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Measurements and Predictions of Binary Component Aerosol Particle Viscosity

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ABSTRACT

Organic aerosol particles are known to often absorb/desorb water continuously with change in gas phase relative humidity (RH) without crystallisation. Indeed, the prevalence of metastable ultraviscous liquid or amorphous phases in aerosol is well-established with solutes often far exceeding bulk phase solubility limits. Particles are expected to become increasingly viscous with drying, a consequence of the plasticising effect of water. We report here measurements of the variation in aerosol particle viscosity with RH (equal to condensed phase water activity) for a range of organic solutes including alcohols (diols to hexols), saccharides (mono-, di- and tri-) and carboxylic acids (di-, tri- and mixtures). Particle viscosities are measured over a wide range (10⁻³ to 10¹⁰ Pa s) using aerosol optical tweezers, inferring the viscosity from the timescale for a composite particle to relax to a perfect sphere following the coalescence of two particles. Aerosol measurements compare well with bulk phase studies (well-within an order of magnitude deviation at worst) over ranges of water activity accessible to both. Predictions of pure component viscosity from group contribution approaches combined with either non-ideal or ideal mixing reproduce the RH-dependent trends particularly well for the
alcohol, di- and tri-carboxylic acid systems extending up to viscosities of $10^4$ Pa s. By contrast, predictions over-estimate the viscosity by many orders of magnitude for the mono-, di-, and tri-saccharide systems, components for which the pure component sub-cooled melt viscosities are $>10^{12}$ Pa s. When combined with a typical scheme for simulating the oxidation of $\alpha$-pinene, a typical atmospheric pathway to secondary organic aerosol (SOA), these predictive tools suggest that the pure component viscosities are less than $10^6$ Pa s for $\sim$97% of the 50,000 chemical products included in the scheme. These component viscosities are consistent with the conclusion that the viscosity of $\alpha$-pinene SOA is most likely in the range $10^5$ to $10^8$ Pa s. Potential improvements to the group contribution predictive tools for pure component viscosities are considered.

I. Introduction

Viscosity is a fundamental physicochemical property that characterises the resistance of a material to deformation and provides insights into related properties such as the phase of a material, the diffusion constants of molecules in the material and intermolecular interactions in non-ideal mixtures. For atmospheric aerosols, particle viscosities can influence mass transfer rates, morphologies and shapes, deposition efficiencies and mechanisms of particle formation. Higher bounce efficiencies of viscous or solid particles from solid substrates can influence aerosol sampling in impactors which can be used to infer the phase of particles. Particles of high viscosity can be expected to respond more slowly to changes in gas composition than low viscosity particles through kinetically limited bulk diffusive transport, leading to slow heterogeneous reaction rates, non-equilibrium partitioning of semi-volatile components between the condensed and gas phases and long range transport of reactive pollutants in the environment. The viscosity of aerosol has the potential to influence ice nucleation efficiency and the activity of organic aerosol as cloud condensation nuclei. In addition, the morphology and shape of particles can be influenced by viscosity, both in the formation of inhomogeneous particles (e.g. the formation of particles with internal gradients in composition) and in the shapes of composite particles formed by coalescence.

Although viscosity can be an important indicator of aerosol properties, bulk phase measurements using conventional rheometry techniques may not allow measurements of viscosity for the metastable phases adopted in aerosol. The deliquescence-efflorescence hysteresis cycle is well-established for many simple
aqueous-solute systems. A crystalline solid absorbs water to become an aqueous solution-droplet at the deliquesce point with a solute concentration equal to the solubility limit. On drying, the phase transition is not reversible at the same water activity; instead, the re-crystallisation (efflorescence) of the solute occurs at much lower water activity and higher solute concentration, consistent with a highly supersaturated solution, due to the inherent slowness of nucleation kinetics. Indeed, many organic solutes may actually take up and desorb water continuously as the relative humidity (RH) is increased and decreased, respectively, with solute super-saturations that are unachievable in a bulk phase. Clearly then, aerosol particles may adopt a metastable phase that cannot be accessed in a bulk sample, raising questions over the validity of bulk phase measurements when applied to predicting aerosol properties and suggesting the prevalence of a sub-cooled liquid phase in organic aerosol. In addition, dilute aqueous solution droplets at high water activity may form amorphous semi-solid or even glassy particles at low RH and low temperature, spanning a viscosity range from $10^{-3}$ to $>10^{12}$ Pa s, an extremely wide dynamic range that may be inaccessible to bulk instruments. Even though the viscosity may surpass that associated with substances such as bitumen ($\sim 10^8$ Pa s), the small size of nanometre-sized particles may still lead to dynamics on a reasonable timescales (e.g. days in the atmosphere); thus, particles that may even be apparently solid cannot be considered to be completely inert.

To resolve the impact of aerosol phase state and viscosity on the properties of ambient particles, new approaches are required to both measure and predict the viscosities of typical atmospheric aerosol constituents. Many approaches for predicting the viscosities of pure components are based on group contribution methods, although they largely remain unevaluated for systems exhibiting viscosities $>1$ Pa s, a viscosity that is still only representative of a viscous liquid. As an example, the group contribution method described by Nannoolal et al. gives the pure component viscosity for the liquid state (or the sub-cooled liquid state if estimating the viscosity below the melting point) with the fragmentation of groups chosen to be the same as that of the estimation methods for boiling point and vapour pressure provided by the same author. Typical mixing rules for estimating the viscosities of mixtures of components include the group contribution thermodynamic viscosity mode method GC-UNIMOD, which includes interaction parameters derived from fits to vapour-liquid equilibrium (VLE) data and gives a model similar in concept to UNIFAC. A second mixing rule used is that of Bosse, which relates the viscosity of a mixture to its excess Gibbs energy and for which an activity coefficient model, such as the Aerosol Inorganic-Organic Mixtures Functional groups
Activity Coefficients (AIOMFAC) model\textsuperscript{46,47} can be used. Booth et al. have recently used this method to predict the temperature dependence of the viscosity of a mixture of dicarboxylic acids, with the estimated values (of order 1 Pa s) found to be six orders of magnitude smaller than the viscosity measured below 70 °C, suggesting that the measurements were made on a bulk sample of different phase.\textsuperscript{9}

Direct approaches to measure the viscosity of aerosol particles are limited. A number of groups have shown that the phase and viscosity of both organic and inorganic particles can be investigated by a “poke-flow” method.\textsuperscript{28,48} A mechanical force from a needle is applied to a particle collected on a substrate (~20 μm diameter). The immediate deformation in shape of the particle is then observed and the recovery to the initial state monitored, with the driving force arising from the minimisation of the surface energy of the particle. From the time for recovery in shape, a range in viscosity can be inferred for particles with viscosities less than 10^8 Pa s, typically spanning 3 – 5 orders of magnitude; for more viscous particles, only a lower limit for viscosity of 10^8 Pa s can be inferred. A more refined approach involves monitoring the diffusional motion of 1 μm diameter beads within a host droplet. From measurements of bead mobility, the viscosity can be inferred with an order of magnitude accuracy up to ~10^3 Pa s.\textsuperscript{48,49} A more accurate measurement for measuring the viscosity of sampled aerosol (but over a limited range for any one measurement) can be achieved from fluorescence lifetime measurements using molecular rotors, with the fluorescence lifetime sensitive to the local viscosity experienced by the rotor.\textsuperscript{31,50} Measurements up to a viscosity of ~10^2 Pa s have been possible using this approach and it has recently been extended to measurements of the viscosity of optically tweezed droplets.\textsuperscript{51}

By careful comparison of the rebound fractions for particles sampled by an impactor with calibration standards, the range of RHs over which an accumulation mode aerosols transitions from a liquid-like to solid-like aerosol can be inferred for secondary organic aerosol.\textsuperscript{5,8} Indeed, Kidd et al.\textsuperscript{7} observed the actual bounce patterns of particles on an impactor plate following sampling to further confirm the varying viscosity of sampled aerosol. Depolarisation in the light scattering from aerosol ensembles in the CERN CLOUD chamber was used to infer the viscous state of α-pinene secondary organic aerosol (SOA), with the asymmetries in particle shape following coalescence leading to a fraction of depolarised scatter.\textsuperscript{3} At RHs near the deliquescence RH, the
depolarising properties of non-spherical SOA formed from coalescence processes were shown to transform to a signature characteristic of a non-depolarising spherical particle.

