

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

James W. Grayson¹, Erin Evoy¹, Mijung Song^{1,a}, Yangxi Chu², Adrian Maclean¹, Allena Nguyen¹, Mary Alice Upshur³, Marzieh Ebrahimi⁴, Chak K. Chan^{2,5,6}, Franz M. Geiger³, Regan J. Thomson³, and Allan K. Bertram¹

¹Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1, Canada ²Division of Environment and Sustainability, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

³Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA

⁴Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall,

Vancouver, BC, V6T 1Z3, Canada

⁵Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

⁶School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China ^anow at: Department of Earth and Environmental Sciences, Chonbuk National University, Jeollabuk-do, Republic of Korea

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

Received: 26 July 2016 – Discussion started: 4 August 2016 Revised: 21 March 2017 – Accepted: 15 May 2017 – Published: 13 July 2017

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 1,2,3butanetriol) 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 log₁₀ (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 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 oligomerization of highly oxidized compounds in atmospheric secondary organic aerosol (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; 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 underpredicted by 1-3 orders of magnitude by each of the models.



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

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., 2012, 2013). Phase transitions and hygroscopic properties of SOA are also susceptible to particle viscosity (Bodsworth et al., 2010; Bones et al., 2012; Hawkins et al., 2014; Ignatius et al., 2016; 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 Fig. 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 1,2,3,4butanetetrol 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.

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 oxidized organic molecules with largely similar ele-

J. W. Grayson et al.: The effect of hydroxyl functional groups and molar mass on viscosity

Compound	Chemical formula	O:C ratio	Molar mass (g mol ⁻¹)	Phase state of bulk at 0 % RH	Phase state of particles at 0 % RH prepared from dilute solutions
2-Methyl-1,4-butanediol	C ₅ H ₁₂ O ₂	0.40	104	Liquid	Liquid
1,2,3-Butanetriol	$C_{4}H_{10}O_{3}$	0.75	106	Liquid	Liquid
1,2,3,4-Butanetetrol	$C_{4}H_{10}O_{4}$	1.00	122	Crystalline	Non-crystalline
Glucose	$C_{6}H_{12}O_{6}$	1.00	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 1. Properties of polyol and saccharide compounds studied experimentally.

mental oxygen-to-carbon (O:C) ratios and containing similar functional groups.

The average O:C ratio of SOA has been determined to range from 0.3 to 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 to 1.0 (Table 1), similar to that of SOA, and the saccharides studied have an O:C ratio of 0.86-1.0 (Table 1), which is similar to that of the more highly oxidized components of SOA.

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 Sect. 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.

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 $\geq 5 \text{ mL}$ and samples that were non-crystalline in the bulk phase, the bead mobility technique was limited to viscosities $\leq 10^3$ Pa s, and the poke-and-flow technique was limited to viscosities $\geq 10^2$ Pa s. The lone exception is 2-methyl-1,4-butanediol, which is a liquid in the bulk phase, but it was 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.

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 to 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 micronsized melamine beads was subsequently nebulized 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 N₂ 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 welldefined 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



Figure 2. Optical images recorded during poke-and-flow experiments using particles of (a) raffinose–water and (b) maltohexaose–water mixtures. Panels (a1) and (b1) correspond to the particles prior to being poked, with the white haloes being an optical effect. Panels (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 (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 (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 (a1) and (b1) correspond to 20 µm.

converted to viscosities using a calibration curve created using sucrose–water and glycerol–water particles (Sect. S1 and Figs. S1–S3 in the Supplement). Experiments were performed at room temperature (294–295 K).

The bead mobility technique is capable of measuring viscosities up to $\approx 10^3$ 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 if 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 $1 \mu m$), during the experiments the diameter of the alcohol particles remained unchanged.

2.4 Poke-and-flow technique

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 $(25-80 \,\mu\text{m} \text{ in diameter})$ 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 $< 10^8$ Pas), 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 2a 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, $\tau_{exp,flow}$, was determined, where $\tau_{exp,flow}$ 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 $> 10^8$ Pas), the action of poking the particles with a needle caused the material to crack with no flow being detected over a period of several hours. Figure 2b provides an example of images recorded during an experiment where the material cracked when poked, and exhibited no observable flow over the subsequent 3 h.

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 **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 (mN m ⁻¹)	Density $(g cm^{-3})$	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 $r < 2R$),
	Upper limit	10 000 ^b	125.8 ^e	1.9 ^f	67 (if r > 2R) 67 (if r < 2R), 58 (if r > 2R)
Maltohexaose	Lower limit	5 ^b	72.0 ^c	1.0 ^d	63 (if $r < 2R$),
	Upper limit	10 000 ^b	138.2 ^e	2.0 ^f	73 (if $r > 2R$) 73 (if $r < 2R$), 63 (if $r > 2R$)

^a Contact angles were determined from optical images of millimetre-sized droplets deposited on hydrophobic substrates. Millimetre-sized droplets were deposited onto hydrophobic substrates and allowed to equilibrate for 30 min. 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 that glucose-water and sucrose-water solutions at 293 K 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 http://www.chemspider.com. 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 http://www.chemspider.com.

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 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 $\geq 10^2$ 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 (Sect. S2 and Table S1).

