

Prof. Gordon McFiggans,  
Co-Editor of Atmospheric Chemistry and Physics

Dear Gordon,

Listed below are our responses to the comments from the reviewers of our manuscript. For clarity and visual distinction, the referee comments or questions are listed here in black and are preceded by bracketed, italicized numbers (e.g. **[1]**). Authors' responses are in red below each referee statement with matching numbers (e.g. **[A1]**). We thank the reviewers for carefully reading our manuscript and for their very helpful suggestions!

Sincerely,

Allan Bertram  
Professor of Chemistry  
University of British Columbia

### **Anonymous Referee #1**

The authors present a new dataset of viscosities of four polyols with different numbers of hydroxyl groups and of aqueous solutions with different water activities for three saccharides with different molar masses. They compare their (and literature) data to two different structure-property models for the polyols. In the recent past it became evident that secondary organic aerosol is often highly viscous or even glassy under atmospheric conditions with potentially significant consequences for heterogeneous chemistry and hygroscopicity of atmospheric aerosol. Since secondary organic aerosol consists of thousands of different compounds, prediction methods need to be validated for model systems before they may be used within a chemical oxidation scheme to predict viscosity of aged aerosol. However, data on viscosities for highly concentrated organic model systems are still sparse. The study of Grayson et al. will help in progressing towards the development of reliable prediction models for viscosity of atmospheric aerosol and as such well suited for publication in ACP. The paper is well written, clear and with conclusions appropriately supported by experimental data. The paper should be published as is.

Minor comments:

**[1]** I understand why the authors focus with the polyols on the change of viscosity with increasing functionalization. However, it would be also beneficial for testing prediction models to measure the effect of water content, i.e. performing measurements as different humidities. If the authors did perform such measurements they should be added to the paper.

[A1] To address the reviewer's comments we will go back and measure viscosity as a function of RH for at least one of the polyols studied.

[2] In the description of the experimental techniques, I suggest to add the range of viscosities accessible with each technique to the respective sections.

[A2] This information will be added to the revised document as suggested.

Technical comments:

[3] I do not like too much the notation the authors use to write the values for the viscosities in the text: "approximately  $1e1 \text{ Pa s}$ ". I suggest to use write those as 10 or whatever power of 10 is needed. Similarly, at the end of section 3, change "0.1 orders of magnitude". Just write by a factor of xxx (I do not know what you mean by 0.1 orders of magnitude, 10%?).

[A3] As suggested, in the revised manuscript scientific notation will be used. Also we will use "by a factor of xxx" rather than fractional orders of magnitudes.

[4] I do not see the need for having Fig. 6. Since you show all data in Fig. 7 showing just it should be sufficient for the reader.

[A4] Figure 6 will be removed as suggested in the revised manuscript.

### **Anonymous Referee #2**

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:

[5] 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.

[A5] To address the referee's comments the source of the data will be added in each figure caption. We will also add additional measurements to the manuscript so that results from the poke-and-flow technique can be directly compared with measurements from a commercial viscometer.

[6] 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.

[A6] The reason why the rheometer was not used for the saccharides and all the polyols will be made clear in the revised manuscript.

[7] 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.

[A7] For raffinose at low relative humidities (< 40% RH) we only report lower limits to the viscosity. In the revised manuscript we will improve the presentation in Figure 5 to improve clarity of the message. The referee also recommends a quantitative discussion that could tie together section 2.4 (description of the poke-and-flow experiments) with section 3.2 (results for viscosity of saccharides). Unfortunately, we are not exactly sure what discussion the referee would like to see added.

[8] 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?

[A8] Information on the expected phase state in the experiments will be added to the revised manuscript for clarity.

[9] 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.

[A9] In the revised manuscript we will add information on the phase state of the particles. In addition, for the saccharide experiments we will add information on the time allowed for the particles to condition to a given RH.

[10] 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.

[A10] As suggested we will add caveats to the comment at the end of section 3.1.

[11] 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.

[A11] Yes, we have assumed a sub-cooled liquid organic in the QSPRs. In the revised manuscript, we will make this clear.

[12] 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.

[A12] As suggested, the predicted vapour pressure values will be added to the manuscript.