Recently, we have shown that the timescale for the relaxation in shape of two coalescing particles following contact can be investigated using aerosol optical tweezers and the viscosity of the coalesced particle inferred over an exceptionally wide dynamic range (10^{-3} to >10^{9} Pa s).^{34,52,53} Two particles are first captured in two optical traps and then moved to the point of coagulation. For particles of low viscosity (<10^{-2} Pa s), the relaxation in shape occurs on a timescale of order 50-200 µs; backscattered elastic light from the optical traps is used to monitor the relaxation in shape and the viscosity estimated from the damping time. Once the relaxation time increases above 1 ms, the change in shape can be followed routinely by brightfield microscopy and the viscosity inferred with the shortest time commensurate with a viscosity of ~10 Pa s. If the viscosity is larger than ~10^{8} Pa s, the relaxation in shape takes longer than 1 day; the exact image frame that the droplets become a perfect single sphere is identified through observing the reappearance of the whispering gallery modes in the Raman spectrum. The dependence of viscosity on RH can be investigated using this approach, which also benefits from the extremely accurate measurements of size and composition (through refractive index retrievals) that come from cavity enhanced Raman spectroscopy.^{54,55}

In this publication, we will provide a comprehensive account of the measurement of aerosol viscosity using the optical tweezers approach, presenting data for a range of binary aqueous-organic aerosols. The systems chosen include a progression of compounds that includes diols, triols, tetraols and hexols, specifically: 1,4-butanediol, 1,2,3-propanetriol (glycerol), 1,2,4-butane triol, 1,2,6-hexanetriol, 1,2,3,4-butane tetraol (erythritol) and 1,2,3,4,5,6-hexanehexol (sorbitol). We also report measurements from the sequence formed by a monosaccharide (glucose), three disaccharides (sucrose, trehalose, maltose) and a tri-saccharide (raffinose). Finally, measurements are reported for aqueous solutions of a saturated dicarboxylic acid, an unsaturated dicarboxylic acid, and a tricarboxylic acid, specifically glutaric acid, maleic acid and citric acid, respectively. For comparison with a previous study,^{9} we also report measurements for a mixture of nine dicarboxylic acids consisting of equimolar proportions of the C_{3}-C_{10} and C_{12} dicarboxylic acids as used by Cappa et al.^{56} and referred to as the Cappa mixture. This is taken as a mixture of organic acids representative of atmospheric organic aerosol.
We first describe predictive tools for estimating viscosity of binary aerosol. The accuracy of aerosol optical tweezers measurements will then be assessed through comparison with conventional bulk phase measurements and predictions. Our aim here is to provide a robust account of measurements and predictions of the viscosity of binary aerosol, recognising that these experimental and theoretical tools must be rigorously benchmarked for simple systems before they can be used with any confidence for more complex systems.


Prediction of the viscosities of mixtures of organic components with water (i.e. the dependence on RH) often requires the application of mixing rules and knowledge of the pure liquid values of each component. The equilibrium phase state is a crystal for many of the low vapour pressure organic components typically found in the condensed phase in atmospheric aerosol. However, the sub-cooled liquid viscosity is required when predicting the viscosity of aqueous solutions. Techniques for predicting pure component and mixture viscosities are based on group contribution methods with tuning to experimental data, but remain largely unevaluated for systems exhibiting viscosities >1 Pa s.\(^9\) For pure component values, estimates from the method of Nanoolal et al.\(^{42}\) are based on using the same fragmentation patterns used in estimating saturation vapour pressures.\(^{44,45}\) These techniques have been described in detail in these previous publications and we refer the reader to these earlier sources for a comprehensive account. Here, we use the UManSysProp parsing suite for each compound to generate the required functional groups used in the method.\(^{57}\)

The viscosity of SOA derived from the oxidation of \(\alpha\)-pinene has been considered as a benchmark system in a number of previous experimental studies; here, we consider predictions of the pure component viscosities of organic compounds that are formed in oxidation schemes of \(\alpha\)-pinene.\(^{3,7,27,48,58}\) In Figure 1(a) we report predictions for the ~3500 organic components formed in the Master Chemical Mechanism simulations described by Barley et al.,\(^{59}\) showing values as a function of predicted saturation vapour pressure\(^{45}\) and O:C ratio. In Figure 1(b), viscosity predictions for the ~50,000 compounds from the \(\alpha\)-pinene oxidation simulation appearing in the GECKO-A model\(^{60}\) are shown for comparison (also shown for comparison as grey symbols...
in Figure 1(a)). The purpose of Figure 1 is to present general trends in individual component viscosity as trajectories move through the commonly used 2D basis set space of Donahue et al., whilst also demonstrating the information ‘bias’ one might attain depending on choice of chemical mechanism. Each component in these figures was taken from studies using basic absorptive partitioning theory without any consideration of condensed phase processes or autoxidation. Recent studies suggest mechanistic models still suffer from a lack of well-constrained process descriptions that would impact mixed solution properties, including viscosity. An in-depth discussion on the difference between both chemical mechanisms is beyond the scope of this study, yet results in Figure 1 at least qualitatively indicate the potential to arrive at different solution viscosity predictions. The general trends observed are as expected with the values displayed spanning from $10^{-3}$ to $10^{12}$ Pa s. Figure 1(c) shows that the distribution (number of compounds) of viscosities for individual components derived from the GECKO-A model, indicating that the majority of compounds have viscosities less than $10^6$ Pa s but that there remain an appreciable number of compounds with considerably higher viscosities.

