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. Again, sorry for the delay in responding to the referee's comments. As mentioned, we needed additional time since the referee's asked for additional measurements and the student leading the paper moved on to another position. The revised manuscript includes additional co-authors, since we had to recruit additional people into the project to respond to the referee's comments.

Since our paper was first submitted to ACPD, two important papers on a similar topic have been published in the literature: Song et al. (2016) and Rothfuss and Petters (2017). Rothfuss and Petters (2017) investigated the influence of functional groups on the viscosity of organic aerosols, whilst Song et al. (2016) investigated the viscosity of particles containing polyols and saccharides as a function of RH. Where appropriate, in the revised manuscript we have compared our measurements with the results from these important manuscripts.
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 have measured viscosity as a function of RH for 1,2,3,4-butanetetrol, and included the results in Table 4, and a new Figure (Figure 5 in the revised manuscript). In addition, we have expanded significantly our measurements of the viscosity of glucose particles as a function of RH for a better comparison with values reported in the literature (see Figure 6 and Table 5 in the revised manuscript).

[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] To address the referee's comments, the following text has been added to the revised manuscript (Section 2.1):

"Three different techniques were used to determine viscosity: a rotational rheometer, a bead mobility technique and a poke-and-flow technique, depending on the amount of material available, the viscosity of the material, and the physical state (e.g. crystalline vs. non-crystalline) of the bulk material. The rotational rheometer used here was limited to volumes ≥ 5 mL and samples that were non-crystalline in the bulk phase, the bead mobility technique was limited to viscosities ≤ 10^3 Pa s, and the poke-and-flow technique was limited to viscosities ≥ 10^2 to Pa s. The lone exception is 2-methyl-1,4-butanediol, which is a liquid in the bulk phase, but only studied using the bead mobility technique due to the cost of 5 mL of this material. Each technique is described in greater detail below."

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 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 has been used. Also we have used "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] As suggested, the original Figure 6 has been removed from the 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 has been added in each figure caption.

[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] See *[A2]* above.

[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 have improved the presentation in Figure 5. The referee also recommended 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 has been added to Table 1 in the revised manuscript.

[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] Information on the expected phase state in the experiments has been added to Table 1. We have also gone back and carried out some additional viscosity measurements with the poke-and-flow technique using longer equilibration times with the gas-phase water vapor to ensure equilibration. Information on the time allowed for the particles to condition to a given RH has been added to Section S2 and Table S1.

[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] To address the referee's comment, the comment at the end of Section 3.1 has been removed from the manuscript, and in the revised manuscript we have added a discussion on how the level of prior functionalization can impact the sensitivity to a single OH functional group (see revised 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 have added the following sentence to make this clear (Section 2.7):

“Two quantitative structure-property relationship (QSPR) models were used to estimate the viscosities of the polyols studied here in the non-crystalline state.”

[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] In the original manuscript we used E-AIM to calculate vapour pressures for the method of Sastri and Rao (1992). Since then, we found an additional method to calculated vapor pressures, which is outlined in Rothfuss and Petters (2016), that results in more accurate predictions of viscosity when combined with the method of Sastri and Rao (1992). Hence, we have decided to use this more accurate method in the revised manuscript. In the revised manuscript, we have added a table that lists the vapor pressures predicted by this method (Table S2).

[13] 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%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] See response *[A12]*.

[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 has been 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] This sentence has been removed from the revised manuscript. Previous studies of the viscosities of glucose are now referenced in Figure 6.

[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 have improved the presentation of Figure 5. See Figures 6 and 7 in the revised manuscript.

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 *[A8]* above.

[18] Volatility of polyols: For some of the shorter chain alcohols presented in this work with the fewest OH groups, volatilzation 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 have added the following text to the manuscript (Section 2.3):

"To determine whether the flow of gas over the particles caused evaporation of the alcohols studied, the size of particles was monitored using the optical microscope. Within the uncertainty of the measurements (approximately 1 μm), during the experiments the diameter of the alcohol particles remained unchanged."

[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] See response *[A1]*.

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] To address the referee's comments we have revised the title to the following: "The effect of hydroxyl functional groups and molar mass on the viscosity of non-crystalline organic and organic-water particles"

[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 has been removed from the abstract, in part, because in the revised manuscript we have used a more accurate method for using this model to predict viscosity (see response *[A12]*).

[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 have been combined as suggested. See Figure 3 in the revised manuscript.

[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 10ˆ8 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 have used these suggestions to improve the figure. See Figures 6 and 7 in the revised manuscript.

The effect of hydroxyl functional groups and molar mass on the viscosity of non-crystalline organic and organic-water particles

James W. Grayson[1], Erin Evoy[1], Mijung Song[1*], Yangxi Chu[2], Adrian Maclean[1], Allena Nguyen[1], Mary Alice Upshur[3], Marzieh Ebrahimi[4], Chak K. Chan[2,5,6], Franz M. Geiger[3], Regan J. Thomson[3], and Allan K. Bertram[1]

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Correspondence to: Allan Bertram (bertram@chem.ubc.ca)

Abstract

The viscosities of three polyols and three saccharides, all in the non-crystalline state, have been studied. Two of the polyols (2-methyl-1,4-butanediol and 1,2,3-butanetriol) were studied under dry conditions, the third (1,2,3,4-butanetetrol) was studied as a function of relative humidity (RH), including under dry conditions, and the saccharides (glucose, raffinose, and maltohexaose) were studied as a function of RH. The mean viscosities of the polyols under dry conditions range from 1.5×10^{-1} to 3.7×10^{1} Pa s, with the highest viscosity being that of the tetrol. Using a combination of data determined experimentally here and literature data for alkanes, alcohols and polyols with a C3 to C6 carbon backbone, we show 1) there is a near linear relationship between $\log_{10}$(viscosity) and the number of hydroxyl groups in the molecule, 2) that on average the addition of one OH group increases the viscosity by a factor of approximately 22 to 45, 3) the sensitivity of viscosity to the addition of one OH group is not a strong function of the number of

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OH functional groups already present in the molecule up to three OH groups, and 4) higher sensitivities are observed when the molecule has more than three OH groups. Viscosities reported here for 1,2,3,4-butanetetrol particles are lower than previously reported measurements using aerosol optical tweezers, and additional studies are required to resolve these discrepancies. For saccharide particles at 30 % RH, viscosity increases by approximately 2-5 orders of magnitude as molar mass increases from 180 to 342 g mol^{-1}, and at 80 % RH, viscosity increases by approximately 4-5 orders of magnitude as molar mass increases from 180 to 991 g mol-1. These results suggest oligomerisation of highly oxidised compounds in atmospheric SOA could lead to large increases in viscosity, and may be at least partially responsible for the high viscosities observed in some SOA. Finally, two quantitative structure-property relationship models (Sastri and Rao (1992) and Marrero-Morejón and Pardillo-Fontdevila (2000)) were used to predict the viscosity of alkanes, alcohols, and polyols with a C3-C6 carbon backbone. Both models show reasonably good agreement with measured viscosities for the alkanes, alcohols, and polyols studied here except for the case of a hexol, the viscosity of which is underpredcited by 1-3 orders of magnitude by each of the models.

1 Introduction

Secondary organic aerosol (SOA) is formed in the atmosphere through the oxidation of volatile organic compounds emitted from the Earth's surface by a range of natural and anthropogenic sources (Hallquist et al., 2009). In most regions of the atmosphere, SOA is estimated to account for 30-70 % of the mass of submicrometer atmospheric particulate matter (Kanakidou et al., 2005). SOA directly and indirectly affects Earth's climate (Stocker et al., 2013) and can negatively affect human health (Baltensperger et al., 2008).

Despite its importance, many of the physical properties of SOA, such as its viscosity, remain poorly understood. Information on the viscosity of SOA is important for several reasons. For example, viscosity information is needed to predict the mass and size distribution of SOA in the atmosphere (Shiraiwa et al., 2013; Shiraiwa and Seinfeld, 2012; Zaveri et al., 2014), as well as to predict heterogeneous chemistry, photochemistry and the long range transport of pollution by SOA (Berkemeier et al., 2016; Hinks et al., 2016; Houle et al., 2015; Kuwata and Martin, 2012; Lignell et al., 2014; Shiraiwa et al., 2011; Steimer et al., 2015; Wang et al., 2015; Zelenyuk et al., 2012; Zhou et al., 2013, 2012). Phase transitions and hygroscopic properties of

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SOA are also susceptible to particle viscosity (Bodsworth et al., 2010; Bones et al., 2012; Hawkins et al., 2014; Ignatius et al., 2015; Ladino et al., 2014; Lienhard et al., 2015; Lu et al., 2014; Murray and Bertram, 2008; Price et al., 2014, 2015; Schill et al., 2014; Song et al., 2012; Tong et al., 2011; Wang et al., 2012; Wilson et al., 2012). Methods for predicting the viscosity of SOA from other properties, such as molar mass, organic functional groups, and water content, may be especially beneficial (Rothfuss and Petters, 2017; Song et al., 2016).

