The development of a group-contribution model to predict the viscosity of organic aerosol

Natalie R. Gervasi

Department of Atmospheric and Oceanic Sciences McGill University, Montreal July 2019

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

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Acknowledgements

First and foremost, I am extremely thankful to my research supervisor, Prof. Andreas Zuend, who has been so supportive and generous with his time in guiding me through this work. I am especially grateful for his insightful discussions, his enthusiasm for my work, and his professional advice. I would also like to extend my gratitude to Prof. Parisa Ariya who has been very encouraging of my research and who has been a wonderful role model for me.

I am very appreciative of Prof. Thomas Preston for his review of this thesis and to Camilo Serrano Damha for his generous help on the French translation of the abstract. Special thanks are also due to the Department of Atmospheric and Oceanic Sciences (AOS) administrative staff for their valuable help over the past two years.

To my wonderful AOS friends and colleagues, thank you for sharing this chapter of life with me. You are the reason my experience at McGill has been incredible and I feel so lucky to have spent this time with such an intelligent, caring, and hilarious group. Lunches will never be the same without you all.

Finally, I extend my deepest gratitude and love to my parents, Marie and Gino, and my brother, Matthew, for their unconditional support and belief in me.

Abstract

Atmospheric aerosol particles have an unequivocal effect on the climate system and human health. They influence Earth's energy budget through their impact on cloud formation and lifetime, and by scattering and absorbing solar radiation. Aerosol particles are ubiquitous in Earth's troposphere. Having a near–global spatial extent, they have been found in both pristine and anthropogenically impacted regions. The Intergovernmental Panel on Climate Change considers our understanding of aerosol particles to be lacking, despite their importance as radiative forcing agents and their role in the Earth's hydrological cycle (IPCC, 2013). The uncertainties regarding aerosol particles and by extension, the difficulty in quantifying their climatic affects, is owing to their chemical and physical complexity. Aerosol particles can have a variety of compositions, morphologies, and phase states. In addition, these aerosol properties can evolve drastically through physiochemical processes over the course of a particle's lifetime in the atmosphere.

Recent findings have demonstrated that organic aerosol (OA) can exist in a highly viscous (semi-solid) or even an amorphous glassy state in typical tropospheric conditions (Zobrist et al., 2008; Virtanen et al., 2010; Slade et al., 2019). In highly viscous OA, the gas-particle partitioning of organic molecules and heterogeneous reactions in the particle bulk are kinetically limited by slow diffusion (Abramson et al., 2013; Liu et al., 2018). As a consequence, the characteristic equilibration time of OA may be minutes, hours or even as long as days—orders of magnitude longer than their well-mixed liquid counterparts. Therefore, precise knowledge of OA phase state is necessary for understanding their growth, aging, and evapouration in the atmosphere.

To this end, the aim of this thesis is to investigate the complexity of OA phase state through the development of a thermodynamic-based group-contribution model to predict the aerosol particulate matter (PM) dynamic mixture viscosity. The mixture viscosity model, AIOMFAC-VISC presented here is a robust tool for predicting the viscosity of aqueousbinary, multicomponent, and SOA surrogate mixtures across the liquid, semi-solid, and amorphous glassy regime ($\sim 10^{-3} - 10^{12+}$ Pa s). Future work will involve using the mixture viscosity predictions from AIOMFAC-VISC to determine characteristic equilibration times in OA via the Stokes–Einstein equation or a modified, Fractional Stokes–Einstein relation.

Abrégé

Les particules d'aérosols atmosphériques (AO) ont un effet incontestable sur le système climatique et la santé humaine. Ils influencent le bilan énergétique de la Terre à travers leur impact sur la formation et la durée de vie des nuages, ainsi que par la diffusion et l'absorption du rayonnement solaire. Les particules d'aérosols sont omniprésentes dans la troposphère terrestre. Ayant une étendue spatiale presque planétaire, ils se retrouvent tant dans les régions vierges que dans celles fortement influencées par l'activité humaine. Le Groupe d'experts intergouvernemental sur l'évolution du climat (GIEC) estime que notre compréhension des particules d'aérosols est limitée malgré leur importance en tant qu'agents de forçage radiatif et leur rôle dans le cycle hydrologique de la Terre (IPCC, 2013). Les incertitudes liées aux particules d'aérosols et, par le fait même, la difficulté à quantifier leurs effets climatiques sont dues à leur complexité chimique et physique. Les aérosols peuvent avoir différentes compositions, différentes morphologies et divers états. De plus, ces propriétés peuvent évoluer de manière drastique par le biais de processus physico-chimiques au cours de la vie d'une particule dans l'atmosphère.

Des découvertes récentes ont démontré que les aérosols organiques (AO) peuvent exister dans des états très visqueux (semi-solides) ou même amorphes vitreux dans des conditions troposphériques typiques (Zobrist et al., 2008; Virtanen et al., 2010; Slade et al., 2019). Dans le domaine hautement visqueux, le partitionnement des molécules organiques entre la phase gazeuse et particulaire, ainsi que les réactions hétérogènes dans la masse des particules sont limitées cinétiquement par la diffusion lente (Abramson et al., 2013; Liu et al., 2018). De ce fait, le temps caractéristique d'équilibrages des aérosols organiques (AO) peut s'étendre de quelques minutes jusqu'à quelques heures, voire même quelques jours, ce qui représente des ordres de grandeur de temps plus longs que dans le cas d'aérosols liquides bien mélangés. Par conséquent, une connaissance précise de l'état de la matière des aérosols organiques (AO) est nécessaire afin de comprendre leur croissance, leur vieillissement et leur évaporation dans l'atmosphère.

À cette fin, l'objectif de cette thèse est d'étudier la complexité de l'état de matière de

l'aérosol organique (AO) à travers le développement d'un modèle de contribution de groupes basé sur la thermodynamique, afin de prédire la viscosité du mélange dynamique de matière particulaire (MP) d'aérosol. Le modèle de viscosité du mélange AIOMFAC-VISC présenté ici est un outil robuste pour prédire la viscosité des mélanges aqueux binaires, à constituants multiples, et de substituts d'aérosols organiques secondaires (AOS) dans le régime liquide, semi-solide et amorphe vitreux (~ $10^{-3} - 10^{12+}$ Pa s). Les travaux futurs consisteront à utiliser les prévisions de viscosité du mélange établies par AIOMFAC-VISC pour déterminer les temps caractéristiques d'équilibrages dans l'aérosol organique (AO) en utilisant l'équation de Stokes-Einstein ou une variante de la relation de Stokes-Einstein fractionnaire.

Thesis Structure and Author Contributions

The following thesis consists of a brief research background, a manuscript, and recommendations for future work. The manuscript, which consists of Chapter 2, plus the accompanying manuscript reference list, will be submitted to the journal, Atmospheric Chemistry and Physics (ACP). Chapter 1 outlines the background and motivation for the work and Section 2.2 is the introduction of the manuscript. Both serve as a literature review for the thesis. Sections 2.3, 2.4, 2.5, and 2.7 constitute the main body of the research. Section 2.3 outlines the theory and methodology used to construct the predictive group-contribution mixture viscosity model. Section 2.4 presents the main results of the model along with a discussion of the model performance and the areas in need future model development. Section 2.5 demonstrates how the model can be used as a tool to make mixture viscosity predictions relevant to atmospheric organic aerosol. Section 2.7, like an appendix, contains information complimentary to the main manuscript. Section 2.6 provides a summary of the work done in the manuscript. Finally, Chapter 3 highlights the potential uses of the model and provides suggestions for future work.

I carried out the research and wrote the manuscript with Prof. Andreas Zuend and in collaboration with Dr. David Topping at the School of Earth, Atmospheric and Environmental Science at the University of Manchester. The original research framework was designed by Prof. Andreas Zuend and the manuscript is a reflection of editorial suggestions from all co-authors. All chapters in this work were done with research direction and editorial guidance provided by Prof. Andreas Zuend.

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Chapter 1

Background

1.1 Overview and motivation

Aerosol PM are often composed of both inorganic and organic chemical components, although the model described here has been designed thus far to predict the mixture viscosity of aqueous organic matter. Organic matter constitutes a significant fraction of the mass of global aerosol. Of the submicrometer aerosol population, organic matter can represent more than 50 % of the total mass (Reid et al., 2018). Organic matter is pervasive in the atmosphere as primary or secondary organic aerosol (POA and SOA, respectively), as coatings around aqueous–inorganic particle cores, or as existing in complex organic–inorganic morphologies.

In general, the chemical properties and structures of typical organic compounds found in aerosol PM are thought to make organic mixtures more readily viscous than inorganic compounds. This has also been experimentally observed for a limited number of surrogate aerosol particle systems, where the addition of inorganic compounds resulted in a reduction of particle mixture viscosity. For example, aqueous–sucrose–sodium chloride particles have a lower viscosity by several orders of magnitude when compared to aqueous–sucrose particles at the same relative humidity (Power et al., 2013). This is due to the sodium chloride driven increase in hygroscopicity. In essence, inorganic compounds may contribute an indirect plasticizing effect in internally mixed aerosol particles. Notwithstanding, should the particles be externally mixed, the aerosol may have domains of differing viscosity. In the case of phase separated particles with an organic shell covering an aqueous-inorganic core, quantifying the viscosity of the organic coating will be important for understanding viscosity–limited bulk– phase physiochemical processes. Therefore, the model development detailed here is focused on aqueous organic mixtures, making it directly applicable to predicting the mixture viscosity of pure, aqueous OA and aqueous OA coatings/domains.

1.2 Measurements of organic mixture viscosity

The first indication that aerosol may exist in a highly-viscous state came from laboratory viscosity measurements of binary-aqueous surrogate aerosol particles (Zobrist et al., 2008). Shortly thereafter, field measurements of SOA demonstrated that ambient aerosol particles may also exhibit this behaviour (Virtanen et al., 2010). In the years following these seminal findings, there has been extensive work in adopting existing methods and developing novel experimental techniques to measure aerosol viscosity across the liquid, semi-solid, and glassy regimes.

1.2.1 Laboratory techniques

Conventional measurements of viscosity are made on bulk samples using viscometer or rheometer, which have a measurement range of approximately 10^{-3} – 10^{8} Pa s (Reid et al., 2018). Despite their robustness, there are limited bulk measurements of atmospherically relevant mixtures given the disparity in size between aerosol and the required large sample volumes of conventional techniques. Booth et al. (2014) performed measurements on anhydrous and aqueous equimolar mixtures of nine di-carboxylic acids, first presented by Cappa et al. (2008) and Song et al. (2016c) and Grayson et al. (2017) made bulk viscosity, conventional viscometry and rheology measurements are typically made to assess the validity of an original technique for simple organic mixtures of readily available compounds.

Measurements of in situ aerosol viscosity for laboratory-generated, surrogate OA are necessarily inventive due to both the size of the sample being measured and the difficulty in probing ultra-high viscosities on experimental timescales. It is noteworthy to briefly describe some of these techniques because the model developed in this work was trained and validated using measurement sets from both conventional methods and novel experimental techniques. Some of the methods that have been created or adapted from other disciplines include aerosol optical tweezers; Dimer Coagulation, Isolation and Coalescence (DCIC); depolarization detection; poke-and-flow; Fluorescence Lifetime IMaging (FLIM); and bead mobility.

Aerosol optical tweezers are used to trap and coalesce particle pairs, whereby the shape relaxation time from coalescence to sphericity is used to estimate viscosity (Power et al., 2013; Song et al., 2016c; Marsh et al., 2018; Rovelli et al., 2019). Similarly, coalescence and shape relaxation is also exploited in the DCIC method. Dimers are created by coagulation of oppositely charged particles. The dimers are passed through a conditioning tube where they can be exposed to varying temperature and relative humidity. An increase in temperature or relative humidity can cause the agglomerate to coalesce and as before, the coalescence relaxation time of the dimers is used to estimate viscosity (Rothfuss and Petters, 2016, 2017a; Marsh et al., 2018). Similarly, Järvinen et al. (2016) have measured the change in the depolarization ratio of light scattered through agglomerates as they coalesce, which is used to infer a viscosity transition as relative humidity is changed.

Lastly, shape relaxation is capitalized by the poke–and–flow method (Renbaum-Wolff et al., 2013; Grayson et al., 2017; Rovelli et al., 2019). Large particles (25–70 μ m in diameter) are deposited onto a hydrophobic surface. They are then poked with a needle and observed with an optical microscope. The needle creates a deformation in the particle, where the speed of relaxation from the deformed state is used to infer viscosity. Aside from aerosol optical tweezers, which can make both liquid viscosity and semi-solid viscosity measurements, other coalescence and shape relaxation techniques are only capable of estimating semi-solid viscosities or inferring a change in viscosity.

The FLIM of viscosity–sensitive fluorophores, called molecular rotors, allows for the mea-

surement of liquid and semi-solid viscosities. The fluorescence lifetime of the molecular rotors are related to the viscosity of their microenvironment. By inserting a small concentration of molecular rotors in proxy-aerosol droplets this technique has been used to measure the viscosity of particles deposited on microscopic slides in varying ambient conditions (Hosny et al., 2013; Fitzgerald et al., 2016). In a similar manner, the bead mobility technique relies on the insertion of inert submicron beads in a microscopic particle (30–70 μ m in diameter) resting on a hydrophobic substrate. The beads move within their environment in response to a surface stress applied to the particle. The viscosity of the particle can then be estimated from a calibration of bead velocity and viscosity (Renbaum-Wolff et al., 2013; Grayson et al., 2017). Both FLIM and the bead mobility technique only have measuring capabilites in the liquid and lower semi-solid regime (~ 10^{-3} – 10^{3} Pa s) (Reid et al., 2018).

For the aforementioned experimental techniques, the uncertainties on their viscosity measurements are higher than uncertainties with conventional rheology or viscometry, sometimes spanning orders of magnitude. Additionally, there can be large discrepancies in viscosity measurements made with different methods. Nonetheless, these experiments have demonstrated consistent findings in terms of the expected viscosity behaviour of aerosol particles. In the case of laboratory–generated particles of known composition and unknown composition, like secondary organic aerosol (SOA), it has been observed that relative humidity and temperature are strong modulators of viscosity. Water, being a strong plasticizer, will cause a decrease in viscosity when water activity, or relative humidity if the mixture is in equilibrium, is increased. A decrease in temperature will cause a decrease in the molecular mobility of constituents in the particle and viscosity will increase as a result (Rothfuss and Petters, 2016).

Aside from relative humidity and temperature, dry particle composition is also a predictor of viscosity. In general, the number of functional groups on molecular constituents modulates viscosity (Grayson et al., 2017; Rothfuss and Petters, 2017), with the addition of carboxylic acids and hydroxyl groups resulting in the largest viscosity increases.

