Viscosity of erythritol and erythritol-water particles as a function of water activity: new results and an intercomparison of techniques for measuring the viscosity of particles

Yangxi Chu, Erin Evoy, Saeid Kamal, Young Chul Song, Jonathan P. Reid, Chak K. Chan and Allan K. Bertram

Abstract

A previous study reported an uncertainty of up to three orders of magnitude for the viscosity of erythritol (1,2,3,4-butanetetrol) – water particles. To help reduce the uncertainty in the viscosity of these particles, we measured the diffusion coefficient of a large organic dye (rhodamine B isothiocyanate-dextran, average molecular weight ~ 70,000 g mol⁻¹) in erythritol-water matrix as a function of water activity using rectangular area fluorescence recovery after photobleaching (rFRAP). The diffusion coefficients were then converted to viscosities of erythritol-water particles using the Stokes-Einstein equation. In addition, we carried out new viscosity measurements for erythritol-water particles using aerosol optical tweezers. Based on the new experimental results and viscosities reported in the literature, we conclude the following: 1) the viscosity of pure erythritol is 247.1±0.1 Pa s (two standard deviations), 2) the addition of a hydroxyl (OH) functional group to a linear C₄ carbon backbone increases the viscosity on average by a factor of 27 ± 5 (two standard deviations), and 3) the increase in viscosity from the addition of one OH functional group to a linear C₄ carbon backbone is not a strong function of the number of OH functional groups already present in the molecule up to the addition of three OH functional groups, but the increase in viscosity may be larger when the linear C₄ carbon backbone already contains three OH functional groups. These results should help improve the understanding of the viscosity of secondary organic aerosol particles in the atmosphere. In addition, these results show that the rFRAP technique, aerosol optical tweezer technique, and bead-mobility technique give results in reasonable agreement if the uncertainties in the measurements are considered.
1 Introduction

Secondary organic aerosol (SOA) is produced by the oxidation of volatile organic compounds followed by condensation of oxidation products (Hallquist et al., 2009). SOA contributes approximately 20 to 70% to the mass of fine aerosol particles, depending on location (Hallquist et al., 2009; Jimenez et al., 2009; Kanakidou et al., 2005; Zhang et al., 2007). Despite the abundance of SOA in the atmosphere, some physical and chemical properties of SOA remain poorly understood.

An example of one such poorly understood physical property is particle viscosity (Cappa and Wilson, 2011; Koop et al., 2011; Mikhailov et al., 2009; Perraud et al., 2012; Reid et al., 2018; Vaden et al., 2011; Virtanen et al., 2010; Zobrist et al., 2008). The viscosity of SOA particles has implications for predicting the size and mass distribution of SOA particles (Lu et al., 2014; Maclean et al., 2017; Saleh et al., 2013; Shiraiwa and Seinfeld, 2012; Zaveri et al., 2014). Particle viscosity also influences reaction rates (Berkemeier et al., 2016; Chu and Chan, 2017a; Chu and Chan, 2017b; Gatzsche et al., 2017; Houle et al., 2015; Kuwata and Martin, 2012; Li et al., 2015; Liu et al., 2018; Steimer et al., 2015; Wang et al., 2015; Zhou et al., 2012), photochemistry (Hinks et al., 2016; Lignell et al., 2014; Wong et al., 2015), phase state (Baustian et al., 2013; Bones et al., 2012; Shiraiwa et al., 2017), and ice nucleating ability of SOA (Bodsworth et al., 2010; Ignatius et al., 2016; Ladino et al., 2014; Murray and Bertram, 2008; Schill et al., 2014; Wilson et al., 2012).

Particulate viscosity also has implications for the long-range transport of pollutants (Bastelberger et al., 2017; Shrivastava et al., 2017; Zelenyuk et al., 2012) and the optical properties of particles (Adler et al., 2013; Robinson et al., 2014).

To improve the understanding of the viscosity of SOA particles, researchers have investigated the viscosity of SOA in the atmosphere (Bateman et al., 2016; Bateman et al., 2017; O’Brien et al., 2014; Pajunoja et al., 2016; Virtanen et al., 2010), the viscosity of SOA material generated in environmental chambers (Grayson et al., 2016; Pajunoja et al., 2014; Renbaum-Wolff et al., 2013; Song et al., 2015, 2016a; Virtanen et al., 2011; Ye et al., 2016), the viscosity of compounds identified in SOA particles (Abramson et al., 2013; Bateman et al., 2015; Hosny et al., 2016), and the viscosity of simple proxies of SOA material (Chenyakin et al., 2017; Marshall et al., 2016; Power et al., 2013). In addition, researchers have investigated the dependence of viscosity on molar mass and the number and type of functional groups (Grayson et al., 2017; Rothfuss and Petters, 2017; Song et al., 2016b). For example, Grayson et al. (2017) investigated the dependence of viscosity on the number of hydroxyl (OH) functional groups on a carbon backbone and found that viscosity increased, on average, by a factor of 22 – 45 following the addition of an OH functional group to linear C_{3}, linear C_{4}, branched C_{3}, and linear C_{6} carbon backbones. However, the study by Grayson et al. revealed a large discrepancy between the viscosity of erythritol (1,2,3,4-butane-tetrol) measured with the bead-mobility technique (Grayson et al., 2017) and measured with the aerosol optical tweezer technique (Song et al., 2016b) at ≤ 25% relative humidity (RH). This led to uncertainties when predicting the effect of adding OH functional groups to a linear C_{4} carbon backbone on viscosity. This also led to
uncertainties regarding the viscosity of tetrols, which have been observed in ambient SOA particles and SOA particles generated in environmental chambers (Claeys, 2004; Edney et al., 2005; Surratt et al., 2006, 2010).