Even though the accuracies of absolute values remain unevaluated, some trends in relation to varying O:C ratio and volatility can be observed from Figure 1. When studying Figure 1(b), results qualitatively suggest the predicted viscosity decreases with increasing O:C ratio for any given volatility (saturation vapour pressure). However, this should not be taken in isolation as indicative of a strict relationship: the interplay between level of oxidation, change in molecular weight and functionality together dictate the change in viscosity in any given series of compounds. Any given vertical transect in Figure 1(b) crosses multiple classes of compounds. Indeed, results from the MCM compounds in Figure 1(a) given an example of the general decrease in viscosity with increasing O:C ratio around a vapour pressure of $10^{-15}$ atm. In Figure 1(b), the viscosity increases with decreasing saturation vapour pressure for a given O:C ratio, which again results from the interplay between changing molecular weight and functionality. The differing ranges of O:C ratio and vapour pressures resulting from the two mechanistic models along with the corresponding variation in viscosity predictions, highlight the potential differences that can result when predicting the viscosity of the resulting SOA in a fully speciated model. Assuming the pure component values are a useful guide to the actual values, viscosity predictions for the SOA will likely depend on the complexity of the mechanistic simulations and the relative abundances of individual components. However, these predictions do demonstrate that pure component values can be
adequately constrained and that generalising expected viscosity ranges, as a function of volatility, might be able to supplement semi-empirical frameworks such as the 2D volatility basis set.\textsuperscript{61}

Moving beyond pure component properties, it is essential to also evaluate the accuracy of predictive approaches for mixed component aerosol viscosities. Here, we compare the GC-UNIMOD mixing rule method\textsuperscript{61} with the ideal and non-ideal mixing rules presented by Bosse.\textsuperscript{43} GC-UNIMOD is a group contribution method that uses interaction parameters to predict the viscosity of a mixture,\textsuperscript{46} relying on pure component values and using equations similar to the UNIFAC model.\textsuperscript{65} The techniques presented by Bosse\textsuperscript{43} are based on Eyrings absolute reaction rate theory, accounting for contributions from the excess Gibbs energy of the solution by an appropriate activity coefficient model:

$$
\ln(h_{\text{mix}}) = x_1 \ln(h_1) + x_2 \ln(h_2) - \frac{g^e}{cRT}
$$

\(\eta_1\) and \(\eta_2\) are the pure component viscosities, \(g^e\) is the excess Gibbs energy of the mixture at any given composition, \(R\) is the ideal gas constant, \(T\) is the temperature and ‘\(c\)’ is a scaling factor tuned according to comparison with experimental data (kept at 0.2, as suggested by Bosse).\textsuperscript{43} In the predictions presented here, we use AIOMFAC to calculate \(g^e\),\textsuperscript{46} which reduces to UNIFAC for organic systems; these predictions are designated as “non-ideal mixing” in the discussion that follow. In addition, we assume an ideal solution (\(g^e=0\)) as one model permutation, designated as “ideal mixing” in the discussion that follows.

Predictions of the RH-dependent mixture viscosities for binary aqueous-organic aerosols for all of the systems studied in Section III (described at the end of Section I) are presented in the Supporting Information (see sections SI.1 to SI.15). For comparison with experimental data, we provide predictions for aqueous mixtures derived from pure component values obtained from Nanoolal et al.\textsuperscript{45} In addition, we provide scaled predictions based on a separate fixed pure-component viscosity value that is estimated from the fits to the measured mixture data presented here or constrained to a value of 10\(^{12}\) Pa s at the known RH of the moisture driven glass transition. This approach demonstrates the potential to estimate values of pure component sub-cooled liquid melt viscosities by comparing our experimental mixture data to predictions from a chosen method and the possibility of rescaling/revising the predictive tools used for viscosity.
Although we will consider the accuracy of the predictions for mixture viscosities in Section III, some immediate general conclusions can be made when comparing the methods. Two typical examples with predictions of the viscosities of aqueous-glucose and aqueous-1,4-butanediol mixtures are provided in Figure 2, chosen as two systems with very different pure component viscosities. Including non-ideality in the prediction of mixture viscosity using the Bosse mixing rule leads to a systematic increase in the viscosity: the increase is much less than an order of magnitude for systems with pure component organic viscosities <1 Pa s but can be larger than an order of magnitude when the pure component viscosity exceeds 10^{12} Pa s. As should be expected, predictions from ideal and non-ideal mixing converge as the limits of pure solute or pure solvent are approached.

A further generalisation that can be made from Figure 2 is that predictions from the GC-UNIMOD and Bosse mixing rule show qualitatively different variations with RH: GC-UNIMOD consistently shows a much steeper increase in viscosity as the RH decreases from the saturation RH, clearly indicating that the plasticising effect of water only comes significantly into play at very high RH/high water contents in the GC-UNIMOD model. Predictions from both the ideal and non-ideal Bosse mixing rules show a much more steady increase in viscosity as the RH decreases from 100 to 0 %. The differences in predicted values, while marginal for mixtures of water with organic compounds of low viscosity (e.g. 1,4-butanediol), becomes increasingly significant as the viscosity of the pure organic component increases (e.g. glucose). However, the differences in shape/curvature at high RH remain consistent for all systems.

III. Experimental Section: Measurements of Aerosol Viscosity

In this section we introduce the method and the uncertainties associated with determining the viscosities of aerosol droplets directly from the optical tweezers technique before reviewing measurements made with a bulk phase rheometer.

III.a. Underdamped and Overdamped Coalescence Dynamics

When the coalescence of two particles first occurs, the shape of the composite particle is highly distorted from sphericity and capillary forces require that it must relax to a sphere to minimise the surface energy. The ensuing oscillations in particle shape can be represented as a sum of damped normal modes,
\[ A(t) = \sum_l \exp \left( \frac{t}{\tau_l} \right) A_{0,l} \cos(\omega_l t - \alpha) , \]  

where \( A(t) \) is the time-dependent amplitude of the oscillation. \( l \) designates the particular deformation mode of the oscillating particle defined in terms of spherical harmonics with an initial mode amplitude given by \( A_{0,l} \), a modal phase shift of \( \alpha \) and frequency \( \omega_l \). The frequency for the lowest order mode (\( l=2 \)) of a water droplet of radius \( \approx 10 \mu m \) is \( \approx 200 \) kHz. The characteristic damping time for a given mode, \( \tau_l \), is strongly dependent on particle size and is given by:

\[ \tau_l = \frac{a^2 \rho}{(l-1)(2l+1)\eta} \]  

where \( a \) is the radius of the relaxed sphere, \( \rho \) is the density of the particle and \( \eta \) is the viscosity. For a 10 \( \mu m \) radius water droplet of viscosity 1 mPa s, the damping time for such rapidly decaying inertial modes is \( \approx 30 \) \( \mu s \). The time constant for the \( l=2 \) mode can be written as:

\[ \tau_l = \frac{a^2 \rho}{5\eta} \]  

If the viscosity of the particle is higher than a size-dependent critical value (\( \approx 20 \) mPa s for a 10 \( \mu m \) radius droplet),\(^{34}\) the relaxation mechanism is characterised by over-damping and is dominated by a slowly creeping viscous mode with no oscillations in shape. When over-damped, the characteristic time for relaxation in shape is given by:

\[ \tau_l = \frac{2(2l^2 + 4l + 3) \eta a}{l(l+2)(2l+1) \sigma} \approx \frac{\eta a}{\sigma} \]  

where the time-constant for only the primary \( l=2 \) mode need be considered.