1.2.2 Field techniques

The two most commonly used field techniques to probe ambient SOA viscosity are particle rebound and Scanning Electron Microscopy (SEM). Particle rebound involves capturing a population of SOA and measuring the particles' propensity to bounce off an impactor plate. If the particles are liquid they will likely splash or adhere to the impactor, whereas if they are semi-solid or glassy, they are more likely to bounce upon impact. A sigmoidal bounce fraction versus size or relatively humidity can be used to infer the number of liquid, semisolid, or glassy particles in the SOA population (Virtanen et al., 2010; Bateman et al., 2015; Pajunoja et al., 2016; Slade et al., 2019). Similarly, particles that have been captured on an impactor plate can be probed with SEM imaging. SEM can be used to observe the shape of adhered particles, allowing for a measurement of the particles' "height-to-base" ratio, which can then be used to infer their phase (Slade et al., 2019).

While field measurements cannot provide an exact measurements of viscosity, they have been critical in affirming that laboratory observations of semi-solid and amorphous, glassy SOA are applicable to the real atmosphere. They have also remained consistent with the temperature and relative humidity dependent viscosity trends observed in laboratory experiments. And recently, Slade et al. (2019) demonstrated a diurnal variability in SOA viscosity in a mixed terpene–isoprene emission forest. Their findings suggest that in certain environments, SOA composition may dominate over relative humidity in determining particle viscosity.

1.3 Existing models of organic aerosol mixture viscosity

The simplest modelling approach for predicting organic mixture viscosity postulates that the mixture viscosity can be described as a sum of the pure component viscosity of individual mixture constituents, where the pure component viscosities are scaled in a prescribed manner. The most robust mixing rule model was first described by Bosse (2005), which scales the pure

component viscosity by the mole fraction of individual components. The Bosse (2005) model has been shown to perform well for binary aqueous organic mixtures up to 10^4 Pa s, however the model predictions deviate largely from experimental viscosity measurements of multicomponent anhydrous (Booth et al., 2014) and multi-component aqueous mixtures (Rovelli et al., 2019), making its applicability to viscosity predictions of OA dubious. Furthermore, the Bosse (2005) model and other methods that rely on knowledge of the pure component viscosity of individual constituents suffer from a lack of experimental measurements of pure component viscosity. This is especially true for compounds with ultra-high viscosities, whose measurements are experimentally inaccessible.

More often, viscosity estimation tools rely on knowledge of the calorimetric glass transition temperature (herein called the glass transition temperature, $T_{\rm g}$), which is more easily measured experimentally, typically via differential scanning calorimetry (DSC). Several approaches exist for estimating the viscosity of organic mixtures based on mixture $T_{\rm g,mix}$ values. These approaches have been adopted from glass and polymer physics for mixtures of atmospheric relevance.

Most commonly, values of $T_{g,mix}$ are predicted using the Gordon–Taylor equation (Gordon and Taylor, 1952), which was originally formulated for binary mixtures,

$$T_{\rm g,mix} \cong \frac{w_1 T_{\rm g,1} + w_2 \frac{1}{k_2} T_{\rm g,2}}{w_1 + w_2 \frac{1}{k_2}},\tag{1.1}$$

where w and T_g are the mass fraction and pure component glass transition temperature for component 1 and 2 in the mixture. Assuming component 1 is water, k_2 is the Gordon–Taylor constant for the solute, which can be expressed generally as,

$$k_{i} = \frac{\left(c_{1}^{l} - c_{1}^{g}\right)M_{i}}{\left(c_{i}^{l} - c_{i}^{g}\right)M_{1}},$$
(1.2)

where c_i^l and c_i^g are the molar heat capacities of a given component at constant pressure in the liquid and glassy state respectively. M_1 and M_i are the molar masses of water and the solute, *i*. The equation for the $T_{g,mix}$ of multi-component aqueous mixtures, where water is component 1, is described by (Lienhard et al., 2012) as,

$$T_{\rm g,mix} \cong \frac{w_1 T_{\rm g,1} + \sum_{i=2}^n w_i \frac{1}{k_i} T_{\rm g,i}}{w_1 + \sum_{i=2}^n w_i \frac{1}{k_i}}.$$
(1.3)

Finally, the viscosity of the mixture can be estimated from $T_{g,mix}$ via a modified Vogel– Tammann–Fulcher (VTF) equation (Marsh et al., 2018; DeRieux et al., 2018; Rovelli et al., 2019). Originally developed for pure components, the VTF equation is an empirical formulation that describes the non-Arrhenius temperature dependence of viscosity for certain compounds (see Angell (1995) and references therein). The VTF equation is described in further detail in Chapter 2.3.

The theoretical basis for the Gordon–Taylor constants, Eqs. (1.1), and (1.3) is rooted in thermodynamics, under the assumption that the glass transition is a second order phase transition. In practice, the Gordon–Taylor equation relies on measurements, parameterizations, or model predictions of the pure component values of $T_{\rm g}$ and the Gordon–Taylor constants.

Aside from experimental measurements, the most straightforward approach to determining the pure component $T_{\rm g}$ of a compound is via the relationship to its melting temperature, $T_{\rm m}$, where $T_{\rm g} \approx \frac{2}{3}T_{\rm m}$, although it is not widely applicable to many glass formers (Angell, 1997; Angell et al., 2002). This rule was initially developed for polymers and by adjusting the scaling of $T_{\rm m}$ from 0.5–0.8 its applicability can be extended to some inorganics and organics (Debenedetti and Stillinger, 2001). Adaptations of this relationship, called the Boyer-Kauzmann rule, where $T_{\rm g} = 0.7T_{\rm m}$, have been applied to atmospheric systems (Koop et al., 2011). Furthermore, estimations of pure component $T_{\rm g}$ using the Boyer-Kauzmann rule, along with measured $T_{\rm g}$ values were used to develop two elemental–contribution models that predict $T_{\rm g}$ values of organics (Shiraiwa et al., 2017; DeRieux et al., 2018).

The Gordon–Taylor constants remain more elusive than values of $T_{\rm g}$ because there are fewer experimental measurements. There are some measurements of k that range from 1 to 5.5 for compounds used as proxies for SOA constituents (Zobrist et al., 2008; Koop et al., 2011; Rothfuss and Petters, 2017a); however, as Berkemeier et al. (2014) note, there is not a distinct relationship between k and molecular structure, which makes it challenging to estimate k for SOA constituents. Moreover, DeRieux et al. (2018) demonstrate that varying k from 1 to 4 for SOA systems result in mixture viscosity predictions that differ by several orders of magnitude. Despite the large uncertainties and the lack of theoretical basis for assigning Gordon–Taylor constants to SOA, the Gordon–Taylor and VTF approaches remain the most widely used tools to estimate mixture viscosity for atmospheric applications.

Chapter 2

A predictive group-contribution model for the viscosity of aqueous organic aerosol

Natalie R. Gervasi¹, David O. Topping², and Andreas Zuend¹

¹Department of Atmospheric and Oceanic Sciences, McGill University, Montreal, Quebec, Canada

²School of Earth, Atmospheric and Environmental Science, University of Manchester, Manchester M13 9PL, U.K.

The following chapter is a manuscript to be submitted to the journal, Atmospheric Chemistry and Physics (ACP). I performed the research, wrote the manuscript, and created the figures. Prof. Andreas Zuend created the original research framework, provided research direction, and edited the manuscript. Dr. David Topping provided model data for this work.

2.1 Abstract

The viscosity of primary and secondary organic aerosol (SOA) has important implications for the processing of aqueous organic aerosol phases in the atmosphere, their involvement in climate forcing, and transboundary pollution. Here we introduce a new thermodynamics-based group-contribution model, which is capable of accurately predicting the dynamic viscosity of a mixture over several orders of magnitude ($\sim 10^{-3}$ to $> 10^{12}$ Pa s) as a function of temperature and mixture composition, accounting for the effect of relative humidity on aerosol water content. The mixture viscosity modelling framework builds on the thermodynamic activity coefficient model AIOMFAC (Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients) for predictions of liquid mixture non-ideality, including liquid-liquid phase separation, and the calorimetric glass transition temperature model by DeRieux et al. (2018) for pure-component viscosity values of organic components. Comparing this new model with simplified modelling approaches reveals that the group-contribution method is the most accurate in predicting mixture viscosity, although accurate pure-component viscosity predictions (and associated experimental data) are key and one of the main sources of uncertainties in current models, including the model presented here. Nonetheless, we find excellent agreement between the viscosity predictions and measurements for systems in which mixture constituents have a molar mass below 350 g mol^{-1} . As such, we demonstrate the validity of the model in quantifying mixture viscosity for aqueous binary mixtures (glycerol, citric acid, sucrose, and trehalose), aqueous multicomponent mixtures (citric acid + sucrose and a mixture of nine dicarboxylic acids), and aqueous SOA surrogate mixtures derived from the oxidation of α -pinene, toluene, or isoprene. We also use the model to assess the expected change in SOA particle viscosity during idealized adiabatic air parcel transport from the surface to higher altitudes within the troposphere. This work demonstrates the capability and flexibility of our model in predicting the viscosity for organic mixtures of varying degrees of complexity and its applicability for modelling SOA viscosity over a wide range of temperatures and relative humidities.

2.2 Introduction

Viscosity measurements of laboratory-made proxy aerosol particles were the first evidence suggesting that secondary organic aerosol (SOA) particles could exist in a highly viscous state (Zobrist et al., 2008; Murray, 2008). Shortly after, field measurements demonstrated that ambient SOA exhibit semi-solid or glassy behaviour in certain environments (Virtanen et al., 2010). In the decade since these discoveries, the implications of highly viscous aerosols (or organic-rich phases thereof) have been a focus of intense study. Viscosity can impact the chemical and physical properties of organic aerosol (OA) particles, prolonging their equilibration with the surrounding gas phase. As an example, the gas-particle partitioning of water (Bones et al., 2012; Berkemeier et al., 2014; Price et al., 2015), semivolatile organics (Abramson et al., 2013; Marshall et al., 2016), and oxidizing compounds (Berkemeier et al., 2016) have been shown to be kinetically limited by slow diffusion in highly viscous or glassy particles. The slowed uptake of semivolatile organics from the gas phase can retard SOA formation and growth. Conversely, the slow diffusion of these molecules out of the particle bulk can impede evaporation. Oxidation reactions within a particle or diffusion of reactants to the particle surface are also slowed, leading to the extended preservation of organic species within aerosol phases that would otherwise undergo photodegradation (Zelenyuk et al., 2017). Reduced evaporation and shielding from oxidation may increase the residence time or organic species, giving these particles and their constituents an advantage in undergoing long-range transport (Schum et al., 2018; Zhou et al., 2019) and in turn, contributing to transboundary pollution (Shrivastava et al., 2017).

Oxidation or multiphase reactions in viscous SOA not only have implications for air quality, but for climate as well. Liu et al. (2018) demonstrated that the production of brown carbon aerosol can be viscosity-limited. SOA that would normally undergo browning due to multiphase chemical reactions instead remain translucent due to slowed reaction kinetics. Their translucency causes them to preferentially scatter, rather than absorb, solar radiation. While the prevention of brown carbon by viscous organics has a direct influence on aerosolradiation-climate effects, in addition, SOA phase state may impact climate and weather indirectly via its potential role in ice nucleation. There is potential for extremely viscous, glassy SOA particles to act as ice nuclei and therefore play a role in ice cloud formation and related optical and lifetime properties of cold clouds (Berkemeier et al., 2014; Lienhard et al., 2015; Knopf et al., 2018; Fowler et al., 2019).

In order to fully understand the implications of viscous SOA we must be able to quantify how frequently SOA precursors and atmospheric conditions, namely relative humidity (RH) and temperature, favour their formation. Semi-solid anhydrous SOA can be formed from biogenic precursors, like monoterpenes (Renbaum-Wolff et al., 2013; Grayson et al., 2016) and isoprene (Song et al., 2015) or from anthropogenic precursors, like polycyclic aromatic hydrocarbons (Zelenyuk et al., 2017). The type of precursor as well as the degree of oxidation governs the degree of functionalization of the resulting SOA species. The pure-component viscosity of an organic species is more sensitive to certain oxygen-bearing functional groups compared to others; although, oxygen-bearing functional group addition is directly proportional to viscosity (Rothfuss and Petters, 2017). Indeed, prolonged oxidation, leading to increased functionalization of precursor and derived hydrocarbons has been shown to increase SOA viscosity at low relative humidity (Saukko et al., 2012).

The hygroscopicity of the SOA mixture also dictates particle viscosity. For a given ambient relative humidity (of typically > 20 %), less hygroscopic SOA components will tend to form more viscous mixtures as compared to their more hygroscopic counterparts of similar molar mass due to the plasticizing effect of absorbed water under equilibrium conditions (Zobrist et al., 2008). Therefore, closely related to hygroscopicity in effect, relative humidity (or water activity in the particle) is a strong modulator of particle viscosity (Price et al., 2015; Ye et al., 2016). We can expect SOA particles of a given composition to have a higher viscosity under dry conditions and it is possible for organics to undergo a moisture-driven glass transition at typical surface-level temperatures (Dette et al., 2014). More ubiquitous is temperature-driven vitrification, where a compound/mixture is cooled rapidly enough to avoid crystallization and instead, the motions of the molecules are slowed to such an extent that they cannot reach the most stable equilibrium positions (i.e. those at lattice positions of a crystal) on experimental timescale. Of course, the effects of temperature and relative humidity cannot be fully decoupled in the atmosphere. Close to the Earth's surface, highly viscous SOA are found in colder, dryer regions (Virtanen et al., 2010), whereas primarily liquid-like SOA dominate in warmer, humid locations (Bateman et al., 2016). The viscosity of SOA at higher tropospheric altitudes remains an open question due to the competing effects of decreasing temperature and increasing relative humidity (Knopf et al., 2018). Recently, a similar ambiguity was observed on diurnal time scale at the surface in a mixed forest environment, where SOA particles were found to be more viscous during the night as compared to during the day, despite a lower daytime relative humidity. The observed diel cycle of viscosity appears to be dominated by chemical changes in submicron-sized SOA composition (Slade et al., 2019). Therefore, for an advanced assessment of the climate impact of aerosol viscosity, it is imperative that we understand the interplay of chemical composition, ambient temperature, and relative humidity in order to quantify the spatiotemporal range of aerosol viscosity in different geographic regions and vertical levels of the atmosphere.

To this end, several groups have developed novel techniques to measure both laboratorymade, proxy particles and ambient SOA viscosity (see Reid et al. (2018) and references therein). Work has also been carried out for developing predictive tools to model SOA viscosity; although, a lack of experimental data to constrain the models, coupled with an incomplete characterization of SOA chemical composition has made this work challenging. Most of the models developed so far have been trained and tested with simple organic mixtures in the liquid regime (where the dynamic viscosity $\eta_{mix} < 10^2$ Pa s). These models vary in complexity, for example, Cao et al. (1993a) employ a group-contribution approach adopted from a statistical thermodynamics treatment (Cao et al., 1993b), while the work by Bosse (2005) outlines a simple, mole-fraction-based mixing rule. Song et al. (2016c) demonstrated the validity of the Bosse (2005) mixing rule for binary aqueous mixtures with alcohol, di- or tricarboxylic acids up to a mixture viscosity of 10⁴ Pa s. They also showed this simple model overestimated the viscosity of binary aqueous mono-, di- and trisaccharide mixtures. Recently, Rovelli et al. (2019) compared the Bosse (2005) model with their own water-activity-dependent viscosity mixing rule. They show that the water-activitydependent predictions outperformed the Bosse (2005) for most of their ternary aqueous sucrose-citric acid and aqueous sucrose-NaNO₃ mixtures up to $\eta_{\text{mix}} \sim 10^6 - 10^7$ Pa s. Shiraiwa et al. (2017) were the first to use a semi-empirical modelling approach to constrain the phase state of SOA based on estimations of the (calorimetric) glass transition temperature of SOA species. DeRieux et al. (2018) expanded on that approach, using glass transition temperature estimations to predict the viscosity of α -pinene SOA, toluene SOA, isoprene SOA, and biomass burning particles.