To help reduce the uncertainty in the viscosity of erythritol-water particles, we measured the diffusion coefficient of a large organic dye (rhodamine B isothiocyanate-dextran, referred to as RBID in the following, average molecular weight ~ 70,000 g mol$^{-1}$) in erythritol-water matrix as a function of water activity ($a_w$) using the rectangular area fluorescence recovery after photobleaching (rFRAP) technique (Deschout et al., 2010). The diffusion coefficients were then converted to viscosities using the Stokes-Einstein equation, which is expressed as

$$D = k_B T / (6\pi\eta R_h),$$

where $D$ is the diffusion coefficient (m$^2$ s$^{-1}$); $k_B$ is the Boltzmann constant (1.38 $\times$ 10$^{-23}$ J K$^{-1}$); $T$ is the temperature (K); $\eta$ is the viscosity (Pa s) of the matrix and $R_h$ is the hydrodynamic radius (m) of the diffusing species, i.e., RBID. RBID has an $R_h$ that is more than 16 times larger than that of erythritol (Table 1 and Fig. 1). We assume that the viscosity of an erythritol-water particle can be accurately calculated from the diffusion coefficient of RBID and the Stokes-Einstein equation, since the Stokes-Einstein equation accurately predicts diffusion coefficients when the diffusing molecules are large in size relative to the matrix molecules, and when the matrix viscosity is $\lesssim$ 10$^4$ Pa s (Chenyakin et al., 2017; Price et al., 2016), which is the case for erythritol-water particles (Grayson et al., 2017; Song et al., 2016b).

In addition to determining viscosities from the rFRAP diffusion measurements, we carried out new viscosity measurements for erythritol-water particles at $a_w < 0.1$ using the aerosol optical tweezer technique. The new viscosity results from the rFRAP experiments and the aerosol optical tweezer technique were then used to update our understanding of the viscosity of erythritol-water particles and the effect of adding OH functional groups to a linear C$_4$ carbon backbone on viscosity. The new results also allowed us to perform an intercomparison between three techniques (rFRAP, aerosol optical tweezers and bead-mobility) used for measuring the viscosity of organic-water particles.

2 Experimental method

2.1 rFRAP

As mentioned above, the rFRAP technique was used to measure the diffusion coefficient of RBID in erythritol-water matrix as a function of $a_w$. The rFRAP experiments were similar to those described in Chenyakin et al. (2017). The current rFRAP experiments required thin films (30–50 µm thick) with a known $a_w$, containing erythritol, water, and trace amounts of RBID. Section 2.1.1 describes the preparation of the thin films. Section 2.1.2 describes the rFRAP technique and the extraction of diffusion coefficients from the rFRAP data.
2.1.1 Preparation of thin films containing erythritol, water, and trace amounts of RBID with a known $a_w$

The solubility of erythritol in water at 293 K is $\sim$ 38 weight percent (Haynes, 2015), which corresponds to an $a_w \approx 0.92$, based on Raoul’s law and assuming erythritol does not dissociate in water (Koop et al., 2011). In our experiments, all thin films were conditioned at $a_w < 0.92$ and were therefore supersaturated with respect to crystalline erythritol. To prepare these supersaturated thin films, a bulk solution containing 20 weight percent erythritol in water and 0.056 weight percent (0.01 mmol L$^{-1}$) RBID were prepared gravimetrically. The prepared bulk solution was then filtered using a 0.45 μm Millex®-HV syringe filter unit (Millipore Sigma Ltd., Etobikoe, ON, Canada) to eliminate solid impurities. Next, the solution was nebulized onto a siliconized hydrophobic glass slide (22×22 mm, VWR, Radnor, PA, USA), which had been rinsed with Milli-Q® water (18.2 MΩ cm). This resulted in droplets with radii ranging from 100 to 170 μm on the hydrophobic glass slide.

The slide holding the droplets was then transferred into a flow cell in an inflatable glove bag (Glass-Col, Terre Haute, IN, USA) for conditioning at a particular $a_w$. A handheld hygrometer (OMEGA, Norwalk, CT, USA) with an accuracy of $\pm$ 2.5% was used to measure the RH at the flow cell outlet and in the glove bag. The $a_w$ was calculated from the measured RH (i.e. $a_w = RH(\%) / 100$) (Seinfeld and Pandis, 2006). The time used for conditioning droplets ranged from 21.5 to 96 h. See Sect. S1 and Table S1 (Supporting Information) for details. After conditioning the droplets at a particular $a_w$, thin films were formed by placing a second hydrophobic glass slide on top of the original glass slide supporting the droplets. A pair of aluminum spacers, with a thickness of 30–50 μm, were placed between the two slides to control the thickness of the thin films. A seal was formed between the two slides by lining the perimeter of one slide with high-vacuum grease prior to sandwiching the droplets.