2.6 Compounds studied

2-Methyl-1,4-butanediol ($\geq 97\%$ purity), 1,2,3,4butanetetrol ($\geq 99\%$ purity), β -D-glucose ($\geq 99.5\%$ purity), raffinose ($\geq 98\%$ purity), and maltohexaose ($\geq 65\%$ purity) were obtained from Sigma-Aldrich. 1,2,3-



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 triangle corresponding to measurements using a rotational rheometer, and error bars corresponding to ± 5 %, and circles corresponding to measurements using the bead mobility technique, with error bars corresponding to an uncertainty of 2σ . Literature values (Czechowski et al., 2003; Haynes, 2015; Viswanath et al., 2007; Sheely, 1932; Sigma-Aldrich, 1996; Song et al., 2016; Jarosiewicz et al., 2004) are shown in red. Solid lines shown on each plot are a linear fit on each of the plots with the corresponding values for the slope (m) and the coefficient of determination (R^2) , with standard error being used to determine the uncertainty in the gradient. The structures of the relevant carbon backbones are included in the top left corner of each panel.

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 where 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 $0.01 \cdot k$ 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 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.

Butanetriol (\geq 90 % purity) was obtained from TCI America. Experiments were also carried out on syn-2-methyl-1,2,3,4butanetetrol 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 paper.

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 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 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 viscosities 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

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 (Pas)
2-Methyl-1,4-butanediol	< 0.5	Bead mobility	$1.5 imes 10^{-1}$	3.2×10^{-2}	$7.1 imes 10^{-1}$
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 25 50 75	Bead mobility Bead mobility Bead mobility Bead mobility	$\begin{array}{c} 3.7 \times 10^{1} \\ 4.9 \times 10^{0} \\ 4.5 \times 10^{-1} \\ 3.8 \times 10^{-2} \end{array}$	5.7×10^{0} 1.9×10^{0} 1.3×10^{-1} 1.6×10^{-2}	$\begin{array}{c} 2.4 \times 10^2 \\ 1.2 \times 10^1 \\ 1.6 \times 10^0 \\ 8.9 \times 10^{-2} \end{array}$

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 summarized 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 $(1 \times 10^{-3}$ Pa s) and that of peanut butter $(1 \times 10^{3}$ 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 are consistent with values for similar compounds reported in the literature. Rothfuss and Petters (2017) reported viscosities of 0.058 and 0.111 Pa s at 295 K for 1,2-pentanediol and 1,5pentanediol, respectively, in reasonable agreement with the 0.15 Pas measured here for 2-methyl-1,4-butanediol. Song et al. (2016) reported the viscosity of 1,2,4-butanetriol to be 1.65 Pas based on bulk measurements and 1.8 Pas based on aerosol optical tweezers measurements, in reasonable agreement with the 1.6 Pas measured here for 1,2,3-butanetriol. On the other hand, the viscosity measured here for 1,2,3,4butanetetrol 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 2 orders of magnitude greater than the 3.7×10^1 Pa s measured here. The reason for the discrepancy between the results obtained here and by Song et al. (2016) for 1,2,3,4-butanetetrol at dry RH is unclear, and additional studies are required to resolve it.

Shown in Fig. 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 C_3 carbon backbone, (b) a linear C_4 carbon backbone, (c) a branched C_5 carbon backbone, and (d) a linear C_6 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 Fig. 3b 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, where 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, lin-



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.

ear C₄, branched C₅, and linear C₆ respectively, with each having a coefficient of determination (R^2) \ge 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



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 (Haynes, 2015) is shown as a blue circle.

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:

$$S_{\eta} = \frac{\Delta \log_{10} \eta}{\Delta N},\tag{1}$$

where $\Delta \eta$ is the change in viscosity, and ΔN is the change in the number of OH functional groups. Shown in Fig. 4 are the values of S_n , 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-hexanehexanol, the difference in viscosity between 1,2,3,4,5,6-hexanehexanol 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_n . For compounds with a linear C_3 , linear C_4 , branched C_5 , 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_n is larger for $N \ge 3$ compared to $N \le 2$. In general, the results show that S_{η} is not strongly dependent on prior func-



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 (Haynes, 2015) is shown as a blue circle in each panel. Additional literature viscosities are represented with the following symbols: regular crosses (Haynes, 2015; Achard et al., 1992), diagonal crosses (Barbosa-Canovas et al., 2007), and upward-pointing triangles (Song et al., 2016).

tionalization 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 or-



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.

ganic molecule, also consistent with conclusions from Rothfuss and Petters (2017).

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

Shown in Fig. 5 are measurements of the viscosity of 1,2,3,4butanetetrol as a function of RH using the bead mobility technique. Our results suggest that viscosity increases by more than 4 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 **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. Mean viscosities are not calculated using the poke-and-flow technique, and hence are represented as n/a in the table.

Compound	Relative	Viscosity measurements			
	humidity (%)	Technique (Pa s)	Mean (Pa s)	Lower limit (Pas)	Upper limit
	80	Bead mobility	4.0×10^{-2}	2.5×10^{-2}	$6.8 imes 10^{-2}$
	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}
Glucose	55	Bead mobility	7.9×10^{0}	4.5×10^{0}	1.4×10^{1}
Glueose	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	$1.8 imes 10^{-1}$	$5.8 imes 10^{-2}$	$6.3 imes 10^{-1}$
	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
	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

included in Fig. 5 are measurements by Song et al. (2016) obtained with aerosol optical tweezers and a commercial rheometer. At \geq 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 (\leq 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 it 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).