In this study, we introduce our thermodynamics-based group-contribution approach developed to predict the viscosity of aqueous OA phases covering several orders of magnitude in viscosity (~ 10^{-3} to > 10^{12} Pa s) as a function of organic mixture composition, temperature, and relative humidity. To this end, our mixing model is coupled with pure-component glass transition temperature estimations by the DeRieux et al. (2018) method. This new development aims for extending the predictability and accuracy beyond the range of existing approaches. The rest of this article is structured as follows: we begin by detailing the model framework and discussing model limitations, followed by comparing the performance of the model with simplified mixing rules. We then discuss the training of the model for a dozen binary aqueous organic mixtures followed by presenting the model's predictive ability for well-constrained multicomponent aqueous organic mixtures. Furthermore, model predictions of the RH-dependent mixture viscosities of α -pinene SOA, toluene SOA, and isoprene SOA are compared to viscosity measurements of laboratory generated SOA. Finally, we discuss atmospheric implications of our model's predictions by exploring the mixture viscosity of the aforementioned SOA systems across the atmospherically relevant temperature and relative humidity space.

2.3 Theory and Methods

We have built a method to predict the viscosity of (aqueous) organic mixtures within the Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficient (AIOMFAC) model framework (Zuend et al., 2008, 2011); this new method is abbreviated as AIOMFAC- VISC. In general terms, our model combines temperature-dependent physicochemical purecomponent properties of organic molecules and water with a non-linear mixing model for dynamic viscosity. Hence, the general approach is similar to predictions of the equilibrium vapour pressures of solution components, which also involves pure-component properties and mixing effects.

At the core of AIOMFAC-VISC are a set of equations relating the viscosity of a mixture to the structural features of chemical components, their relative abundance in a phase and to temperature. These equations are based on those from an existing group-contribution thermodynamics-viscosity model called GC-UNIMOD (Cao et al., 1993a), but modified in several important ways. Within AIOMFAC-VISC, AIOMFAC supplies predictions of nonideal thermodynamic mixing effects in a solution phase in the form of component activity coefficients, while two additional parameterizations are used for pure-component properties. First, the parameterization described by Dehaoui et al. (2015) is used to estimate the viscosity of water as a function of temperature. Second, the method introduced by DeRieux et al. (2018) is used to estimate the pure-component viscosity of individual organic molecules for a given temperature. In the following, we describe the combination of models and parameterizations that comprise the AIOMFAC-VISC method.

2.3.1 Mixture viscosity predictions

We have modified the semi-empirical viscosity equations of GC-UNIMOD to better represent atmospherically relevant organic mixtures. Following Cao et al. (1993a), the natural logarithm of the dynamic viscosity of a mixture, η_{mix} , is expressed in AIOMFAC-VISC as

$$\ln(\eta_{\rm mix}) = \sum_{i=1}^{n} \left[\xi_i^C + \xi_i^R\right].$$
 (2.1)

Here, n is the number of individual mixture components (molecules), and ξ_i^C and ξ_i^R are the combinatorial and residual viscosity contributions of the i^{th} molecule, respectively. The combinatorial contributions represent the geometric properties of each molecule in a simplified



Figure 2.1: A flow chart showing a simplified schematic of the AIOMFAC-VISC model framework. The colour shadings of the boxes denote the model or parameterization being used at a given point in the framework. Blue indicates the use of the DeRieux et al. (2018) model to predict the pure-component calorimetric glass transition temperature, green indicates the use of the modified Vogel–Tammann–Fulcher equation to predict the pure-component viscosity of the organic components, red indicates the use of the Dehaoui et al. (2015) parameterization to estimate the pure-component viscosity of water, and yellow indicates the use of AIOMFAC-VISC to calculate the mixture viscosity.

form, whereas the residual contributions account for the inter-molecular interactions, e.g. due to van der Waals forces. Specifically, and unlike the equation for ξ_i^C in GC-UNIMOD, we introduce the combinatorial contribution of the i^{th} molecule as the product of pure-component viscosity times combinatorial activity,

$$\xi_i^C = \gamma_i^C x_i \ln(\eta_i^0), \qquad (2.2)$$

where $\gamma_i^{\rm C}$ is the combinatorial activity coefficient, x_i is the molar fraction (with respect to the mixture of molecules), and η_i^0 is the temperature-dependent pure-component viscosity. The mole-fraction-based combinatorial activity ($a_i^{\rm C} = \gamma_i^{\rm C} x_i$) is routinely computed as part of the Universal Quasi-Chemical Functional group Activity Coefficients (UNIFAC) model (Fredenslund et al., 1975) equations within the AIOMFAC model. It can be considered an effective measure of composition – a modification of the mole fraction composition scale to account for differences in shapes and sizes of molecules, which is important when mixtures contain small molecules like water as well as significantly larger molecules like sucrose, raffinose or various oligomers.

The residual contributions are written as

$$\xi_i^R = \Phi_i \left[\sum_k \nu_k^{(i)} \Xi_k^{(i)} - \sum_k \nu_k^{(i)} \Xi_k^{(i), \text{ref}} \right], \qquad (2.3)$$

where $\Xi_k^{(i)}$ is the residual viscosity of (sub)group k for component i (indicated by the superscript) in the mixture of components and with $\nu_k^{(i)}$ being the number of groups k within molecule i. $\Xi_k^{(i),\text{ref}}$ is the group residual viscosity of group k for component i in the purecomponent solution of the i^{th} component, representing a reference value for each component. Both terms are expressed as

$$\Xi_k^{(i)} = \frac{Q_k}{R_k} N_{k,i}^{vis} \sum_m \left[\Gamma_{m,k} \ln \left(\Psi_{m,k} \right) \right], \qquad (2.4)$$

where for the i^{th} molecule there exist functional subgroups k, while subgroup-index m covers here all subgroups from all molecules of the mixture (with the definition of a subgroup as in UNIFAC, AIOMFAC). Hence, in the reference value calculation for $\Xi_k^{(i),\text{ref}}$, index *m* covers all subgroups of that molecule (*i*). For subgroup *k*, Q_k and R_k are its relative van der Waals surface area and volume parameters, respectively (Hansen et al., 1991). The parameter $N_{k,i}^{vis}$ is computed as follows (Cao et al., 1993a):

$$N_{k,i}^{vis} = Q_k \left(\frac{q_i - r_i}{2} - \frac{1 - r_i}{z} \right),$$
(2.5)

where,

$$q_i = \sum_k \nu_k^{(i)} Q_k$$
 and $r_i = \sum_k \nu_k^{(i)} R_k.$ (2.6)

Variables q_i and r_i are the molecule-specific relative surface area and volume parameters, respectively. The lattice coordination number, z, is set as a constant of value 10 (Zuend et al., 2008).

Next, we note that the local interaction composition of subgroups, $\Gamma_{m,k}$ (Eq. 2.4), is described by the following set of expressions involving the fractional relative subgroup surface area Θ_m :

$$\Theta_m = \frac{X_m Q_m}{\sum_k X_k Q_k} \quad \text{and} \quad \Gamma_{m,k} = \frac{\Theta_m \Psi_{m,k}}{\sum_k \Theta_k \Psi_{m,k}},\tag{2.7}$$

where

$$\Psi_{m,k} = \exp\left[\frac{-a_{m,k}}{T}\right].$$
(2.8)

Here $\Psi_{m,k}$ is a function of the AIOMFAC subgroup interaction parameter, $a_{m,k}$ and temperature, T. X_m in Eq. (2.7) is the molar fraction of subgroup m within the mixture of subgroups. For additional information regarding Θ_m and $\Psi_{m,k}$ we refer the reader to Zuend et al. (2008).

Finally, returning to Eq. (2.3), the volume fraction, Φ_i , which is here based on the relative van der Waals molecular volumes (Eq. 2.6), can be expressed as

$$\Phi_i = \frac{x_i r_i}{\sum_{j=1}^n x_j r_j}.$$
(2.9)

We note that the residual contribution to viscosity, ξ_i^R is nearly identical to the formulation

of GC-UNIMOD, except for the expression for $N_{k,i}^{vis}$; our expression (Eq. 2.5) differs from its counterpart in GC-UNIMOD by a factor -1 (both are semi-empirical expressions and not fundamentally derived from theory). Doing so allows for significantly better agreement between AIOMFAC-VISC and measurements of dynamic viscosity for binary aqueous mixtures (see Supplementary Information, SI, Section S5).

2.3.2 Pure-component viscosity predictions

Water

AIOMFAC-VISC requires knowledge of the pure-component dynamic viscosity (η^0) of the individual mixture components. The pure-component viscosity is the viscosity of a given component in its pure liquid, semi-solid or amorphous solid state as a function of temperature. Bulk measurements for a range of pure-component viscosity values ($10^{-3} - 10^8$ Pa s) can be made using conventional equipment, like a viscometer or rheometer at temperatures typically between -40 and 200 °C (Reid et al., 2018). With a sufficient number of measurements, the pure-component viscosity can be described empirically or semi-empirically for the temperature range over which the measurements were made.

For example, in this work we estimate the pure-component viscosity of water using the semi-empirical power law parameterization given by Dehaoui et al. (2015):

$$\eta_{\rm H_2O}(T) = A \left(\frac{T - T_{\rm s}}{T_{\rm s}}\right)^{-B},$$
(2.10)

where $\eta_{\rm H_2O}$ is the pure-component viscosity of water, T is the temperature in Kelvin (K), A and B are constants with values of $(1.3788 \pm 0.0026) \times 10^{-4}$ Pa s and 1.6438 ± 0.0052 , respectively. $T_{\rm s}$ is theorized to be the mode-coupling temperature of water with a value of 225.66 ± 0.18 K. The Dehaoui et al. (2015) parameterization is supported by experimental data over the temperature range $\sim 230 - 400$ K (and likely reasonable to lower T), covering most of the atmospherically relevant temperature range (see Fig. 2.9 in the SI).

Organic compounds

It should be noted that AIOMFAC-VISC typically does not consider the crystallization of organic compounds; rather, the model assumes that all components remain amorphous over the entire temperature and relative humidity space. In practice, this is a reasonable assumption because crystallization in complex SOA mixtures is likely suppressed owing to the variety of compounds that comprise the SOA phase. As a result, this assumption necessitates supplying AIOMFAC-VISC with the pure-component viscosity for all individual components.

Given the abundance of experimental data and the quality of the Dehaoui et al. (2015) power law fit, we have a high degree of confidence in the predicted temperature-dependent pure-component viscosity of water for a range of atmospherically relevant temperatures. However, the estimate of the temperature-dependent pure-component viscosity for organic components is a significantly more nuanced problem. First, for most atmospherically relevant organics there are no measurements of their pure-component viscosity. Often the lack of data is a result of the organics having ultra-high pure-component viscosities (> 10⁸ Pa s) near room temperature, making their measurement experimentally inaccessible. For those organics whose pure-component viscosities have been measured, the experiments are typically performed at room temperature (~ 20 - 25 °C), which limits our ability to determine the temperature dependence and to parameterize the functional form to lower temperatures. Therefore, the lack of available data precludes our use of empirically determined pure-component viscosity values.

The scarcity of high-viscosity experimental data motivated us to instead use the group contribution model developed by Nannoolal et al. (2009) for the prediction of the purecomponent viscosity values. However, the Nannoolal et al. (2009) model was developed/validated only for predicting liquid-like viscosities $\ll 1$ Pa s and, therefore, it is not reliable for predicting viscosity in the semi-solid and glassy regime for the compounds we are interested in. Sastri and Rao (1992) have developed a group-contribution model for pure-component viscosity based on a relationship of viscosity with pure-component vapour pressure; however, this model was also developed for liquid-state viscosities only.



Figure 2.2: Prediction of the pure-component viscosity (η^0) as a function of temperature using the method by DeRieux et al. (2018) for (a) glycerol, (b) citric acid, (c) sucrose, and (d) trehalose. The three curves in each panel show the effect of different fragility parameters on the pure-component viscosity prediction (solid, D = 10; dashed, D = 5; dash-dotted, D = 30). The pink lines illustrates which fragility parameter the model uses as a function of temperature, i.e. when $T \downarrow T_g$ then D = 10 and when $T \downarrow T_g$ then D = 30. The grey symbols are reference values of T_g (either measured or parameterized) where horizontal error bars have been omitted for clarity (additional information and the sources of the T_g values can be found in Table 2.1). The reference values of T_g have been plotted using the convention that $\eta^0(T_g) = 10^{12}$ Pa s. The vertical grey dotted lines denote 0 °C and 22 °C.

We also attempted to determine a semi-empirical relationship between pure-component viscosity and pure-component vapour pressure. We compared experimentally-determined and modelled values of pure-component viscosity with modelled pure-component vapour pressures. Modelled viscosity values were calculated using the Nannoolal et al. (2009) group-contribution approach and vapour pressure values were determined using the on-line tool UManSysProp (http://umansysprop.seaes.manchester.ac.uk) (Topping et al., 2016) with the model by Nannoolal et al. (2008) or by using the EVAPORATION model (Compernolle et al., 2011) without the empirical factor for functionalized dicarboxylic acids. At lower viscosity and vapour pressure, the relationship is linear in double logarithmic space; however, this relationship does not apply sufficiently well at higher viscosity values (see Fig. 2.10).

