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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of varying experimental conditions on the viscosity of α-pinene derived secondary organic material" *by* J. W. Grayson et al.

Anonymous Referee #2

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The paper presents very interesting results on how the viscosity of complex aerosol produced from a given precursor is likely to depend on total mass loadings. This fits in well with other chamber studies that suggest approaching atmospheric loadings is important to embed relevant compositional dependent properties. There are many methods now presenting work to infer or directly measure viscosity. The poke flow technique offers a nice angle to those systems for which inferring diffusion from shrinkage might be prone to errors introduced from phase separation/solubility considerations. I found the paper very well written. In fact, raising points for discussion is relatively hard as the authors are careful in inferring potential for solid conclusions and artefacts from experimental conditions. The paper should be published in ACP. My points below are

aimed at continuing the interesting discussions raised and would value the response of the authors to clarify a few issues.

Section 2.1 – 2.2: This is likely covered in previous publications, so apologies in advance, but how much confidence is there that the method does not force a given face state by virtue of impaction of the suspended droplets, ignoring any semi-volatile loss? I guess I'm asking if there is any evidence that a meta stable liquid state in a suspension, left for long enough on an impacted filter, would change phase state by virtue of impaction? Atomising droplets from mixtures for which inferred viscosity is different between suspension and bulk methods would easily test this.

Would it be possible to pass your collected samples through a differential scanning calorimeter (DSC) perhaps to infer any expected phase change with temperature rate dependency?

Section 2.3

One angle to add to this, that is interesting and you discuss in page 32976 (section 2.3) and throughout, is also the prospect of losing any semi-volatile material during collection. The idea you discuss is that if we can very roughly associate an increased plasticiser effect with increased volatility of compound (take water as an example), there also a chance that loss of that material from collected particles over 4 days, for example, might alter results. Your viscosity increase from very high to high mass loadings would suggest that the impact of plasticisers would be expected to roughly correlate with viscosity. The same might be true for techniques including bounce measurements where vigorous drying of the particle could perhaps force loss of key semi-volatile species. With typical mixing rules used to correlate composition change to diffusion coefficients, one might expect a relatively small amount of plasticiser loss to have a larger subsequent effect on viscosity. As before, have you characterised systems for which a range of volatilities, and viscosities, are known in pre-defined mixtures? In this paper you study this potential from a system with a mass concentration of 6000 micrograms.

This is still high for atmospheric systems and it isn't clear to me whether the chemical mechanisms 'present' under such conditions are impacting on the expected physical properties. Of course, one could argue that at lower mass loadings, say < 100 micrograms, the volatility and products required to maintain mass loadings might have higher viscosities (non liquid perhaps), but it would still be interesting to confirm this.

How does the potential presence of non Newtonian fluids affect any inferred viscosity from your simulations? Would a variable 'poke rate' infer this? I guess for atmospheric systems, we only really need to know the magnitude scale for viscosity but it is interesting nonetheless.

On page 32976 you state that 'This result suggests it is possible that a small volume of semi-volatile material may have evaporated during the exposure to dry nitrogen, below the detection limit of the measurements of particle volume, but enough to result in a small increase in viscosity.' One might eexpect this. Taking water as an example, the mixing rules used to predict changing diffusion coefficients with changing composition suggest a relatively small amount of water is needed to significantly alter equilibration timescales. Have you modeled this effect from your measurements assuming a simple mixing rule and loss of a range of semi-volatiles?

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 32967, 2015.