In the following we determine the viscosity of three polyols (2-methyl-1,4-butanediol, 1,2,3-butanetriol, and 1,2,3,4-butanetetrol) under dry conditions (relative humidity (RH) < 0.5 %), the structures and properties of which are detailed in Figure 1 and Table 1, respectively. The viscosities of polyols were measured to quantify the relationship between viscosity and the number of hydroxyl (OH) functional groups in a molecule. Polyols were also chosen for study due to their atmospheric importance, as, for example, tetrols have been observed in ambient particles and particles generated in environmental chambers (Claeys et al., 2004; Edney et al., 2005; Surratt et al., 2006, 2010). The viscosity of 1,2,3,4-butanetetrol was also determined as a function of RH, as RH and water content are closely related and organic particles in the atmosphere will adjust their water content in order to maintain equilibrium with the surrounding water vapour. The water content of an organic particle increases is directly related to RH, which typically leads to a decrease in viscosity due to the plasticizing effect of water (Koop et al., 2011; Power et al., 2013).

In addition to polyols, we determined the viscosity as a function of RH for three saccharides (glucose, raffinose and maltohexaose), the structures and properties of which are also detailed in Fig. 1 and Table 1, respectively. Saccharides including levoglucosan, glucose, xylose, sucrose, and maltose have been observed in wood smoke (Nolte et al., 2001), and may be responsible for the majority of the organic mass in ambient submicron particles in remote marine boundary layers (Russell et al., 2010). The saccharides were studied to quantify both the relationship between viscosity and RH, and between viscosity and molar mass at a given RH, for highly oxidised organic molecules with largely similar elemental oxygen-to-carbon ratios (O:C) and containing similar functional groups.

The average O:C of SOA has been determined to range from 0.3-1.1 (Chen et al., 2011; Jimenez et al., 2009; Lambe et al., 2015). The polyols studied here range in O:C from 0.4-1.0 (Table 1), similar to that of SOA, and the saccharides studied have an O:C of 0.86-1.0 (Table 1),

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which is similar to that of the more highly oxidised components of SOA.

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Although bulk samples of the tetrol and the saccharides studied here are crystalline under dry conditions, all our studies were carried out on non-crystalline samples (Table 1), with non-crystalline states being generated by aerosolizing dilute aqueous solutions followed by drying the aerosolized particles in the absence of surfaces that promote crystallization (see Section 2 for further details).

Finally, the measured viscosities of the polyol compounds under dry conditions, as well as literature viscosity values for related alkanes, alcohols, and polyols under dry conditions, were compared to predictions produced using two structure activity models (Marrero-Morejón and Pardillo-Fontdevila, 2000; Sastri and Rao, 1992). These two models have been derived and validated using organic compounds with viscosities <100 Pa s. As such, their applicability to organic compounds with viscosities >100 Pa s is uncertain.

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The work here is complementary to the recent studies by Rothfuss and Petters (2017) and Song et al. (2016). Rothfuss and Petters (2017) investigated the influence of functional groups on the viscosity of organic aerosols, whilst Song et al. (2016) investigated the viscosity of particles containing polyols and saccharides as a function of RH.

2 Experimental

2.1 Viscosity measurements

Three different techniques were used to determine viscosity: a rotational rheometer, a bead mobility technique and a poke-and-flow technique, depending on the amount of material available, the viscosity of the material, and the physical state (e.g. crystalline vs. non-crystalline) of the bulk material.. The rotational rheometer used here was limited to volumes ≥ 5 mL and samples that were non-crystalline in the bulk phase, the bead mobility technique was limited to viscosities ≤ 10^3 Pa s, and the poke-and-flow technique was limited to viscosities ≥ 10^2 to Pa s. The lone exception is 2-methyl-1,4-butanediol, which is a liquid in the bulk phase, but only studied using the bead mobility technique due to the cost of 5 mL of this material. Each technique is described in greater detail below.

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2.2 Rotational rheometry

The rotational rheometer technique has been described in detail previously (Collyer and Clegg, 1988). For these measurements, a commercial rotational rheometer with a cup and bob fixture was used (MCR 501, Anton Paar, Austria, as described in Behzadfar and Hatzikiriakos (2014)). A temperature-controlled sample compartment on the rheometer was used to perform measurements at 295 K, using a shear rate ranging from 1-100 s^{-1}.

2.3 Bead mobility technique

The bead mobility technique has been described in detail previously (Renbaum-Wolff et al., 2013a). Briefly, an aqueous solution of the material was nebulized onto a hydrophobic substrate (either a Teflon substrate or a glass slide coated with an organosilane), forming super-micron sized particles on the hydrophobic substrate. A solution containing micron-sized melamine beads was subsequently nebulised over the top of the substrate, resulting in the incorporation of the melamine beads into the particles. The substrate was then fixed inside a flow cell, and the flow cell subsequently mounted to an optical microscope. A humidity-controlled flow of N_2 gas was passed through the flow cell, which imparted a shear stress on the surface of the particles. This shear stress caused the material in the particle to circulate in well-defined patterns. The speeds at which beads were observed to circulate within a particle were determined from images recorded during the experiments, and the bead speeds were converted to viscosities using a calibration curve created using sucrose-water and glycerol-water particles (Section S1 and Figures S1-S3). Experiments were performed at room temperature (294-295 K).

The bead mobility technique is capable of measuring viscosities up to ≈10^3 Pa s in super-micron sized particles (30-50 μm in diameter). By aerosolizing an aqueous solution to produce super-micron sized particles on a hydrophobic substrate, which often do not promote crystallization, the technique can be used to measure the viscosity of supersaturated liquids (Bodsworth et al., 2010; Pant et al., 2006; Wheeler and Bertram, 2012).

To determine whether the flow of gas over the particles caused evaporation of the alcohols studied, the size of particles was monitored using the optical microscope. Within the uncertainty of the measurements (approximately 1 μm), during the experiments the diameter of the alcohol particles remained unchanged.

2.4 Poke-and-flow technique

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The poke-and-flow technique has been described in detail previously (Grayson et al., 2015; Renbaum-Wolff et al., 2013b). The technique builds on the qualitative approach described by Murray et al., (2012). An aqueous solution of the material was nebulized onto a hydrophobic substrate, forming super-micron sized particles (30-70 µm in diameter) on the hydrophobic substrate. The substrate was fixed inside a flow cell, and the flow cell subsequently mounted to an optical microscope. Particles were allowed to equilibrate at a given RH and room temperature (294-295 K). Then the particles were poked using a needle attached to a micromanipulator. If the viscosity of the material was low (approximately $<10^8$ Pa s), the action of poking the particles with a needle caused the material to form a half-torus geometry. When the needle was removed, the material flowed and reformed the energetically favourable hemispherical morphology. Figure 2, Panel a, provides an example of images recorded during an experiment where the material flowed and reformed the hemispherical geometry after poking. From images recorded during the experiments, the experimental flow time, $\tau_{\text{exp,flow}}$, was determined, where $\tau_{\text{exp,flow}}$ is the time taken for the diameter of the hole after poking to decrease to half of its original value. If the viscosity of the material was high (approximately $>10^8$ Pa s), the action of poking the particles with a needle caused the material to crack with no flow being detected over the period of several hours. Figure 2, Panel b, provides an example of images recorded during an experiment where the material cracked when poked, and exhibited no observable flow over the subsequent three hours.

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To determine viscosities from the poke-and-flow experiments, the behaviours observed in the experiments and described above were subsequently simulated using a multiphysics program (COMSOL multiphysics). For experiments where flow was observed, a half-torus geometry was used in the simulations with dimensions based on the dimensions observed in experiments. For more details of the simulations used when flow was observed see Grayson et al., (2015). Input to the simulations included the slip length (which describes the interaction between the material and the hydrophobic glass slide), the surface tension of the material, the contact angle between the material and hydrophobic glass surface and the density of the material. Physical parameters used in the simulations where flow was observed are listed in Table 2. For experiments where particles exhibited cracking behaviour, simulations were used to determine the lower limit of viscosity of the particles. In this case, the geometry used in the simulations was a quarter-sphere geometry, with one flat surface in contact with a solid substrate, which represents the

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hydrophobic glass surface (Renbaum-Wolff et al., 2013b). In these simulations the viscosity of the material was varied until the sharp edge at the top of the quarter-sphere moved by 0.5 μm over the experimental time. A movement of 0.5 μm would be discernible in the microscope experiments and, as no movement was observed in the experiments, the simulated viscosity represents a lower limit to the viscosity of the particle. The physical properties used for the cases where particles were observed to crack and no flow was observed over the course of the experiment are given in Table 3. Additional details for this type of simulation is provided in Renbaum-Wolff et al. (2013b).