Ultimately, at present it is not possible to rely on directly measured or predicted purecomponent viscosity values of organic compounds over the atmospheric temperature range. As a result, we employ the method developed by DeRieux et al. (2018), which uses the calorimetric glass transition temperature, T_g (herein called the glass transition temperature) to predict the pure-component viscosity of organic compounds. This method is an updated T_g parameterization based on previous work done by Shiraiwa et al. (2017). Compared to the Shiraiwa et al. (2017) method (validated for compounds $M < 450 \text{ g mol}^{-1}$), the DeRieux et al. (2018) method was designed to perform better also for higher molar mass compounds. With the DeRieux et al. (2018) method, we first predict T_g of the organic compounds. We then use the glass transition temperature to calculate the pure-component viscosity of the organics via the modified Vogel–Tammann–Fulcher equation (Angell, 1991; DeRieux et al., 2018). A semi-empirical, elemental-contribution model is used by DeRieux et al. (2018) to predict the glass transition temperature for a given organic molecule:

$$T_{\rm g} = (y_{\rm C^0} + \ln(y_{\rm C})) b_{\rm C} + \ln(y_{\rm H}) b_{\rm H} + \ln(y_{\rm C}) \ln(y_{\rm H}) b_{\rm CH} + \ln(y_{\rm O}) b_{\rm O} + \ln(y_{\rm C}) \ln(y_{\rm O}) b_{\rm CO} \quad (2.11)$$

where $y_{\rm C}$, $y_{\rm H}$, and $y_{\rm O}$ are the number of carbon, hydrogen and oxygen atoms of the molecule. $b_{\rm C}$, $b_{\rm H}$, $b_{\rm O}$, $b_{\rm CH}$, and $b_{\rm CO}$ are model parameters determined by optimisation using $T_{\rm g}$ training data from experiments. For the parameter values and a full description of the model, the reader is referred to the aforementioned work. The estimated glass transition temperature is then used to calculate the Vogel temperature, T_0 and subsequently, the pure-component viscosity (Angell, 1991):

$$T_0 = \frac{39.17 \, T_{\rm g}}{D + 39.17} ; \qquad \log_{10}(\eta^0) = -5 + 0.434 \frac{T_0 D}{T - T_0} \tag{2.12}$$

where Angell (1991) has assumed,

$$\lim_{T \to \infty} \eta = 10^{-5} \text{ Pa s} \text{ and } \eta^0(T_{\rm g}) = 10^{12} \text{ Pa s.}$$
(2.13)

The Vogel temperature, T_0 , and the fragility parameter, D, are component-specific properties. T_0 is thought to be related to the Kauzmann temperature (the ideal glass transition temperature) (Angell, 1997). The fragility parameter, D indicates whether the (liquid) compound is a "strong" or "fragile" glass-former. Strong glass-formers show an approximately linear increase in $\log_{10}(\eta^0)$ (Arrhenius behaviour) as they are cooled toward their glass transition (Debenedetti and Stillinger, 2001). In other words, the activation energy for viscous flow in strong liquids is temperature independent (i.e. $T_0 = \text{constant}$ in Eq. 2.12). Conversely, as a fragile glass-former undergoes cooling it will show very little increase in viscosity until near the glass transition, whereupon it will experience a steep increase in viscosity (so-called super-Arrhenius behaviour). In the case of a fragile glass-former, the activation energy for viscous flow is temperature dependent (i.e. $T_0 = T_0(T)$ in Eq. 2.12). In practice, D is calculated from a so-called Arrhenius plot. An Arrhenius plot illustrates the curve produced on a graph of $\log_{10}(\eta_i^0)$ vs. $\frac{T_g}{T}$. The slope of the curve at $\frac{T_g}{T} = 1$ produces the fragility index, m, from which the fragility parameter is derived via $D = \frac{665.89}{m-17}$ (DeRieux et al., 2018).

Predictions of pure-component viscosity as a function of temperature using Eqs. (2.11) and (2.12) are shown for glycerol, citric acid, sucrose, and trehalose in Fig. 2.2. Grey symbols indicating reference $T_{\rm g}$ values (either measured or parameterized) are also shown according to the convention that $\eta^0(T_{\rm g}) = 10^{12}$ Pa s. Although, it is important to note that for fragile glass-formers $\eta^0(T_{\rm g})$ may be up to four orders of magnitude lower than 10^{12} Pa s (Angell, 1995). As such, including the reference $T_{\rm g}$ values does not provide a clear picture of the

performance of the DeRieux et al. (2018) method for individual components; however, it allows us to make relative comparisons among certain components. For example, sucrose and trehalose, both disaccharides, are structural isomers differing in their composition from two monosaccharides, with reference $T_{\rm g}$ values that reflect this difference; however, both compounds have the same number of carbon, hydrogen and oxygen atoms, so the DeRieux et al. (2018) method produces identical pure-component viscosity predictions. The inherent omission of more detailed structural information illustrates one potential limitation of that pure-component viscosity prediction method. Nonetheless, the fact that the pure-component viscosity prediction can be made for any organic over a large temperature range affords a level of flexibility and predictability that, at present, outweighs the potential inaccuracies. More importantly, the potential inaccuracy of this method may be largely associated with our choice of the fragility parameter. For organic compounds, D values typically range from \sim 5 – 30 (Angell, 1997; DeRieux et al., 2018) and for most organics at or around room temperature, assuming a fragility parameter of 10 has been shown to be appropriate (Shiraiwa et al., 2017; DeRieux et al., 2018). We believe this to be especially true in the context of complex SOA mixtures where individual components may have fragility parameters that deviate from D = 10, but with a sufficient number of components in the mixture, these deviations will be offset. Moreover, for some organics whose $T_{\rm g}$ is close to the temperature of interest in a mixture viscosity calculation, the choice of fragility parameter may only have a small influence on the pure-component viscosity prediction. Figure 2.2 illustrates that for citric acid near 298 K any value of D between 5 and 30 will produce nearly identical values of pure-component viscosity. However, we highlight this case in particular because it appears to be the exception. For glycerol, sucrose, and trehalose in Fig. 2.2 the choice of D at room temperature presents a large discrepancy (several orders of magnitude) in the pure-component viscosity. This is true for most organics studied in this work.

In general, the choice of D becomes most influential in the supercooled regime, specifically beyond the organic's $T_{\rm g}$ if $T_{\rm g}$ occurs at the conventionally assigned viscosity of 10^{12} Pa s. For example, D = 10 will produce similar values of pure-component viscosity at either room temperature or at 273 K for glycerol, however the opposite is true for citric acid, sucrose, and trehalose (Fig. 2.2). As such, we must consider our choice of D not only for comparison with laboratory (room temperature) data, but for temperatures representative of where we expect viscous aerosol to be most relevant (around and below 15 °C). The temperature at which we must begin to concern ourselves with the influence of the fragility parameter varies from compound to compound, but for each compound this issue always presents itself above and below its $T_{\rm g}$.

There is also recent evidence to suggest that some liquid glass-formers undergo a fragileto-strong crossover (FSC) at a temperature T_{\times} , where $T_{\rm g} < T_{\times} < T_{\rm M}$, with $T_{\rm M}$ being the melting temperature. The physical reason behind the FSC is poorly understood at present, but it is thought to be related to a spatially inhomogeneous arrest of molecules in the liquid/amorphous phase during cooling. This phenomenon, known as "spatially heterogeneous dynamics" postulates that correlated domains in a liquid may exhibit different relaxation dynamics than the average over the entire bulk (Ediger, 2000). The FSC has been observed for water (Jagla, 2001) and silicon dioxide (La Nave et al., 2002; Saika-Voivod et al., 2004) and recently for a number of organics (see Novikov and Sokolov (2003) and Mallamace et al. (2010) and references therein). Both of these latter works suggest there is a universal, material-independent FSC pure-component viscosity based on experiments of relaxation dynamics for glass-forming liquids. Novikov and Sokolov (2003) suggest that η^{\times} is on the order of 10⁶ Pa s. However Mallamace et al. (2010) find that η^{\times} is on the order of 10³ Pa s. Notwithstanding this discrepancy, the presence of the FSC motivates our choice to change the assignment of D from 10 to 30 on a per-component basis if the temperature of a simulation case is below the component's $T_{\rm g}$. We note that the results of the aforementioned studies would suggest that for at least some organics the FSC occurs at temperatures warmer than $T_{\rm g}$. This is also supported by recent measurements of a super-Arrhenius to Arrhenius transition observed in citric acid, having occured at 302 – 312 K, which is approximately 20 – 30 K warmer than average values of the citric acid glass transition reported in the literature. While it would be more appropriate to change the D assignment at the FSC viscosity, we do not have a clear scientific basis to assign universal pure-component FSC. At least for temperatures below $T_{\rm g}$ it is reasonable to assume that the FSC has occurred.



Figure 2.3: Prediction of $T_{\rm g}$ using the methods presented in (a) DeRieux et al. (2018) and (b) Shiraiwa et al. (2017) versus measured reference $T_{\rm g}$ values for some of the binary aqueous mixtures considered in this study. The grey markers represent individual reference $T_{\rm g}$ values and the coloured markers represent the average $T_{\rm g}$. Error bars for reference values have been omitted for clarity. For a list of the reference values and their uncertainties see Table 2.1. The grey dashed 1:1 lines represent perfect agreement between predicted and reference values.

2.3.3 Estimation of pure-component viscosity uncertainty

The uncertainty in the pure-component viscosity as predicted by the DeRieux et al. (2018) method arises from the uncertainty in the prediction of $T_{\rm g}$ and the uncertainty in D. Given that the $T_{\rm g}$ model is parameterized using a collection of measured $T_{\rm g}$ values, any uncertainty in $T_{\rm g}$ measurements will be propagated into the fitted DeRieux et al. (2018) model parameters. In addition, the fragility parameter is derived from measurements of $T_{\rm g}$, so any uncertainty in $T_{\rm g}$ will also propagate into the value of D. Therefore, we assess the uncertainty in the pure-component viscosity prediction by prescribing an uncertainty for $T_{\rm g}$. $T_{\rm g}$ measurements are made by cooling a compound until a liquid-to-glass phase transition occurs. For example, differential scanning calorimetry reveals a change in heat capacity of the single-component substance when $T_{\rm g}$ is reached (e.g. Angell et al., 2002; Lienhard et al., 2012). However, in some ways the glass transition temperature is a misnomer; the measured vitrification temperature of a liquid is dependent on the cooling rate from liquid (or the heating rate starting from the glassy state). In reality, the calorimetric glass transition temperature is not a discrete value; rather, it describes a range of temperatures (or a retrieved average temperature) corresponding to appropriate cooling rates that induce vitrification. Faster cooling rates will result in a slightly warmer $T_{\rm g}$ value than if the same substance were cooled at a slower rate (Debenedetti and Stillinger, 2001; Angell et al., 2002). For cooling rates that differ by an order of magnitude the resulting $T_{\rm g}$ range is approximately 3 – 5 K (Debenedetti and Stillinger, 2001). Another, more consequential factor that contributes to experimental $T_{\rm g}$ measurement uncertainty is the purity of the substance being measured. In essence, depending on laboratory conditions and sample preparation procedure, it is possible that the substance being measured is not entirely anhydrous – and trace amounts of water, being an excellent plasticizer, may cause a lower measured $T_{\rm g}$ value than what is true for the anhydrous compound.

Factoring in the effects of cooling rate and the substance purity on $T_{\rm g}$, we choose to assign a 5 % uncertainty. For a compound whose glass transition is within the range of atmospherically relevant temperatures, an uncertainty of ~ 10 – 20 K is produced. This is also in good agreement with findings from DeRieux et al. (2018), who state that for the
compounds they investigated, their model can estimate $T_{\rm g}$ within ± 21 K based on a 68 % prediction interval. We also note that this appears to be a reasonable uncertainty based on the spread in reference $T_{\rm g}$ values for the components we have studied, where glass transition temperature data are available (see Table 2.1). The reference values of $T_{\rm g}$ are either values measured experimentally or extrapolated from parameterizations of measurements of pure-component viscosity. Independent reference values of $T_{\rm g}$ for the same pure-component can differ by as little as one or two Kelvin, but in the most extreme case (citric acid) considered here, values span almost 50 K.

Figure 2.3 shows a comparison of the $T_{\rm g}$ values predicted by the DeRieux et al. (2018) and Shiraiwa et al. (2017) models with the reference values listed in Table 2.1. The average relative difference between the predicted values and the mean of the reference values are 6.76 % and 8.71 % for the DeRieux et al. (2018) and Shiraiwa et al. (2017) models, respectively. This demonstrates that, for the compounds studied here, the DeRieux et al. (2018) model is more appropriate. In addition, we note that a 5 % uncertainty in $T_{\rm g}$ is in good agreement with the difference between the predicted and reference $T_{\rm g}$ values.

2.3.4 Estimation of AIOMFAC-VISC sensitivity

We calculated the sensitivity of AIOMFAC-VISC as a proxy for the uncertainty in the mixture viscosity prediction. We chose to prescribe the AIOMFAC-VISC sensitivity as the response of the mixture viscosity prediction to a small change in mixture composition. The mixture composition adjustment was done by adjusting the mixture water content by a small amount. This is meant to represent the uncertainty in the composition measurement in a laboratory setting, which would be typical of all experiments. The calculation of AIOMFAC-VISC sensitivity is described in Section S3 of the SI.

2.3.5 Treatment of Secondary Organic Aerosol Systems

For SOA mixtures we used the AIOMFAC-VISC method within the MCM–EVAPORATION– AIOMFAC equilibrium gas–particle partitioning framework (Zuend and Seinfeld, 2012) to account for complex aerosol composition and the potential for liquid–liquid phase separation (LLPS). The Master Chemical Mechanism (MCM; Jenkin et al., 1997; Saunders et al., 2003; Jenkin et al., 2015) simulates the oxidation of parent hydrocarbons in the gas phase and provides a set of reaction products and stoichiometric yields for prescribed environmental conditions. We select a subset of the MCM reaction products, using those to generate surrogates mixtures of 14 - 21 components as a representation of the SOA composition formed from a specific precursor, as is done frequently when molecular-structure input information is required by models (e.g. Zuend and Seinfeld, 2012; Rastak et al., 2017; Gorkowski et al., 2019). The procedures used to determine the molar concentrations of SOA components along with the lists of MCM products used for the three SOA systems studied are provided in Section S6 of the SI.

2.4 Results and Discussion

2.4.1 Comparison with simplified models

A group-contribution model like AIOMFAC-VISC has the potential to offer a high degree of fidelity, owing to its relatively detailed description of a given mixture of organics plus water. However, it is important to question whether the estimation of mixture viscosity actually requires the complexity offered by a group-contribution model – or if a simpler mixing rule would suffice. To this end, we have compared the performance of AIOMFAC-VISC with three different expressions:

$$\ln(\eta_{\rm mix}) = \sum_{i}^{n} x_i \ln(\eta_i^0) \quad ; \quad \ln(\eta_{\rm mix}) = \sum_{i}^{n} \phi_i \ln(\eta_i^0) \quad ; \quad \ln(\eta_{\rm mix}) = \sum_{i}^{n} \sigma_i \ln(\eta_i^0). \quad (2.14)$$

Here, x_i is the mole fraction, ϕ_i is the volume fraction, and σ_i is the surface area fraction of the i^{th} mixture component. Implicit in these expressions is the assumption that mixture viscosity can be described simply as a weighted mean of the pure-component viscosities of the mixture components. The weighting is representative of the fractional amount of each component present in the mixture, either by their number of moles, their occupied volume, or their surface area.

