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Supplement of

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

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Supplemental Information

S1. Calibration curve for the bead mobility technique.

Measurements of beads speeds were converted to viscosities using a calibration curve developed using sucrose-water and glycerol-water particles. To generate a calibration curve, bead speeds in sucrose-water particles and glucose-water particles were measured over a range of RH values. The RH in each experiment was converted to viscosity based by using literature data to determine the relationship between viscosity and RH. For glycerol-water, the relationship between viscosity and RH was taken from Renbaum-Wolff et al. (2013). For sucrose-water, the relationship between viscosity and RH has been updated from that used by Renbaum-Wolff et al. to include recent measurements such as those by Power et al. (2013), and is shown as Figure S1.

Shown in Figures S2 and S3 are the two calibration curves used in this study to convert bead speeds to viscosities. Two different calibration curves were used, one for each of the two flow cells used in the study, as the two flow cells had different geometries and flow velocities.

S2. Equilibration times with the surrounding RH.

To estimate the time needed for water vapour to come to equilibrium with the particles in our experiments, we used the following equation from Shiraiwa et al. (2011):

$$\tau_{diff,H2O} = \frac{{d_p}^2}{4\pi^2 D_{H2O}}, \qquad [1]$$

where $\tau_{\mathrm{diff,H2O}}$ is the characteristic time of mass-transport and mixing of water by molecular diffusion within the particle, d_{p} is the particle diameter, and D_{H2O} is the diffusion coefficient of water within the droplet.

In the bead mobility experiments, viscosities were $\leq 1\times 10^3$ Pa s, which corresponds to $\tau_{\mathrm{diff,H2O}} \leq 10$ min, based on Equation 1 and the relation between viscosity and D_{H2O} in sucrose-water particles shown in Marshall et al. (2016). In the bead mobility experiments the particles were allowed to come to equilibration with the water vapor for at least 10 min before measuring bead speeds.

In the poke-and-flow experiments, viscosities were $> 1\times 10^2$ Pa s. Shown in Table S1 is the calculated characteristic time of mass-transport and mixing ($\tau_{\mathrm{diff,H2O}}$) in the poke-flow experiments, based on Eq. 1 and the relation between viscosity and D_{H2O} in sucrose-water particles shown in Marshall et al. (2016). Also included in Table S1 are the equilibration times (t_{exp}) used in the poke-and-flow experiments, which is the time a particle was exposed to a given RH before poking. In cases where flow was observed t_{exp} was greater than or equal to $\tau_{\mathrm{diff,H2O}}$. This was not the case for the experiments when particles cracked. However, this was not a concern since in the experiment when cracking was observed we only reported a lower limit to viscosity and non-equilibrium between the water activity in the gas phase and water activity in the particle phase would only lead to higher viscosities due to the method the particles were conditioned (experiments were started from a high relative humidity and then the relative humidity was decreased to the relative humidity used during poking).

Tables

Table S1. Experimental parameters used in the poke-flow experiments for saccharide-water particles. The variable t_{exp} represents the time the particles were exposed to a given relative humidity (conditioning time), while $\tau_{diff,H2O}$ is the characteristic time of mass-transport and mixing of water by molecular diffusion within the particle.

Compound	Relative humidity (%)	d_p (µm)	$\tau_{diff,H2O}$ (min)	t_{exp} (min)	Droplet flowed or cracked
Glucose	36	57-73	≤34 to ≤56	240	Flowed
	30	40-70	≤45 to ≤138	240	Flowed
	19	55-80	≤365 to ≤771	1080	Flowed
Raffinose	62	29-35	≤23 to ≤35	60	Flowed
	55	66-80	≤525 to ≤772	1080	Flowed
	40	36-42	≥608 to ≥827	120	Cracked
Maltohexaose	80	57-70	≤55 to ≤83	300	Flowed
	77	34-42	≤48 to ≤74	60	Flowed
	60	25-35	≥264 to ≥517	120	Cracked
	50	25-30	≥380 to ≥517	120	Cracked

Table S2. Vapor pressure data used in the QSPR model of Sastri and Rao (1992) to predict the viscosity of the C3-C8 alkanes, alcohols, and polyols shown in Figure 3. Vapour pressures were determined following the procedure outlined in Rothfuss and Petters (2017). Specifically, the normal boiling point of the compound was determined using a group contribution method, and the vapour pressure was determined from the normal boiling point using an equation from Sastri and Rao (1992).

