THE RELATIONSHIP BETWEEN DIFFUSION COEFFICIENTS AND VISCOSITY IN ORGANIC-WATER MATRICES AS PROXIES FOR SECONDARY ORGANIC AEROSOL

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Erin Evoy

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

The relationship between diffusion coefficients and viscosity in organic-water matrices as proxies for secondary organic aerosol

submitted by Erin Evoy in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Examing Committee:

Allan Bertram, Chemistry
Supervisor

Grenfell Patey, Chemistry
Supervisory Committee Member

David Chen, Chemistry
University Examiner

John Grace, Chemical and Biological Engineering
University Examiner

Additional Supervisory Committee Members:

Dan Bizzotto, Chemistry
Supervisory Committee Member

Russ Algar, Chemistry
Supervisory Committee Member
Abstract

The diffusion coefficients of large and small molecules in organic-water mixtures are important to atmospheric chemistry, as organic-water mixtures are useful proxies for atmospheric organic aerosol. Diffusion coefficients of large molecules (molecules with radius $R_{\text{diff}} \geq$ the radius of the organic matrix molecule, $R_{\text{matrix}}$) and small molecules ($R_{\text{diff}} < R_{\text{matrix}}$) in organic-water mixtures have been presented in the literature. However, these data are limited.

Frequently, the Stokes-Einstein relation, which relates diffusion and viscosity ($D \propto 1/\eta$), where $D$ is the diffusion coefficient and $\eta$ is the viscosity, is used to calculate diffusion coefficients. An alternative relation is the fractional Stokes-Einstein relation ($D \propto 1/\eta^{\xi}$), where $\xi$ is a fractional exponent. However, the accuracy of neither of these relations has been thoroughly assessed for predicting diffusion coefficients in organic-water mixtures.

This thesis combines new diffusion measurements with literature data to test the Stokes-Einstein and fractional Stokes-Einstein relations. When $R_{\text{diff}}/R_{\text{matrix}} \geq 1$, the Stokes-Einstein relation is able to describe most diffusion coefficients within a factor of 10, up to a viscosity of $10^6$ Pa s. However, a fractional Stokes-Einstein relation with a single $\xi$ value does a better job of describing the data. When a data set includes both $R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and $R_{\text{diff}}/R_{\text{matrix}} < 1$, the Stokes-Einstein relation describes only 75% of the data. A fractional Stokes-Einstein relation, where $\xi$ is a function of $R_{\text{diff}}/R_{\text{matrix}}$, is able to describe 98% of the data. These equations are tested in more realistic and chemically complex aerosol samples. The Stokes-Einstein relation is able to accurately describe diffusion coefficients of organic molecules in one lab-generated organic aerosol sample, while the fractional Stokes-Einstein relation is required to describe the diffusion coefficients in the second sample.

Finally, diffusion measurements of a very large organic molecule ($R_{\text{diff}} >> R_{\text{matrix}}$) are combined with the Stokes-Einstein relation to calculate the viscosity of an organic-water mixture, resolving a discrepancy in the literature between two previously published viscosity data sets.

The results presented here increase our ability to quantify the relationship between diffusion of large and small molecules and the viscosity of organic-water mixtures, which are useful proxies for atmospheric organic aerosol.
Lay Summary

Atmospheric aerosols affect visibility, climate, the transportation of pollutants, and human health. Those effects depend on physical properties such as the diffusion rates of molecules within atmospheric aerosol. While there are limited diffusion data available, there is a relatively large amount of viscosity information for these aerosols in the literature. These viscosity data may be used to predict diffusion rates, however there is currently no simple and accurate method to relate diffusion and viscosity in these aerosols. Here, diffusion rates are measured in proxies for atmospheric aerosol, and combined with literature data to evaluate the accuracy of different equations used to calculate diffusion. Parameters are developed for an equation which accurately relates diffusion and viscosity, resulting in a unified description of diffusion rates in proxies for atmospheric aerosol. These results will improve our ability to quantify the effects of atmospheric aerosols on human and environmental health.
Preface

Chapters 2, 3, and 5 are adapted from co-authored peer-reviewed journal articles and Chapter 4 is a co-authored work in preparation for submission as a peer-reviewed journal article. My specific contributions to each research chapter are detailed below.