Figure S1 (Supporting Information) shows a schematic of the thin films used in the rFRAP experiment. The process of creating the thin films was carried out inside the inflated glove bag, to prevent the sample from being exposed to the uncontrolled room RH. After conditioning the droplets to a known $a_w$ and creating the thin films, the concentration of RBID in the thin films ranged from 0.2 to 0.3 weight percent. At this concentration, the fluorescence intensity of the thin films was proportional to the RBID concentration (Sect. S2 and Fig. S2, Supporting Information).

Even though all thin films were supersaturated with respect to crystalline erythritol, crystallization was not observed, likely because 1) the bulk solution was filtered to remove impurities, and 2) the glass slides were highly hydrophobic, which reduced the possibility of heterogeneous nucleation of organic crystals (Bodsworth et al., 2010; Pant et al., 2004, 2006; Wheeler and Bertram, 2012; Yeung et al., 2009).

2.1.2 rFRAP technique and data extraction

In the rFRAP experiments, a confocal laser scanning microscope was used to photobleach RBID
molecules in a small volume of the thin film. After photobleaching, a gradual recovery of fluorescence within the photobleached region occurred due to the diffusion of unbleached fluorescent molecules from outside the bleached region into the bleached region. The diffusion coefficient of the fluorescent dye was determined by monitoring the time-dependent recovery of the fluorescence intensity using the same confocal laser scanning microscope used for photobleaching.

In this work, a Zeiss LSM510 confocal laser scanning microscope with a 10×0.30 numerical aperture objective was used. The pinhole was set at 120 μm. Photobleaching was performed using a helium-neon laser with an emission wavelength of 543 nm, at a power of 330 μW. The photobleached area ranged from 3×3 to 6×6 μm². The bleach parameters, including the number of iterations and scanning speed of the laser, were adjusted to obtain a reduction in fluorescence intensity of ~30% in the bleached region, as recommended by Deschout et al. (2010). After photobleaching, images were taken using the same laser at a power of 4 μW, at time intervals ranging from 2 to 30 s, depending on the speed of recovery of the fluorescence signal, with longer intervals used when the fluorescence recovery was slower. All experiments were performed at room temperature (292–294 K).

Figure 2 shows an example of a series of images recorded during an rFRAP experiment. All of the images recorded after photobleaching were normalized against an image captured prior to photobleaching, using the ImageJ software. After normalization, the images were downsized from 512×512 pixels to 128×128 pixels by averaging pixels to reduce the level of noise (Chenyakin et al., 2017).

The following is the analytical solution given by Deschout et al. (2010) for the fluorescence intensity at position (x,y) and time t after photobleaching a rectangle area in a thin film:

$$F(x,y,t) = F_0(x,y) \left[ 1 - \frac{K_0}{4} \left[ \text{erf} \left( \frac{x-l_x^2}{\sqrt{\pi} \sqrt{4Dt}} \right) - \text{erf} \left( \frac{x+l_x^2}{\sqrt{\pi} \sqrt{4Dt}} \right) \right] \times \left[ \text{erf} \left( \frac{y-l_y}{\sqrt{\pi} \sqrt{4Dt}} \right) - \text{erf} \left( \frac{y+l_y}{\sqrt{\pi} \sqrt{4Dt}} \right) \right] \right]$$

where $F(x,y,t)$ is the fluorescence intensity at position (x,y) and time t after photobleaching, $F_0(x,y)$ is the fluorescence intensity at position (x,y) prior to photobleaching, $l_x$ and $l_y$ are the lengths of the rectangular photobleached area, $K_0$ is related to the fraction of molecules photobleached in the bleach region, r is the resolution of the microscope, $t$ is the time after photobleaching, and $D$ is the diffusion coefficient of the fluorescent dye.

Following the rFRAP experiments, individual images were fit to Eq. (2) using a Matlab script, with $K_0$ and $r^2 + 4Dt$ left as free parameters. A normalization factor was also included as a free parameter, and it returned a value close to 1, as expected. From Eq. (2), a value of $r^2 + 4Dt$ was obtained for each image taken after photobleaching. Next, $r^2 + 4Dt$ was plotted as a function of time after photobleaching, and a straight line was fit to the plotted data. An example plot of $r^2 + 4Dt$ versus $t$
and a linear fit to the data are shown in Fig. 3. Diffusion coefficients were determined from the slope of the fitted line. The diffusion coefficient at each \( x \) reported in Sect. 3 is the average of at least four measurements.