Class	Compound	Predicted Vapor Pressure (Pa)
Alkanes	Butane	1.22×10^{5}
	Hexane	1.78×10^{4}
	2-methyl-butane	8.43×10^{4}
Alcohols	1-propanol	8.59×10^{3}
	1-butanol	3.25×10^{3}
	1-hexanol	4.91×10^{2}
	2-methyl-1-butanol	2.22×10^{3}
Diols	1,2-propanediol	5.81×10^{2}
	1,2-butanediol	2.33×10^{2}
	1,2-hexanediol	4.08×10^{1}
	2-methyl-1,4-butanediol	7.26×10^{1}
Triols	1,2,3-propanetriol	2.20×10^{1}
	1,2,3-butanetriol	2.08×10^{1}
	1,2,6-hexanetriol	2.23×10^{0}
	1,2,4-butanetriol	9.92×10^{0}
Tetrol	1,2,3,4-Butanetetrol	1.26×10^{0}
Hexol	Hexane-1,2,3,4,5,6-hexol	$2.20 \text{ x } 10^{-2}$

Table S3. List of literature data included in Figure 3, along with literature sources.

Class	Compound	Viscosity at 295 K / Pa s	Reference(s)
Alkanes	Butane	1.7×10^{-4} [a]	Viswanath et al. (2007) and references therein
	2-Methylbutane	2.2×10^{-4} [a]	Haynes (2015)
	Hexane	3.1×10^{-4} [a]	Viswanath et al. (2007) and references therein
Alcohols	1-Propanol	2.1×10^{-3} [a]	Viswanath et al. (2007)and references therein
	1-Butanol	2.8×10^{-3} [a]	Viswanath et al. (2007) and references therein
	2-Methyl-1-butanol	5.0×10^{-3} [a]	Viswanath et al. (2007) and references therein
	1-Hexanol	5.0×10^{-3} [a]	Viswanath et al. (2007) and references therein
Diols	1,2-Propanediol	5.1×10^{-2} [a]	Haynes (2015)
	1,2-Butanediol	6.0×10^{-2}	Czechowski and Jadżyn (2003)
	1,2-Hexanediol	7.4×10^{-2}	Jarosiewicz et al. (2004)
Triol	1,2,3-Propanetriol	1.2×10^{0} [a]	Haynes (2015) and Sheely (1932)
	1,2,4-Butanetriol	1.8×10^{0} (1.0×10^{0}-3.1×10^{0}) [b]	Song et al. (2016)
	1,2,6-Hexanetriol	2.3×10^{0} [c]	Sigma-Aldrich (1996)
	1,2,6-Hexanetriol	1.2×10^{1} (6.1×10^{0}-2.4×10^{1}) [b]	Song et al. (2016)
Tetrol	1,2,3,4-Butanetetrol	4.0×10^{3} (1.1×10^{3}-1.4×10^{4}) [b]	Song et al. (2016)
Hexol	1,2,3,4,5,6-Hexanehexol	1.7×10^{6} (2.3×10^{5}-1.2×10^{7}) [b]	Song et al. (2016)

[a] Value at 295 K interpolated using a polynomial fit of literature temperature dependent values of $\log_{10}$(viscosity).

[b] Value at 293 K extrapolated using the polynomial fit determined by Song et al. (2016) to their experimental values of viscosity as a function of RH at 293 K based on their optical tweezer work.