Chapter 2 (first author on a published journal article that was adapted for this thesis):
- Formulated and designed the research with A. K. Bertram
- Performed diffusion experiments using the rFRAP technique
- Performed analysis of experimental data
- Wrote the manuscript with A. K. Bertram
- Additional contributions from co-authors:
  - A. M. Maclean, Y. Li, A. P. Tsimpidi, V. A. Karydis, J. Leliveld, and M. Shiraiwa provided calculations of mixing times as a function of altitude and latitude
  - G. Rovelli and J. P. Reid provided viscosity data
  - S. Kamal provided assistance with the diffusion experiments and wrote the code used to analyze the experimental data

Chapter 3 (first author on a published journal article that was adapted for this thesis):
• Formulated and designed the research with A. K. Bertram
• Performed diffusion experiments using the rFRAP technique
• Performed analysis of experimental data
• Performed case study of application of results to degradation of PAH in the planetary boundary layer
• Wrote the manuscript with A. K. Bertram
• Additional contributions from co-authors:
  • S. Kamal provided assistance with the diffusion experiments, and wrote the code used to analyze the experimental data
  • G. N. Patey and S. T. Martin provided assistance in interpreting the data and writing the manuscript

Chapter 4 (first author on a work in preparation for submission as a peer-reviewed journal article):
Evoy, E., Kiland, K., Huang, Y., Schnitzler, E., Kamal, S., Abbatt, J. P., and Bertram, A. K.
• Formulated and designed the research with A. K. Bertram
• Performed diffusion experiments in β-caryophyllene SOA with K. Kiland
• Performed diffusion experiments in biomass burning organic aerosol
• Performed analysis of experimental data
• Wrote the manuscript with A. K. Bertram
• Additional contributions from co-authors:
  • K. Kiland and Y. Huang provided the β-caryophyllene SOA
  • E. Schnitzler and J. Abbatt provided the biomass burning organic aerosol samples

Chapter 5 (co-first author on a published journal article that was adapted for this thesis):
• Assisted in research formulation and design
• Assisted in performing viscosity measurements using the rFRAP technique
• Assisted in analyzing the rFRAP experimental data
• Assisted in writing the manuscript
• Additional contributions from co-authors:
  • Y. Chu and A. K. Bertram also formulated and designed the research
  • Y. Chu also performed viscosity measurements using the rFRAP technique
  • Y. Chu also analyzed the rFRAP experimental data
  • S. Kamal provided assistance with the diffusion experiments and wrote the code used to analyze the experimental data
  • Y. C. Song and J. P. Reid performed viscosity measurements using the optical tweezers technique
  • Y. C. Song and J. P. Reid analyzed the optical tweezers experimental data
  • Y. Chu, A. K. Bertram, Y. C. Song, and J. P. Reid also wrote the manuscript
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The image of tar pitch is part of an image from the pitch drop experiment (image courtesy of Wikimedia Commons, GNU Free Documentation License, University of Queensland, John Mainstone).

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**Figure 3.2** Average fluorescence intensity as a function of cresyl violet mass fraction in raffinose-water thin films at $a_w = 0.90 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \ \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for cresyl violet in raffinose-water thin films. rFRAP experiments were performed using cresyl violet concentrations within the linear range indicated here. .......................................................... 47

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**Figure 3.5** A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of cresyl violet in a sucrose-citric acid matrix at $a_w = 0.43$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

**Figure 3.6** Double log plots of (a) log $D$ versus log $\eta$ and (b) log $D - \log (kT/6\pi R_{diff})$ versus log $\eta$. Closed symbols indicate diffusion coefficients measured in this work, and open symbols represent diffusion coefficients taken from the literature (Table B.3 and Appendix B, Section B1). The solid line in (b) represents the Stokes-Einstein relation and the dashed lines represent an order of magnitude uncertainty in the Stokes-Einstein relation (an order of magnitude uncertainty corresponds to roughly the uncertainty in the original viscosity measurements). In both panels the colour of the data points corresponds to $R_{diff}/R_{matrix}$, where $R_{diff}$ is the radius of the diffusing molecules and $R_{matrix}$ is the radius of the organic molecules in the organic-water mixture. $R_{diff}/R_{matrix}$ was determined using the values listed in Table 3.2.