The poke-and-flow technique is capable of measuring viscosities ≥ 10^2 Pa s in super-micron sized particles, and, as for the bead mobility technique, the poke-and-flow technique can also study the viscosity of supersaturated liquids.

2.5 Equilibration times in bead mobility and poke-and-flow experiments

The particles were allowed to equilibrate with the humidity level in the flow cells prior to being studied using the bead mobility and the poke-and-flow techniques. The equilibration times used are discussed in the Supplement (Section S2 and Table S1).

2.6 Compounds studied

2-Methyl-1,4-butanediol (≥97 % purity), 1,2,3,4-butanetetrol (≥99 % purity), β-D-glucose (≥99.5 % purity), raffinose (≥98 % purity), and maltohexaose (≥65 % purity) were obtained from Sigma-Aldrich. 1,2,3-Butanetriol (≥90 % purity) was obtained from TCI America. Experiments were also carried out on syn-2-methyl-1,2,3,4-butanetetrol using the bead mobility technique. This tetrol was prepared based on the procedure described in Ebben et al. (2014). However, particles consisting of syn-2-methyl-1,2,3,4-butanetetrol were determined to have particle-substrate contact angles < 55° on the hydrophobic substrates used for bead mobility experiments. As the bead mobility technique has only been verified using particles with contact angles between 55° and 100°, these results are omitted from the manuscript.

The RHs at which viscosities were measured for each of the compounds are detailed in Tables 4 and 5. Raffinose particles were studied at RH values ≥ 40 %. At 40 % RH the particles cracked when poked, and did not flow on a laboratory timescale. The same results were expected

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as lower RH values, and so lower RH values were not covered. Maltohexaose particles were studied at RH values ≥ 50 %. Maltohexaose did not flow at either 60 % RH or 50 % RH, and so experiments were not carried out at lower RH values.

2.7 Predictions of viscosity using quantitative structure-property relationship models

Two quantitative structure-property relationship (QSPR) models were used to estimate the viscosity of the polyols studied here in the non-crystalline state. QSPR models relate physical, chemical, or physicochemical properties of compounds to their structures. The first QSPR model used, which was developed by Sastri and Rao (1992), estimates the viscosity of a compound at a given temperature (295 K was used here) based on its vapour pressure at that temperature, along with the number and type of functional groups in the molecule. Vapour pressures were determined following the procedure outlined in Rothfuss and Petters (2017). Specifically, the normal boiling point of the compound was determined using the group contribution method of Joback and Reid (1987) (as revised by Stein and Brown (1994)), and the vapour pressure was determined from the normal boiling point using an equation from Sastri and Rao (1992). The vapour pressures used to calculate viscosities are listed in Table S2.

The second QSPR model used to predict viscosity was proposed by Marrero-Morejón and Pardillo-Fontdevila (2000) and estimates the viscosity of a compound only at 293 K based on its molar mass and the type and number of bonds and functional groups within the molecule. Although 293 K is slightly lower than the temperature at which viscosities measurements were made in this study, the small difference in temperature between the model and experiments (1-2 K) should not lead to large discrepancies.

3 Results and discussion

3.1 Viscosity of polyols under dry conditions

The measured viscosities of the polyols under dry conditions are summarised in Table 4. The mean viscosities of the polyols range from 1.5×10^{-1} to 3.7×10^{1} Pa s, with the tetrol having the highest viscosity. For reference, these viscosities lie between that of water (1×10^{-3} Pa s) and that of peanut butter (1×10^{3} Pa s), whilst the viscosity of honey is approximately 1×10^{1} Pa s (Koop et al., 2011). The values measured here for 2-methyl-1,4-butanediol and 1,2,3-butanetriol

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are consistent with values for similar compounds reported in the literature, with Rothfuss and Petters (2017) reporting viscosities of 0.058 Pa s and 0.111 Pa s at 295 K for 1,2-pentanediol and 1,5-pentanediol, respectively, in reasonable agreement with the 0.15 Pa s measured here for 2-methyl-1,4-butanediol, and Song et al. (2016) reporting the viscosity of 1,2,4-butanetriol to be 1.65 Pa s based on bulk measurements and 1.8 Pa s based on aerosol optical tweezers measurements, in reasonable agreement with the 1.6 Pa s measured here for 1,2,3-butanetriol. On the other hand, the viscosity measured here for 1,2,3,4-butanetetrol at dry RH is significantly lower than that reported by Song et al. (2016) using optical tweezers, the only other study of the viscosity of 1,2,3,4-butanetetrol. Using aerosol optical tweezers, Song et al. (2016) measured the viscosity of 1,2,3,4-butanetetrol as a function of RH (their RH dependent results are discussed in more detail below), and used a polynomial function to fit their data, which predicts a viscosity at dry conditions of 4.0×10^3 Pa s, more than two orders of magnitude greater than the 3.7×10^1 Pa s measured here. The reason for this discrepancy is unclear, and additional studies are required in order to resolve these discrepancies.

Shown in Figure 3 are the viscosities under dry conditions at 294-295 K as a function of the number of OH functional groups in a given molecule for compounds with (a) a linear C3 carbon backbone, (b) a linear C4 carbon backbone, (c) a branched C5 carbon backbone, and (d) a linear C6 carbon backbone. Individual panels include only molecules comprised of a specific carbon backbone in order to isolate the effect on viscosity of adding an OH functional group to a compound. Experimental viscosities measured here feature in Panels b and c (black symbols). The sources and values of the literature data shown in Fig. 3 (red symbols) are detailed in Table S3.

Included on each panel is a linear fit to the data to give an estimate of the average change in viscosity with the addition of an OH functional group, with a direct, near linear, relationship between $\log_{10}$(viscosity) and the number of OH functional groups in a compound can be observed. The slopes of the fits are 1.34, 1.61, 1.41, and 1.65 for the linear C3, linear C4, branched C5, and linear C6 respectively, with each having a coefficient of determination (R^2) ≥ 0.91. This suggests viscosity increases on average by a factor of approximately 22 to 45 with the addition of an OH functional group to one of these carbon backbones. This observation is consistent with the recent work by Rothfuss and Petters (2017) that showed the addition of an OH functional group to a carbon backbone leads to an increase in viscosity by a factor of approximately 13 to 24, up to a total of at least three OH functional groups at room temperature.

However, this analysis does not consider the extent to which the sensitivity to the addition of a single OH functional group can depend on the level of prior functionalization. Following Rothfuss and Petters (2017), to evaluate the effect of the prior level of functionalization, we calculated the following sensitivity parameter:

$$S_\eta = \frac{\Delta\eta}{\Delta N} \qquad (1)$$

where Δη is the change in viscosity, and ΔN is the change in the number of OH functional groups. Shown in Figure 4 are the values of S_η, calculated from the data shown in Fig. 3, as a function of the number of OH functional groups in a molecule. S_η was calculated by starting from the alkane and determining the change in viscosity with the addition of each successive OH functional group. For the case of 1,2,3,4,5,6-hexanehexaol, the difference in viscosity between 1,2,3,4,5,6-hexanehexaol and 1,2,6-hexanetriol and a ΔN value of 3 was used. In cases with multiple measurements of viscosity for a single alcohol or multiple species with the same carbon backbone and same number of OH groups, the mean of their viscosities was used to calculate S_η. For compounds with a linear C3, linear C4, branched C5, or linear C6 carbon backbone, S_η does not appear to be very sensitive to the addition of OH functional groups up to three, three, two, and two OH groups, respectively. For the addition of a fourth OH functional group to the linear C4 carbon backbone, discrepancies between the measurements prohibit the drawing of a strong conclusion. For the C6 carbon backbone, S_η is larger for N ≥3 compared to N ≤2. In general, the results show that S_η is not strongly dependent on prior functionalization with OH groups of the carbon backbone, up to the addition of three OH groups for two or three out of the four carbon backbones studied here. These results are consistent with the previous studies by Rothfuss and Petters (2017), who concluded that each of the first three OH groups added to a carbon backbone at room temperature result in comparable increases in viscosity. For the linear C6 carbon backbone, S_η was larger for the addition of 3 or more OH groups, indicating that the addition of an OH group to a highly oxidized organic molecule may have a larger effect on viscosity than the addition of an OH group to a less oxidized organic molecule, also consistent with conclusions from Rothfuss and Petters (2017).