Once the relaxation mechanism (either over- or under-damped) can be identified, the time-constant for the relaxation in shape can be used to infer the viscosity of the coalescing particle (from equation 3 or 5), provided the radius, density and surface tension of the particle are known. Indeed, for viscosities below critical damping both the viscosity and surface tension can be retrieved independently from the measurement and no assumptions about surface tension need be made.\(^{66}\) Using this approach we have measured the viscosities of aqueous sucrose solutions and aqueous mixtures of sucrose-sodium chloride over a wide RH and composition...
range (from $>90\%$ RH to $<20\%$ RH)\textsuperscript{34} with estimated viscosities spanning from $10^{-3}$ to $>10^9$ Pa s and for aqueous sodium nitrate aerosol spanning the range $10^{-3}$ to $>10^1$ Pa s.\textsuperscript{67}

In the measurements presented here, the radius and refractive index of the final particle can both be determined with accuracies of $<\pm0.05\%$.\textsuperscript{34,55} The refractive index can be used to infer the particle density from the molar refraction mixing rule using an approach previously described by us.\textsuperscript{68} Even a $1\%$ error in radius and density would lead to only $\sim2\%$ in the inferred viscosity (following from equation (3)) and so we do not consider errors arising from size determination and density any further here. Aqueous salt solution aerosols may have surface tensions in excess of that of water (72.8 mN m$^{-1}$ at 293 K) while organic aerosol may have surface tensions of $<30$ mN m$^{-1}$. Even assuming a single surface tension value of $55\pm30$ mN m$^{-1}$ for all aerosol, as used here, the uncertainty in the viscosity inferred from over-damped relaxation would remain $<\pm50\%$. Even this degree of uncertainty allows an excellent characterisation of the viscosity dependence of an aerosol when varying over as much as 12 orders of magnitude. As already stated, for aerosol droplets with viscosities below $\sim20$ mPa s, no assumptions need be made, with viscosity and surface tension both retrieved from the time-dependent damping behaviour. Indeed, there are other uncertainties that can lead to a larger spread of an order of magnitude in viscosity for particles of the same composition. Before presenting further details of the analysis of coalescing droplets, we briefly review the experimental approach as used for the measurements presented here.

\textit{III.b. The Aerosol Optical Tweezers Technique}

A schematic of the optical tweezers instrument for manipulating aerosol droplets and studying droplet coalescence is shown in Figure 3. An aerosol mist is generated with an ultrasonic nebuliser from an aqueous solution containing involatile (or low volatility) solutes. Droplets of $\sim10\mu$m radius are captured in two optical traps formed from a conventional holographic optical tweezers arrangement using either a Hamamatsu spatial light modulator (SLM, X10468) or a Holoeye SLM (LC-R 2500), mounted in a conjugate plane to the back-aperture of the microscope objective (Olympus ACH, 100x/1.25, oil), and using a laser beam at 532 nm (Laser Quantum Opus 3W).\textsuperscript{34,66} Sequential kinoforms are displayed by the SLM allowing direct control of the separation of the traps and leading to eventual droplet coalescence.\textsuperscript{34,69} A laser power of order $10$ mW in each
optical trap is typical. A high-frame rate camera (Vision Research, Phantom v. 7.3) capable of a time-resolution of 10 μs is used to record brightfield images for low viscosity measurements with relaxation timescales less than 1 ms.\textsuperscript{52} When imaging at less than 1 kHz (>1 ms time-resolution), a Dalsa Genie HM 640 camera was used. A silicon photodetector (Thorlabs DET 110) is used to record the backscattered light intensity from the trapped droplets in combination with a low-load, high bit-rate oscilloscope (either a LeCroy HDO 6034-MS or Wavesurfer 454). Similar to previous studies, backscattered Raman light can be imaged onto the entrance slit of a 0.5 m focal length spectrograph, dispersed by a 1200g/mm grating and equipped with a CCD detector. The Raman spectrum from a droplet consists of a broad underlying spontaneous Stokes’ band with superimposed resonant structure at wavelengths commensurate with whispering gallery modes (WGMs) from which the radius and refractive index of the droplet, both of which can be determined with accuracies of better than ±0.05 %.\textsuperscript{54,55} The RH in the trapping cell is controlled by varying the relative flow rates of dry and humidified nitrogen gas flows, allowing fine control over the water activity of the solution droplet and, thereby, control over solute concentrations. The RH is measured using a capacitance probe mounted in the gaseous outflow from the trapping cell (Honeywell, HIH-4202A). More coarsely, the solute concentration can be varied by changing the solute concentration in the original solution used at nebulisation and trap loading.

\textbf{III.c. Analysis and Determination of the Damping Time for Relaxation to a Sphere}

The three approaches for recording the damping time have been summarised earlier and we have indicated that the uncertainties associated with the determination of particle size, density (from refractive index) and surface tension are small by comparison with the uncertainties in the damping time constant. In previous measurements for sucrose particles, mean viscosities were reported from a number of coagulation events with a spread that was typically a factor of 5 from the lowest to the highest value at a single RH with viscosities spanning from $10^{-3}$ to $10^9$ Pa s.\textsuperscript{34} This variation represents the variation in the recorded time constant for the relaxation in shape at the RH reported by the capacitance probe. In this publication, we report viscosities inferred from relaxation times determined by elastic light scattering and brightfield imaging. We shall consider these two approaches, describing how the measurements are made and analysed to yield time constants. Examples of measurements in damping time with particle viscosity using these two approaches are shown in Figure 4 for
aqueous-sucrose aerosol at RHs in the range 41 to 95 % RH with damping times spanning from 210 s to 11 μs.

Elastic backscattered light (532 nm) was collected with a silicon photodetector and recorded with a low-load, high bit-rate oscilloscope. As discussed in previous work, the time-dependent elastic backscattered light provides a highly time-resolved measurement of the changing droplet shape for the period around the coalescence event. The oscilloscope was triggered at the onset of coalescence of two trapped droplets when the elastic backscattered light intensity surpassed a user-determined threshold. For underdamped coalescence (low viscosity, <20 mPa s), the relaxation time was determined by fitting the maxima in the oscillations in the elastic backscattered light (for an example, see the inset in Figure 3) to an exponential decay using a nonlinear least-squares algorithm. Initially, the elastic backscattered light intensity does not follow an exponential decay due to the high level of distortion in droplet shape; thus, the number of oscillation maxima included in the fit was systematically varied to produce the fit most consistent with the later portion of the backscatter signal. For overdamped (higher viscosity) coalescence (as in the examples in Figure 4), the portion of the elastic backscattered light signal after the maximum was fit to an exponential decay. The uncertainty in the fitted relaxation time constant was determined by systematically varying the initial time point included in the least squares fit and taking the average and standard deviation of the best fits. This approach generally agrees with expected values to better than 0.5 mPa·s for particles with viscosity up to ~100 mPa s, and the elastic backscattered light is in quantitative agreement with extraction of the relaxation time constant from high frame rate images for relaxation times ≤1 ms. For relaxation times longer than ~1-2 ms, the time-dependent position of the composite droplet in the optical trap complicates interpretation of the elastic backscattered light as the composite droplet moves towards the equilibrium trap position. For these higher viscosity droplets, the analysis of the brightfield images provides a more accurate determination of the relaxation time constant.

The time-dependence of the aspect ratio of the coalescing pair of droplets can be determined from a sequence of brightfield images following initial contact; examples are shown in Figure 4. The image corresponding to the time of contact between the two droplets is identified as the time at which there is no longer a detectable gap between the two droplets and when the two droplets no longer move independently. The brightfield image for which these conditions are satisfied is tagged as the t=0 s image for the coalescence event and the aspect
ratio of the two connected droplets is reported as X/Y for subsequent times. X is the largest distance between the edges of the coalescing particle and Y is the maximum distance between the edges along an axis orthogonal to X; these need not correspond simply to the horizontal/vertical dimensions on the image, but may vary as the position and orientation of the trapped composite droplet fluctuates during shape relaxation. The aspect ratio at the point of contact may not be exactly 2 as the two droplets are unlikely to have the same diameter. Immediately after contact, one of the spherical halves of the relaxing particle remains tightly held within the optical trap and within the plane of focus, while the other often rotates out of the focal plane; an example is shown in Figure S.16. As a consequence, the aspect ratio of the two conjoined halves cannot be accurately measured for a period of time (at times from <10 to ~300 s in Figure S.16). Once the composite particle has progressed significantly towards a relaxed sphere (at times longer than ~300 s in Figure S.16), the aspect ratio can once again be determined. The damping time, τ, can then be readily calculated from an exponential fit to the time-dependence in the aspect ratio inferred from the in-plane image. Typical uncertainties in the fitted damping time are ±5 %; the specific uncertainty for each coalescence event is used to estimate viscosity.