**Figure 3.7** The exponent value to be used in the fractional Stokes-Einstein relation, $\zeta$, plotted as a function of $R_{diff}/R_{matrix}$ (black squares) and an exponential best fit to that data (red line). The equation of the exponential best fit line is Eq. 3.2 with $A = 0.73$ and $B = 1.79$. Closed symbols correspond to $\zeta$ values based on diffusion data sets measured in this work, and open symbols correspond to $\zeta$ values based on diffusion data sets from the literature. $R_{diff}/R_{matrix}$ was determined using the values listed in Table 3.2. X-axis error bars represent the uncertainty in $R_{diff}/R_{matrix}$ determined from the uncertainty in reported $R_{diff}$ values and the range of $R_{matrix}$ values if two
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**Figure 3.8** Double log plots of measured and calculated $D$ using (a) the Stokes-Einstein relation and (b) the fractional Stokes-Einstein relation, with $\zeta$ calculated using Eq. 3.2. Closed symbols indicate diffusion coefficients measured in this work and open symbols represent diffusion coefficients taken from the literature. The colours of the data points correspond to $R_{\text{diff}}/R_{\text{matrix}}$, where $R_{\text{diff}}$ is the radius of the diffusing molecules and $R_{\text{matrix}}$ is the radius of the organic molecules in the organic-water mixture. $R_{\text{diff}}/R_{\text{matrix}}$ was determined using the values listed in Table 3.2. The solid black line in each panel is a 1-to-1 line. The dashed lines represent an order of magnitude uncertainty, corresponding to roughly the uncertainty in the viscosity data used to calculate the diffusion coefficients (Appendix B, Section B2). There is also uncertainty in the predicted diffusion coefficients in panel (b) due to the uncertainty in the $\zeta$ values calculated using Eq. 3.2. This uncertainty is not included in the figure for the sake of clarity.

**Figure 3.9** Degradation time of PAHs due to the bulk-phase reaction between PAHs and $O_3$ within a 200 nm diameter organic-water particle. Black squares indicate degradation times calculated using diffusion coefficients of $O_3$ and PAHs based on the Stokes-Einstein relation, while red circles indicate diffusion coefficients based on the fractional Stokes-Einstein relation. The dashed red lines indicate the upper and lower limits for degradation times calculated using the fractional Stokes-Einstein relation when the 95 % confidence band in Figure 3.7 is used to calculate upper
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**Figure 4.1** Upper and lower limits of \(\beta\)-caryophyllene SOA viscosity measured using the poke-flow technique (Table 4.1) and a linear best fit to the upper limits of viscosity, used to calculate the time required for thin films containing the SOA to come to equilibrium with the surrounding \(a_w\) as described in Section 4.2.3.

**Figure 4.2** Configuration of the glass slides holding the fluorescent SOA thin films. Top view (panel A) and side view (panel B) of a thin film of a lab-generated SOA sample deposited on a plain glass slide previously coated with a uniform layer of R6G molecules. The sample is sandwiched with a hydrophobic glass slide and contained within two hydrophobic glass slides sealed with vacuum grease, for use in rFRAP experiments.

**Figure 4.3** Upper and lower limits of BBOA viscosity measured using the poke-flow technique and a linear best fit to the upper limits of viscosity, used to calculate the conditioning times given in Table 4.4.

**Figure 4.4** Fluorescence images of films containing R6G, \(\beta\)-caryophyllene SOA, and water, at \(a_w = 0.85 \pm 0.025\) (a-d) and at \(a_w = 0.23 \pm 0.025\) (e-h), collected using a confocal laser scanning microscope during a rFRAP experiment. Images (a) and (e) were taken prior to photobleaching and used to normalize all images after photobleaching. Images (b) and (f) were taken immediately following the photobleaching event and images (c-d) and (g-h) were taken during the recovery period. The white square in images (a) and (e) represents a 20 \(\mu m^2\) region for photobleaching, while the size of the imaged region is 2000 \(\mu m^2\).