Viscosity of 1,2,3,4-butanetetrol as a function of relative humidity

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Shown in Figure 5 are measurements of the viscosity of 1,2,3,4-butanetetrol as a function of RH using the bead mobility technique. Our results suggest that viscosity increases by more than four orders of magnitude as the RH decreases from 100 % to <0.5 %. This inverse relationship between viscosity and RH is due to the behaviour of water as a plasticizer (a component that reduces the viscosity of a solution) and the greater water content in particles at higher RHs (Koop et al., 2011). Also included in Fig. 5 are measurements by Song et al. (2016) obtained with aerosol optical tweezers and a commercial rheometer. At ≥ 50 % RH the values determined here overlap with those determined by Song et al. (2016) when uncertainties in the measurements are considered. At low RH values (≤ 25%) the values determined here are lower than those determined by Song et al. (2016), even when experimental uncertainties are considered. The reason for this discrepancy is unclear, though may be resolved by using other techniques that can access supersaturated conditions and high viscosities such as fluorescence lifetime imaging (e.g. Hosny et al., 2016).

3.2 Viscosity of saccharides

The viscosities of three binary saccharide-water mixtures were determined at a range of RHs using the bead mobility and poke-and-flow techniques. The viscosities measured for each of the saccharide particles are grouped by RH and summarised in Table 5 and shown with literature data in Figure 6. The viscosity of each saccharide was observed to increase as RH decreased, as expected due to the plasticizing effect of water. For maltohexaose, the most extreme case, viscosity increased by more than eight orders of magnitude as the RH decreased from 100% to approximately 60% RH. At 60 % RH, the viscosity of maltohexaose is greater than or equal to the viscosity of tar pitch (approximately 10^8 Pa s), illustrating that organic particles can have extremely high viscosities even at 60 % RH.

The measured values determined here for glucose-water particles using the bead mobility and poke-and-flow techniques show good overlap with the values determined by Song et al. (2016) at 80 % and 19 % RH, however, the values determined here are lower than those determined by Song et al. (2016) in the 30-60 % RH range, even when experimental uncertainty is taken into account (Figure 6a). Measurements of the viscosity of raffinose-water particles determined here using the bead mobility and poke-and-flow techniques are in good agreement with measurements by Song et al. (2016) using aerosol optical tweezers (Figure 6b).

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Shown in Figure 7 is a plot of log$_{10}$(viscosity) vs. molar mass for saccharide particles at three different RH values (30 %, 55%, and 80%). These plots were generated using 1) viscosities measured experimentally here and shown in Fig. 6 for glucose-water particles, raffinose-water particles and maltohexaose-water particles, 2) viscosity measurements as a function of RH for sucrose-water particles reported by Power et al. (2012) and 3) the parameterizations provided in the Supplemental Information of Song et al. (2016) for the viscosities of glucose-water, sucrose-water, raffinose-water, and maltohexaose-water particles as a function of RH.

Figure 7 illustrates that, at 30 % RH, viscosity is measured to increase by approximately 2-5 orders of magnitude as the molar mass of the saccharide increases from 180 to 342 g mol^{-1}, and at 80 % RH the viscosity increased by roughly 4-5 orders of magnitude as the molar mass of the saccharide increased from 180 to 991 g mol^{-1}. This pattern is consistent with the measurements by Song et al. (2016), who also observed an increase in viscosity with an increase in molar mass for a given RH based on studies with a series of saccharides. These observations are also consistent with prior studies that suggest a relationship between viscosity and molar mass (Hiemenz and Lodge, 2007; Pachaiyappan et al., 1967; Rothfuss and Petters, 2017), whilst prior studies have also shown a relationship between molar mass and glass transition temperature (Koop et al., 2011; Zobrist et al., 2008) and a relationship between molar mass and the bounce of particles off surfaces (Li et al., 2015; Saukko et al., 2012).

3.3 Comparison of measured and predicted viscosities

Two QSPR models have been used to predict the viscosities of the polyols studied here. The first model (Sastri and Rao, 1992) relates viscosity to the molecular structure and vapor pressure of a compound, whilst the second (Marrero-Morejón and Pardillo-Fontdevila, 2000) relates viscosity to the molecular structure and molar mass of a compound. Figure 8 compares the measured and predicted viscosities for all the alkanes, alcohols and polyols shown in Fig. 3., with symbols being used to identify the number of OH groups in a molecule. The ability of both models to predict the measured viscosities is similar. For alkanes, alcohols, and diols the model of Marrero-Morejón and Pardillo-Fontdevila (2000) predicts all the measured viscosities within a factor of 5, whist the model of Sastri and Rao (1992) predicts all but one of the measured viscosities within a factor of 5. For triols, both models predict all but one of the measurements within a factor of 5. Due to the discrepancies between the measurements reported here and by

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Song et al. (2016) for 1,2,3,4-butanetetol, no firm conclusion can be reached with regards to the ability of the models to predict its viscosity. For the hexaol, both models under predict the measured viscosity by a minimum of approximately one order of magnitude and a maximum of three orders of magnitude.

4 Atmospheric implications

An estimated 500-750 Tg of isoprene is emitted annually from the Earth's surface (Guenther et al., 2006). Once in the atmosphere, isoprene molecules react predominantly with hydroxyl (OH) radicals (Worton et al., 2013), leading to products with oxygen containing functional group(s). Previous characterisation studies of SOA produced via the oxidation of isoprene by OH radicals have identified the presence of triols and tetraols (Claeys et al., 2004; Edney et al., 2005). Recently, Song et al. (2015) measured the viscosity of SOA produced via the oxidation of isoprene in the absence of NO_X, and determined it to range between 2×10^4 and 4×10^6 Pa s at <1 % RH. Based on our measurements and the aerosol optical tweezers measurements by Song et al. (2016), the viscosity of tetrols under dry conditions is between approximately 3.7×10^1 and 4.0×10^3 Pa s, implying that individual components in the SOA studied by Song et al. (2015) have viscosities greater than that of the tetrols studied either here or by Song et al. (2016).

The results from the experiments with polyols, along with literature data for alkanes, alcohols, and polyols suggest that adding a hydroxyl (OH) functional group to a carbon backbone can increase the viscosity of the organic compound by y, on average, a factor of 22 to 45. These results may be useful for estimating the viscosity of some components of SOA.

The results from the experiments with saccharides illustrate the strong dependence of viscosity on molar mass for highly oxidised organic compounds. Oligomerisation reactions are known to occur in SOA, and increase the molar mass of a compound whilst keeping its O:C roughly constant. Oligomers have been estimated to account for up to 50 % of the mass of SOA (Baltensperger et al., 2005; Gao et al., 2004; Hallquist et al., 2009; Tolocka et al., 2006). The formation of oligomer products may proceed via a mechanism such as dehydration (Muller et al., 2009), or the elimination of oxygen or carbon dioxide (Zhang et al., 2015). Consistent with previous suggestions (Kidd et al., 2014; Virtanen et al., 2010), our results with saccharides suggest that these types of reactions may play an important role in producing the high viscosities observed in SOA (Booth et al., 2014; Grayson et al., 2016; Pajunoja et al., 2014; Renbaum-

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Deleted: Figure 6 is a plot of measured vs. predicted viscosity for the polyols measured here. The QSPR model of Sastri and Rao (1992) (Figure 6(a)) over-predicts the viscosity of 2-methyl-1,4-butanediol by 2.7-3.0 orders of magnitude, the viscosity of 1,2,3-butanetriol by 6.5-7.8 orders of magnitude, the viscosity of 2-methyl-1,2,3,4-butanetetrol by 14.7-18.7 orders of magnitude, and the viscosity of 1,2,3,4-butanetetrol by 7.2-10.3 orders of magnitude. ... [15]

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Wolff et al., 2013b; Song et al., 2015; Zhang et al., 2015).

Two QSPR models were tested for their ability to predict the viscosity of alkanes, alcohols and polyols. Both models show reasonably good agreement with measured viscosities for alkanes, alcohols, and polyols. As such, these models show potential for predicting the viscosity of SOA components.