3.3 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 grouped by RH are summarized in Table 5 and shown with literature data in Fig. 6. The viscosity of each saccharide was observed to increase as RH decreased, as expected due to the platicizing effect of water. For maltohexaose, the most extreme case, viscosity increased by more than 8 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 (Fig. 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 (Fig. 6b).

Shown in Fig. 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 Supplement 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 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 Fig. 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.

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).

3.4 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 vapour 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 those reported in Song et al. (2016) for 1,2,3,4-butanetetrol, no firm conclusion can be reached with regards to the ability of the models to predict its viscosity. For the hexaol, both models underpredict the measured viscosity by a minimum of approximately 1 order of magnitude and a maximum of 3 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 one or more functional groups. Previous characterization studies of SOA produced via the oxidation of isoprene by OH radicals have identified the presence of triols and tetrols (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 reported here, 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, 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 oxidized organic compounds. Oligomerization reactions are known to occur in SOA, and increase the molar mass of a compound whilst keeping its O: C ratio 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 via 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-Wolff et al., 2013b; Song et al., 2015; Zhang et al., 2015).

Two QSPR models were tested for their ability to predict the viscosities 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.

Data availability. Underlying material and related items for this paper are located in the Supplement.

The Supplement related to this article is available online at https://doi.org/10.5194/acp-17-8509-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. This work was supported by the Natural Sciences and Engineering Research Council of Canada. Regan J. Thomson and Franz M. Geiger gratefully acknowledge support from the National Science Foundation (CHE 1212692). Mary Alice Upshur gratefully acknowledges support from a National Aeronautics and Space Administration Earth and Space (NASA ESS) Fellowship and a National Science Foundation (NSF) Graduate Research Fellowship (NSF GRFP). The authors also thank D. A. Ullmann for help generating a calibration curve for the bead mobility experiments.

Edited by: Gordon McFiggans Reviewed by: three anonymous referees

References

- Achard, C., Dussap, C. G., and Gros, J.-B.: Prédiction de l'activité de l'eau, des températures d'ébullition et de congélation de solutions aqueuses de sucres par un modèle UNIFAC, Ind. Aliment. Agric., 109, 93–101, 1992.
- Baltensperger, U., Kalberer, M., Dommen, J., Paulsen, D., Alfarra, M. R., Coe, H., Fisseha, R., Gascho, A., Gysel, M., Nyeki, S., Sax, M., Steinbacher, M., Prevot, A. S. H., Sjögren, S., Weingartner, E., and Zenobi, R.: Secondary organic aerosols from anthropogenic and biogenic precursors, Faraday Discuss., 130, 265–278, https://doi.org/10.1039/b417367h, 2005.
- Baltensperger, U., Dommen, J., Alfarra, M. R., Duplissy, J., Gaeggler, K., Metzger, A., Facchini, M. C., Decesari, S., Finessi, E., Reinnig, C., Schott, M., Warnke, J., Hoffmann, T., Klatzer, B., Puxbaum, H., Geiser, M., Savi, M., Lang, D., Kalberer, M., and Geiser, T.: Combined determination of the chemical composition and of health effects of secondary organic aerosols: The POLYSOA project, J. Aerosol Med. Pulm. Deliv., 21, 145–154, https://doi.org/10.1089/jamp.2007.0655, 2008.
- Barbosa-Canovas, G. V.: Water activity in foods: Fundamentals and applications, Wiley-Blackwell, Hoboken, NJ, 2007.
- Baudry, J., Charlaix, E., Tonck, A., and Mazuyer, D.: Experimental evidence for a large slip effect at a nonwetting fluid-solid interface, Langmuir, 17, 5232–5236, https://doi.org/10.1021/la0009994, 2001.
- Behzadfar, E. and Hatzikiriakos, S. G.: Rheology of bitumen: Effects of temperature, pressure, CO₂ concentration and shear rate, Fuel, 116, 578–587, https://doi.org/10.1016/j.fuel.2013.08.024, 2014.
- Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Pöschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy, semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, Phys. Chem. Chem. Phys., 18, 12662–12674, https://doi.org/10.1039/C6CP00634E, 2016.
- Bodsworth, A., Zobrist, B., and Bertram, A. K.: Inhibition of efflorescence in mixed organic-inorganic particles at temperatures less than 250 K, Phys. Chem. Chem. Phys., 12, 12259–12266, https://doi.org/10.1039/c0cp00572j, 2010.
- Bones, D. L., Reid, J. P., Lienhard, D. M., and Krieger, U. K.: Comparing the mechanism of water condensation and evaporation in glassy aerosol, P. Natl. Acad. Sci. USA, 109, 11613–11618, https://doi.org/10.1073/pnas.1200691109, 2012.
- Booth, A. M., Murphy, B., Riipinen, I., Percival, C. J., and Topping, D. O.: Connecting bulk viscosity measurements to kinetic limitations on attaining equilibrium for a model aerosol composition, Environ. Sci. Technol., 48, 9298–9305, https://doi.org/10.1021/es501705c, 2014.
- Chen, Q., Liu, Y., Donahue, N. M., Shilling, J. E., and Martin, S. T.: Particle-phase chemistry of secondary organic material: Modeled compared to measured O:C and H:C Elemental ratios provide constraints, Environ. Sci. Technol., 45, 4763–4770, https://doi.org/10.1021/es104398s, 2011.
- Cheng, J.-T. and Giordano, N.: Fluid flow through nanometerscale channels, Phys. Rev. E., 65, 031206-1–031206-5, https://doi.org/10.1103/PhysRevE.65.031206, 2002.
- Choi, C. H. and Kim, C. J.: Large slip of aqueous liquid flow over a nanoengineered superhydrophobic