Figure 2.4 shows a comparison of these different mixture viscosity models at T = 293.15 K for two binary systems: water + glycerol and water + citric acid. To remove the influence of a potential inaccuracy in the pure-component viscosity prediction on the model intercomparison, the panels on the left in Fig. 2.4 show the systems with the pure-component viscosities taken from measurements or a case-specific model estimation. For glycerol, the pure-component viscosity has been determined experimentally while for citric acid experimental data exists at very low mass fractions of water, allowing an extrapolation to the pure-component viscosity by leaving the pure-component viscosity of citric acid at the system temperature as a single fit parameter of our AIOMFAC-VISC model. With assigned pure-component viscosities, it becomes clear that the mixing rules based on molecular volume fraction or surface area fraction in the mixture are unsuitable predictors of mixture viscosity. The mole-fraction-weighted mixing rule performs reasonably for glycerol, but AIOMFAC-VISC remains the most accurate mixing model. For the aqueous citric acid system, the mole-fraction-weighted mixing rule and the AIOMFAC-VISC predictions are similar and both are in good agreement with the available experimental data. At least for binary aqueous systems, the mole-fraction-weighting appears to be the best simple mixing rule.

Comparing the panels from the left column with the right column in Fig. 2.4 highlights the effect of uncertainty in the pure-component viscosity prediction on the mixture viscosity and the variability in the quality of this prediction depending on the component. For glycerol, the DeRieux et al. (2018) method only slightly overpredicts the pure-component viscosity. For citric acid, the overprediction of η_{org}^0 spans almost four orders of magnitude. It should also be noted that while the pure-component viscosity is overpredicted for both citric acid and glycerol, this is not the case for every organic. For eleven single-organic component systems studied for which we have reference values of $T_{\rm g}$, $\eta_{\rm org}^0$ was overpredicted for six of the components and underpredicted for five of the components, related to over-/underpredictions of the corresponding $T_{\rm g}$ values (Fig. 2.3).

Figure 2.4 demonstrates that the AIOMFAC-VISC prediction of mixture viscosity is highly sensitive to the pure-component viscosity value. With the appropriate pure-component viscosity value (either from experiment or a model fit) we have the ability to make the mixture viscosity prediction highly accurate (in these specific cases, but not generally). In using the DeRieux et al. (2018) method we sacrifice some accuracy in predicting mixture viscosity in order to have the flexibility of predicting the mixture viscosity for systems containing organics for which we have no information about their pure-component viscosity from experimental data. This is especially important in the context of SOA systems.

2.4.2 Binary aqueous organic mixtures

Before running AIOMFAC-VISC for multicomponent mixtures, including a selection of SOA systems, the model was first tested with a dozen binary aqueous mixtures, which were chosen based on the availability of experimental data covering the low-viscosity and semi-solid regimes. The binary aqueous mixtures were used to test and validate the model, i.e., we tested potential adjustments to the AIOMFAC-based viscosity equations (Eqs. 2.2 – 2.3) to optimally predict the viscosity of as many binary aqueous mixtures as possible. Figure 2.5 shows the results for four of these systems. For aqueous glycerol and aqueous citric acid mixtures, the AIOMFAC-VISC model (solid line) slightly overpredicts the mixture viscosity at lower mass fractions of water due to the overestimation in η^0 . The experimental data at low mass fractions of water lie within the η^0 uncertainty (grey shaded region) for glycerol, although not for citric acid. At higher mass fractions of water, the experimental data for both systems agree very well with the model prediction. For sucrose we observe a similar pattern; the model shows higher predictive power at higher mass fractions of water. The agreement of the model with experimental data where $\eta_{mix} > 10^8$ Pa s is especially encouraging for modelling ultra-high viscosities. However, we note that the logarithmic



Figure 2.4: Model intercomparison of mixture viscosity predictions as a function of mass fraction of water at T = 293.15 K. The mixing models shown are AIOMFAC-VISC (black solid lines) and three simple viscosity mixing rules (Eq. 2.14): molecular mole-fractionweighted (pink dashed lines), volume-fraction-weighted (blue dash-dotted lines) and surfacearea-fraction-weighted (yellow dotted lines) means of pure-component viscosities. Top row: the binary mixture of glycerol and water, with the pure-component viscosity of glycerol assigned from (**a**) the measured value or (**b**) predicted by the DeRieux et al. (2018) method. Bottom row: the binary mixture of citric acid and water, with the pure-component viscosity of citric acid assigned (**c**) based on an AIOMFAC-VISC fit of η_{org}^0 using the shown experimental data or (**d**) predicted by the DeRieux et al. (2018) method. Grey markers show experimental data from different methods (see key).



Figure 2.5: AIOMFAC-VISC mixture viscosity predictions as a function of mass fraction of water at 293.15 K for: (a) glycerol, (b) citric acid, (c) sucrose, and (d) trehalose. The solid black line is the AIOMFAC-VISC mixture viscosity prediction. The dashed black lines show the AIOMFAC-VISC sensitivity. The model sensitivity is assessed by calculating the response of the model to a small change in mixture composition (see Sect. 2.3.4). The grey shaded area denotes a 5 % uncertainty in the prediction of $T_{\rm g}$. Markers show experimental data. Error bars have been omitted when the length of the error bar does not exceed the width of the marker.

scale leads to seemingly good agreement at higher viscosities and seemingly higher scatter among experimental data at lower viscosity, while in absolute (non-logarithmic) terms, the agreement at lower viscosity is typically far better.

For compounds with a small molar mass ($< 200 \text{ g mol}^{-1}$) the AIOMFAC-VISC mixture viscosity prediction works well. Assessing the validity of the AIOMFAC-VISC viscosity prediction for compounds with larger molar masses (> 200 g mol⁻¹) is challenging, because experimental data are available only for a select few binary aqueous mixtures with large molecules (sucrose, trehalose, maltose, and raffinose). Moreover, these data sets are all for cyclic sugars, so it is questionable whether they serve as a widely-applicable assessment for AIOMFAC-VISC validity at higher molar mass or just AIOMFAC-VISC validity for mono, di, and tri-saccharides. Nonetheless, it appears as molar mass increases, the AIOMFAC-VISC prediction starts to deviate from experimental data for the binary mixtures tested that contain larger, highly-functionalized organic molecules. For example, this is evident for binary aqueous mixtures with trehalose. This reduction in predictability may be occurring for two reasons. First, the η^0 prediction becomes less accurate for larger molecules, particularly those with a molar mass above > 350 g mol^{-1} . Second, AIOMFAC-VISC may not be able to capture certain structural characteristics of the mixture components with the groupcontribution approach. Namely, as the mass fraction of water decreases, the movement of trehalose molecules in the mixture may become restricted due to an increase in the so-called free volume of each molecule. The free volume of trehalose molecules would be greater than the volume predicted based on the sum of contributing group volumes.

2.4.3 Multicomponent aqueous organic mixtures

A direct way to assess the accuracy of AIOMFAC-VISC mixture viscosity predictions is by evaluating model predictions against available experimental data for aqueous multicomponent mixtures for which we know the mass or mole fractions of components in the mixture. An example of an aqueous multicomponent system is shown in Fig. 2.6, where AIOMFAC-VISC is tested for aqueous sucrose and citric acid systems of different organic mixing ratios



Figure 2.6: (a) AIOMFAC-VISC-AIOFMAC mixture viscosity predictions as a function of relative humidity (lines) for a aqueous mixtures of sucrose and citric acid compared with aerosol optical tweezer experimental data (symbols) and poke-and-flow experimental data (shaded regions). The colours of the markers and curves correspond to mixtures with different concentrations of sucrose and citric acid. The three mixtures are composed of dry compositions of 40:60 (pink), 60:40 (blue), and 80:20 (yellow) percent mass fraction of sucrose:citric acid. (b) AIOMFAC-VISC mixture viscosity for the equimolar dicarboxylic acid mixture presented in Cappa et al. (2008). The solid line shows the AIOMFAC-VISC predicted mixture viscosity, dashed lines represent model sensitivity, and the shaded region represents a 5 % uncertainty in $T_{\rm g}$. Grey markers show the viscosity measurements in a limited RH range.

(40:60, 60:40, and 80:20 percent mass fraction of sucrose : citric acid). The model is run at the same temperature of 295 K as the mixture viscosity measurements conducted by Marsh et al. (2018) and Rovelli et al. (2019). We have omitted the model sensitivity envelope in Fig. 2.6 for clarity. Fitted pure-component viscosity values were used for this simulation for citric acid and sucrose in order to assess the AIOMFAC-VISC mixture viscosity prediction without introducing uncertainty from the DeRieux et al. (2018) pure-component viscosity prediction method. The model shows good agreement with the aerosol optical tweezers data for the 40:60 and 60:40 aqueous sucrose : citric acid mixtures. The model is less accurate for the 80:20 mixture, in which case the model consistently underestimates the measured viscosities. Based on Fig. 2.5, it appears the model is more accurate for predicting the mixture viscosity of binary, aqueous citric acid than for binary, aqueous sucrose. This may explain the better model performance in case of the 40:60 and 60:40 sucrose : citric acid mixtures as compared to the 80:20 mixture. Furthermore, we note that these optical tweezers measurements do not provide an independent estimation of the water contents at given RH; hence, a part of the model-measurement deviations may also be attributed to over-/underestimations of the actual mixture water content by AIOMFAC.

Well-characterized mixtures of known molecular compositions for viscosity purposes are scarce. The only other multicomponent mixture data to which we can compare our model to is shown in Fig. 2.6b. This multicomponent mixture (herein termed the "Cappa mixture") was first presented in Cappa et al. (2008). The Cappa mixture is comprised of equimolar amounts of nine dicarboxylic acids ($C_3 - C_{12}$). As before, the solid line in Fig. 2.6b indicates the AIOMFAC-VISC prediction, the dashed lines indicate the model sensitivity and the shaded region represents the 5 % uncertainty in T_g . Both the anhydrous and aqueous viscosity was measured experimentally by Booth et al. (2014) (diamond marker) and Song et al. (2016a) (degree le markers) for the Cappa mixture. Booth et al. (2014) measured the water-free viscosity to be approximately 6×10^6 Pa s and they also reported that the aqueous mixture viscosity remained semi-solid > 10^5 Pa s above ~ 0.8 mole fraction of water. This appears to differ from experimental data on the same system by Song et al. (2016a), which suggests that the viscosity of the Cappa mixture is in the liquid regime (~ 10^{-2} Pa s) even



Figure 2.7: AIOMFAC-VISC mixture viscosity predictions (solid line) for (a) α -pinene SOA at T = 293 K, (b) toluene SOA at T = 295 K, and (c) isoprene SOA at T = 295 K. The dashed lines represent the model sensitivity and the grey shaded regions represent a 5 % uncertainty in estimated $T_{\rm g}$ values. The markers and colour shaded regions represent experimental data obtained by different methods (see legend). T = R.T. indicates the measurements were taken at room temperature ($\sim 293 \pm 4$ K).

between 60 and 70 % RH. The AIOMFAC-VISC prediction does not agree well with either set of experimental data, although it falls in between the measured range and it does exhibit the same trend of moderate viscosity at low relative humidity, which steeply declines with increasing relative humidity.

2.4.4 Secondary organic aerosol systems

Finally, we test the AIOMFAC-VISC predictions against experimental data for three secondary organic aerosol systems, SOA derived from the oxidation of α -pinene, toluene, or isoprene (Fig. 2.7). In the case of α -pinene SOA, there are several distinct experimental data sets from the literature, which we used to compare to the AIOMFAC-VISC prediction. Most of the measurements were carried out at/near room temperature (T = R.T.), without a clearly quantified temperature range. A few sets of measurements are specified to have been taken between 293 – 295 K. Here we assume room temperature to be approximately 20 °C and so we have chosen to run the AIOMFAC-based gas-particle partitioning computations as well as AIOMFAC-VISC at 293 K. In the case of toluene- and isoprene-derived SOA, there are fewer experimental data sets and most measurements have been made at ~ 295 K, so for these two systems we matched our simulation temperature accordingly. For further details about the surrogate mixtures and compositions for all SOA defined in AIOMFAC-VISC see Section S6 of the SI.

SOA formed from α -pinene oxidation

In the case of laboratory measurements, α -pinene SOA is the most studied SOA system in the viscosity literature. Despite this, its viscosity remains poorly constrained in relative humidity space, i.e. there are large discrepancies in viscosity measurements taken at approximately the same relative humidity. Some of these discrepancies span several orders of magnitude. For example, at \sim 30 % RH, measurements of viscosity range from \sim 10⁴ – 10⁹ Pa s (Fig. 2.7a). The differences between those data sets occur likely for two reasons. First, a range of novel experimental techniques are used to measure the aerosol viscosity. The novelty of these techniques is owing to the non-trivial challenge of measuring ultra-high viscosities in situ. As a result, these techniques have a high degree of uncertainty and often only a range of possible viscosities can be provided, rather than a precise viscosity measurement. With large experimental uncertainties it is unsurprising that we also see a disparity between data sets. Second, the laboratory-made α -pinene SOA mixtures may vary greatly in composition from data set to data set depending on the method of SOA generation and sample extraction/preparation for viscosity measurements. For example, an SOA particle that experiences a longer oxidation time (or higher exposure to ozone and/or OH radicals) may contain a mixture with a higher average O:C ratio when compared to a particle that experienced a shorter oxidation time. A higher average O:C ratio for the particle mixture suggests it may contain a larger fraction of molecules with oxygen-bearing functional groups and potentially more diversity in the branching characteristics of molecular structures from the parent hydrocarbon. The molecules may also be larger and of higher molar mass on average (barring substantial fragmentation). As a result, the SOA particle that was given more time to oxidize may have a higher mixture viscosity (particularly at low RH). Grayson et al. (2016) also provide evidence that production aerosol mass concentrations are inversely proportional to the SOA viscosity. From gas-particle partitioning theory and experimental evidence, a higher abundance of less-oxidized components in the SOA is expected for high aerosol loading chamber experiments. This provides further evidence that the production method of α -pinene SOA can have a non-trivial influence on the measured viscosity. It also suggests that the viscosity of laboratory-generated SOA may underestimate ambient SOA viscosity, because laboratory-generated SOA mass concentrations (for viscosity measurement purposes) have often been several orders of magnitude higher than the concentrations typical in ambient air.

Ultimately, the spread in experimental data makes it difficult to assess AIOMFAC-VISC's viscosity prediction capabilities in great detail. Of course, AIOMFAC-VISC cannot simultaneously agree with all experimental data sets. However, we can compare the AIOMFAC-VISC prediction with specific measurements by adjusting our representative α -pinene SOA mixture in the model. Specifically, we adjust the molar ratios of products in our representative α -pinene SOA mixture, such that its average O:C ratio is similar to the average O:C of the SOA reported for the experimental data set in question. For the viscosity simulations, we further turn off partitioning of organics between the particle and the gas phase in order to ensure that the O:C remains constant and the particle composition remains fixed (except for water content) regardless of relative humidity. This approach mimics the conditions under which viscosity measurements at different RH levels are typically done with a specific SOA sample extracted during a laboratory experiment. We have chosen to "target" the data set of bead mobility measurements from Renbaum-Wolff et al. (2013) because they report an expected O:C for the mixtures used in their bead mobility experiments and this is the data set with the smallest experimental uncertainty across all measurements (for RH > 70 %). The small uncertainties are likely a result of the higher relative humidity and therefore lower mixture viscosity. Consequently, if we have a high degree of confidence in this data set then we can assume AIOMFAC-VISC's prediction to be an extrapolation of the SOA properties from these measurements over the whole RH range.