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Figures and Tables

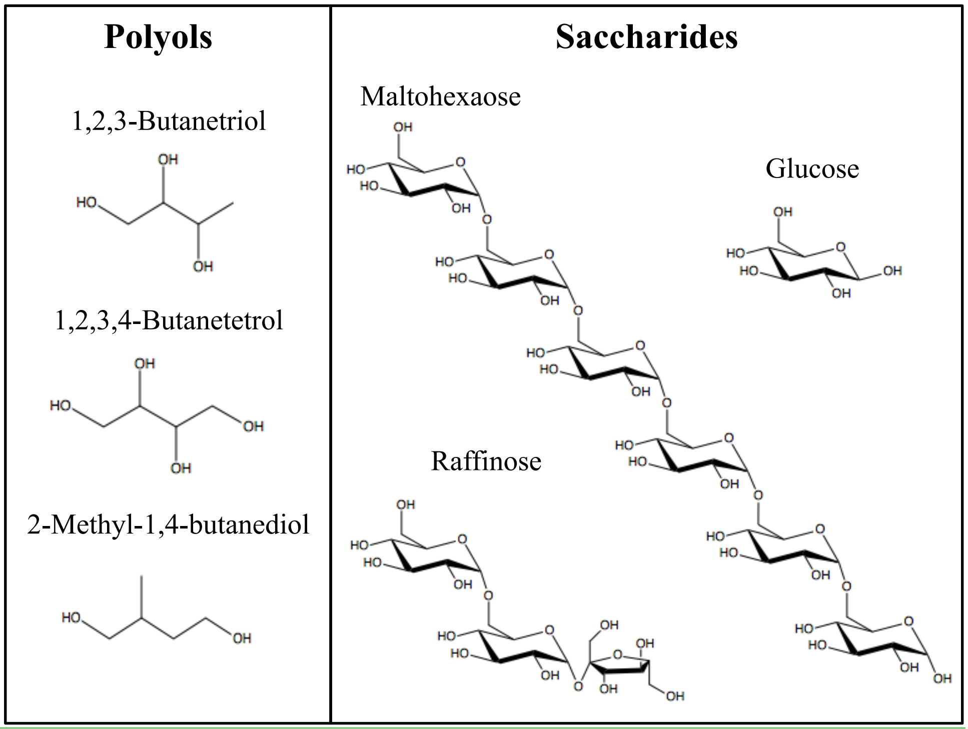

Figure 1. The structure of the polyols and saccharides studied experimentally in this work.

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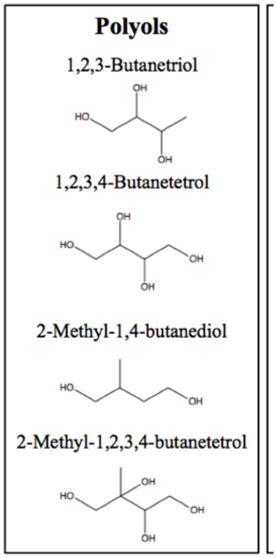

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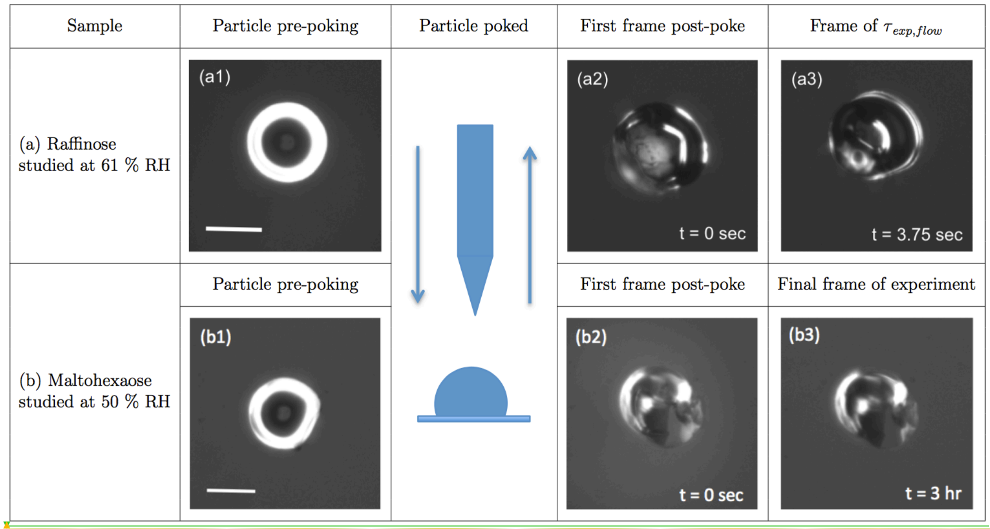

Figure 2. Optical images recorded during poke-and-flow experiments using particles of a) raffinose-water and b) maltohexaose-water mixtures. Images a1 and b1 correspond to the particles prior to being poked, with the white haloes being an optical effect. Images a2 and b2 correspond to the first frame after the needle has been removed. The particle comprised of raffinose and studied at 61 % RH exhibited flow, and image a3 corresponds to an image of the particle at its experimental flow time, $\tau_{exp,flow}$, the point at which the diameter of the hole at the centre of the torus has decreased to 50 % of its original size. The particle composed of maltohexaose and studied at 50 % RH exhibited cracking behaviour and, as shown in image b3, no change in the size or shape of the cracks can be observed 3 h after the particle has been poked. The scale bars in images a1 and b1 correspond to 20 µm.

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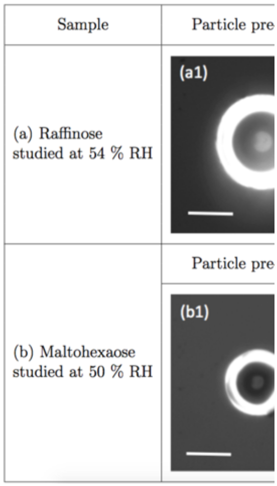

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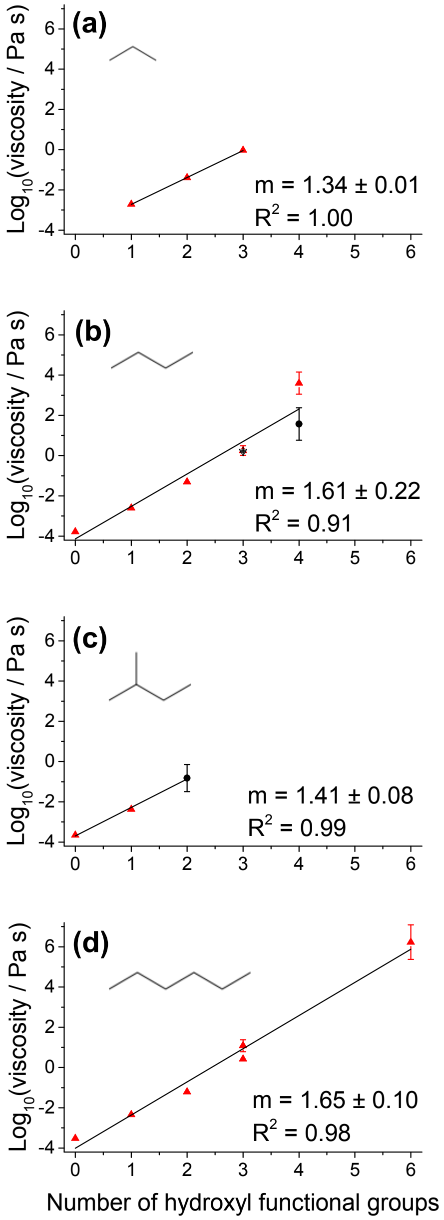

Figure 3. Plot of $\log_{10}$(viscosity / Pa s) vs. the number of hydroxyl (OH) functional groups for compounds with (a) linear C3, (b) linear C4, (c) branched C5, and (d) linear C6 carbon backbones. Experimental values determined here are shown in black, with the upward pointing

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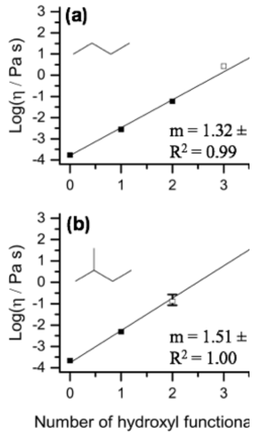