[c] Value at 295 K interpolated using a linear fit of literature temperature dependent values of $\log_{10}$(viscosity). A linear fit was used as only two experimental points were available, at 293 K and 303 K.

Figures

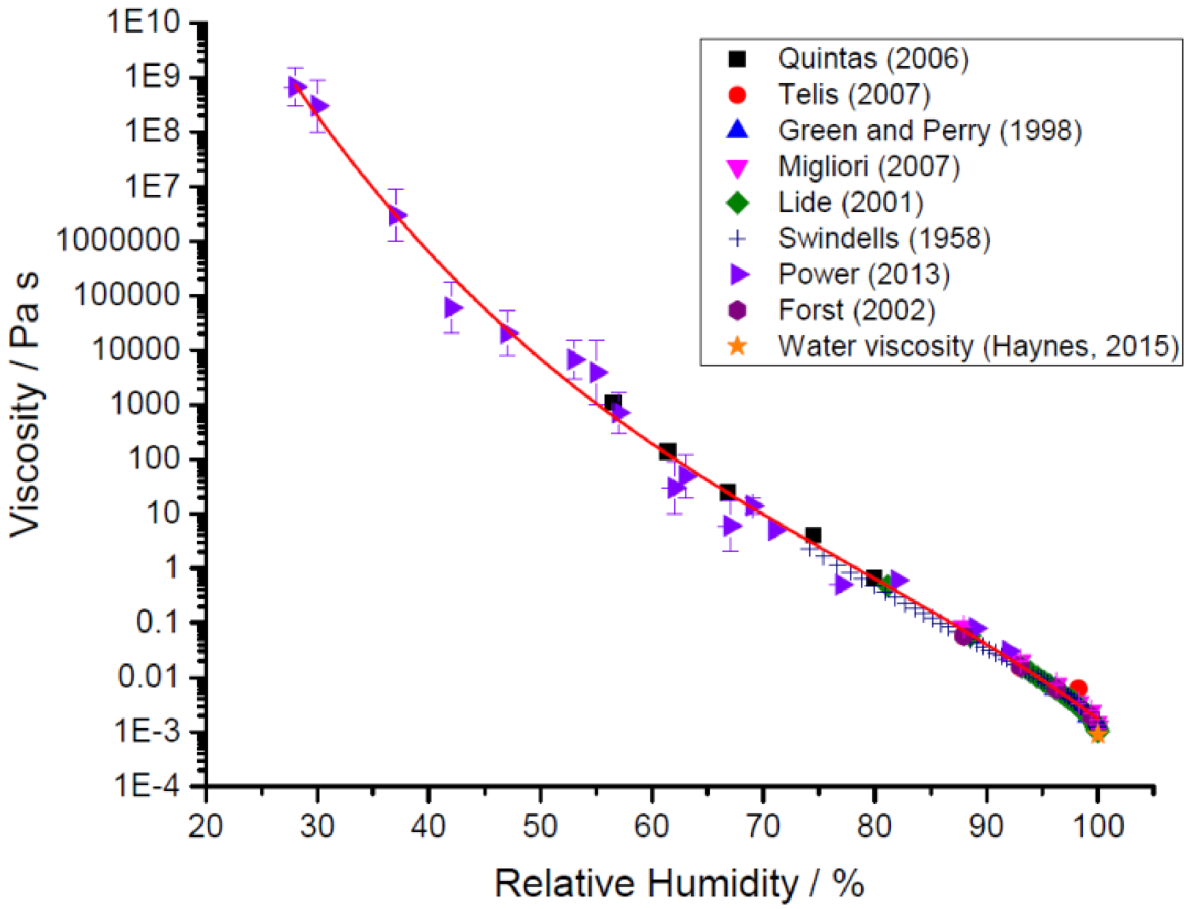

Figure S1. Relation between viscosity and RH for sucrose-water particles. This relation is used to construct the calibrations curves shown in Figures S2-S3. Data come from Först et al. (2002), Green and Perry (2007), Haynes (2015), Lide (2001), Migliori et al. (2007), Power et al. (2013), Quintas et al. (2006), Swindells