Cross-sectional views of the fluorescence intensity along the x-axis for different times after photobleaching are shown in Fig. 4. The cross-sections for the measured intensities (blue dots) were generated by averaging the normalized fluorescence intensities \( (F/F_0) \) over the width of the photobleached region in the y direction, at each position \( x \). Calculated cross-sections of the fluorescence intensities (red lines) were generated from fits of Eq. (2) to the experimental data. The close agreement between the measured and calculated cross-sections illustrates that Eq. (2) describes our experimental data well.

Equation (2) was derived by assuming no diffusion in the axial direction (i.e. \( z \)-direction). Deschout et al. (2010) have shown that Eq. (2) gives accurate diffusion coefficients when the numerical aperture of the microscope is low (\( \leq 0.45 \)) and the thickness of the films is small (\( \leq 120 \mu m \)), consistent with the numerical aperture of 0.30 and film thickness of 30–50 \( \mu m \) used in our experiments. Equation (2) also assumes that the only mechanism for recovery in the photobleached region is diffusion. An additional possible mechanism is reversible photobleaching, which has been observed in some fluorescence imaging experiments (Chenyakin et al., 2017; Long et al., 2011; Sinnecker et al., 2005). In a separate set of experiments, we showed that this is not an important mechanism in our experiments (Sect. S3 and Fig. S3, Supporting Information).

2.2 Aerosol optical tweezer

The application of the aerosol optical tweezer technique to measure the viscosity of aerosol particles has been discussed in detail in previous publications (Bzdek et al., 2016; Song et al., 2016b) and will only be briefly reviewed here. Two optical traps are formed using a holographic optical tweezers instrument equipped with a laser at 532 nm (Laser Quantum Opus 3W). The holographic arrangement uses a spatial light modulator (Hamamatsu, X10468) to encode phase information into the expanded laser-light wavefront, creating an interference pattern in the trapping plane that resembles two tightly focused beams. Aerosol droplets are captured from a cloud of aerosol generated from a medical nebulizer and introduced into a RH-controlled trapping cell with the RH recorded by a capacitance probe (Honeywell, HIH-4202A). Typical particle diameters are 9–16 \( \mu m \).

Droplet sizes and refractive indices are inferred from the discrete wavelengths commensurate with whispering gallery modes (WGMs) that are observed in the Raman scattering fingerprints recorded from the two droplets. Particle size and refractive index are estimated from comparison with calculated WGM wavelengths using Mie scattering theory and can be determined with an accuracy of \( < \pm 2 \) nm and \( < \pm 0.0005 \), respectively (Preston and Reid, 2013).
Following a conditioning period of many hours, identified by a steady droplet size over a period of tens of minutes, the particles are coalesced by manipulating the optical trap positions. Once brought into contact, the shape of the composite particle relaxes over a timescale of microseconds to hours, dependent on the viscosity. One of three methods is then chosen to infer particle viscosity from the shape relaxation based on the relaxation timescale:

1. For relaxation timescales of < 1 ms (equivalent to viscosities < 10 Pa s) (Power and Reid, 2014), the time-dependence of the backscattered light intensity can be used to monitor the change in shape using a silicon photodetector (Thorlabs, DET 110) and oscilloscope (LeCroy, HDO 6034-MS). At timescales longer than this, the movement of the trapped particle relative to the laser beam focus (i.e. the relaxation in trapped position) contributes to the change in light scattering signal and becomes convoluted with the change arising from the relaxation in shape. Thus, light scattering measurements cannot be used for viscosities > 10 Pa s (Bzdek et al., 2016).

2. For longer timescales, the relaxation in shape can be directly viewed from brightfield microscopy over a period spanning from 5 – 10 ms (equivalent to viscosities > 10 Pa s) to as long as 10^3 s (equivalent to viscosities ~ 10^7 Pa s) (Bzdek et al., 2016). Images are recorded by a camera (Dalsa Genie HM 640, CMOS) with 5 – 10 ms time resolution. The change in aspect ratio for the relaxing particle is determined and used to determine the relaxation time constant (Song et al., 2016b).

3. The disappearance followed by the reappearance of WGMs from the Raman spectrum from the coalesced dimer (recorded with 1 s time resolution) can be used to infer the slow disappearance of a spherical cavity on one side of the dimer and reemergence of a single spherical particle at the end of the relaxation process (Power et al., 2013). With a coarse time resolution of 1 s, this method should only be used to infer the viscosity when higher than 10^4 Pa s (Power and Reid, 2014).

With three analysis methods, viscosity measurement can cover a wide range, from 10^-3 Pa s to > 10^9 Pa s. However, it should be noted that there are ranges where two techniques may overlap but with varying accuracy (e.g. imaging and Raman for viscosities 10^4 – 10^5 Pa s with relaxation times of 1 – 10 s).

3 Results and Discussion

3.1 Diffusion coefficients in and viscosities of erythritol-water particles as functions of aw measured by the rFRAP technique

Shown in Fig. 5(a) and listed in Table S2 (Supporting Information) are the measured diffusion coefficients of RBID in erythritol-water matrices as a function of aw. The diffusion coefficient
decreased by 2 – 3 orders of magnitude as $a_w$ decreased from approximately 0.5 to 0. This decrease in the diffusion coefficients with a decrease in $a_w$ is due to the plasticizing effect of water (Koop et al., 2011; Power et al., 2013).