[13] The Nannoolal 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%20Methods%20-%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.

[A13] We will also try and compare our measurements with the method mentioned above.

[14] 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.

[A14] To address the referee's comments, the discussion on adding 1 OH group to a carbon backbone in the atmospheric implications will be removed since the most relevant mechanism is the conversion of isoprene to a tetrol, which is already discussed in the preceding paragraph.

Minor comments:

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

[A15] A reference will be added in the revised manuscript.

[16] 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.

[A16] In the revised manuscript we will improve the presentation of Figure 5.

### **Anonymous Referee #3**

The manuscript describes a systematic comparison of new measurements of viscosity along with a compilation of data appearing in the literature for a series of polyols and saccharides. Measurements are made using the previously developed bead mobility and poke-flow techniques for particles deposited on a substrate. This contributes a set of benchmark data that help to expand the availability of viscosity measurements in the literature, providing greater insight into the factors that govern the phase and viscosity of secondary organic aerosol. As such, it should be published once the authors have had an opportunity to respond and address the following comments.

Major points:

[17] Equilibrium phase state of alcohols: The authors do not clearly state the equilibrium phase of any of the polyols studied. From a brief investigation, 1,2,3,4-butanetetrol is a solid at room temperature, it is less clear for some of the others. This should be stated for each compound in Section 2.5. Indeed, if the compounds are liquids, it is not clear what is gained by making the measurements by the approaches described here rather than conventional rheological measurements. In addition, some discussion of the expected phase state in the aerosol phase would be beneficial. For the particles prepared for this work, it is clear that the deposited particles probed are all in a liquid state.

[A17] See response to question [8] above.

[18] Volatility of polyols: For some of the shorter chain alcohols presented in this work with the fewest OH groups, volatilization of the alcohol may occur fairly quickly. This could lead to additional temperature gradients driving circulation in the droplets, and compromising the bead mobility measurement, possibly leading to a lower reported viscosity than might be the reality. Has this been considered? It would be helpful if the authors could present data for one of the alcohols that can be compared with previous bulk phase measurements. They should at least discuss the possible effect of volatility and temperature depression, particularly as they are probing pure liquid droplets.

[A18] To address the referee's comments we will add additional data to the manuscript so that results from the poke-and-flow technique can be directly compared with measurements from a commercial viscometer. The issue of volatility will also be addressed in the revised manuscript.

[19] Relative humidity: Water clearly acts as a plasticizer but there is very little consideration of the role of water, particularly for the systematic studies presented for the polyol systems. I recommend the authors consider including RH dependent data if they can easily be measured or if they have already determined them. The distinction between systems for which RH dependence has been examined and those for which it has not should be made clearly in the abstract. Indeed, there is very little new data in this manuscript, particularly for the polyols, 4 points out of 16 points in Figures 3 and 4.

[A19] To address the reviewer's comments we will go back and measure viscosity as a function of RH for at least one of the polyols studied.

Minor Points:

[20] - The title leaves some ambiguity as to what is reported. I suggest the authors replace "viscosity of organics" by "viscosity of pure liquid phases of organics".

[A20] The title will be changed as suggested.

[21] - Abstract: "with the over-prediction being up to 19 orders of magnitude" - is there really any significance to this? Surely this just suggests the model is fundamentally flawed?

[A21] This clause will be removed from the abstract.

[22] - For ease of comparison, it would make sense to combine Figures 3 and 4 into one figure given they both consider sequences of polyol compounds.

[A22] Figure 3 and 4 will be combined as suggested.

[23] - Figure 5: The authors present viscosity data for sucrose in Figure 5(a) but this is the system used to calibrate the bead mobility measurements so I am a little confused if this is really new data? Or is it just the data from the literature? I also recommend the authors remove the shaded areas above  $10^8$  Pa s as these are just a lower limit - at a first glance, the reader might be deceived into thinking these systems show constant values over these ranges. If it is new data, it could be helpful to see the comparison with previous RH dependent measurements directly in the Figure, particularly if it gives an indication of the level of uncertainty in the current approach. More generally, Figure 5 is poorly produced.

[A23] For sucrose, the data is from the literature. Thanks for the suggestions on Figure 5. We will improve this figure in the revised manuscript for clarity.