surface, Phys. Rev. Lett., 96, 066001-1–066001-4, https://doi.org/10.1103/PhysRevLett.96.066001, 2006.

- Craig, V. S. J., Neto, C., and Williams, D. R. M.: Shear-dependent boundary slip in an aqueous newtonian liquid, Phys. Rev. Lett., 87, 054504-1–054504-4, https://doi.org/10.1103/PhysRevLett.87.054504, 2001.
- Churaev, N. V., Sobolev, V. D., and Somov, A. N.: Slippage of liquids over lyophobic solid surfaces, J. Colloid Interf. Sci., 97, 574–581, https://doi.org/10.1016/0021-9797(84)90330-8, 1984.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173–1176, https://doi.org/10.1126/science.1092805, 2004.
- Collyer, A. A. and Clegg, D. W.: Rheological Measurement, Elsevier Applied Science Publishers Ltd, New York, NY, 1988.
- Czechowski, G. and Jadzyn, J.: The viscous properties of diols I. The homologous series of 1,2- and 1,n-alkanediols, Z. Naturforsch., 58, 317–320, https://doi.org/10.1515/zna-2003-5-612, 2003.
- Ebben, C. J., Strick, B. F., Upshur, M. A., Chase, H. M., Achtyl, J. L., Thomson, R. J., and Geiger, F. M.: Towards the identification of molecular constituents associated with the surfaces of isoprene-derived secondary organic aerosol (SOA) particles, Atmos. Chem. Phys., 14, 2303–2314, https://doi.org/10.5194/acp-14-2303-2014, 2014.
- Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W., and Claeys, M.: Formation of 2methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States, Atmos. Environ., 39, 5281–5289, https://doi.org/10.1016/j.atmosenv.2005.05.031, 2005.
- Gao, S., Keywood, M. D., Ng, N. L., Surratt, J., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and α-pinene, J. Phys. Chem. A, 108, 10147–10164, https://doi.org/10.1021/jp047466e, 2004.
- Grayson, J. W., Song, M., Sellier, M., and Bertram, A. K.: Validation of the poke-flow technique combined with simulations of fluid flow for determining viscosities in samples with small volumes and high viscosities, Atmos. Meas. Tech., 8, 2463–2472, https://doi.org/10.5194/amt-8-2463-2015, 2015.
- Grayson, J. W., Zhang, Y., Mutzel, A., Renbaum-Wolff, L., Böge, O., Kamal, S., Herrmann, H., Martin, S. T., and Bertram, A. K.: Effect of varying experimental conditions on the viscosity of α-pinene derived secondary organic material, Atmos. Chem. Phys., 16, 6027–6040, https://doi.org/10.5194/acp-16-6027-2016, 2016.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, https://doi.org/10.5194/acp-6-3181-2006, 2006.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-

Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, https://doi.org/10.5194/acp-9-5155-2009, 2009.

- Hawkins, L. N., Baril, M. J., Sedehi, N., Galloway, M. M., De Haan, D. O., Schill, G. P., and Tolbert, M. A.: Formation of semisolid, oligomerized aqueous SOA: Lab simulations of cloud processing, Environ. Sci. Technol., 48, 2273–2280, https://doi.org/10.1021/es4049626, 2014.
- Haynes, W. M.: CRC Handbook of Chemistry and Physics, 96th Edn., CRC Press/Taylor and Francis Group, Boca Raton, FL, 2015.
- Hiemenz, P. C. and Lodge, T. P.: Polymer Chemistry, 2nd Edn., CRC Press, Boca Raton, FL, 2007.
- Hinks, M. L., Brady, M. V, Lignell, H., Song, M., Grayson, J. W., Bertram, A., Lin, P., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Effect of Viscosity on Photodegradation Rates in Complex Secondary Organic Aerosol Materials, Phys. Chem. Chem. Phys., 18, 8785–8793, https://doi.org/10.1039/C5CP05226B, 2016.
- Hosny, N. A., Fitzgerald, C., Vyšniauskasm, A., Athanasadis, A., Berkemeier, T., Uygur, N., Pöschl, U., Shiraiwa, M., Kalberer, M., Pope, F. D., and Kuimova, M. K.: Direct imaging of changes in aerosol particle viscosity upon hydration and chemical aging, Chem. Sci., 7, 1357–1367, https://doi.org/10.1039/c5sc02959g, 2016.
- Houle, F. A., Hinsberg, W. D., and Wilson, K. R.: Oxidation of a model alkane aerosol by OH radical: the emergent nature of reactive uptake, Phys. Chem. Chem. Phys., 17, 4412–4423, https://doi.org/10.1039/C4CP05093B, 2015.
- Ignatius, K., Kristensen, T. B., Järvinen, E., Nichman, L., Fuchs, C., Gordon, H., Herenz, P., Hoyle, C. R., Duplissy, J., Garimella, S., Dias, A., Frege, C., Höppel, N., Tröstl, J., Wagner, R., Yan, C., Amorim, A., Baltensperger, U., Curtius, J., Donahue, N. M., Gallagher, M. W., Kirkby, J., Kulmala, M., Möhler, O., Saathoff, H., Schnaiter, M., Tomé, A., Virtanen, A., Worsnop, D., and Stratmann, F.: Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene, Atmos. Chem. Phys., 16, 6495–6509, https://doi.org/10.5194/acp-16-6495-2016, 2016.
- Jarosiewicz, P., Czechowski, G., and Jadzyn, J.: The viscous properties of diols. V. 1,2-hexanediol in water and butanol solutions, Z. Naturforsch., 59, 559–562, https://doi.org/10.1515/zna-2004-0905, 2004.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kumala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A.