**III.d. Representation of Viscosity Data and Uncertainties Arising from Environmental Conditions**

When reporting the dependence of viscosity on RH/water activity (see, for example, Figure 5(a)), it must be remembered that the uncertainty associated with the RH capacitance probes used in this experiment is ±2 %, even when routinely calibrated. Thus, variability in the reported dependence of viscosity on RH will arise from this imprecision in RH determination and control. In the case of a glass forming aerosol, such as that formed from an aqueous-glucose mixture, the viscosity can increase by 15 orders of magnitude with decrease in RH from 100 to 0 %. This corresponds to an average increase of an order of magnitude in viscosity over a change in RH of ~7 %, typically a factor of ~5 across the uncertainty range set by the RH probe, similar to the level of reproducibility we have observed in previous measurements for glass forming aerosol. Another method for reporting the compositional dependence of the viscosity is to report the variability with inferred particle refractive index from the fitting of the WGMs appearing in the Raman spectrum (see Figure 5(b) for the analogous plot for the example shown in Figure 5(a)). The mass fraction of solute can then be inferred from refractive index by applying the molar refraction mixing rule. Although a potentially more accurate measurement of aerosol composition than inferring from RH, radial inhomogeneities in particle composition can be formed during conditioning/drying to the RH of a specific measurement, leading to systematic errors.
in composition. As a consequence, there is no noticeable improvement in the reproducibility of the compositional dependence of viscosity, as seen in the comparison shown in Figure 5(c) (note that the aqueous-glucose system is merely used as an example). The different dependencies in the viscosity with composition reported in Figure 5(c) arise from the different systematic errors incurred when estimating the mass fraction of solute from RH or from the RI. For the former conversion, the inaccuracies of thermodynamic models at high mass fractions of solute (i.e. under dry conditions) are well known. In the latter case, the determination of composition from RI requires knowledge of the density and refractive index of the pure organic component as a supercooled melt, both quantities similarly associated with large uncertainties.

Generally, we report parameterisations of viscosity with the measured RH for the measurements presented here, concluding that this allows the most general characterisation of the aerosol state across all measurements, and is independent of chemical system, particle viscosity or conditioning time. For a subset of systems (for aqueous-maltose, aqueous-raffinose, aqueous-1,2,4-butanetriol, aqueous-erythritol, aqueous-1,2,6-hexanetriol, aqueous-sorbitol, aqueous-glutaric acid, aqueous-maleic acid, aqueous-Cappa mixture), measurements of viscosity have been made at RHs greater than 90 %. For these measurements, the RH-probes are considerably less accurate and the values of the droplet RIs have been used to estimate the RHs using the molar refraction mixing rule. Indeed, at these high RHs, the water activity can be retrieved with high accuracy as the solute concentrations may be below the solubility limit, allowing direct comparison with sub-saturation bulk phase measurements. Given the viscosities are mostly <<1 Pa s at these high RHs, a droplet composition equilibrates quickly to the gas phase RH; thus, an assumption of a homogeneous refractive index when fitting WGM fingerprints is valid, ensuring that an accurate determination of droplet RI results. All experimental data are reported as RH-dependent viscosities (mostly as linear or quadratic functions of RH) providing the most general form for any future use. All viscosities reported are inferred from individual coalescence events.

A further source of variability in the reported viscosities arises from the conditioning time allowed for the pair of particles to equilibrate at the RH of the measurement prior to coalescence. When the droplets are viscous, water transport is inhibited and may take many thousands of seconds. In Figure 6 we show an example of the influence of the conditioning time on the measured viscosity for aqueous-sucrose particles at 60 % RH. Sucrose
solution droplets, initially at 80 % RH, were dried to 60 % RH; the coalescence between different pairs of droplets was initiated at times of 0, 120, 240, 600, 1400, 2000 s following the initiation of the RH change, corresponding to different degrees of drying and equilibration towards the final composition expected at 60 % RH. With increase in conditioning time and, hence, increase in time for drying, the reported viscosity increases towards a steady value. The relationship of the inferred viscosity to the timescale for water transport kinetics can be clearly identified (with an example also shown in Figure 6 for one specific droplet drying event). Both the time-dependence of particle size and the conditioning-time dependence of the measured viscosity can be fit to the Kohlrausch-Williams-Watts equation: 

\[ F(t) \approx \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right] \]  

(6)

where \( \tau \) is the characteristic relaxation time and \( \beta (< 1) \) decreases markedly as the system approaches a glass transition. The response function, \( F(t) \), takes the form:

\[ F(t) = \frac{\sigma(t) - \sigma(\infty)}{\sigma(0) - \sigma(\infty)} \]  

(7)

where \( \sigma(t) \) is the evolving time response of a relaxing parameter (viscosity or size) and \( \sigma(0) \) and \( \sigma(\infty) \) are the values for the initial and final states, respectively. The KWW equation has been shown to provide a robust functional form for characterising the relaxation timescales for viscous aerosol following a perturbation.74,75 The time-constants are of similar magnitude for the viscosity response and size response, although the response in viscosity is consistently slower than the water transport. The reason for this is not clear and will be the subject of a future study. However, we can conclude that typical conditioning times for particles with viscosities \( >10^6 \) Pa s must be extended beyond 1 hour for a reliable measurement of viscosity to be achieved, otherwise the viscosity determined may be considerably lower than reality. It must be recognised that, even with this extended period of conditioning, the compositions and viscosities of the coalescing particles may not be fully relaxed/uniform for the most viscous aerosol studied.

III.e. Bulk Phase Measurements of Viscosity

Bulk viscosity measurements were made using a TA Instruments DH-1 Rheometer, as described in Booth et al.9 Details of the method are summarised here. The system consists of an upper and lower plate, the upper plate is mechanically controlled and sensors monitor the radial displacement, torque and the lateral force. The lower plate has a peltier element for precise temperature control of the sample. The upper plate (diameter 40
mm) is lowered onto the sample with the distance between plates set to 1500 µm. For some highly viscous samples, the samples are heated to improve the flow properties before the plate distances are set. The rheometer can be operated in rotational mode to obtain stress vs. strain measurements where the slope is the viscosity or, alternately, it can be operated in oscillation mode which provides additional information (see Supporting Information, Section SI.17). For our oscillation experiments we chose a small displacement of $1 \times 10^{-4}$ radians based on experience with polymer melt samples and an oscillation frequency of 1 Hz. Heating and cooling temperature ramps were from -20 to 40°C to cover cold tropospheric regions to the hottest. The temperature rate was 5°C/min to match typical differential scanning calorimetry rates and is typically of maximum possible cooling rates an aerosol particle might experience during rapid convection in a cloud system. The coefficient of expansion of the steel parallel plates was measured over the range of temperatures to allow us to compensate for the thermal expansion of the metal plates. To account for volume changes in the sample, the distance between the plates was constantly adjusted to maintain a constant lateral (perpendicular to plate) force of 4 N for solid–like samples, with a viscosity of $10^{12}$ Pa.s noted as the upper limit.