The Stokes-Einstein equation and measured diffusion coefficients were used to calculate the viscosity of erythritol-water particles. It has been found that the Stokes-Einstein equation significantly underestimates the diffusion coefficients of small molecules such as water and ozone within a matrix containing larger molecules (Bastelberger et al., 2017; Li et al., 2015; Marshall et al., 2016; Price et al., 2014; Shiraiwa et al., 2011). On the other hand, as discussed in Sect. 1, the Stokes-Einstein equation gives accurate diffusion coefficients when the diffusing species is similar in size or larger than the matrix molecules and when the viscosity of the matrix is comparable to or lower than $10^8$ Pa s (Chenyakin et al., 2017; Price et al., 2016). Hence, in this study, we assume that the viscosity of erythritol-water particles can be accurately calculated using the measured RBID diffusion coefficient and the Stokes-Einstein equation, because RBID is much larger than the matrix molecules (Table 1) and the highest reported viscosity of erythritol in the literature is on the order of $10^7$ Pa s (Grayson et al., 2017; Song et al., 2016b).

Figure 5(b) and Table S2 show the viscosity of erythritol-water particles (calculated using diffusion coefficients from Fig. 5(a) and the Stokes-Einstein equation) as a function of $a_w$. As $a_w$ decreased from approximately 0.5 to 0, the viscosity increased from approximately $1 \times 10^{-1}$ to $5 \times 10^1$ Pa s.

The symbols in Fig. 5 are color-coded by the time allowed to condition the samples to a particular $a_w$ value before measuring the diffusion coefficient. The color scale in the top left corner applies to both panels (a) and (b). No clear trend is observed between the conditioning time and diffusion coefficient or particle viscosity.

To further investigate the effect of the time used to condition the samples to a particular $a_w$ value, in Fig. 6, the measured RBID diffusion coefficients in erythritol-water matrices are plotted as a function of conditioning time at $a_w \leq 0.105$. The data shown in Fig. 6 were taken from the data shown in Fig. 5(a). Included as a second x-axis is the sample conditioning time in multiples of $\tau_w$, where $\tau_w$ is the characteristic time for water diffusion within the sample droplets used in the conditioning experiments (see Sect. S1 for details, Supporting Information). Consistent with Fig. 5(a), Fig. 6 illustrates that there is no clear trend between diffusion coefficient and the time allowed for conditioning the samples prior to the diffusion measurements. Figure 6 also suggests that a sample conditioning time of $\geq 21.5$ hours, or $\geq 6.5 \tau_w$ was sufficient to reach near equilibrium between the RH used for conditioning and the $a_w$ in particles.

3.2 Viscosity of erythritol-water particles as a function of $a_w$ measured by the aerosol optical tweezer technique
Erythritol viscosity measurements using the aerosol optical tweezer technique are shown in Fig. 7. The viscosity of pure water at 293 K (Korson et al., 1969) is also included for comparison. The red circles represent the new aerosol optical tweezer measurements obtained in this work (also listed in Table S3, Supporting Information), based solely on brightfield images. The gray circles represent the viscosities reported in Song et al. (2016b). The new averaged viscosities reported here based on the aerosol optical tweezer technique are lower than those reported by Song et al. (2016b) at $a_w < 0.1$, although the error bars (representing two standard deviations) overlap.

In the previous aerosol optical tweezer measurements at $a_w < 0.1$ (Song et al., 2016b), the timescale for relaxation to a sphere was estimated from two methods: the change in coalesced particle shape as recorded by the brightfield images and the reappearance of WGMs in the Raman spectrum. Upon re-evaluation of the data previously obtained at $a_w < 0.1$ (Song et al., 2016b) and comparison with the new measurements, it was determined that erythritol viscosity measurements under dry conditions using the Raman spectral measurements were compromised by the limited time resolution (1 s, equivalent to ~ $10^4$ Pa s) and higher than those estimated from brightfield imaging, yielding an overestimate of the viscosity. Since the new aerosol optical tweezer measurements in this work are based solely on the brightfield images, they are more accurate than the previous results at $a_w < 0.1$ as a consequence of the higher time resolution of the brightfield imaging measurement compared to the Raman spectroscopy measurement. The viscosity at $a_w = 0.22$ reported by Song et al. (2016b) was based on brightfield images alone and those at $a_w \geq 0.43$ were based on back-scattered light intensity (where viscosities were < 10 Pa s, see Sect. 2.2).