Renbaum-Wolff et al. (2013) report that the expected O:C of their SOA mixtures is approximately 0.3 to 0.4, which they justify from previous measurements of O:C for α -pinene

generated via ozonolysis in an environmental chamber (see the Supporting Information from Renbaum-Wolff et al. (2013)). In Fig. 2.7a we have adjusted the composition of the representative α -pinene SOA mixture such that AIOMFAC-VISC is in excellent agreement with bead mobility viscosity measurements from Renbaum-Wolff et al. (2013). Although, the adjustments made to achieve this agreement results in an average O:C of 0.51. If SOA constituent concentrations are modified to produce an average mixture O:C of ~ 0.4, then the model is in agreement with the measurements from Grayson et al. (2016), but not with those of Renbaum-Wolff et al. (2013). By choosing to fit the model to the data of Renbaum-Wolff et al. (2013), the general shape of the AIOMFAC-VISC prediction curve appears reasonable and ensures most of the experimental data fall within the uncertainty in $T_{\rm g}$ values. Furthermore, the $T_{\rm g}$ value predictions produce a water-free mixture viscosity for the SOA mixture that agrees well with the data by Zhang et al. (2015) for RH < 1 %. Although, we acknowledge that this approach removes an element of predictability from AIOMFAC-VISC.

We also note that AIOMFAC-VISC is capable of predicting the mixture viscosity of multiple aerosol phases should liquid–liquid phase separation (LLPS) occur. For example, in α -pinene SOA free of ammonium sulfate, LLPS is still expected to occur at high RH, although it is not resolved in Fig. 2.7 because LLPS occurs in this case at very high water activity only.

SOA formed from toluene and isoprene oxidation

Similarly, for comparison with the toluene SOA experimental data we also adjusted the representative toluene SOA mixture (see Supplementary Information). Song et al. (2016b) determined an average O:C ratio of 1.08 for SOA particles they generated with a mass concentration of $60 - 100 \ \mu g \ m^{-3}$ during production. They also note that this is in agreement with previous measurements of toluene SOA O:C of 0.9 – 1.3 generated under similar conditions. The toluene SOA particles investigated by Li et al. (2015) also have an O:C in the range of 1.0 - 1.2. Therefore, we adjusted our representative mixture in terms of relative surrogate compound composition, such that an O:C of 1.2 resulted. The AIOMFAC-VISC viscosity predictions for the adjusted toluene SOA system can be found in (2.7b). Accounting

for error and model sensitivity, the predictions agree very well with the data for RH > 40 %, while the agreement decreases below 40 % RH. It seems the model lacks the curvature necessary to fully capture the experimental data at low relative humidity; however, both the experimental uncertainty and model sensitivity span orders of magnitude in mixture viscosity for RH < 30 %. In addition, as mentioned above, the chemical makeup of toluene SOA was likely different in different experiments, with the specific O:C having an influence on the water uptake and thereby viscosity, which may lead to a lower viscosity of higher-O:C SOA samples, especially for RH > 10 %, where water uptake is non-negligible in these systems of relatively high average O:C.

Neither Song et al. (2016a) nor Bateman et al. (2015) have provided O:C values for their isoprene SOA; however, Li et al. (2015) produced isoprene SOA under similar conditions and they measure an O:C of 0.8 - 1.0. After adjustment, the O:C of our representative isoprene SOA mixture is 1.1 (see SI for details) and the AIOMFAC-VISC viscosity prediction for this mixture is shown in (2.7c). Here, the model slightly underpredicts the viscosity of isoprene SOA at high relative humidity and slightly overpredicts at low relative humidity. However, considering the combination of experimental error and model uncertainty, there is reasonable agreement between the AIOMFAC-VISC predictions and most data points. Overall, the model does a reasonable job of representing isoprene SOA in comparison to these experimental data sets.

2.5 Atmospheric Implications

While SOA reside largely in the planetary boundary layer (PBL) (Tsigaridis and Kanakidou, 2003), there are aircraft (Heald et al., 2006) and ground-based measurements (Schum et al., 2018) of significant SOA concentrations in the free troposphere (FT). As such, we can expect SOA to be exposed to a wide range of temperature and relative humidity conditions. Shiraiwa et al. (2017) investigated the phase state of SOA for ambient temperature and relative humidity conditions for the PBL and the FT. Using a global chemistry climate model and estimating SOA phase state based on a glass transition temperature approach, they conclude



Figure 2.8: Mixture viscosity predicted by AIOMFAC-VISC as a function of temperature and relative humidity for simulated (a) α -pinene SOA, (b) toluene SOA, and (c) isoprene SOA. Dashed contour lines denote the values of $\log_{10} (\eta_{\text{mix}}$ Pa s). Coloured regions indicate conventional, viscosity-based classifications of liquid (blue), semi-solid (yellow), and amorphous solid (green) physical states. The green horizontal lines in (a) denote ranges of RH and T for which Järvinen et al. (2016) measured a viscosity "phase" transition from solid or semi-solid to liquid in α -pinene SOA. They determined this viscosity transition to occur at $\eta_{\text{mix}} = 10^7$ Pa s. The solid coloured lines indicate three trajectories in temperature versus RH space for an idealized adiabatic air parcel uplift containing SOA particles for different initial conditions. The assigned initial conditions are T = 288 K, RH = 20 % (blue); T = 300 K, RH = 30 % (pink); and T = 300 K, RH = 70 % (yellow). The dash-dotted blue line depicts the possible range of relative humidity experienced by SOA particles should they survive cloud processing and remain at their saturation altitude.

that SOA phase state is largely dependent on relative humidity in the PBL. Their results showed SOA exist mostly in the liquid state in the tropics and polar regions while SOA are in semi-solid phase state in arid, continental regions. Shiraiwa et al. (2017) also predict that SOA would be almost entirely semi-solid and/or glassy in the FT.

The aforementioned work is also consistent with the results from Maclean et al. (2017) for the PBL. Maclean et al. (2017) used a parameterization of viscosity as a function of temperature and relative humidity based on experimental data for laboratory-generated α pinene SOA. They found that the mixing times within α -pinene SOA particles were less than one hour in the PBL, where SOA concentrations were most spatially and temporally significant, suggesting SOA would be mostly liquid or somewhat semi-solid.

Both Shiraiwa et al. (2017) and Maclean et al. (2017) consider the phase state of SOA strictly based on averaged ambient temperature and relative humidity conditions. In effect, this approach provides a snapshot of SOA phase state for a given location in the atmosphere. but it ignores the temperature and relative humidity changes the SOA particles are exposed to during transport. The snapshot approach may overestimate the significance of semi-solid and glassy SOA at higher tropospheric altitudes. Indeed, SOA transported from the PBL to the FT may be lifted in convective updrafts, in which they will experience a decrease in temperature, but simultaneously an increase in relative humidity. Due to the plasticising effect of water, initially viscous SOA carried in an updraft may transition from semi-solid to liquid and go on to activate as cloud condensation nuclei or experience in-cloud scavenging. Alternatively, SOA may undergo some plasticising in an updraft, but remain viscous enough to avoid substantial cloud processing, depending on their CCN ability and whether cloud formation conditions are reached during transport. SOA may avoid such drastic temperature and relative humidity changes altogether if they meander to higher altitudes in slowly moving air masses. Of course, these scenarios are all contingent on the initial SOA viscosity and hygroscopicity and the extent of relative humidity increase the SOA experiences, which is linked to the type and duration of upward/downward transport. Ultimately, the history of the SOA is important for understanding the potential of viscous aerosol particles to act as ice nuclei or to be involved in long-range transport of pollutants.

To this end, we have used the AIOMFAC-VISC model to simulate the change in viscosity during an idealized adiabatic uplift of an air parcel containing α -pinene, toluene, or isoprene SOA. In Fig. 2.8, we first compute the relationship between SOA viscosity, temperature, and relative humidity as predicted by the model. We note that the simulated SOA mixtures used to generate Fig. 2.8 are the same as those shown in Fig. 2.7. Comparing the three SOA cases investigated, α -pinene SOA is highly viscous for a larger area of the tropospherically-relevant temperature–relative humidity space than toluene or isoprene SOA. With the enhanced hygroscopicities of the latter contributing to their lower viscosity at higher temperatures and RH > 60 %. Overlaid on the contour plots of Fig. 2.8 are three idealized adibatic air parcel updrafts represented by their temperature and relative humidity relationship prior to cloud formation (i.e. for RH < 100 %). Each updraft has a temperature lapse rate of 10 K km⁻¹ and is assumed to start near 0 m above sea level, where the mean air pressure is 1000 hPa.

The three convective updrafts have different initial temperature and RH conditions, meant to represent different surface climates. Colder and rather dry surface conditions are represented by the blue curves, which have an initial temperature of 288 K and relative humidity of 20 %, where the lifting condensation level (RH = 100 %) of the SOA-containing air parcel is ~ 2712 m above sea level. These initial conditions are meant to mirror the ambient conditions of the field experiments done by Virtanen et al. (2010). By considering the conventional viscosity-based phase state classifications, the viscosity for all three SOA in this simulation are initially semi-solid, but all transition to liquid at higher altitudes. If we consider that fragile organic compounds may transition to a glassy state at viscosities up to four orders of magnitude lower than 10^{12} Pa s, then the α -pinene SOA may be glassy just above the surface. In this case, the final altitude of the SOA before saturation, suggests it can reach the free troposphere if we assume the PBL does not extend beyond 1 km altitude, which may be a reasonable assumption for cold and dry regions during day time.

The pink curves in Fig. 2.8 show relatively warm (300 K) and dry (30 % RH) surface conditions, meant to represent arid climates. Here the lifting condensation level of the parcel is reached at ~ 2272 m altitude. Again, all three SOA types are semi-solid near the sur-

face where the intermediate relative humidity level dominates over the warmer temperature concerning mixture viscosity. At higher altitudes, the transition from semi-solid to liquid occurs. In subtropical arid regions, we expect the PBL to extend to higher altitudes, so it is possible for SOA-containing updrafts to reach water saturation prior to entering the free troposphere. Finally, warm and wet climates are represented by the yellow curves with an initial temperature of 300 K and RH of 70 %, where the parcel altitude reached at 100 % RH is 717 m. In this case, none of the three SOA mixtures will have viscosities greater than that of a liquid and they will experience water saturation within the PBL.

The initial conditions of the updrafts were chosen to demonstrate examples of mixture viscosity values we can expect for ambient SOA at equilibrium with their environment. This is to say that we do not expect to frequently see drier conditions at the surface than what is represented with the blue curves in Fig. 2.8. As a result, we can expect that SOA carried adiabatically to higher altitudes have the potential to become highly viscous, but not necessarily glassy before they experience their first cloud-processing event. After spending time in a cloud along their parcel trajectory, in the absence of wet removal via precipitation, such SOA particles (potentially cloud-processed) may remain at similar altitude in the upper PBL or the FT and experience there conditions of lower RH (moving horizontally in the diagrams of Fig. 2.8), leading to evaporative loss of aerosol water accompanied by an increase in viscosity. Hence, while the aerosols may end up remaining for hours to days in the FT in a semi-solid or glassy viscosity range at lower temperatures, these particles may have experienced conditions of liquid-like viscosity and associated fast internal mixing and gas–aerosol exchange during certain times of their journey to the free troposphere.

2.6 Conclusion

The main product of this work is a new model, AIOMFAC-VISC, which predicts the viscosity of atmospherically relevant mixtures as a function of temperature, relative humidity, and mixture composition over a wide range of phase states. The model uses a thermodynamic group-contribution approach to predict mixture viscosity. The mixture viscosity prediction is constrained by parameterizations of the pure-component viscosity values of the individual mixture components. For water we use a parameterization by Dehaoui et al. (2015). For the organic components we use the method of DeRieux et al. (2018). Over the course of developing the model we found that the parameterization of the pure-component viscosity of the organic constituents is likely the largest source of uncertainty in the AIOMFAC-VISC predictions. This uncertainty arises from an underlying uncertainty in the prediction of pure-component glass transition temperatures and the choice of the fragility parameter.

We have assessed the validity of the AIOMFAC-VISC mixture viscosity predictions for binary as well as multicomponent aqueous mixtures where the pure-component viscosities of the organics are well constrained by experimental data. In those cases we did not use the DeRieux et al. (2018) pure-component viscosity prediction method; instead we supplied the mixing model with known pure-component viscosity values. By doing so, we demonstrate that AIOMFAC-VISC can predict mixture viscosity over a range of > 12 orders of magnitude (validated by data from $\sim 10^{-3} - 10^9$ Pa s). Using the DeRieux et al. (2018) pure-component viscosity prediction method for the same cases can introduce a notable error in the predicted mixture viscosity. However, at present, the DeRieux et al. (2018) method is the most widelyapplicable and reliable way for the prediction of pure-component viscosities of multifunctional organics of atmospheric relevance. Ultimately, in order to fully realize the predictive power of AIOMFAC-VISC, the pure-component viscosity prediction will need to be improved.

Notwithstanding, the AIOMFAC-VISC mixture viscosity prediction alongside the De-Rieux et al. (2018) pure-component viscosity prediction method is shown to be valid for SOA mixtures where the model can be compared to room temperature experimental data (α -pinene, toluene, and isoprene SOA) and where adequate SOA surrogate mixtures can be established. Mixture viscosity was also simulated for relevant ranges in temperature (230 – 300 K) and relative humidity (0 – 100 %) to determine expected viscosity regimes for ambient SOA. The validity of the AIOMFAC-VISC prediction for SOA mixtures provides insight into the viscosity of SOA formed near the Earth's surface that are then transported to higher altitudes. By simulating an idealized adiabatic updraft, we determine that under most conditions α -pinene, toluene, and isoprene SOA will either be semi-solid or liquid close to the surface, but that an increase in relative humidity with upward transport will result in a transition to the liquid state. Only in the coldest and driest conditions can we expect SOA to approach a glassy state and remain semi-solid during transport into the free troposphere. In the lower troposphere at temperatures above 0 °C, given the slight to moderate hygroscopicity of SOA phases, our model predicts that such particles are typically semi-solid or liquid-like. Associated diffusion times for water are fast; however, the gas-particle equilibration time of organic compounds is on the order of seconds to minutes (Koop et al., 2011). While relatively fast, such viscosities may impact the interpretation of ground-based or aircraft aerosol measurements with instruments within which the aerosol sample experiences a residence time of order ten seconds or less (Shingler et al., 2016).

The ability of AIOMFAC-VISC to provide mixture viscosity predictions for complex multicomponent mixtures is owing to the flexibility afforded by the group-contribution approach and the DeRieux et al. (2018) pure-component viscosity prediction method. While further investigation will be needed to refine the pure-component viscosity prediction, at present AIOMFAC-VISC is suitably robust to make predictions of SOA mixture viscosity from the liquid to the amorphous glassy regime. Future work will involve extending AIOMFAC-VISC to account for the effect of dissolved inorganic electrolyte components present in aerosol phases.