M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525–1529, https://doi.org/10.1126/science.1180353, 2009.

- Jin, B. J. and Padula, M.: Steady flows of compressible fluids in a rigid container with upper free boundary, Math. Ann. 329, 723– 770, https://doi.org/10.1007/s00208-004-0535-0, 2004.
- Joback, K. G. and Reid, R. C.: Estimation of pure-component properties from group-contributions, Chem. Eng. Comm., 57, 233– 243, 1987.
- Joly, L., Ybert, C., Bocquet, L., and Trizac, E.: Effets électrocinétiques sur surfaces glissantes, Houille Blanche, 1, 53–58, https://doi.org/10.1051/lhb:200601006, 2006.
- Joseph, P. and Tabeling, P.: Direct measurement of the apparent slip length, Phys. Rev. E., 71, 035303-1–035303-4, https://doi.org/10.1103/PhysRevE.71.035303, 2005.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, https://doi.org/10.5194/acp-5-1053-2005, 2005.
- Kidd, C., Perraud, V., Wingen, L. M., and Finlayson-Pitts, B. J.: Integrating phase and composition of secondary organic aerosol from the ozonolysis of α -pinene, P. Natl. Acad. Sci. USA, 111, 7552–7557, https://doi.org/10.1073/pnas.1322558111, 2014.
- Koop, T., Bookhold, J., Shiraiwa, M., and Pöschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Phys. Chem. Chem. Phys., 13, 19238, https://doi.org/10.1039/c1cp22617g, 2011.
- Kuwata, M. and Martin, S. T.: Phase of atmospheric secondary organic material affects its reactivity, P. Natl. Acad. Sci. USA, 109, 17354–17359, https://doi.org/10.1073/pnas.1209071109, 2012.
- Ladino, L. A., Zhou, S., Yakobi-Hancock, J. D., Aljawhary, D., and Abbatt, J. P. D.: Factors controlling the ice nucleating abilities of α-pinene SOA particles, J. Geophys. Res.-Atmos., 119, 9041– 9051, https://doi.org/10.1002/2014JD021578, 2014.
- Lambe, A. T., Chhabra, P. S., Onasch, T. B., Brune, W. H., Hunter, J. F., Kroll, J. H., Cummings, M. J., Brogan, J. F., Parmar, Y., Worsnop, D. R., Kolb, C. E., and Davidovits, P.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol chemical composition and yield, Atmos. Chem. Phys., 15, 3063–3075, https://doi.org/10.5194/acp-15-3063-2015, 2015.
- Lee, J. Y. and Hildeman, L. M.: Surface tension of solutions containing dicarboxylic acids with ammonium sulfate, d-glucose, or humic acid, J. Aerosol Sci., 64, 94–102, https://doi.org/10.1016/j.jaerosci.2013.06.004, 2013.
- Li, Y. J., Liu, P., Gong, Z., Wang, Y., Bateman, A. P., Bergoend, C., Bertram, A. K., and Martin, S. T.: Chemical reactivity and liquid/nonliquid states of secondary organic material, Environ. Sci. Technol., 49, 13264–13274, https://doi.org/10.1021/acs.est.5b03392, 2015.
- Li, Z., D'eramo, L., Monti, F., Vayssade, A.-L., Chollet, B., Bresson, B., Tran, Y., Cloitre, M., and Tabeling, P.: Slip length measurements using muPIV and TIRF-based velocimetry, ISR J.

Chem., 54, 1589–1601, https://doi.org/10.1002/ijch.201400111, 2014.