3.3 Update on the viscosity of erythritol-water particles as a function of $a_w$ and an intercomparison of techniques for measuring the viscosity of particles

In Fig. 8, we have summarized the previous and current measurements of the viscosity of erythritol-water particles as a function of $a_w$. The black triangles represent measurements by Grayson et al. (2017) using the bead-mobility technique. The blue squares represent the rFRAP results from this work, where experimental data at similar $a_w$ have been binned together so as not to give extra weight to the rFRAP data. The red circles indicate aerosol optical tweezer measurements from Song et al. (2016b) (open circles) and this study (solid circles). The previous measurements at $a_w \leq 0.1$ by Song et al. (2016b) were excluded from Fig. 8, because the new aerosol optical tweezer measurements reported in this study at $a_w \leq 0.1$ are thought to be more accurate. Considering the uncertainties in the measurements, the results from the three techniques (bead-mobility, rFRAP and aerosol optical tweezer) are in reasonable agreement.

To determine the viscosity of pure erythritol under dry conditions ($a_w = 0$), a straight line was fit to the data in Fig. 8 (shown as the red line) and then extrapolated to $a_w = 0$. The intercept on the y-axis was $2.393 \pm 0.246$ (two standard deviations), corresponding to a viscosity of pure erythritol of
3.4 Effect of the addition of OH functional groups to a linear C₄ carbon backbone

Grayson et al. (2017) previously estimated the effect of adding OH functional groups on the viscosity of a linear C₄ compound. Here we repeat this analysis (Fig. 9) based on the updated viscosity of pure erythritol ($247^{±18}_2$ Pa s) determined above. For those compounds with the same number but different positions of OH functional groups, the average of their viscosities was taken from the literature (Grayson et al., 2017; Rothfuss and Petters, 2017; Song et al., 2016b). Table S4 (Supporting Information) lists the values and sources of literature data used. The data in Fig. 9 were fit to a linear equation, resulting in a slope of $1.437 ± 0.090$ (two standard deviations), which indicates that the viscosity of a linear C₄ molecule increases on average by a factor of $27^{±9}_6$ per addition of an OH functional group.

The viscosity increase from the addition of OH functional groups to a carbon backbone may depend on the level of prior functionalization. To investigate this aspect further, we calculated the sensitivity parameter ($S_\eta$) for a linear C₄ carbon backbone using the viscosity data presented in Fig. 9 and the following equation (Rothfuss and Petters, 2017):

$$S_\eta = \Delta \log_{10}(\eta \text{ Pa s}) / \Delta N,$$

where $\Delta \log_{10}(\eta \text{ Pa s})$ is the change in viscosity on a log₁₀ scale, and $\Delta N$ is the change in the number of OH functional groups. $S_\eta$ was estimated based on the addition of one OH functional group ($\Delta N = 1$), starting from n-butane. The relationship between $S_\eta$ and $N$ is shown in Fig. 10 for a linear C₄ carbon backbone. $S_\eta$ is between 0.7 and 1.9 for $N = 1 – 3$. On the other hand, $S_\eta$ is between 1.7 and 2.7 for $N = 4$, suggesting $S_\eta$ increases with the addition of the fourth OH functional group to the linear C₄ carbon backbone. However, additional studies are needed in order to reduce the uncertainties of the measurements and make stronger conclusions.

4 Summary and Conclusion

In this work, viscosities of erythritol-water particles as a function of $a_w$ at 292 – 295 K were measured using the rFRAP and aerosol optical tweezer techniques. In the rFRAP measurements, a trace amount of RBID (0.2 – 0.3 weight percent) was added to the erythritol-water matrix and viscosities of erythritol-water particles were estimated based on the measured diffusion coefficients of RBID and the Stokes-Einstein equation. In the new measurements using the aerosol optical tweezer technique, viscosity was measured at $a_w < 0.1$ based solely on brightfield imaging (Song et al., 2016b).

In general, considering the uncertainties in the measurements, viscosities measured using the bead-mobility (Grayson et al., 2017), rFRAP and aerosol optical tweezer techniques are in reasonable
agreement. A linear fit was performed for the experimentally determined viscosities of erythritol-water particles against $a_w$ and extrapolated to $a_w = 0$. Based on the extrapolation, the viscosity of pure erythritol at 292 – 295 K is estimated at $247^{+188}_{-107}$ Pa s (two standard deviations). Based on these results, the addition of an OH functional group to a linear C$_4$ carbon backbone increased the viscosity by a factor of $27^{+9}_{-5}$ (two standard deviations), on average. In comparison, Grayson et al. (2017) reported a factor of $41^{+27}_{-16}$ based on previous measurements.

The sensitivity parameter was calculated to determine the dependency of viscosity on the degree of prior functionalization for a linear C$_4$ carbon backbone. Based on the sensitivity parameter analysis, the increase in viscosity due to the addition of one OH functional group to a linear C$_4$ carbon backbone is not a strong function of the number of OH groups already present in the molecule, up to the addition of three OH functional groups. On the other hand, the degree of increase in viscosity is likely larger when the linear C$_4$ carbon backbone already contains three OH groups. These results should help improve the understanding of the viscosity of SOA particles in the atmosphere.
Data availability.

Data for this paper are available in the Supporting Information.

Competing interests.

The authors declare that they have no conflict of interest.

Acknowledgments.