IV. Results and Discussion: Comparison of Aerosol and Bulk Phase Measurements with Predictions of Viscosity for Benchmark Systems

We report here measurements of the viscosity of aqueous-organic aerosol droplets extending over an RH range from close to 0 % to 100 % RH. As described earlier, uncertainties in RH are those associated with the reported uncertainties in the capacitance RH probe or, at high RHs in the underdamped regime, from the uncertainties in the particle refractive indices used to estimate the water activity of the measurement. The uncertainties in the reported viscosities are the standard deviations associated with an average of multiple measurements made over a narrow range in RH about the reported RH value. All measurements were made at 293 K. Where possible, these data are compared with new bulk phase measurements or data available in the literature. We also compare the measurements with predictions from the models described in Section II.

IV.a. Molecules with an Alcohol Functionality

In Figure 7(a), we present measurements of the viscosities of a sequence of aqueous solutions of alcohols with increasing carbon chain length and increasing number of hydroxyl groups, specifically: 1,4-butanediol, 1,2,4-butanetriol, 1,2,6-hexanetriol, 1,2,3,4-butanetetraol (erythritol), 1,2,3,4,5,6-hexanhexol (sorbitol) and 1,2,3-
propanetriol (glycerol, dry conditions only). The RH dependencies are fit to a log-linear dependence on RH and constrained to the viscosity of pure water at 100 % RH, infinite dilution of the alcohol. The functional forms for these fits and the numerical values for the measured points are presented for each system in the Supporting Information. Some general trends become apparent. At a specific RH, the viscosity increases with increasing carbon chain length. For example, the viscosity increases by approximately one order of magnitude on progressing from 1,2,3-propanetriol to 1,2,4-butanetriol to 1,2,6-hexanetriol, an increase in the carbon chain length of 3 units, with two of the alcohol groups being in the 1,2-positions and the third at the opposite end of the molecule. More significantly, the viscosity under dry conditions increases by more than 4 orders of magnitude on progressing from 1,4-butanediol (~0.09 Pa s) to 1,2,4-butanetriol (~2 Pa s) to 1,2,3,4-butanetetraol (~3000 Pa s), clearly indicating the critical factor that the number of OH groups plays in determining the viscosity.

Detailed comparisons of predicted RH dependencies with measurements are presented for all systems in the Supporting Information with a representative trend shown for 1,2,4-butanetriol in Figure 7(b). While the predicted pure component viscosity for the least viscous system (0.102 Pa s) is accurate to within ~10 % (see Section SI.6), the errors in the predictions become larger for the more viscous systems (see SI.7 and SI.8); notably, there is even an overestimate by an order of magnitude for 1,2,4-butanetriol (~24 Pa s) which has a viscosity only one order of magnitude outside the viscosity range for which previous model benchmarking has been possible. It should also be noted that the bulk phase measurements for the pure organic liquids and aqueous solutions are in excellent agreement with most of the aerosol optical tweezers measurements when comparison can be made, i.e. when the stable thermodynamic phase is a liquid at room temperature or when a solution phase measurement can be made at a concentration below the solubility limit. Good agreement is seen between aerosol and bulk measurements for aqueous-1,2,4-butanetriol (SI.7), aqueous-sorbitol (SI.10) and aqueous-glycerol (SI.15) solutions, while for aqueous-erythritol (SI.8), agreement is within one order of magnitude.

Close examination of the data presented in the Supporting Information indicates that the inclusion of non-ideality in the Bosse model is best able to represent the viscous properties of the mixture. The only exception are the bulk data for the viscosity of aqueous-1,4-butanediol (SI.6). Although the aerosol measurements are
consistent with predictions from the Bosse model, the water activity dependence from the bulk measurements is much more in line with predictions from GC-UNIMOD. It should be noted that the discrepancy may come about from inaccuracies in estimates of mixture water activities derived from the known bulk mixture compositions; here we used AIOMFAC to perform this conversion. Alternatively, it is interesting that there appears to be a step in viscosity from $\sim 10^{-2}$ Pa s to $\sim 10^{-1}$ Pa s at an RH below 40 % RH; this transition is around the viscosity estimate for critical damping and could reflect the incompleteness of the treatment used here for analysing the droplet damping time in this transition regime (Section III.a). Although this requires further exploration, the focus of this study is on systems with viscosity larger than 1 Pa s.

The level of agreement between the model predictions and the measurements at all RHs is summarised in Figure 8(a), clearly showing the worsening level of accuracy in the predictions of the pure component as the viscosity of the pure component increases. Pure component values of a liquid phase could only be measured for three systems, with the values for both of the systems with viscosities above 1 Pa s in error by more than an order of magnitude. In Figure 8(b) we compare the viscosity predictions with measurements if the predicted pure component value is scaled to provide agreement with the value at 0 % RH determined from the bulk data or an extrapolation of the parameterisation of the RH-dependent aerosols data if the bulk data is not available. From this rescaling, it is clear that the level of agreement is generally improved across the full RH range although some errors of more than an order of magnitude remain at intermediate RHs, presumably a consequence of the failure to adequately represent the non-ideality in the intermolecular interactions.

**IV.b. Aqueous Aerosol Containing Saccharides**

A comparison of the RH-dependent trends in viscosity of the series of saccharides is provided in Figure 9(a) with a comprehensive report of all of the data available in the Supporting Information. Generally, at a particular RH, there is clearly a general trend towards higher viscosity with progression from mono-saccharide (glucose) to di-saccharide (sucrose, trehalose, maltose) to tri-saccharide (raffinose). Unlike for the straight-chain alcohols, the predictions of pure component viscosities from the Nanoolal et al. model for the pure organic melts are in significant error, leading to very large overestimates in the viscosities of the aqueous solutions by many orders of magnitude, as reported in Table 1.
Aerosol measurements and predictions for aqueous-sucrose mixtures are shown in Figure 9(b) as an example. Notably, there is excellent agreement between bulk and aerosol measurements for the systems where comparison can be made, specifically: aqueous-glucose (above ~85 % RH, SI.1), aqueous-sucrose (above ~85 % RH, SI.2), aqueous-trehalose (above 90 % RH, SI.3). Both the bulk and aerosol measurements most clearly follow mixture predictions using either the Bosse non-ideal mixing or ideal mixing treatments, with GC-UNIMOD showing a significantly stronger dependence at higher RH that is not seen experimentally. This conclusion is also clear from the correlation analysis shown in Figure 8(a). Unlike the sequence of alcohols, for which the pure component values can be directly measured in the bulk phase or estimated from the RH-dependent trends, we have constrained the model predictions for the saccharides to pass through $10^{12}$ Pa s at the known moisture driven glass transition RH. The scaled predictions provide a much closer representation of the experimental data, Figure 8(b), although the pure component values can still be in very large error (Table 1).

**IV.c. Aqueous Aerosol Containing Di- and Tri-Carboxylic Acid**

Finally, measurements of the viscosities of aqueous aerosol droplets containing di-carboxylic acids (glutaric acid, maleic acid) and tri-carboxylic acids (citric acid) are shown in Figure 10, along with measurements for the mixture of 9 dicarboxylic acids referred to as the Cappa mixture. As for the sequence of alcohol systems, the addition of a further functional group, in this case the addition of a carboxylic acid group, can lead to a significant change in the viscosity at a chosen water activity. From the measurements, an increase of viscosity of ~8 orders of magnitude under dry conditions is observed for the pure component on progressing from a di- to a tri-carboxylic acid. Predictions of pure component viscosities from the Nanoolal model suggest a considerably weaker dependence on number of carboxylic acid groups, with values of $1.5\times10^5$ Pa s and 0.5 Pa s estimated for citric acid and the Cappa mixture, respectively.