2.7 Supplementary Information

2.7.1 Estimation of the pure component viscosity of water

The pure component viscosity of water was estimated using the parameterization developed by Dehaoui et al. (2015) for all model simulations in this work; see Eq. (10) of main text. The experimental data used for developing the Dehaoui et al. (2015) parameterization extends from 239.15 K to 491.95 K. The parameterization is in excellent agreement with the data when temperatures are below ~ 400 K. In Fig. 2.9, we compare the Dehaoui et al. (2015) parameterization with a parameterization by Viswanath et al. (2007) and with experimental



Figure 2.9: Parameterizations of the pure-component viscosity of water from Dehaoui et al. (2015) (solid line) and Viswanath et al. (2007) (dashed line). Markers represent experimental data where error bars have been omitted for clarity. The Dehaoui et al. (2015) parameterization is supported by measurements from ~ 230 to 400 K and the Viswanath et al. (2007) parameterization is supported by measurements from ~ 270 to 500 K.

data. The parameterization by Viswanath et al. (2007) is in better agreement with experimental data above ~ 400 K when compared to the Dehaoui et al. (2015) parameterization. The Viswanath et al. (2007) parameterization is also in excellent agreement with the experimental data down to ~ 270 K, below which it begins to deviate substantially from the available experimental data. Between 270 K and ~ 380 K the two parameterizations are almost indistinguishable. Here we choose to use the Dehaoui et al. (2015) parameterization given that it is the more robust parameterization at lower temperatures of relevance in the troposphere.

2.7.2 Exploration of the relationship between pure component vapour pressure and viscosity

In this study, initially an attempt was made to estimate the pure component viscosity of organic compounds from their pure component vapour pressures. The pure component viscosity is shown as a function of pure component vapour pressure in double logarithm space in Fig. 2.10. There is only a weak linear relationship between viscosity and vapour pressure when considering the range of viscosity from liquid to glassy for both the Nannoolal et al. (2008) and EVAPORATION model vapour pressure predictions. A stronger linear relationship exists in the liquid range, but below a vapour pressure of 10^{-5} Pa, the relationship between viscosity and vapour pressure becomes less clear and reliable data are scarce. We still hypothesize a relationship to exist between the two pure-component properties even in the semi-solid and glassy regimes. Although, it is likely this relationship is not resolved with the vapour pressure and viscosity estimation tools used here, given these tools have been trained with compounds that have higher vapour pressure and liquid viscosity only. Just as direct measurements of ultra-high pure-component viscosities are challenging to make, so too are measurements of ultra-low pure component vapour pressures. In order to fully elucidate the relationship between the two material properties, more precise experimental measurements are needed to better constrain pure-component property estimation tools.

Table 2.1: Measured, parameterized, or modelled values of the glass transition temperature (T_g) from the literature. Uncertainty values are listed when they are provided from their source.

Compound	$T_{\rm g}$ (K)	Reference
1,2,4-Butanetriol	200.7	Nakanishi and Nozaki (2011)
1,2,6-Hexanetriol	202	Böhmer et al. (1993)
	206.4 ± 0.5	Dorfmüller et al. (1979)
	201.9	Nakanishi and Nozaki (2011)
	192 ± 2	Zhang et al. (2018)
	193.3 ± 1.3	Zobrist et al. (2008)
1,4-Butanediol	158.4 ± 1.1	Zobrist et al. (2008)

Continued on next page

Compound	$T_{\rm g}~({\rm K})$	Reference
Citric Acid	281 ± 5	Bodsworth et al. (2010)
	286 ± 1.5	Dette et al. (2014)
	273.25 ± 3.4	Hoppu et al. (2009)
	281.9 ± 0.9	Lienhard et al. (2012)
	284.15 ± 0.2	Lu and Zografi (1997)
	286 ± 10	Marsh et al. (2018)
	260 ± 10	Murray (2008)
	$283.35^{\text{in situ}}$	Timko and Lordi (1979)
	286.65^{bulk}	Timko and Lordi (1979)
	307 ± 5	Zhang et al. (2018)
Fructose	283.15	Ablett et al. (1993)
	286	Angell (1997)
	283	Ollet and Parker (1990)
	289^{mid}	Simatos et al. (1996)
Glucose	306	Angell (1997)
	297 ± 2	Dette et al. (2014)
	309	Kawai et al. (2005)
	293.2 ± 0.9	Lienhard et al. (2012)
	304	Ollet and Parker (1990)
	296^{mid}	Simperler et al. (2006)
	$325^{\text{calculated}}$	Simperler et al. (2006)
	296.1 ± 3.1	Zobrist et al. (2008)
Glycerol	187	Angell (1997)
	193	Angell (1997)
	190	Böhmer et al. (1993)
	191 ± 0.9	Lienhard et al. (2012)
	191.7	Nakanishi and Nozaki (2011)
	196	Seidl et al. (2013)
	192 ± 2	Zhang et al. (2018)
Raffinose	377.9 ± 0.9	Lienhard et al. (2012)
	395.7 ± 21.6	Zobrist et al. (2008)
Sorbitol	266	Angell (1997)
	274	Böhmer et al. (1993)
	268.3	Nakanishi and Nozaki (2011)
		Continued on next page

 Table 2.1 – Continued from previous page

Compound	$T_{\rm g}$ (K)	Reference	
	276^{mid}	Simatos et al. (1996)	
Sucrose	323	Angell (1997)	
	331 ± 2	Dette et al. (2014)	
	350 ± 3.5	Hancock et al. (1995)	
	341	Kawai et al. (2005)	
	341	Rothfuss and Petters (2017)	
	333^{mid}	Simperler et al. (2006)	
	$347^{\text{calculated}}$	Simperler et al. (2006)	
	335.7 ± 3.6	Zobrist et al. (2008)	
Trehalose	388	Angell (1997)	
	369 ± 1.5	Dette et al. (2014)	
	386	Kawai et al. (2005)	
	380^{mid}	Simperler et al. (2006)	
	$392^{\text{calculated}}$	Simperler et al. (2006)	

Table 2.1 - Continued from previous page

2.7.3 Estimation of AIOMFAC-VISC sensitivity

We calculated the sensitivity of AIOMFAC-VISC as a proxy for the uncertainty in the mixture viscosity prediction. We chose to prescribe the AIOMFAC-VISC sensitivity as the response of the mixture viscosity prediction to a small change in mixture composition. A small change in mixture composition is meant to represent the uncertainty in the composition measurement in a laboratory setting, which would be typical of all experiments. Therefore, the AIOMFAC-VISC sensitivity of mixture viscosity, s_{η} , is calculated using a molar partial derivative:

$$s_{\eta} = x^{\text{tol}} \left[\frac{\partial \ln(\eta_{\text{mix}})}{\partial n_{\text{H}_2\text{O}}} \right]$$
(2.15)

where x^{tol} is the molar tolerance (the prescribed uncertainty) in the mixture composition. To retrieve x^{tol} we first perturb the mass of water by $\delta_m = 2$ % relative to the mass of the



Figure 2.10: Reference or modelled pure component viscosity as a function of modelled pure component vapour pressure. Vapour pressures have been estimated using (a) the online tool UManSysProp (http://umansysprop.seaes.manchester.ac.uk) with the Nannoolal et al. (2008) vapour pressure model and the Nannoolal et al. (2004) boiling point estimation method and (b) the EVAPORATION model (Compernolle et al., 2011). Purple markers indicate values where the viscosity has been modelled using the method by Nannoolal et al. (2009). Blue markers indicate reference viscosity values either from direct experimental measurements or from an extrapolation with the Vogel–Tamman–Fulcher equation to T = 293.15 K using pure-component viscosity values measured at higher temperatures. All model values have been calculated at 293.15 K. Reference viscosity values are taken at a range of temperatures (295 ± 5 K). Dashed black lines indicate linear regressions (in logarithm space) to the combined reference and model data.

total system,

$$m_{\rm H_2O} = m_{\rm H_2O,init} + \delta_m, \qquad (2.16)$$

where $m_{\rm H_2O,init}$ is the initial mass of water in the mixture (e.g. $m_{\rm H_2O,init} = w_{\rm H_2O,init}$ for 1 kg of total mass of the mixture) and $m_{\rm H_2O}$ is the perturbed mass. Next, the mass fractions of all components are normalized to account for the mass addition via

$$w_i = \frac{w_{i,\text{init}}}{1+\delta_m},\tag{2.17}$$

where w_i represents the normalized mass fraction of a given component *i* given the initial mass fraction $w_{i,init}$. By doing this, we prescribe the model sensitivity as strictly a change in water content of the mixture, where the mixing ratio of organic constituents remains fixed. The normalized mass fractions are then converted to mole fractions (x_i) and finally, x^{tol} is calculated as the difference between the mole fractions of the perturbed system and the unperturbed system.

$$x^{\text{tol}} = x_{\text{H}_2\text{O}} - x_{\text{H}_2\text{O,init}}.$$
 (2.18)

2.7.4 Comparison of AIOMFAC-VISC and GC-UNIMOD

Here we compare the performance of the mixture viscosity prediction of AIOMFAC-VISC with the original Cao et al. (1993a), GC-UNIMOD model. To compare the mixture viscosity prediction absent of uncertainty introduced by the pure-component viscosity prediction, we have fixed the pure-component viscosity of citric acid to a fitted value at the temperature of interest here (as described in the main text) and we have used the experimental pure-component viscosity of glycerol. As seen in Fig. 2.11 the AIOMFAC-VISC mixture viscosity prediction is greatly improved from that by the GC-UNIMOD model. The same behaviour was observed for the other binary aqueous mixtures investigated in this work.



Figure 2.11: A comparison of predicted mixture viscosity as a function of mass fraction of water (blue curves) shown for glycerol (top two panels) and citric acid (bottom two panels). The AIOMFAC-VISC mixture viscosity prediction for glycerol (\mathbf{a}) and citric acid (\mathbf{c}) is in significantly better agreement with the experimental data (red markers) as compared to the GC-UNIMOD mixture viscosity prediction for both glycerol (\mathbf{b}) and citric acid (\mathbf{d}).

2.7.5 Binary aqueous mixture viscosity predictions for all training data

To optimize the mixing model of AIOMFAC-VISC, we attempted to simultaneously fit the mixing model prediction to experimental viscosity data for the binary aqueous mixtures shown in Figs. 2.12, 2.13, and 2.14. The fit is captured by an adjustable parameter multiplied by the residual component of the mixture viscosity model. The determination of an optimal fit parameter is a global minimization problem, ideally approached by using a set of global optimization methods. For this, we used the optimization approach described by Zuend et al. (2011). The optimal fit parameter was determined to be ~ 1.0 , therefore no further adjustments were made to the mixture viscosity model aside from those adjustments made to the original Cao et al. (1993a) formulation described in the main text.

2.7.6 Determination of SOA systems

For all three SOA systems simulated in this work, each surrogate compound was assigned a fixed molar concentration in the particulate matter (PM). These fixed molar concentrations in mol m⁻³ (of air) are listed in Tables 2.2, 2.3, and 2.4 for α -pinene-, toluene-, and isoprene-derived SOA, respectively. To determine those molar concentration of constituents for the α -pinene and isoprene SOA systems, we begin by calculating the equilibrium gas-particle partitioning of the surrogate species in each SOA system using the MCM–EVAPORATION–AIOMFAC approach (Zuend et al., 2011) where the initial total molar concentrations (PM plus gas phase) for α -pinene and isoprene SOA were taken from Zuend and Seinfeld (2012) and Rastak et al. (2017), respectively. We extract the molar concentration of each constituent in the PM phase for a relative humidity of 40 %. When relative humidity is held at 40%, the average O:C ratio of the SOA produced via our gas-particle partitioning prediction is representative of known O:C ratios from experiments. We then hold the molar concentrations of organics in the PM constant during calculations of mixture viscosity. In the case of α -pinene SOA, we have made one additional adjustment by scaling the molar amount of surrogate compound C₁₀₈OOH in the PM phase by a factor of 30. This is done to better



Figure 2.12: AIOMFAC-VISC mixture viscosity predictions as a function of mass fraction of water at 293.15 K for (a) 1,2,4-butanetriol, (b) 1,2,6-hexanetriol, (c) 1,4-butanetriol, and (d) erythritol. The solid black line is the AIOMFAC-VISC mixture viscosity prediction. The dashed black lines show the AIOMFAC-VISC sensitivity. The sensitivity is assessed by calculating the response of the model to a small change in mixture composition. The grey shaded region denotes a 5 % uncertainty in the prediction of T_g . Markers show experimental data. Error bars have been omitted when the length of the error bar does not exceed the width of the marker.



Figure 2.13: AIOMFAC-VISC mixture viscosity predictions as a function of mass fraction of water at 293.15 K for (a) fructose, (b) glucose, (c) maltose, and (d) raffinose. The solid black line is the AIOMFAC-VISC mixture viscosity prediction. The dashed black lines show the AIOMFAC-VISC sensitivity. The sensitivity is assessed by calculating the response of the model to a small change in mixture composition. The grey shaded region denotes a 5 % uncertainty in the prediction of $T_{\rm g}$. Markers show experimental data. Error bars have been omitted when the length of the error bar does not exceed the width of the marker.



Figure 2.14: AIOMFAC-VISC mixture viscosity predictions as a function of mass fraction of water at 293.15 K for (a) acetic acid, (b) glutaric acid, (c) maleic acid, and (d) sorbitol. The solid black line is the AIOMFAC-VISC mixture viscosity prediction. The dashed black lines show the AIOMFAC-VISC sensitivity. The sensitivity is assessed by calculating the response of the model to a small change in mixture composition. The grey shaded region denotes a 5 % uncertainty in the prediction of $T_{\rm g}$. Markers show experimental data. Error bars have been omitted when the length of the error bar does not exceed the width of the marker.

Table 2	2.2:	M	CM-de	erivec	l surro	ogate (componer	nts	for a	lpha-	pin	ene
oxidati	ion	by	ozone	and	their	fixed	amounts	in	mol	${\rm m}^{-3}$	in	the
particu	ılat	e m	atter	(PM)) phas	e.						

Name (MCM)	O:C	$M \ (\mathrm{g \ mol}^{-1})$	mol ${\rm m}^{-3}$ in PM phase
C107OOH	0.4	200.231	2.1860×10^{-10}
PINONIC	0.3	184.232	1.2356×10^{-10}
C97OOH	0.44	188.22	2.5175×10^{-9}
C108OOH	0.5	216.231	8.4010×10^{-8}
C89CO2H	0.33	170.206	2.010×10^{-11}
PINIC	0.444	186.205	8.0263×10^{-9}
C921OOH	0.56	204.220	9.2106×10^{-9}
C109OOH	0.4	200.231	1.5748×10^{-11}
C812OOH	0.625	190.194	8.4291×10^{-9}
HOPINONIC	0.4	200.232	2.3266×10^{-9}
C811OH	0.375	158.094	8.9370×10^{-11}
C813OOH	0.75	206.193	3.2969×10^{-9}
ALDOL dimer	0.375	368.421	5.9996×10^{-10}
ESTER dimer	0.375	368.421	2.3998×10^{-9}

¹ The ALDOL dimer and ESTER dimer are not predicted by MCM. Justification for including the dimers can be found in Zuend and Seinfeld (2012).