- Lienhard, D. M., Huisman, A. J., Krieger, U. K., Rudich, Y., Marcolli, C., Luo, B. P., Bones, D. L., Reid, J. P., Lambe, A. T., Canagaratna, M. R., Davidovits, P., Onasch, T. B., Worsnop, D. R., Steimer, S. S., Koop, T., and Peter, T.: Viscous organic aerosol particles in the upper troposphere: Diffusivity-controlled water uptake and ice nucleation?, Atmos. Chem. Phys., 15, 13599– 13613, https://doi.org/10.5194/acp-15-13599-2015, 2015.
- Lignell, H., Hinks, M. L., and Nizkorodov, S. A.: Exploring matrix effects on photochemistry of organic aerosols, P. Natl. Acad. Sci. USA, 111, 13780–13785, https://doi.org/10.1073/pnas.1322106111, 2014.
- Lu, J. W., Rickards, A. M. J., Walker, J. S., Knox, K. J., Miles, R. E. H., Reid, J. P., and Signorell, R.: Timescales of water transport in viscous aerosol: measurements on sub-micron particles and dependence on conditioning history, Phys. Chem. Chem. Phys., 16, 9819–30, https://doi.org/10.1039/c3cp54233e, 2014.
- MacDonald, G. A., Lanier, T. C., Swaisgood, H. E., and Hamann, D. D.: Mechanism for stabilization of fish actomyosin by sodium lactate, J. Agr. Food Chem., 44, 106–112, https://doi.org/10.1021/jf940698y, 1996.
- Marrero-Morejón, J. and Pardillo-Fontdevila, E.: Estimation of liquid viscosity at ambient temperature of pure organic compounds by using group-interaction contributions, Chem. Eng. J., 79, 69– 72, https://doi.org/10.1016/S1385-8947(99)00173-4, 2000.
- Muller, L., Reinnig, M.-C., Hayen, H., and Hoffmann, T.: Characterization of oligomeric compounds in secondary organic aerosol using liquid chromatography coupled to electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Rapid Commun. Mass Spectrom., 23, 971–979, https://doi.org/10.1002/rcm.3957, 2009.
- Murray, B. J. and Bertram, A. K.: Inhibition of solute crystallisation in aqueous H⁺-NH₄⁺-SO₄²⁻-H₂O droplets., Phys. Chem. Chem. Phys., 10, 3287–3301, https://doi.org/10.1039/b802216j, 2008.
- Murray, B. J., Haddrell, A. E., Peppe, S., Davies, J. F., Reid, J. P., O'Sullivan, D., Price, H. C., Kumar, R., Saunders, R. W., Plane, J. M. C., Umo, N. S., and Wilson, T. W.: Glass formation and unusual hygroscopic growth of iodic acid solution droplets with relevance for iodine mediated particle formation in the marine boundary layer, Atmos. Chem. Phys., 12, 8575–8587, https://doi.org/10.5194/acp-12-8575-2012, 2012.
- Neto, C., Evans, D. R., Bonaccurso, E., Butt, H.-J., and Craig, V. S. J.: Boundary slip in Newtonian liquids: a review of experimental studies, Rep. Prog. Phys., 68, 2859–2897, https://doi.org/10.1088/0034-4885/68/12/R05, 2005.
- Nolte, C. G., Schauer, J. J., Cass, G. R., and Simoneit, B. R. T.: Highly polar organic compounds present in wood smoke and in the ambient atmosphere, Environ. Sci. Technol., 35, 1912–1919, https://doi.org/10.1021/es001420r, 2001.
- Pachaiyappan, V., Ibrahim, S. H., and Kuloor, N. R.: Simple correlation for determining viscosity of organic liquids, Chem. Eng., 74, 193–196, 1967.
- Pajunoja, A., Malila, J., Hao, L., Joutsensaari, J., Lehtinen, K. E. J., and Virtanen, A.: Estimating the Viscosity Range of SOA Particles Based on Their Coalescence Time, Aerosol Sci. Tech., 48, i–iv, https://doi.org/10.1080/02786826.2013.870325, 2014.
- Pant, A., Parsons, M. T., and Bertram, A. K.: Crystallization of aqueous ammonium sulfate particles internally mixed

with soot and kaolinite: Crystallization relative humidities and nucleation rates, J. Phys. Chem. A, 110, 8701–8709, https://doi.org/10.1021/jp060985s, 2006.