**Figure 4.5** Fluorescence images of films containing BBOA including an intrinsic fluorescent molecule, and water, at \(a_w = 0.43 \pm 0.025\) (a-d) and at \(a_w = 0.23 \pm 0.025\) (e-h), collected using a...
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Figure 4.6 A plot of $r^2 + 4Dt$ as a function of time after photobleaching R6G in a sample of β-caryophyllene SOA at $a_w = 0.85 \pm 0.025$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

Figure 4.7 A plot of $r^2 + 4Dt$ as a function of time after photobleaching intrinsic fluorescent molecules in a sample of biomass burning aerosol at $a_w = 0.43 \pm 0.025$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

Figure 4.8 Diffusion coefficients of R6G in β-caryophyllene SOA as a function of water activity ($a_w$). The x error bars represent the uncertainty in the measured $a_w$ and the y error bars are equal to 2 times the standard deviation of the measured diffusion coefficients. Each data point represents the average of a minimum of 4 measurements. For diffusion coefficients predicted using the Stokes-Einstein relation, the lower limit was calculated using the upper limit in viscosity and the upper limit was calculated using the lower limit in viscosity. For diffusion coefficients predicted using the fractional Stokes-Einstein relation, the lower limit was calculated using the upper limit in viscosity and the lower limit of the hydrodynamic radius of β-caryophyllene SOA molecules, while the upper limit in diffusion was calculated using the lower limit in viscosity and the upper
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**Figure 4.9** Diffusion coefficients of an intrinsic fluorescent molecule in BBOA as a function of water activity ($a_w$). The x error bars represent the uncertainty in the measured $a_w$ and the y error bars are equal to 2 times the standard deviation of the measured diffusion coefficients. Each data point represents the average of a minimum of 5 measurements. For diffusion coefficients predicted using the Stokes-Einstein relation, the lower limit was calculated using the upper limit in viscosity and the upper limit for the hydrodynamic radius of the diffusing intrinsic fluorescent molecule. The upper limit of diffusion was calculated using the lower limit in viscosity and the lower limit for the hydrodynamic radius of the diffusing intrinsic fluorescent molecules. The secondary y axis shows mixing times for the intrinsic fluorescent molecules in a 200 nm BBOA particle. ........... 85

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**Figure 5.2** Average fluorescence intensity as a function of RBID mass fraction in erythritol-water thin films at $a_w = 0.630 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately 30×30 μm². The laser scanning microscope settings used were identical to those used in the rFRAP experiments for RBID in erythritol-water thin films. rFRAP experiments were performed using RBID concentrations within the linear range indicated here................................................................. 91

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**Figure 5.5** Average fluorescence intensity as a function of time following the uniform photobleaching of an entire droplet. The average fluorescence intensities after photobleaching were normalized against an image taken prior to photobleaching. The RBID mass fraction within the conditioned droplets was approximately 0.3 weight percent. P0 represents a non-photobleached reference droplet. P1 and P2 represent two droplets chosen for the experiments.

**Figure 5.6** An example of the captured brightfield images as a function of time after the coalescence of two erythritol particles in optical tweezers at $a_w = 0.04 ± 0.02$. The relaxation to a spherical particle occurred within 56 milliseconds.

**Figure 5.7** (a) The measured diffusion coefficients of RBID as a function of $a_w$. (b) The viscosity of erythritol-water particles as a function of $a_w$ based on the measured RBID diffusion coefficients and the Stokes-Einstein relation. Results from rFRAP measurements are color-coded by the sample conditioning time prior to the rFRAP experiments. The color scale applies to both panel (a) and (b). Horizontal error bars indicate the upper and lower limits of $a_w$. Vertical error bars correspond to two standard deviations of diffusion coefficient (in panel a) and log (viscosity) (in panel b).

**Figure 5.8** The diffusion coefficient of RBID as a function of the time allowed for conditioning erythritol-water particles at $a_w = 0 – 0.046$ (open squares) and $0 – 0.105$ (filled squares). The secondary (top) x-axis represents the conditioning time expressed in multiples of $\tau_{mix,H2O}$ (characteristic time for the diffusion of water molecules within the erythritol-water droplets).
the calculation of $\tau_{\text{mix}, \text{H}_2\text{O}}$, the lower limit of $a_w$ (i.e., 0) was taken, leading to maximum $\tau_{\text{mix}, \text{H}_2\text{O}}$ values of 3.3 h for droplets with a radius of 100 μm. Error bars represent two standard deviations of RBID diffusion coefficients.