Considering the tricarboxylic acid alone in Figure 10(a) (and section SI.11), excellent consistency is observed between the trends from bulk and droplet measurements, although bulk measurements are inaccessible under the supersaturated conditions reported in the aerosol phase measurements. Again, both the ideal and non-ideal mixing model of Bosse are more closely able to represent the measured trend that the predictions of GC-UNIMOD, consistent with the measurements within their experimental error. It is rather interesting to note
that the prediction of the pure component viscosity of citric acid from the Nanoolal et al. model\textsuperscript{42} is an underestimate of the measured value by approximately one order of magnitude.

In contrast to the comparison for the tri-carboxylic acid system, the pure component estimates for the di-carboxylic acid systems are an over estimate by an order of magnitude or more, although this is based on a significant extrapolation of the experimental data. The measurement range is limited to relatively high RHs compared to other systems, as indicated in Figure 10(b). As the viscosity approaches the critical damping viscosity of \( \approx 20 \) mPa s for droplets of the size studied here, large errors in estimated viscosities can result as the droplet transitions from under- to over-damped coalescence dynamics.\textsuperscript{34} Within the accessible RH range, the viscosity measurements are extremely accurate and there is excellent agreement (within factor of 2) between bulk and aerosol measurements at RHs above \( \approx 93 \% \) (see section SI.12). The measured values of viscosity for the mixture of di-carboxylic acids, the Cappa mixture, suggest that the dry aerosol viscosity should remain less than \(<1\) Pa s. Although this is consistent with all model predictions, previous measurements using the bulk rheometer described here have suggested the viscosity should be \(<10^6\) Pa s.\textsuperscript{9} This highlights the challenges associated with making bulk measurements of viscosity of components that can be expected to surpass their solubility limit and crystallise. Perhaps unsurprisingly, the viscosity of the complex mixture from straight chain dicarboxylic acids follows a very similar trend with RH to the single component studied alone, glutaric acid.

For the carboxylic acids as whole, it can be concluded that the viscosities of aqueous mixtures are reasonably well represented by predictions from the combination of the Nannolal et al.\textsuperscript{42} model of pure component viscosities and the Bosse non-ideal mixing rule. This trend is observed in the correlation analyses shown in Figures 8(a) and 8(b). Indeed, the predictions seem better able to represent the organic acid systems than the small sample set of alcohols and saccharides considered here, although it should be recognised that citric acid contains one alcohol group as well as three carboxylic acid groups.

**V. Conclusions**

In summary, we have explored the accuracy of predicting mixed component aerosol viscosities using a combination of pure component viscosity predictions from the method of Nanoolal et al.\textsuperscript{42} with the use of the
GC-UNIMOD mixture prediction model,\textsuperscript{41} ideal mixing or non-ideal mixing using the model of Bosse.\textsuperscript{43} The accuracy of these predictive tools has not been rigorously tested before at viscosities above 1 Pa s. Measurements of coalescence relaxation times following the coagulation of pairs of aqueous-organic droplets can be used to infer the viscosity of aerosol from low viscosity liquids formed from dilute solutes in water (10\textsuperscript{-3} Pa s) up to a viscosity approaching the glass transition (10\textsuperscript{10} Pa s) for a pure sub-cooled melt formed by the solute. The combination of Nanoolal et al. predictions of pure component viscosity with either non-ideal or ideal mixing reproduce the RH-dependent trends particularly well for the sequence of straight chain alcohols studied and for the di- and tri-carboxylic acid systems (Figures 8(a) and 8(b)), even at viscosities extending up to 10\textsuperscript{6} Pa s. By contrast, predictions can be an over-estimate by many orders of magnitude for the mono-, di-, and tri-saccharide systems, components for which the pure component sub-cooled melt viscosities could be >>10\textsuperscript{12} Pa s. In all cases, predictions from the GC-UNIMOD method\textsuperscript{41} for treating the mixtures perform poorly when compared with both Bosse methods,\textsuperscript{43} suggesting that water has a much lower plasticising effect on mixture viscosities than is actually observed.

We consider again the predicted viscosities of organic components expected to be observed in typical atmospheric aerosol oxidation schemes (i.e., Figure 1 for the oxidation of \(\alpha\)-pinene). The decreasing accuracy of the predictive tools as the viscosity increases, particularly above 10\textsuperscript{6} Pa s, may be expected to lead to increasing errors in the viscosity predictions at high O:C ratio and low vapour pressure, and inaccuracies in the distribution of viscosities predicted, Figure 1(c). However, it can also be seen that components with expected viscosities higher than 10\textsuperscript{6} Pa s (recognising this itself is from the model prediction!) number only \textasciitilde1400 out of a total number of >50,000 in the oxidation scheme in the GECKO-A simulations. Although not making any allowance for gas-particle partitioning here, it seems unlikely that the viscosity of \(\alpha\)-pinene SOA is much larger than 10\textsuperscript{6} Pa s. Not only does water act as a plasticiser, but lower viscosity organic components can act as plasticisers reducing the viscosity of the organic matrix; indeed, we have recently show that maleic acid can significantly reduce the viscosity of sucrose containing aerosol in ternary maleic acid-sucrose-water aerosol.\textsuperscript{76} Further, volatilisation measurements of semi-volatile components and measurements dependent on aerosol mixing timescales both suggest that the viscosity of \(\alpha\)-pinene SOA is most likely in the range 10\textsuperscript{5} to 10\textsuperscript{8} Pa s.\textsuperscript{19,23} Hosny et al.\textsuperscript{31} report a value that is consistent with a value of 10\textsuperscript{5} to 10\textsuperscript{6} Pa s although the lowest
RH of their measurement is 70 %. Zhang et al.\textsuperscript{77} report a value of between $10^7$ and $10^9$ Pa s at an RH of <5 %, based on measurements that examine the RH dependence of the dynamic shape factor of aerosol produced by coalescence of viscous SOA particles. By contrast, poke-flow measurements suggest the value is larger than $10^9$ Pa s.\textsuperscript{48} Future work on more complex mixtures would further allow the refinement of these predictive viscosity tools and provide greater insights into the rheological properties of complex atmospheric aerosol.

**Supporting Information**

The supporting information available with this paper contains comprehensive tables of all measured data points (bulk and aerosol measurements), tables of the polynomial fits, figures that show the comparisons between measurements and predictions for each system and further figures on the analysis methods used.

**Acknowledgements**

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Table 1. A comparison of the inferred values of the viscosities of pure amorphous saccharide aerosol from the parameterisations of the experimental data with the unscaled Nanooolal et al. predictions or with the values from the Bosse non-ideal mixing model if the predictions are constrained to go through the reported RH of the moisture driven glass transition.  