- Power, R. M., Simpson, S. H., Reid, J. P., and Hudson, A. J.: The transition from liquid to solid-like behaviour in ultrahigh viscosity aerosol particles, Chem. Sci., 4, 2597–2604, https://doi.org/10.1039/C3SC50682G, 2013.
- Price, H. C., Murray, B. J., Mattsson, J., O'Sullivan, D., Wilson, T. W., Baustian, K. J., and Benning, L. G.: Quantifying water diffusion in high-viscosity and glassy aqueous solutions using a Raman isotope tracer method, Atmos. Chem. Phys., 14, 3817– 3830, https://doi.org/10.5194/acp-14-3817-2014, 2014.
- Price, H. C., Mattsson, J., Zhang, Y., Bertram, A. K., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., Rickards, A. M. J., and Murray, B. J.: Water diffusion in atmospherically relevant α-pinene secondary organic material, Chem. Sci., 6, 4876–4883, https://doi.org/10.1039/C5SC00685F, 2015.
- Renbaum-Wolff, L., Grayson, J. W., and Bertram, A. K.: Technical Note: New methodology for measuring viscosities in small volumes characteristic of environmental chamber particle samples, Atmos. Chem. Phys., 13, 791–802, https://doi.org/10.5194/acp-13-791-2013, 2013a.
- Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity, P Natl. Acad. Sci. USA, 110, 8014–8019, https://doi.org/10.1073/pnas.1219548110, 2013b.
- Rothfuss, N. E. and Petters, M. D.: Influence of Functional Groups on the Viscosity of Organic Aerosol, Environ. Sci. Technol., 51, 271–279, https://doi.org/10.1021/acs.est.6b04478, 2017.
- Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., Bates, T. S., and Finlayson-Pitts, B. J.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, P. Natl. Acad. Sci. USA, 107, 6652–6657, https://doi.org/10.1073/pnas.0908905107, 2010.
- Sastri, S. R. S. and Rao, K. K.: A new group contribution method for predicting viscosity of organic liquids, Chem. Eng. J., 50, 9–25, https://doi.org/10.1016/0300-9467(92)80002-R, 1992.
- Saukko, E., Lambe, A. T., Massoli, P., Koop, T., Wright, J. P., Croasdale, D. R., Pedernera, D. A., Onasch, T. B., Laaksonen, A., Davidovits, P., Worsnop, D. R., and Virtanen, A.: Humiditydependent phase state of SOA particles from biogenic and anthropogenic precursors, Atmos. Chem. Phys., 12, 7517–7529, https://doi.org/10.5194/acp-12-7517-2012, 2012.
- Schill, G. P., De Haan, D. O., and Tolbert, M. A.: Heterogeneous ice nucleation on simulated secondary organic aerosol, Environ. Sci. Technol., 48, 1675–1692, https://doi.org/10.1021/es4046428, 2014.
- Schnell, E.: Slippage of water over nonwettable surfaces, J. Appl. Phys., 27, 1149–1152, https://doi.org/10.1063/1.1722220, 1956.
- Sheely, M. L.: Glycerol viscosity tables, Ind. Eng. Chem., 24, 1060– 1064, https://doi.org/10.1021/ie50273a022, 1932.
- Shiraiwa, M. and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, 1–6, https://doi.org/10.1029/2012GL054008, 2012.
- Shiraiwa, M., Ammann, M., Koop, T., and Poschl, U.: Gas uptake and chemical aging of semisolid organic aerosol

particles, P. Natl. Acad. Sci. USA, 108, 11003–11008, https://doi.org/10.1073/pnas.1103045108, 2011.

- Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gasparticle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Phys. Chem. Chem. Phys., 15, 11441–11453, https://doi.org/10.1039/c3cp51595h, 2013.
- Sigma-Aldrich: 1,2,6-Hexanetriol, Milwaukee, WI, available at: https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/ Aldrich/Bulletin/al_techbull_al128.pdf (last access: 6 February 2017), 1996.
- Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 2691–2712, https://doi.org/10.5194/acp-12-2691-2012, 2012.
- Song, M., Liu, P. F., Hanna, S. J., Li, Y. J., Martin, S. T., and Bertram, A. K.: Relative humidity-dependent viscosities of isoprene-derived secondary organic material and atmospheric implications for isoprene-dominant forests, Atmos. Chem. Phys., 15, 5145–5159, https://doi.org/10.5194/acp-15-5145-2015, 2015.
- Song, Y. C., Haddrell, A. E., Bzdek, B. R., Reid, J. P., Bannan, T., Topping, D. O., Percival, C., and Cai, C.: Measurements and predictions of binary component aerosol particle viscosity, J. Phys. Chem. A, 120, 8123–8137, https://doi.org/10.1021/acs.jpca.6b07835, 2016.
- Steimer, S. S., Berkemeier, T., Gilgen, A., Krieger, U. K., Peter, T., Shiraiwa, M., and Ammann, M.: Shikimic acid ozonolysis kinetics of the transition from liquid aqueous solution to highly viscous glass, Phys. Chem. Chem. Phys., 17, 31101– 31109, https://doi.org/10.1039/C5CP04544D, 2015.
- Stein, S. E. and Brown, R. L.: Estimation of normal boiling points from group contributions, J. Chem. Inf. Comput. Sci., 34, 581– 587, https://doi.org/10.1021/ci00019a016, 1994.
- Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M. M. B., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgely, P. M. (Eds.): IPCC Climate Change 2013: The Physical Science Basis, in: Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK and New York, NY, USA, 2013.
- Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110, 9665–9690, https://doi.org/10.1021/jp061734m, 2006.
- Surratt, J. D., Chan, A. W., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, a J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, P. Natl. Acad. Sci. USA, 107, 6640–6645, https://doi.org/10.1073/pnas.0911114107, 2010.
- Tretheway, D. C. and Meinhart, C. D.: Apparent fluid slip at hydrophobic microchannel walls, Phys. Fluids, 14, L9–L12, https://doi.org/10.1063/1.1432696, 2002.
- Tolocka, M. P., Heaton, K. J., Dreyfus, M. A., Wang, S., Zordan, C. A., Saul, T. D., and Johnston, M. V.: Chemistry of particle incep-

tion and growth during α -pinene ozonolysis, Environ. Sci. Technol., 40, 1843–1848, https://doi.org/10.1021/es051926f, 2006.