² The average O:C ratio of the predicted α -pinene SOA mixture is 0.507 (for 27.248 μ g m⁻³ of SOA formed at T = 293.15 K).

match the curvature of the experimental viscosity data at high relative humidity. In the case of toluene SOA, we have selected several constituents from the MCM-derived list of surrogate components from toluene photo-oxidation by OH radicals. To determine the molar concentrations of a given constituent (n_i) in the PM phase we use the following formula:

$$n_i = \text{O:C} \times T_g \times 10^{-10}.$$
 (2.19)

Using this scaling results in the O:C of the SOA produced to be similar to what is expected from laboratory chamber experiments. We note here that we have increased the concentration of compound C_{535} OOH by a factor of 5 to increase the average mixture O:C from 0.96 to 1.12.

Table 2.3: MCM-derived surrogate components for toluene oxidation by OH and their fixed amounts in mol m^{-3} in the particulate matter (PM) phase.

Name (MCM)	O:C	$M~({\rm g~mol^{-1}})$	mol m^{-3} in PM phase
C5134CO2OH	0.8	130.099	1.9868×10^{-8}
C5CO234	0.6	114.099	1.3525×10^{-8}
PMALNHY2OH	0.714	174.151	1.9267×10^{-8}
C6H5CH2OOH	0.286	124.137	5.8337×10^{-9}
CRESOOH	0.857	190.151	2.4241×10^{-8}
TLEPOXMUC	0.429	140.137	1.9987×10^{-8}
MALANHY	0.75	98.057	1.6884×10^{-8}
C3DIALOOH	1.333	104.062	3.0168×10^{-8}
C33CO	1.0	86.046	2.2626×10^{-8}
C23O3CCHO	0.8	130.099	1.9868×10^{-8}
C535OOH	1.4	180.113	2.0366×10^{-7}
C534OOH	1.4	180.113	4.0863×10^{-8}

¹ The average O:C ratio of the predicted toluene SOA mixture is 1.12 (for 301 μ g m⁻³ of SOA formed at T = 295.15 K).

Name (MCM)	O:C	$M \ (\mathrm{g \ mol}^{-1})$	mol m ^{-3} in PM phase
IEB1OOH	1.0	150.1120	2.1859×10^{-9}
IEB2OOH	1.0	150.1120	3.8058×10^{-11}
C59OOH	1.0	150.0940	6.4468×10^{-9}
IEC100H	1.0	150.0940	2.2503×10^{-9}
C58OOH	1.0	150.1120	2.2710×10^{-10}
IEPOXA	0.6	118.1308	1.6303×10^{-31}
C57OOH	1.0	150.1120	1.8452×10^{-10}
IEPOXC	0.6	118.1308	3.7912×10^{-21}
HIEB1OOH	1.2	166.1120	2.3492×10^{-9}
INDOOH	1.4	197.1380	1.6072×10^{-9}
IEACO3H	1.0	148.0960	1.8935×10^{-19}
C525OOH	1.2	166.0940	1.7850×10^{-9}
HIEB2OOH	1.2	166.1120	1.0495×10^{-9}
IEC2OOH	1.0	148.0600	2.0814×10^{-17}
INAOOH	1.4	197.1380	7.2618×10^{-10}
C510OOH	1.4	195.1040	5.5325×10^{-13}
INB100H	1.4	197.1380	4.6077×10^{-10}
IECCO3H	1.0	148.1148	1.2558×10^{-17}
INCOOH	1.4	197.1380	8.7075×10^{-11}
INB2OOH	1.4	197.1380	1.8653×10^{-10}
Tetrol dimer	1.43	254.2768	3.9110×10^{-18}

Table 2.4: MCM-derived surrogate components for isoprene photo-oxidation and their fixed amounts in mol m^{-3} in the particulate matter (PM) phase.

¹ The average O:C ratio of the predicted isoprene SOA mixture is 1.12 (for 3.406 $\mu g m^{-3}$ of SOA formed at T = 295.15 K). See the SI of Rastak et al. (2017) for chemical formulas and justification for the tetrol dimer.

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Chapter 3

Future Work

3.1 Bulk diffusion and mixture viscosity in organic aerosol

3.1.1 The Stokes–Einstein relation

Viscous OA are slower to respond to changes in gas-phase composition, suggesting that gas-particle partitioning and heterogeneous chemistry may be kinetically limited by slowly diffusing species in a highly viscous organic matrix. One method to quantify the mixing times of components in viscous OA is to translate viscosity (a mixture property) into bulk diffusion mixing timescales (a kinetic property) via the Stokes–Einstein (SE) relation. The SE relation states that the translational diffusion coefficient, D of a Brownian particle is inversely proportional to the viscosity of the mixture, η_{mix} it is diffusing through,

$$D = \frac{\mathbf{k}_{\mathrm{b}}T}{6\pi r\eta_{\mathrm{mix}}}.\tag{3.1}$$

Here k_b is Boltzmann's constant, T is the temperature in Kelvins, and r is the hydrodynamic radius of the Brownian particle. While the SE relation was originally intended to describe diffusion of Brownian particles, it has been also been derived using a free volume approach where the diffusing species is of similar size to the molecules it is diffusing through (Das, 2011). Its applicability at the molecular scale has also been shown to be valid using molecular dynamics simulations (Bocquet et al., 1994). In this manner, the diffusion coefficients of organic species can be used to determine bulk diffusion mixing timescales of organics in an aerosol particle of a given diameter $d_{\rm p}$,

$$\tau = \frac{d_{\rm p}^2}{4\pi^2 D}.\tag{3.2}$$

Eq. 3.2 equation holds when $D = 10^{-9} - 10^{-25} \text{ m}^2 \text{s}^{-1}$ and $d_p = 1 \text{ nm} - 10 \mu \text{m}$ (Shiraiwa et al., 2011).

In theory, with the mixture viscosity calculations provided by AIOMFAC-VISC, the bulk diffusion of molecules in OA can be readily predicted by using Eqs. (3.1) and (3.2). It should be noted, however, that the SE relation does not hold for the diffusion where the tracer molecule is significantly smaller than the other mixture molecules (Douglas and Leporini, 1998). This calls into question the applicability of the SE relation in predicting the diffusion of water and oxidizing compounds. Additionally, diffusion decouples from viscosity in supercooled liquids (Tarjus and Kivelson, 1995). Therefore, it is not entirely clear how valid the viscosity–diffusion relationship is in predicting the diffusion of organics in ultraviscous aerosol. Ultimately, to understand if or how the SE relation can be applied with AIOMFAC-VISC results, a deeper understanding of the viscosity–diffusion decoupling is required.

While viscosity is a hallmark material property of glasses, the microscopic structural relaxation dynamics of a liquid provides a more detailed picture of the glassy regime than can be determined through viscosity alone. The microscopic structural relaxation of a liquid can be observed through correlations in particle (molecule) density fluctuations. Simply stated, at a given length scale and at some point in the future, the density fluctuations determine to what extent the instantaneous positions of the molecules in the liquid resemble a past configuration (Janssen, 2018).

For a liquid that is not supercooled, structural relaxation occurs homogeneously. In the supercooled case, molecules in the system form spatio-temporally correlated domains with varying relaxation times. It is thought that while some clusters of molecules undergo relaxation, other regions of the liquid remain temporarily frozen, giving rise to a phenomenon known as dynamic heterogeneity (Jung et al., 2004). Both the decoupling of viscosity and diffusion and the fragile-to-strong crossover are thought to be a manifestation of dynamic heterogeneity that arises in a supercooled liquid. It is not entirely understood how diffusion in a highly correlated supercooled liquid occurs. Although, it has been proposed that molecules diffusive via a thermally activated hopping process (Mallamace et al., 2010). At warmer temperatures, the particles diffuse freely because the energy barrier of hopping is similar to the thermal energy of the system, and therefore, the movement of molecules is tied to the viscosity of the system (Ediger, 2000).

A common approach to account both for the decoupling of diffusion from viscosity and for the diffusion of small molecules is the Fractional Stokes–Einstein (FSE) relation. The FSE takes the general form of,

$$D = \left(\frac{\mathbf{k}_{\mathrm{b}}T}{6\pi r\eta}\right)^{\zeta},\tag{3.3}$$

where ζ is an empirical constant. Values of ζ can range from 0.0–1.0 depending on the diffusing species and the components of the solution the species is diffusing through.

Ultimately, overcoming the inaccuracies of the SE relation, either with the FSE relation or another approach is highly desirable because there are more experimental measurements of SOA viscosity than direct measurements of SOA diffusion coefficients. Here it is worth briefly mentioning the experiments done to measure diffusion coefficients in proxy SOA bulk mixtures and particles, both to highlight the range of diffusion coefficients that are to be expected and to compare them to SE and FSE predictions.

3.1.2 Diffusion of water

Several studies report diffusion coefficients of water D_w in binary and ternary aqueous mixtures. Zobrist et al. (2011) extrapolated the diffusion coefficient of water in glassy aqueous sucrose particles near 200 K, where they found ultra-slow diffusion $(D_w \sim 10^{-24} \text{ m}^2 \text{s}^{-1})$. Lienhard et al. (2015) and Davies and Wilson (2016) found similar results for water in aqueous sucrose, although both of these groups investigated additional binary and ternary aqueous mixtures where the diffusion values were not so extreme, especially at higher water activity and temperatures above freezing. The exception to this is aqueous shikimic acid, where values of D_w are similar to those in aqueous sucrose. For water diffusing in pure, atmospherically relevant compounds, excluding sucrose and shikimic acid, D_w values range from ~ 10^{-9} – 10^{-12} m²s⁻¹ at around 295 K and ~ 10^{-11} – 10^{-18} m²s⁻¹ at around 235 K (Steimer et al., 2015; Lienhard et al., 2015). Notably, Davies and Wilson (2016) show that SE drastically underpredicts D_w in aqueous sucrose when compared to their measurements.

The slow diffusion of water in sucrose and shikimic acid is noteworthy because the diffusion of water measured in α -pinene SOA extract is orders of magnitude faster. Price et al. (2015) and Lienhard et al. (2015) found larger values of D_w in α -pinene SOA extract compared to sucrose and shikimic acid for all measured temperatures and water content. This highlights the potential weakness of using sucrose and shikimic acid as proxy SOA consituents. In both aforementioned works, water diffusion was not shown to be kinetically limited on timescales of 1 s at temperatures above freezing. Price et al. (2015) demonstrate with parameterizations down to low temperatures that in mid- and upper-tropospheric conditions, α -pinene SOA may have a glassy core surrounded by a liquid shell. Lienhard et al. (2015) showed that kinetic limitations of water uptake only began at temperatures below 220 K in α -pinene SOA.

3.1.3 Diffusion of organics

Abramson et al. (2013) estimated that $D_{\text{pyrene}} \sim 2.5 \times 10^{-21} \text{ m}^2 \text{s}^{-1}$ for pyrene tracer molecules diffusing through α -pinene SOA produced in an evapouration chamber under ambient laboratory temperature and relative humidity. They observed that after approximately 24 hours only about half of the pyrene had evapourated from the α -pinene SOA. Their experiment is suggestive of ultra-slow diffusing times of organics in SOA proxies under warm conditions; however, their estimation of D_{pyrene} is orders of magnitude lower than measurements of D for other organic diffusion systems studied.

Price et al. (2016) measured the diffusion coefficients of sucrose, D_s at 296 K in aqueous sucrose mixtures of varying water activity. They demonstrated that at low water activity, D_w and D_s varied up to four orders of magnitude, with the diffusion of sucrose always slower than the diffusion of water in the same mixture at any given water activity. They also compared the SE and fitted FSE relations for predicting D_w and D_s . SE was shown to be inappropriate for estimating D_w , however SE predictions of D_s were in reasonable agreement with experimental measurements. Nonetheless, fitted FSE relationships performed better than SE for predicting both D_w and D_s .

Chenyakin et al. (2017) found similar diffusion coefficient values for the diffusion of fluorescent dyes in aqueous sucrose mixtures when compared to the sucrose self-diffusion coefficients reported by Price et al. (2016). At 294.5 K and at the lowest water water activity studied, $a_w = 0.38$, the diffusion coefficients for fluorescein, rhodamine 6G, and calcein were $1.9 \times 10^{-13} \text{ m}^2 \text{s}^{-1}$, $1.5 \times 10^{-14} \text{ m}^2 \text{s}^{-1}$, and $7.7 \times 10^{-14} \text{ m}^2 \text{s}^{-1}$, respectively. At low water activity the SE relationship was shown to slightly underpredict the diffusion coefficients of the dyes; however, SE was in good agreement with experimental values at high water activity $(a_w \ge 0.6)$. Similarly, Ullmann et al. (2019) measured the diffusion coefficients of fluorescent organic molecules in thin films of brown limonene SOA. The diffusion coefficients were similar in magnitude to those reported by Chenyakin et al. (2017). Ullmann et al. (2019) report the mixing times from the measured diffusion coefficients; for a_w ranging from 0.9 to 0.33, mixing times were calculated as 0.001 to 14 seconds in a 200 nm sized particle.

3.2 Outlook

One direction of future work that can be taken to translate AIOMFA-VISC mixture viscosity predictions to bulk diffusion timescales is to use the FSE relation in place of SE. First, it would be beneficial to determine if there is a universal value of the FSE constant, ζ for organic–organic diffusion and water–diffusion. Mallamace et al. (2010) proposed that $\zeta \approx 0.85$ for 84 glass formers, some of which are directly applicable to organic aerosol, such as toluene, acetic acid, and glycerol. Recently, using a FSE relation with a pre-exponential factor, Evoy et al. (2019) suggest universal constants may exist in the case of organic–organic diffusion, at least for proxy SOA particles. More measurements, with a variety of diffusing species will be required to confirm if their suggested FSE constants are widely applicable.

Should the FSE constant not be universal in nature for mixtures of atmospheric relevance, another direction of future work will be to develop an appropriate estimation or model of FSE constants. Molecular dynamics simulations have shown that the FSE constant is related to the fragility of the glass former. The simulations by, Jung et al. (2004) showed that for self-diffusion in strong liquids, $\zeta \sim 0.95$, and for fragile glass formers $\zeta \sim 0.73$. Given this, the relationship between fragility and ζ may be explored through a comparison of fragility measurements and empirically derived values of ζ . Further exploration of the concept of fragility may also improve the pure-component viscosity prediction within AIOMFAC-VISC.

Overall, the pure-component viscosity prediction remains the largest source of uncertainty in AIOMFAC-VISC predictions. In the future, more measurements of T_g may be available to better constrain the pure-component viscosity. Notwithstanding, the model at present is suitable for estimating the mixture viscosity of OA and future work will also involve expanding the model to consider the presence of dissolved inorganic electrolytes, which will be necessary for providing a more complete understanding of the characteristic equilibration times of ambient OA.

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