This work was carried out in the Laboratory for Advanced Spectroscopy and Imaging Research (LASIR) at The University of British Columbia in Vancouver and supported by the Natural Sciences and Engineering Research Council of Canada. Yangxi Chu gratefully acknowledges the support from the Hong Kong PhD Fellowship Scheme by Hong Kong Research Grants Council and the Overseas Research Award at The Hong Kong University of Science and Technology (HKUST). Jonathan P. Reid and Young Chul Song gratefully acknowledge support from the NERC through the award of grant NE/M004600/1.
References


compounds: dependency on molecular properties and implications for secondary organic aerosols in
Kuwata, M. and Martin, S. T.: Phase of atmospheric secondary organic material affects its reactivity,
the ice nucleating abilities of α-pinene SOA particles, J. Geophys. Res. Atmos., 119(14), 9041–9051,
Lignell, H., Hinks, M. L. and Nizkorodov, S. A.: Exploring matrix effects on photochemistry of
Highly Viscous States Affect the Browning of Atmospheric Organic Particulate Matter, ACS Cent.
Long, D., Lin, H. and Scheblykin, I. G.: Carbon nanotubes as photoprotectors of organic dyes:
reversible photoreaction instead of permanent photo-oxidation, Phys. Chem. Chem. Phys., 13(13),
Timescales of water transport in viscous aerosol: measurements on sub-micron particles and
dependence on conditioning history, Phys. Chem. Chem. Phys., 16(21), 9819–9830,
Maclean, A. M., Butenhoff, C. L., Grayson, J. W., Barsanti, K., Jimenez, J. L. and Bertram, A. K.:
Mixing times of organic molecules within secondary organic aerosol particles: a global planetary
boundary layer perspective, Atmos. Chem. Phys., 17(21), 13037–13048, doi:10.5194/acp-17-13037-
Marshall, F. H., Miles, R. E. H., Song, Y.-C., Ohm, P. B., Power, R. M., Reid, J. P. and Dutcher, C. S.:
Diffusion and reactivity in ultraviscous aerosol and the correlation with particle viscosity, Chem. Sci.,


Shikimic acid ozonolysis kinetics of the transition from liquid aqueous solution to highly viscous glass,


Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R.,

Vermeylen, R., Maenhaut, W., Claeyts, 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(31),


Surratt, J. D., Chan, A. W. H., 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, Proc. Natl. Acad. Sci., 107(15), 6640–6645,


of laboratory and ambient secondary organic aerosol, Proc. Natl. Acad. Sci., 108(6), 2190–2195,


Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirilä, P., Leskinen, J., Mäkelä, J. M.,


state of biogenic secondary organic aerosol particles, Nature, 467(7317), 824–827,


Virtanen, A., Kannosto, J., Kuuluvainen, H., Arffman, A., Joutsensaari, J., Saukko, E., Hao, L., Yli-

Pirilä, P., Tiitta, P. and Holopainen, J. K.: Bounce behavior of freshly nucleated biogenic secondary

organic aerosol particles, Atmos. Chem. Phys., 11(16), 8759–8766, doi:10.5194/acp-11-8759-2011,

2011.

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


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(2),


Wilson, T. W., Murray, B. J., Wagner, R., Möhler, O., Saathoff, H., Schnaiter, M., Skrotzki, J., Price,

H. C., Malkin, T. L. and Dobbie, S.: Glassy aerosols with a range of compositions nucleate ice

eheterogeneously at cirrus temperatures, Atmos. Chem. Phys., 12(18), 8611–8632, doi:10.5194/acp-12-


Zobrist, B., Marcolli, C., Pedernera, D. A. and Koop, T.: Do atmospheric aerosols form glasses?

708
709
### Table 1.
The molar masses ($M_w$) and hydrodynamic radii ($R_H$) of erythritol and rhodamine B isothiocyanate-dextran (RBID), which are used as the matrix and diffusing fluorescent dye in this work, respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>$R_H$ (Å)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erythritol</td>
<td>122.12</td>
<td>3.4 ± 0.3</td>
<td>Kiyosawa (1991)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Schultz and Solomon (1961)</td>
</tr>
<tr>
<td>Rhodamine B isothiocyanate-</td>
<td>70,000 (on average)</td>
<td>59 ± 1</td>
<td>Floury et al. (2015)</td>
</tr>
<tr>
<td>dextran (RBID)</td>
<td></td>
<td></td>
<td>Paës et al. (2017)</td>
</tr>
</tbody>
</table>
Figures

(a) Molecular structures of (a) erythritol and (b) rhodamine B isothiocyanate – dextran (RBID) in neutral form. On average, n = 429.