- Tong, H. J., Reid, J. P., Bones, D. L., Luo, B. P., and Krieger, U. K.: Measurements of the timescales for the mass transfer of water in glassy aerosol at low relative humidity and ambient temperature, Atmos. Chem. Phys., 11, 4739–4754, https://doi.org/10.5194/acp-11-4739-2011, 2011.
- Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirilä, P., Leskinen, J., Mäkelä, J. M., Holopainen, J. K., Pöschl, U., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: An amorphous solid state of biogenic secondary organic aerosol particles, Nature, 467, 824–827, https://doi.org/10.1038/nature09455, 2010.
- Viswanath, D. S., Ghosh, T., Prasad, D. H. L., Dutt, N. V. K., and Rani, K. Y.: Viscosity of liquids, Springer, Dordrecht, the Netherlands, 2007.
- Wang, B., Lambe, A. T., Massoli, P., Onasch, T. B., Davidovits, P., Worsnop, D. R., and Knopf, D. A.: The deposition ice nucleation and immersion freezing potential of amorphous secondary organic aerosol: Pathways for ice and mixedphase cloud formation, J. Geophys. Res.-Atmos., 117, 1–12, https://doi.org/10.1029/2012JD018063, 2012.
- Wang, B., O'Brien, R. E., Kelly, S. T., Shilling, J. E., Moffet, R. C., Gilles, M. K., and Laskin, A.: Reactivity of liquid and semisolid secondary organic carbon with chloride and nitrate in atmospheric aerosols, J. Phys. Chem. A, 119, 4498–4508, https://doi.org/10.1021/jp510336q, 2015.
- Watanabe, K., Udagawa, Y., and Udagawa, H.: Drag reduction of Newtonian fluid in a circular pipe with a highly water-repellent wall, J. Fluid Mech., 381, 225–238, https://doi.org/10.1002/aic.690470204, 1999.
- Wheeler, M. J. and Bertram, A. K.: Deposition nucleation on mineral dust particles: A case against classical nucleation theory with the assumption of a single contact angle, Atmos. Chem. Phys., 12, 1189–1201, https://doi.org/10.5194/acp-12-1189-2012, 2012.
- Wilson, T. W., Murray, B. J., Wagner, R., Möhler, O., Saathoff, H., Schnaiter, M., Skrotzki, J., Price, H. C., Malkin, T. L., Dobbie, S., and Al-Jumur, S. M. R. K.: Glassy aerosols with a range of compositions nucleate ice heterogeneously at cirrus temperatures, Atmos. Chem. Phys., 12, 8611–8632, https://doi.org/10.5194/acp-12-8611-2012, 2012.

- Worton, D. R., Surratt, J. D., Lafranchi, B. W., Chan, A. W. H., Zhao, Y., Weber, R. J., Park, J. H., Gilman, J. B., De Gouw, J., Park, C., Schade, G., Beaver, M., Clair, J. M. S., Crounse, J., Wennberg, P., Wolfe, G. M., Harrold, S., Thornton, J. A., Farmer, D. K., Docherty, K. S., Cubison, M. J., Jimenez, J. L., Frossard, A. A., Russell, L. M., Kristensen, K., Glasius, M., Mao, J., Ren, X., Brune, W., Browne, E. C., Pusede, S. E., Cohen, R. C., Seinfeld, J. H., and Goldstein, A. H.: Observational insights into aerosol formation from isoprene, Environ. Sci. Technol., 47, 11403–11413, https://doi.org/10.1021/es4011064, 2013.
- Zaveri, R. A., Easter, R. C., Shilling, J. E., and Seinfeld, J. H.: Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: Representing effects of volatility, phase state, and particle-phase reaction, Atmos. Chem. Phys., 14, 5153–5181, https://doi.org/10.5194/acp-14-5153-2014, 2014.
- Zelenyuk, A., Imre, D., Beránek, J., Abramson, E., Wilson, J., and Shrivastava, M.: Synergy between secondary organic aerosols and long-range transport of polycyclic aromatic hydrocarbons, Environ. Sci. Technol., 46, 12459–12466, https://doi.org/10.1021/es302743z, 2012.
- Zhang, X., McVay, R. C., Huang, D. D., Dalleska, N. F., Aumont, B., Flagan, R. C., and Seinfeld, J. H.: Formation and evolution of molecular products in α-pinene secondary organic aerosol, P. Natl. Acad. Sci. USA, 112, 14168–14173, https://doi.org/10.1073/pnas.1517742112, 2015.
- Zhou, S., Lee, A. K. Y., McWhinney, R. D., and Abbatt, J. P. D.: Burial effects of organic coatings on the heterogeneous reactivity of particle-borne benzo[a]pyrene (BaP) toward ozone, J. Phys. Chem. A, 116, 7050–7056, https://doi.org/10.1021/jp3030705, 2012.
- Zhou, S., Shiraiwa, M., McWhinney, R. D., Pöschl, U., and Abbatt, J. P. D.: Kinetic limitations in gas-particle reactions arising from slow diffusion in secondary organic aerosol, Faraday Discuss., 165, 391–406, https://doi.org/10.1039/c3fd00030c, 2013.
- Zhu, L., Neto, C., and Attard, P.: Reliable measurements of interfacial slip by colloid probe atomic force microscopy. III. Shear-rate-dependent slip, Langmuir, 28, 3465–3473, https://doi.org/10.1021/la204566h, 2012.
- Zobrist, B., Marcolli, C., Pedernera, D. A., and Koop, T.: Do atmospheric aerosols form glasses?, Atmos. Chem. Phys., 8, 5221– 5244, https://doi.org/10.5194/acp-8-5221-2008, 2008.