et al. (1958), and Telis et al. (2007). In cases where viscosity is reported as a function of mass fraction sucrose, the mass fraction is converted to a water activity using the parameterization given by Zobrist et al. (2008), and then to a relative humidity. The equation of the third order polynomial best fit line is $\log_{10}\text{viscosity} = 20.43296 - 0.54892(\text{RH}) + 0.00551(\text{RH}^2) - 2.34\text{E-}5(\text{RH}^3)$.

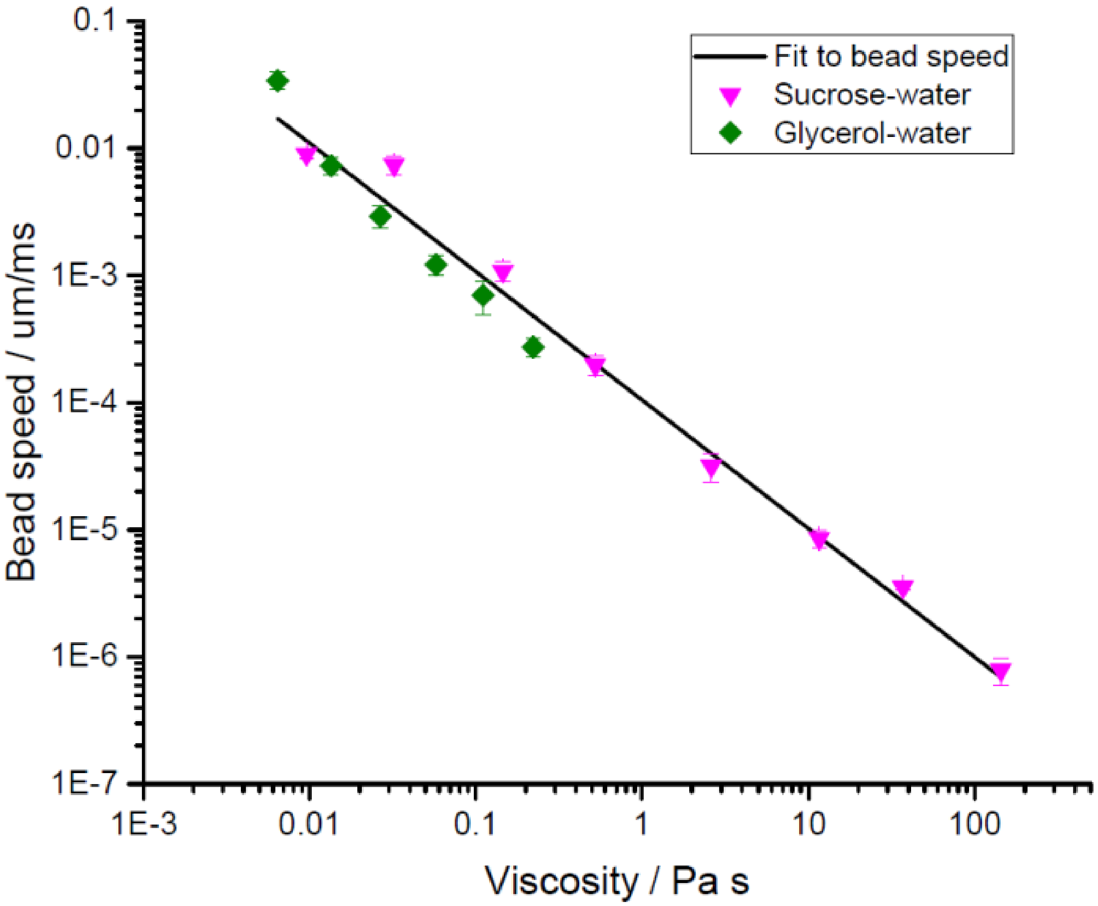

Figure S2. Calibration curve used for the flow cell described in Renbaum-Wolff et al. (2013).