**Figure 5.9** Viscosity of erythritol-water particles as a function of $a_w$, determined using the aerosol optical tweezers technique. Red circles represent experimental results from this study. Gray circles represent experimental results from Song et al. (2016b). The green circle represents the viscosity of pure water at 293 K (Korson et al., 1969). Horizontal error bars indicate the upper and lower limits of $a_w$. Vertical error bars represent two standard deviations of log (viscosity).

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**Figure 5.11** Viscosities of compounds with a linear C₄ carbon backbone at 292 – 295 K plotted against the number of OH functional groups. Black circles represent viscosities of the compounds with 0 – 3 OH functional groups (i.e., n-butane, 1-butanol, 2-butanol, 1,2-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2,3-butanetriol and 1,2,4-butanetriol) taken from literature (Grayson et al., 2017; Rothfuss and Petters, 2017b; Song et al., 2016b). For the literature data points, the
error bars are two standard deviations of log (viscosity) of multiple compounds. The blue circle represents the viscosity of pure erythritol, with error bars of two standard deviations, based on the linear fit in Figure 5.10. The red line is a linear fit to the data, which is weighted based on the uncertainties in viscosity data. The slope and regression coefficient ($R^2$) are shown in the annotation. The uncertainty in the slope corresponds to two standard deviations.

**Figure 5.12** The viscosity sensitivity parameter at 292 – 295 K plotted against the number of OH functional groups for linear C$_4$ compounds (alkane, alcohol and polyols). Black circles represent values estimated using literature data alone (Grayson et al., 2017; Rothfuss and Petters, 2017b; Song et al., 2016b); the blue circle represents the value estimated using experimental results from this work and literature data (Grayson et al., 2017; Song et al., 2016b). The error bars are propagated from the uncertainties shown in Figure 5.11.

**Figure A.1** Parameterization between viscosity and water activity for citric acid solutions. Data come from Song et al. (2016) and include measurements on particles using the optical tweezers technique and measurements in the bulk phase using a rheometer. Measurements were performed at 293 ± 2 K. The equation of the second order polynomial line (red line) is $\log(\eta) = 5.9232 \pm 0.3772 - 14.508 \pm 0.3124(a_w) + 6.30235 \pm 0.3605(a_w^2)$. X-error bars on the data points represent the ± 0.02 $a_w$ and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.

**Figure A.2** Parameterization between viscosity and water activity for sorbitol solutions. Data come from Song et al. (2016) and include measurements on particles using the optical tweezers technique. Measurements were performed at 293 ± 2 K. The equation of the line (red line) is $\log(\eta) = ...$
\( (\eta) = 6.4134 \pm 1.021 - 9.4175 \pm 2.871 (a_w) + 0 \pm 2.708 (a_w^2) \). X-error bars on the data points represent the \( \pm 0.02 \) \( a_w \) and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals. ................................. 137

**Figure A.3** Parameterization between viscosity and water activity for sucrose-citric acid solutions. Data come from Rovelli et al. (2019) and only include measurements on particles using the optical tweezers technique. Measurements performed using the poke-and-flow technique were not included due to the larger uncertainty in viscosity measurements using that technique. Measurements were performed at 293 \( \pm 2 \) K. The equation of the line (red line) is \( \log (\eta) = 9.55 \pm 0.857 - 22.62 \pm 1.97 (a_w) + 10.76 \pm 1.87 (a_w^2) \). X-error bars on the data points represent the \( \pm 0.02 \) \( a_w \) and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals................................................................. 138

**Figure B.1** Viscosity of raffinose-water solutions as a function of \( a_w \). Viscosity data come from Grayson et al. (2017) and Song et al. (2016). A second order polynomial was fit to the data, with the resulting equation \( \log (\eta, \text{ Pa s}) = 22.15 - (34.42 \times a_w) + (8.907 \times a_w^2) \). X-error bars correspond to the uncertainty in the \( a_w \) (0.025 for Grayson et al. (2017) and 0.02 for Song et al. (2016)). Y-error bars represent deviations between multiple measurements at the same \( a_w \). The y-error bars for Grayson et al. (2017) represent two standard deviations, and the y-error bars for Song et al. (2016) represent one standard deviation. Viscosity measurements from Song et al. (2016) were made at a temperature of 293 \( \pm 2 \) K, and viscosity measurements from Grayson et al. (2017) were made at a temperature of 294-295 K........................................................................................................ 150
Figure B.2 Log \((D/D_0)\) as a function of \(\log (\eta_0/\eta)\) for the system cresyl violet in raffinose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope. ................................................................. 151

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**Figure B.6** Log ($D/D_0$) as a function of log ($\eta_0/\eta$) for the system R6G in sucrose-citric acid. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the $\zeta$ value is the standard error of the slope.