Figure 1. Molecular structures of (a) erythritol and (b) rhodamine B isothiocyanate – dextran (RBID) in neutral form. On average, n = 429.
Figure 2. Images captured during an rFRAP experiment for erythritol-water thin films conditioned at $a_w = 0.023 \pm 0.023$. RBID concentration in the films was approximately 0.3 weight percent. The red square in (a) indicates the region selected for photobleaching. Images (b–f) were recorded at 0, 360, 720, 1080 and 1440 s after photobleaching. Dimensions of the images and the red square are $60 \times 60 \mu m^2$ and $6 \times 6 \mu m^2$, respectively.
Figure 3. $r^2 + 4Dt$ as a function of $t$ for the diffusion of RBID in erythritol-water matrix with $a_w = 0.023 \pm 0.023$. RBID concentration in the conditioned films was approximately 0.3 weight percent. The red line represents a linear fit to the data.
Figure 4. Cross-sectional view of the normalized fluorescence intensities ($F / F_0$) along the x-axis during an rFRAP experiment. Blue dots correspond to the measured data, while the red lines represent fits to the experimental data using Eq. (2). The sample films were conditioned at $a_w = 0.023 \pm 0.023$. RBID concentration in the conditioned films was approximately 0.3 weight percent. Panel (a) shows the cross-section prior to photobleaching. $F / F_0$ equals 1 because the image was normalized against itself. Panels (b–f) show the cross-sections at 0, 360, 720, 1080 and 1440 s after photobleaching, corresponding to frames (b–f) in Fig. 2.
Figure 5. (a) The measured diffusion coefficients of RBID as a function of $a_w$. (b) The viscosity of erythritol-water particles as a function of $a_w$ based on the measured RBID diffusion coefficients and the Stokes-Einstein equation. Results from rFRAP measurements are color-coded by the sample conditioning time prior to the rFRAP experiments. The color scale applies to both panel (a) and (b). Horizontal error bars indicate the upper and lower limits of $a_w$. Vertical error bars correspond to two standard deviations of diffusion coefficient (in panel a) and $\log_{10}$ (viscosity / Pa s) (in panel b).
Figure 6. The diffusion coefficient of RBID as a function of the time allowed for conditioning erythritol-water particles at $a_w = 0 - 0.046$ (open squares) and $0 - 0.105$ (filled squares). The secondary (top) x-axis represents the conditioning time expressed in multiples of $\tau_w$ (characteristic time for the diffusion of water molecules within the erythritol-water droplets). For the calculation of $\tau_w$, the lower limit of $a_w$ (i.e., 0) was taken, leading to maximum $\tau_w$ values of 3.3 h for droplets with a radius of 100 μm. Error bars represent two standard deviations of RBID diffusion coefficients.
Figure 7. Viscosity of erythritol-water particles (on a log_10 scale) as a function of $a_w$, determined using the aerosol optical tweezer technique. Red circles represent experimental results from this study. Gray circles represent experimental results from Song et al. (2016b). The green circle represents the viscosity of pure water at 293 K (Korson et al., 1969). Horizontal error bars (± 0.02) indicate the upper and lower limits of $a_w$. Vertical error bars represent two standard deviations of log_10 (viscosity / Pa s).
Figure 8. Viscosity of erythritol-water particles as a function of $a_w$ measured by the bead-mobility technique (black triangles) (Grayson et al., 2017), the rFRAP technique (blue squares) and the aerosol optical tweezer technique (open red circles – from Song et al. (2016b), solid red circles – this study). The viscosity of pure water at 293 K (open green circle) (Korson et al., 1969) is also included for comparison. Horizontal error bars (± 0.02) indicate the upper and lower limits of $a_w$. Vertical error bars represent two standard deviations of $\log_{10} (\text{viscosity} / \text{Pa s})$. The red line is a linear fit to the data shown in the plot using the orthogonal distance regression-fitting algorithm, which is weighted based on the uncertainty in viscosity data. The equation of the linear fit is $\log_{10} (\text{viscosity} / \text{Pa s}) = (2.393 \pm 0.246) + (-0.054 \pm 0.002) \cdot (100 \ a_w)$. Uncertainties in the slope and y-axis intercept correspond to two standard deviations.
Figure 9. Viscosities of compounds with a linear C₄ carbon backbone at 292 – 295 K on a log₁₀ scale plotted against the number of OH functional groups. Black circles represent viscosities of the compounds with 0 – 3 OH functional groups (i.e., n-butane, 1-butanol, 2-butanol, 1,2-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2,3-butanetriol and 1,2,4-butanetriol) taken from literature (Grayson et al., 2017; Rothfuss and Petters, 2017; Song et al., 2016b). For the literature data points, the error bars are two standard deviations of log₁₀ (viscosity / Pa s) of multiple compounds. The blue circle represents the viscosity of pure erythritol, with error bars of two standard deviations, based on the linear fit in Fig. 8. The red line is a linear fit to the data, which is weighted based on the uncertainties in viscosity data. The slope and regression coefficient (R²) are shown in the annotation. The uncertainty in the slope corresponds to two standard deviations.
Figure 10. The viscosity sensitivity parameter at 292 – 295 K plotted against the number of OH functional groups for linear C₄ compounds (alkane, alcohol and polyols). Black circles represent values estimated using literature data alone (Grayson et al., 2017; Rothfuss and Petters, 2017; Song et al., 2016b); the blue circle represents the value estimated using experimental results from this work and literature data (Grayson et al., 2017; Song et al., 2016b). The error bars are propagated from the uncertainties shown in Fig. 9.