments?

Line 60 on: Another important way that viscosity and the diffusion limitations this may

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create in organic aerosols has been assessed is through aerosol population mixing experiments, optical tweezers, and other related methods. These experiments test for diffusion limitations that would prevent prompt mixing of organic components through evaporation and then re-dissolution into the aerosol phase. Please cite and discuss these approaches as well. (Gorkowski et al., 2017; Liu et al., 2016; Ye et al., 2016, 2018).

Like 77: Should state that tetrols are important components of atmospheric aerosols as they are hydrolysis products of IEPOX, which is a major oxidation product of isoprene that has been extensively studied recently. This will help to better motivate this study and focus on erythritol.

Eqn 2: Is “erf” the error function used to describe a lognormal population? Please define so this is clear.

Line 184: If r is the microscope’s resolution, why is r^2 a free parameter? Shouldn’t the microscope’s resolution be fixed and known? Or is just combined as one free term as $r^2 + 4Dt$?

Line 210: Is it aerosol optical tweezers or tweezer? I am used to seeing “tweezers” in the literature.

Line 260: Much more discussion of why adding an –OH group to the carbon backbone would increase viscosity is needed. This will be unclear to non-experts. Please discuss in terms of the intermolecular interactions the alcohol groups create, as intermolecular interactions are what determine viscosity, and to a large extent diffusivity as well. Please also discuss/speculate, again using a structure-activity relationship perspective, why the effect might diminish after the 3rd -OH group is added. What could explain these diminishing returns? A nice concise summary of what is known regarding how structure influences viscosity, especially for -OH and similar functional groups, would be a really helpful addition here.

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Fig. 5: Why weren't more a_w values studied, especially at the higher range to see how consistently the trend holds? Measurements in the apparent transition region of ~ 0.05 - $0.2 a_w$ would be really useful.

Fig. 8: The aerosol optical tweezers results seem consistently biased higher compared to the bead-mobility and rFRAP results presented here. Please discuss. I don't see the "reasonable agreement" (line 335) between all three methods (excluding the old optical tweezers data) that is stated.

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Liu, P., Li, Y. J., Wang, Y., Gilles, M. K., Zaveri, R. A., Bertram, A. K. and Martin, S. T.: Lability of secondary organic particulate matter, *Proc. Natl. Acad. Sci.*, 113(45), 12643–12648, doi:10.1073/pnas.1603138113, 2016.

Ye, Q., Robinson, E. S., Ding, X., Ye, P., Sullivan, R. C. and Donahue, N. M.: Mixing of secondary organic aerosols versus relative humidity, *Proc. Natl. Acad. Sci.*, 113(45), 12649–12654, doi:10.1073/pnas.1604536113, 2016.

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