<table>
<thead>
<tr>
<th></th>
<th>Log (Measured Viscosity / Pa s)</th>
<th>log (Predicted unscaled Viscosity / Pa s)</th>
<th>log (Predicted scaled Viscosity / Pa s)</th>
<th>The glass transition RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>8.719</td>
<td>16.171</td>
<td>11.878</td>
<td>0 %</td>
</tr>
<tr>
<td>Sucrose</td>
<td>15.924</td>
<td>42.766</td>
<td>32.684</td>
<td>23 %</td>
</tr>
<tr>
<td>Maltose</td>
<td>18.652</td>
<td>46.705</td>
<td>41.558</td>
<td>32 %</td>
</tr>
<tr>
<td>Trehalose</td>
<td>19.017</td>
<td>16.171</td>
<td>23.759</td>
<td>22 %</td>
</tr>
</tbody>
</table>
Figures

Figure 1. (a) Predicted viscosities of compounds derived in the atmospheric oxidation of α-pinene in the Master Chemical Mechanism as a function of predicted saturation vapour pressure and O:C ratio. Note that the viscosity is shown as a colour scale with a logarithmic base-10 value. For comparative purposes, compounds generated from the GECKO-A model for α-pinene simulations are marked as grey symbols. (b) Predicted viscosities of compounds derived within the GECKO-A model for α-pinene simulations as a function of predicted saturation vapour pressure and O:C ratio. Note that the viscosity is shown as a colour scale with a logarithmic base-10 value. (c) Predicted distribution of viscosities for the compounds identified in the GECKO-A model.
Figure 2. Comparison of mixing rule predictions for aqueous-glucose (upper curves) and aqueous-1,4-butanediol (lower curves) mixtures. Solid pink lines, GC-UNIMOD; dashed red lines, ideal mixing; dotted blue lines, Bosse with non-ideal mixing. The symbols indicate the measurements for these two systems reported in Section IV with the solid black (grey) lines and orange envelopes indicating the RH-dependent fit to the experimental data.
Figure 3. Schematic of aerosol optical tweezers instrument used to perform measurements of aerosol viscosity. Of particular importance for this work, the image of the coalescing droplet pair can be recorded by brightfield microscopy synchronously with the measurement of the intensity of elastic backscattered light. The droplet pair are manipulated in real-time by controlling the kinoform displayed on the spatial light modulator. The Raman spectra are recorded using the spectrograph/CCD.
Figure 4. Examples of the dependence of the damping time on particle viscosity as measured from the elastic light scattering (lowest viscosity event, open squares) and aspect ratio from brightfield images following coalescence (remaining four events). The measurements shown are for aerosol droplets of aqueous-sucrose at RHs of 95, 89, 79, 52 and to 41 % with damping times increasing from left to right, respectively, and spanning from ~10 µs to 210 s. For comparison, the image panels show the sequence of brightfield images recorded for each of the coalescence events. With the high frame rate imaging (at RHs of 95, 89 and 79 %), the minimum integration time is between 10 and 40 µs, dependent on the region of interest selected on the camera for the imaging measurement.
Figure 5. Example of the dependence of viscosity on (a) RH/water activity and (b) measured refractive index for aqueous-glucose aerosol droplets. (c) Comparison between the compositional dependencies of viscosity inferred from RH (black circles) and from refractive index (red circles), using the AIOMFAC model of the equilibrium solution composition are shown.
Figure 6. (a) Example of the influence of the conditioning time on the measured viscosity for aqueous-sucrose particles at 60% RH. Each points are measured from different conditioning time 0, 120, 240, 600, 1400, 2000s. The red line represents a KWW fit to the viscosity data with a time-constant of 760 s. (b) Example of the response function in particle size of last three points (black, 600 s; green, 1400 s; blue, 2000 s) in panel (a) following the initiation of the droplet drying process (RH decrease from 80% to 60%) and recorded to the coalescence event at the last time recorded for each transition. The red lines indicate the KWW fits for the 3 response functions with time constants of 345, 350 and 356 s for increasing times of 600, 1400 and 2000 s, respectively.
Figure 7. (a) Viscosities of aqueous solutions of a series of straight chain alcohols, bottom to top: 1,4-butandiol, 1,2,4-butanetriol, 1,2,6-hexanetriol, 1,2,3,4-butanetetraol (erythritol), 1,2,3,4,5,6-hexahexol (sorbitol). The red circle at 0% RH indicates the viscosity of pure 1,2,3-propanetriol (glycerol). Experimental points are indicated only for the lowest and highest viscosity mixtures so as to indicate the spread in the data values and indicate the typical level of uncertainty; a more comprehensive account is provided in the SI. The lines and envelopes indicate the linear fits and uncertainties derived from the aerosol measurements. (b) Representative comparison of the predicted and measured RH-dependencies of mixtures of aqueous solutions of 1,2,4-butanetriol. Experimental data: black circles, experimental data (this study); orange line and orange shaded region, parameterisation of all experimental data; red circle, pure solution bulk-phase viscosity measurement. Model predictions: dashed lines, mixture viscosities based on predictions of pure component viscosities from the Nanoolal et al.\textsuperscript{42} model; solid lines, scaled viscosities such that the mixture viscosity passes through 1 Pa s at the measured viscosity value for the pure liquid; red lines, ideal mixing rule; blue lines, Bosse mixing model;\textsuperscript{43} pink lines, GC-UNIMOD.\textsuperscript{41}
Figure 8. (a) Correlation of measured viscosities for aqueous solutions of straight-chain alcohols, saccharides and carboxylic acids with unscaled predictions from the estimates of the pure component viscosities from the model of Nanoolal et al. and the Bosse non-ideal mixing model. Symbols: pink triangles, straight chain alcohols; blue circles; di- and tri-carboxylic acids; black squares; saccharides. The filled symbols indicate the pure component values with the black square indicating that the predicted viscosities for the saccharides are >>10^12 Pa s. (b) Correlation of measured viscosities for aqueous solutions of straight-chain alcohols, saccharides and carboxylic acids with scaled predictions from the estimates of the pure component viscosities from the model of Nanoolal et al., same symbols as in panel (a) (see text for further details).
**Figure 9.** (a) Viscosities of aqueous solutions of a mono-saccharide (glucose, black), three di-saccharides (sucrose, red; trehalose, blue; maltose, pink) and a tri-saccharide (raffinose, orange). (b) Representative comparison of predicted and measured RH-dependencies of mixtures of aqueous solutions of aqueous-sucrose. Experimental data: black circles, experimental data (this study); orange line and orange shaded region, parameterisation of all experimental data; grey circles, previous study of aqueous-sucrose by Power et al. Model predictions: dashed lines, mixture viscosities based on predictions of pure component viscosities from the model of Nanoolal et al.; solid lines, scaled viscosities such that the mixture viscosity passes through a viscosity of $10^{12}$ Pa s at the reported value of the moisture driven glass transition, RH ~ 23 %. Pink lines, GC-UNIMOD; red lines, ideal mixing; blue lines, Bosse with non-ideal mixing.
Figure 10. (a) Measured viscosities of aqueous solutions of the tricarboxylic acid citric acid (orange). Experimental data: black circles, experimental data (this study); orange line and orange shaded region, parameterisation of all optical tweezers data; red circles, bulk solution viscosity measurements. Model predictions: dashed lines, mixture viscosities based on predictions of pure component viscosities from the model of Nanooolal et al.\textsuperscript{42}; solid lines, scaled viscosities such that the mixture viscosity passes through a viscosity of $\sim 10^6$ Pa s for the pure organic component, the value estimated from the fit to the experimental data. Pink lines, GC-UNIMOD; red lines, ideal mixing; blue lines, Bosse with non-ideal mixing. (b) Comparison of RH-dependent viscosities of aqueous solutions of the dicarboxylic acids (blue, glutaric acid; red, maleic acid) and the Cappa mixture (pink). The darker shaded regions of the uncertainty envelopes indicate the RH ranges over which measurements were made.