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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "The effect of adding hydroxyl functional groups and increasing molar mass on the viscosity of organics relevant to secondary organic aerosols" *by* James W. Grayson et al.

Anonymous Referee #2

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This paper presents results on the viscosity of four polyols and three saccharides to infer the importance of adding OH groups and changing molecular weight to atmospheric organics. The use of a small subset to infer general trends for secondary organic aerosol is difficult, but the increase in studies attempting to resolve the importance of organics on the potential to form highly viscous aerosol particles needs data from studies such as that presented here.

Whilst the results are interesting, there are a few factors with regards to the atmospheric relevance, modelling comparisons and information on the experiments that

require addressing before publication:

General comments:

This study seems to provide a perfect opportunity to cross compare data from complimentary instruments for a property that is only partly investigated in the literature. With this in mind, the source of the data should be added in each figure caption, even though it is stated in table 2. It is not clear if there is any reason why the rheometer was not used for the saccharides and all of the polyols. This should be noted in the text. In addition in figure 5a, whilst I struggle a little with the presentation, it seems the Raffinose data from the poke flow technique can vary by a factor of 100 and yet, at the point of convergence at low RH, matches perfectly. It is unfortunate there is no quantitative discussion that could tie together sections 2.4 and 3.2 and refer to this figure and I feel would add to the paper.

The relationship with viscosity and increasing the number of OH groups might be expected, but there is an interesting thought of what phase state might be attainable in suspended aerosols rather than bulk samples. Do the authors have any thoughts on this? Related to that point, in section 3.2 you comment on the behaviour of viscosity versus RH, but there is no feel for what phase state the sample would be in at that time. How long are the samples allowed to equilibrate with a specific concentration of water vapour? If we are to believe existing equilibration timescale investigations, this can take a very long time, a time that increases with particle size? Perhaps I have missed this, apologies if so.

The comment at the end of section 3.1 needs much more data to confirm and I would recommend some caveats. As the models might allude towards, there is a non-linear interplay between viscosity, different functionality on a given molecule and within a given mixture. Even if we can isolate the impact of functionalization on one molecule, if there is enough plasticiser present, as the authors note, the viscosity could remain very low.

In section 2.6 you present the two QSPRs used in this study. Presumably each model is predicting the viscosity of the sub-cooled liquid organic? For comparisons with data extracted from your measurements this is important to state since we have to consider what the measured state represents.

For the method of Sastri and Rao (1992), the authors are clearly aware of a range of issues here, not least the variability in predictions of saturation vapour pressure. The cross-over in data used to fit vapour pressure models and viscosity relations will be highly variable. I would similarly recommend such methods are not used in future studies, certainly if the reliance on accurate vapour pressure data for a wide range of systems is needed. However, please state the predicted vapour pressure values you have derived in the text, as it will guide the reader into deciphering this. It is of course well known that viscosity can be theoretically related to saturation vapour pressure. The Nanoolal methods the authors comment on also provide predictions of viscosity, a method published in 2009, using the same fragmentation patterns as used in the vapour pressure/boiling point technique:

http://chemthermo.ddbst.com/Parameters/Pure%20Component%20Property%20Estimation
%20Overview%20Rarey-Nannoolal.pdf

Would the authors be able to compare with this method? I suspect it will similarly lead to the conclusion that predicted viscosities will suffer from the fact that existing methods are trained the systems which exhibited viscosities less than 100Pa.s. However the functionality coverage is more extensive and might better support your data.

In the atmospheric implications section, a suggestion is made that the relationship between adding 1 OH group to a carbon backbone might be used to estimate the viscosity of some components of SOM. It might help the readers to suggest some exemplar compounds to reflect this, given the problem that might arise from estimating the base viscosity? I would support the proceeding statement that existing predictive techniques might be better constrained by additional laboratory measurements.

Minor comments:

Page 5, line 3. Noting that data for Glucose has been presented before and therefore not required in this study needs a reference.

Figure 5. I found it quite hard to distinguish the open versus closed symbols in the brown area in figure 5a, and more generally struggled with the cyan symbols and figure resolution. I would suggest trying to increase symbol size and resolution.

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