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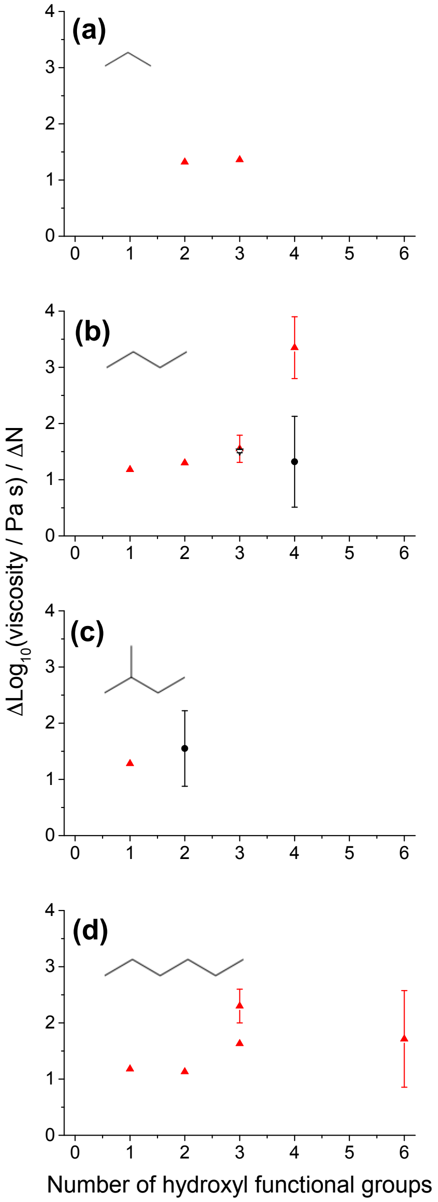

Figure 4. Plot of the change in $\log_{10}$(viscosity / Pa s) per change in hydroxyl functional group (ΔN) for compounds with (a) linear C3, (b) linear C4, (c) branched C5, and (d) linear C6 carbon backbones. The values shown are as in Fig. 3, with experimental values determined in this study shown in black, and literature values shown in red.

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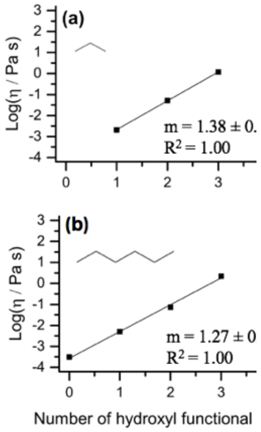

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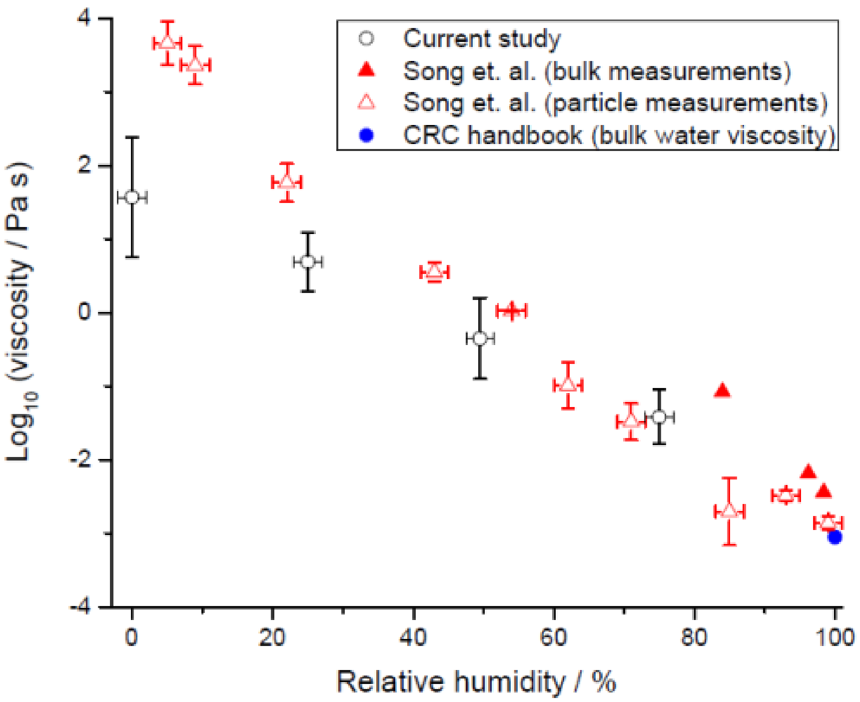

Figure 5: Plot of log$_{10}$(viscosity / Pa s) vs. relative humidity for 1,2,3,4-butanetetrol. Experimental data determined here using the bead mobility technique are shown as black circles, with uncertainties as 2σ. Literature values of Song et al. (2016) are shown as red symbols, and the viscosity of water (CRC Handbook of Chemistry and Physics) is shown as a blue circle.

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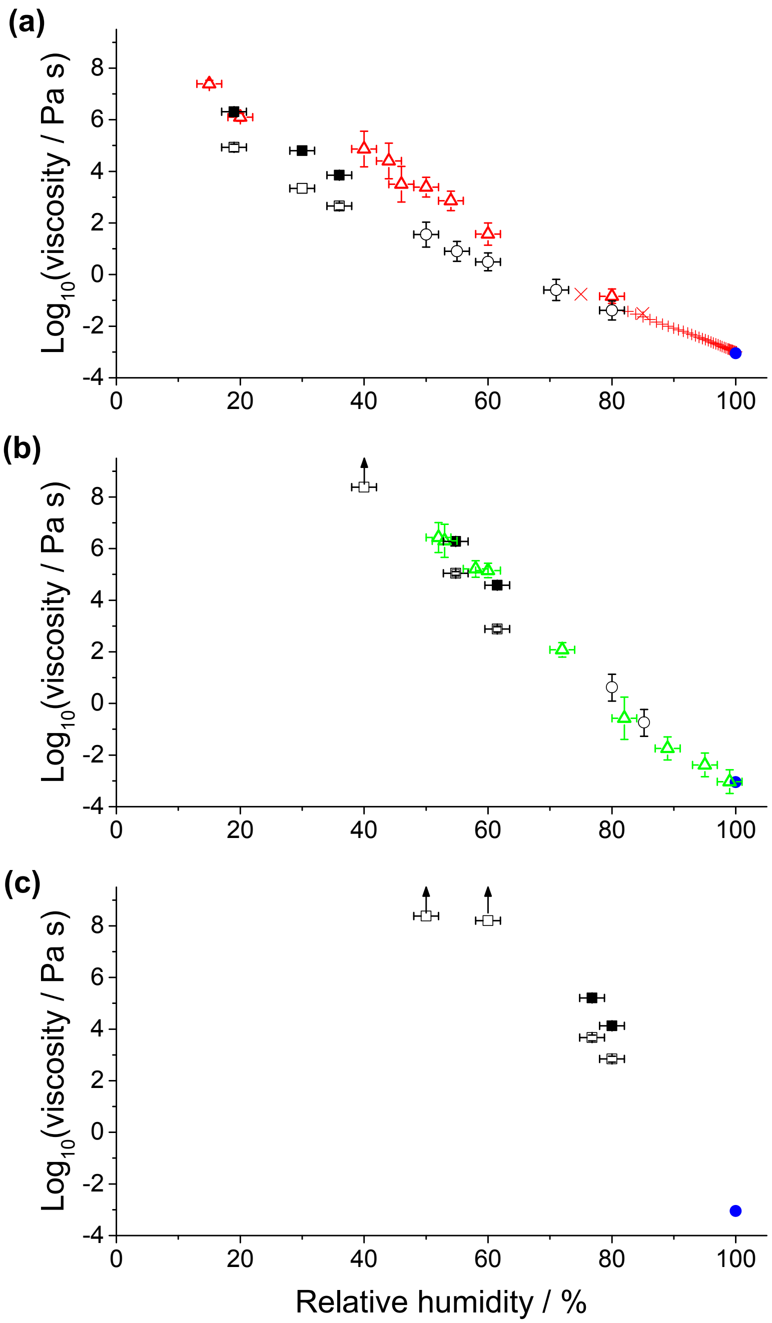

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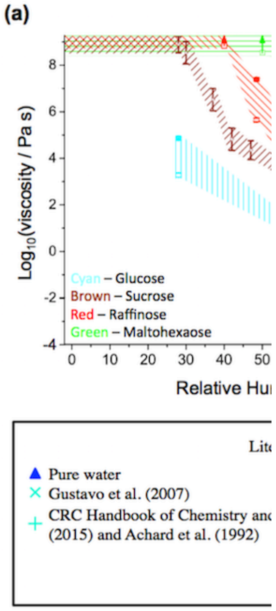

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Figure 6. Plot of $\log_{10}$(viscosity / Pa s) vs. relative humidity for (a) glucose, (b) raffinose, and (c) maltohexaose. Viscosities measured here are shown in black; circle symbols correspond to measurements made using the bead mobility technique, with error bars corresponding to an uncertainty of 2σ, and square symbols correspond to the lower (open symbols) and upper (filled symbols) limits of viscosity determined using the poke-and-flow technique, with uncertainties corresponding to 95 % confidence intervals. The viscosity of water (CRC Handbook of Chemistry and Physics) is shown as a blue circle in each panel. Additional literature viscosities are represented with the following symbols: regular crosses (CRC Handbook of Chemistry and Physics, 2015, and Achard et al., 1992), diagonal crosses (Barbosa-Canovas et al., 2007), and upward pointing triangles (Song et al., 2016).

