Secondary organic aerosol (SOA) constitutes a significant proportion of ambient particulate matter and exhibits substantial chemical complexity. Volatile organic compounds (VOCs) emitted into the atmosphere from biogenic/anthropogenic sources, undergo oxidation forming a variety of products of differing chemical compositions and volatilities. Compounds of sufficiently low volatility can form SOA through new particle formation, or by partitioning onto pre-existing aerosol mass. Gas-particle equilibrium partitioning is a fundamental concept governing the growth and loss of SOA. However, recent literature has suggested that equilibrium partitioning may be kinetically limited, preventing volatilization from the aerosol phase as a result of the physical state of the aerosol (e.g. glassy, viscous) (Vaden et al. 2011). Experimental measurements of diffusion constants within viscous aerosol are limited and do not represent the complex chemical composition observed in SOA (i.e. multicomponent mixtures). These experimental measurements along with detailed SOA chemical speciation are required in order to investigate the effect of viscosity and diffusion on equilibrium partitioning. To understand the dynamic mechanisms occurring during SOA growth and evolution, the equilibrium state of the aerosol must be known.

This work combines a number of key components required to investigate the effect of viscosity and diffusion on equilibrium partitioning. A new medium scale continuous flow reactor (CFR) has been built to generate large quantities of SOA for offline chemical characterization and viscosity/diffusion measurements. The CFR consists of a 300L polyvinylidene difluoride (PVDF) gas sampling bag with an Hg Pen-Ray lamp (254 nm). VOCs and oxidants can be continuously introduced into the CFR at a controlled relative humidity. A range of instruments are used to monitor temperature, humidity, NO$_x$, O$_3$, gas-phase product formation/degradation (proton-transfer reaction mass spectrometry) and SOA mass, number and diameter (electrical low pressure impactor, ELPI). The use of the ELPI allows SOA mass to be collected without substrate, removing any potential artefacts associated with solvent extractions. The SOA mass from a variety of VOCs with differing functionalities (i.e. aromatics, alkenes) will be investigated, under a range of atmospheric conditions (e.g. oxidants, concentrations and relative humidities). The detailed chemical and structural composition of the SOA mass will be investigated using $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy and ultra performance liquid chromatography coupled to ultra-high resolution mass spectrometry. In addition to the detailed chemical speciation, bulk compositional techniques such as Fourier transform infrared spectroscopy and an elemental analyzer (provides the total mass of elements CHNS) will also be used to provide an overview of the chemical speciation. The viscosity and diffusion constants of water in the SOA will be determined using an electrical dynamic balance and optical tweezers. The detailed chemical composition and diffusion/viscosity measurements of the SOA obtained from these experiments will be used to refine predictive tools for viscosity and multicomponent mixtures using a combination of the pure component method of Nannooolal et al. (2009) and relevant mixture methods, driven by the UManSysProp informatics suite (Topping et al. 2016).

The work presented here has the potential to lead to considerable advances in our understanding of the dynamic mechanisms occurring during SOA growth and evolution. To our knowledge, this is the first account where detailed chemical speciation and multicomponent viscosity and diffusion measurements have been combined to investigate the effect of the physical state of SOA on equilibrium partitioning.

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