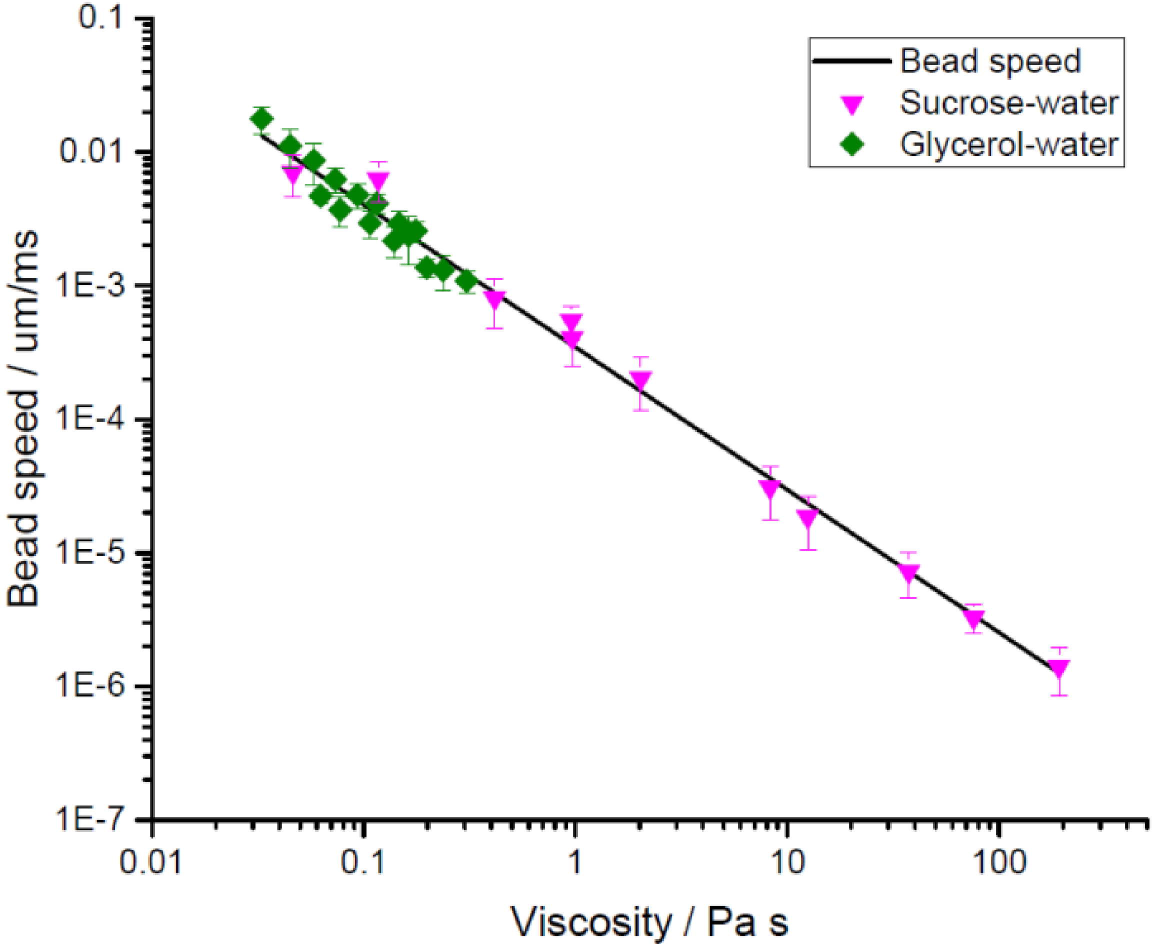

Figure S3. Calibration curve for a new flow cell used in some of the bead-mobility experiments. The new flow cell has a smaller height and larger width, similar to a parallel plate flow cell to ensure a fully developed laminar flow.

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