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Deleted: Plots of $\log_{10}$(viscosity) vs. (a) relative humidity and (b) molar mass for glucose, sucrose, raffinose, and maltohexaose. Values determined experimentally here were measured at 294-295 K. Results determined in the current study using the bead-mobility technique are shown using circle symbols, and those determined using the poke-and-flow technique are shown using squares, with filled squares representing upper limits of viscosity and open squares representing lower limits of viscosity, with y-error bars representing 95 % confidence intervals for both techniques, as detailed in Table 4. Also included are literature viscosity values (measured at 293 or 298 K) for sucrose (Först et al., 2002; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007) and glucose (Achard et al., 1992; Barbosa-Canovas, 2007; Haynes, 2015). The viscosity of glucose at 47 % shown in (b) was determined using a polynomial fit to the data shown in (a). The viscosity of water is also added to (a). Shaded regions are added to (a) and (b) to guide the readers eye.

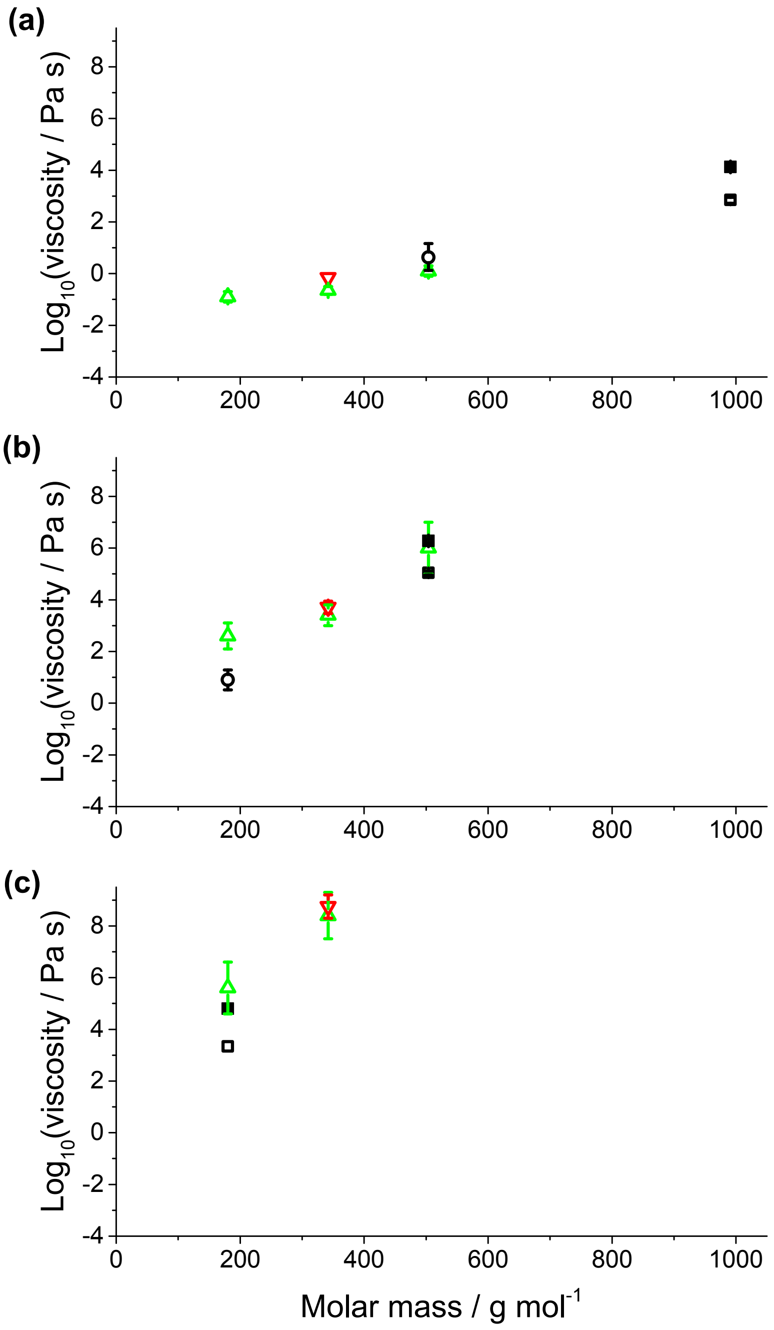

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Figure 7. Plot of $\log_{10}$(viscosity / Pa s) vs. molar mass at relative humidities of (a) 80 %, (b) 55 %, and (c) 30 %. Viscosities measured here are shown in black; circle symbols correspond to measurements made using the bead mobility technique, with error bars corresponding to an uncertainty of 2σ, and square symbols correspond to the lower (open symbols) and upper (filled symbols) limits of viscosity determined using the poke-and-flow technique, with uncertainties corresponding to 95 % confidence intervals. Literature values from Power et al. (2013) and Song et al. (2016) are represented using red downward pointing triangles, and green upward pointing triangles, respectively.

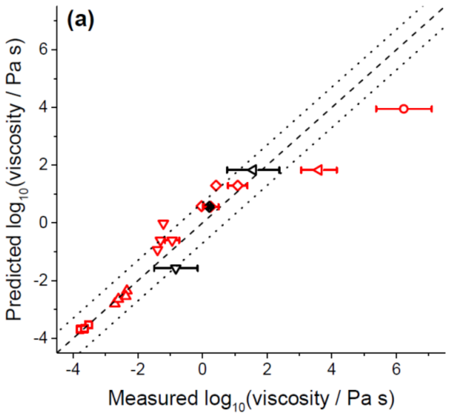

Figure 8. Plot of measured vs. predicted log$_{10}$(viscosity) using the models of a) Sastri and Rao (1992) and b) Marrero-Morejon and Pardillo-Fontdevila (2000) for the C3-C6 alkanes (square symbols), alcohols (upward pointing triangles), diols (downward pointing triangles), triols (diamonds), tetrols (leftward pointing triangles), and hexaol (circle) shown in Figure 3. Values determined experimentally in this study are shown in black, whilst literature viscosity values are shown in red. Dashed lines correspond to the 1:1 lines and dotted lines correspond to 1:5 and 5:1 lines. Error bars indicate uncertainties in the measured viscosities.

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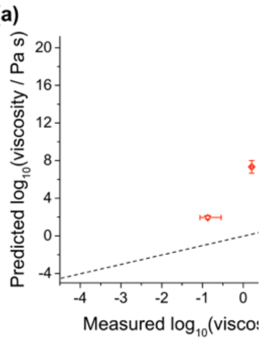

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Deleted: 6. Plot of measured vs.predicted log$_{10}$(viscosity) for the polyols measured in the current study: 2-methyl-1,4-butanediol, 1,2,3-butanetriol, 2-methyl-1,2,3,4-butanetetrol, and 1,2,3,4-butanetetrol. a) Predictions using the model of Sastri and Rao (1992) and b) predictions using the model of Marrero-Morejon and Padillo-Fontdevila (2000). Dashed 1:1 lines are shown on each plot. Error bars on the x-axis represent uncertainty in viscosities for compounds measured experimentally here, whilst error bars on the y-axis observed in (a) are due to the range of predicted vapour pressures using the QSPR models discussed in the text.

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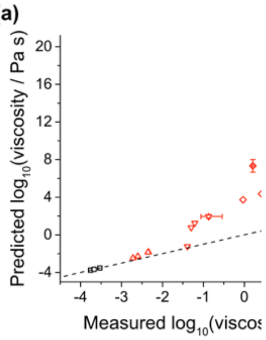

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Table 1. Properties of polyol and saccharide compounds studied experimentally.

Compound	Chemical formula	O:C	Molar mass (g mol^{-1})	Phase state of bulk at 0% RH	Phase state of particles 0% RH prepared from dilute solutions
2-Methyl-1,4-butanediol	$C_5H_{12}O_2$	0.40	104	Liquid	Liquid
1,2,3-Butanetriol	$C_4H_{10}O_3$	0.75	106	Liquid	Liquid
1,2,3,4-Butanetetrol	$C_4H_{10}O_4$	1.00	122	Crystalline	Non-crystalline
Glucose	$C_6H_{12}O_6$	1.0	180	Crystalline	Non-crystalline
Raffinose	$C_{18}H_{32}O_{16}$	0.89	504	Crystalline	Non-crystalline
Maltohexaose	$C_{36}H_{62}O_{31}$	0.86	991	Crystalline	Non-crystalline

Table 2. Physical parameters used in COMSOL Multiphysics simulations for cases where flow was observed in the poke-and-flow experiments. R and r indicate the radius of a tube and the radius of an inner hole, respectively.

		Slip length (nm)	Surface tension ($\mathrm{mN\ m^{-1}}$)	Density ($\mathrm{g\ cm^{-3}}$)	Contact angle (°)[a]
Glucose	Lower limit	5[b]	72.0[c]	1.0[d]	66 (if r<2R), 73 (if r>2R)
	Upper limit	10,000[b]	95.1[e]	1.7[f]	73 (if r<2R), 66 (if r>2R)
Raffinose	Lower limit	5[b]	72.0[c]	1.0[d]	58 (if r<2R), 67 (if r>2R)
	Upper limit	10,000[b]	125.8[e]	1.9[f]	67 (if r<2R), 58 (if r>2R)
Maltohexaose	Lower limit	5[b]	72.0[c]	1.0[d]	63 (if r<2R), 73 (if r>2R)
	Upper limit	10,000[b]	138.2[e]	2.0[f]	73 (if r<2R), 63 (if r>2R)

[a] Contact angles were determined from optical images of millimeter sized droplets deposited on hydrophobic substrates. Millimeter sized droplets were deposited onto hydrophobic substrates and allowed to equilibrate for 30 minutes. Then digital photographs were taken. Contact angles at the particle-substrate interface were determined from the acquired images using ImageJ software.

[b] This slip length range is based on experimental measurements of the slip length for organic-water compounds on hydrophobic surfaces (Baudry et al., 2001; Cheng and Giordano, 2002; Choi and Kim, 2006; Churaev et al., 1984; Craig et al., 2001; Jin and Padula, 2004; Joly et al., 2006; Joseph and Tabeling, 2005; Li et al., 2014; Neto et al., 2005; Schnell, 1956; Tretheway and Meinhart, 2002; Watanabe et al., 1999; Zhu et al., 2012).

[c] The surface tension corresponds to the surface tension of pure water at 293 K. Experimental measurements have determined glucose-water and sucrose-water solutions at 293 K to have a greater surface tension than that of pure water (Lee and Hildemann, 2013; MacDonald et al., 1996). It is assumed that the same is true for raffinose-water and maltohexaose-water solutions.

[d] The lower limit of density corresponds to the density of water.

[e] For upper limits to the surface tension of saccharide-water solutions we use the surface tensions predicted for each of the pure saccharides by ACD/Labs. Values obtained from www.chemspider.com.

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[f]The upper limits of density for glucose, raffinose, and maltohexaose are the upper limits of density predicted for each of the pure compounds by ACD/Labs. Values obtained from www.chemspider.com.

Table 3. Physical parameters used in COMSOL simulations to simulate a lower limit of viscosity for poke-and-flow experiments where particles were observed to crack when impacted by the needle, and no observable flow of material was observed over the course of the experiment.

Slip length (nm)	Surface tension (mN m^{-1})	Density (g cm^{-3})	Contact angle (°)
10-17[a]	72.0[b]	1.8[c]	90[d]

[a] In the simulations a slip length of 0.01*k was used, where k is the grid spacing of the mesh used in the simulation. A grid spacing of 1 to 1.7 μm was used in the simulations, and hence the slip length ranged from 10 nm to 17 nm. Further details are available in Renbaum-Wolff et al. (2013b).

[b] The surface tension corresponds to the surface tension of pure water at 293 K, which is the estimated lower limit of surface tension for raffinose-water and maltohexaose-water solutions. The viscosity determined in simulations increases with surface tension, so the lower limit of surface tension gives rise to the simulated lower limit of viscosity.

[c] The predicted densities of raffinose and maltohexaose based on ACD/Labs are 1.8±0.1 and 1.9±0.1 g cm^{-3}, respectively.

[d] In cases where particles cracked and did not flow, the calculated lower limit of viscosity is independent of the contact angle between 20° and 100° (Renbaum-Wolff et al., 2013b). For the current study we used a contact angle of 90°, which falls within this range.

Table 4. Measured viscosities for the polyols and polyol-water mixtures studied here. The error associated with the rotational rheometer was not available, and so an error of 5 % has been used, greater than the stated error of 0.1 % reported for a similar rotational rheometer (Viscotester 550, Haake, Austria). For experiments using the bead mobility technique, the mean is reported along with lower and upper limits, which correspond to an uncertainty of 2σ.

Compound	RH (%)	Viscosity measurements			
		Technique	Mean (Pa s)	Lower limit (Pa s)	Upper limit (Pa s)
2-Methyl-1,4-butanediol	<0.5	Bead mobility	1.5×10^{-1}	3.2×10^{-2}	7.1×10^{-1}
1,2,3-Butanetriol	<0.5	Rotational rheometer	1.6×10^{0}	1.5×10^{0}	1.7×10^{0}
1,2,3,4-Butanetetrol	<0.5	Bead mobility	3.7×10^{1}	5.7×10^{0}	2.4×10^{2}
	25	Bead mobility	4.9×10^{0}	1.9×10^{0}	1.2×10^{1}
	50	Bead mobility	4.5×10^{-1}	1.6×10^{0}	1.3×10^{-1}
	75	Bead mobility	3.8×10^{-2}	1.6×10^{-2}	8.9×10^{-2}

Table 5. Measured viscosities for the saccharide-water mixtures studied here. For experiments using the bead mobility technique, the mean is reported along with lower and upper limits, which correspond to an uncertainty of 2σ. For experiments using the poke-and-flow technique, lower and upper limits of viscosity are reported, taking account of the 95 % confidence limits of the simulated lower and upper limits of viscosity for the group of particles studied at each RH. N/A represents not applicable.

Compound	Relative humidity (%)	Viscosity measurements			
		Technique	Mean	Lower limit	Upper limit
Glucose	80	Bead mobility	4.0×10^{-2}	2.5×10^{-2}	6.8×10^{-2}
	70	Bead mobility	2.5×10^{-1}	1.3×10^{-1}	4.8×10^{-1}
	60	Bead mobility	3.1×10^{0}	2.1×10^{0}	4.6×10^{0}
	55	Bead mobility	7.9×10^{0}	4.5×10^{0}	1.4×10^{1}
	50	Bead mobility	3.5×10^{1}	1.5×10^{1}	8.5×10^{1}
	36	Poke-and-flow	N/A	3.2×10^{2}	9.2×10^{3}
	30	Poke-and-flow	N/A	2.2×10^{3}	6.3×10^{4}
	19	Poke-and-flow	N/A	5.7×10^{4}	2.7×10^{6}
Raffinose	85	Bead mobility	1.8×10^{-1}	5.8×10^{-2}	6.3×10^{-1}
	80	Bead mobility	4.3×10^{0}	1.3×10^{0}	1.5×10^{1}
	62	Poke-and-flow	N/A	5.9×10^{2}	4.7×10^{4}

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Deleted: **Table 4.** Measured viscosities for the polyol and the saccharide-water mixtures studied here, with results from individual particles grouped by RH. The error associated with the rotational rheometer was not available, and so an error of 5 % has been used, greater than the stated error of 0.1 % reported for a similar rotational rheometer (Viscotester 550, Haake, Austria). For experiments using the bead-mobility technique, the mean is reported along with the 95 % confidence intervals. For experiments using the poke-and-flow technique, lower and upper limits of viscosity are reported, taking account of the 95 % confidence limits of the simulated lower and upper limits of viscosity for the group of particles studied at each RH. N/A represents not applicable.
Relative humidity (%) ... [22]

	55	Poke-and-flow	N/A	9.1×10^{4}	2.2×10^{6}
	40	Poke-and-flow	N/A	6.0×10^{8}	N/A
Maltohexaose	80	Poke-and-flow	N/A	5.2×10^{2}	1.7×10^{4}
	77	Poke-and-flow	N/A	3.5×10^{3}	1.9×10^{5}
	60	Poke-and-flow	N/A	4.0×10^{8}	N/A
	50	Poke-and-flow	N/A	3.0×10^{8}	N/A