**Figure B.7** Log ($D/D_0$) as a function of log ($\eta_0/\eta$) for the system R6G in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the $\zeta$ value is the standard error of the slope.

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an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the $\zeta$ value is the standard error of the slope.

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**Figure B.16** Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system xenon in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.
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### List of Symbols

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<tr>
<td>$R_{\text{diff}}$</td>
<td>radius of a diffusing species</td>
</tr>
<tr>
<td>$R_{\text{matrix}}$</td>
<td>radius of a molecule in a fluid matrix</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>$x^2$</td>
<td>mean squared displacement</td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>viscosity of pure water at 295 K</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>fractional exponent in the fractional Stokes-Einstein relation</td>
</tr>
<tr>
<td>$\tau_{\text{mix}}$</td>
<td>characteristic mixing time due to molecular diffusion</td>
</tr>
<tr>
<td>$\tau_{\text{mix, H2O}}$</td>
<td>characteristic mixing time of water due to molecular diffusion</td>
</tr>
</tbody>
</table>
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBOA</td>
<td>biomass burning organic aerosol</td>
</tr>
<tr>
<td>CLSM</td>
<td>confocal laser scanning microscope</td>
</tr>
<tr>
<td>O:C</td>
<td>elemental oxygen to carbon ratio</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>R6G</td>
<td>rhodamine 6G</td>
</tr>
<tr>
<td>RBID</td>
<td>Rhodamine B isothiocyanate-dextran</td>
</tr>
<tr>
<td>rFRAP</td>
<td>rectangular area fluorescence recovery after photobleaching</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>SOA</td>
<td>secondary organic aerosol</td>
</tr>
<tr>
<td>SOM</td>
<td>secondary organic material</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi-volatile organic compound</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
</tbody>
</table>
List of Units

Å  Angstroms

cm  centimetre

g  grams

h  hours

K  Kelvin

km  kilometre

m  metre

mm  millimeter

mM  millimolar

mol  moles

nm  nanometre

Pa s  Pascal seconds

s  seconds

W  watts

µm  micrometre
Acknowledgements

I am deeply grateful to those who have made this dissertation possible, by providing mentorship, friendship, and support over the last five years.

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To Mum, Dad, and Kate.
Chapter 1: Introduction

1.1 Atmospheric aerosols

1.1.1 Sources and classification of atmospheric aerosols

Atmospheric aerosols are solid and liquid particles suspended in the Earth’s atmosphere. Aerosols are ubiquitous, but their number concentration has great spatial and temporal variation, ranging between $10^2 - 10^8$ cm$^{-3}$, with typical values ranging from $10^2$ to $10^4$ cm$^{-3}$ in the troposphere (Seinfeld and Pandis, 2006). Temporally, concentrations are 2-10 times higher during the summer in many regions (Spracklen et al., 2010). Aerosols can be classified in a number of ways. Aerosols are classified as primary, when they are emitted as solid or liquid particulate matter directly into the atmosphere, or as secondary, when they are formed in situ in the atmosphere, as a result of gases reacting to form low-volatility products, some of which condense to the particle phase.

Both primary and secondary aerosols can arise from natural and anthropogenic sources. Examples of natural primary aerosols include salt from sea spray, mineral dust from deserts, and organic products from biomass burning. Anthropogenic primary aerosols include dust produced through industrial activity. Natural secondary aerosols are formed following the emission of biogenic gaseous precursors, while anthropogenic secondary aerosols are formed, for example, following the emission of precursor gases through the combustion of fossil fuels. Combined, the natural sources of aerosols account for the large majority of the mass of aerosols and aerosol precursors emitted globally (Stocker et al., 2013).

Aerosol particles are also classified on the basis of size, and range in diameter from nanometers to tens of micrometers. The smallest aerosols will coagulate quickly to form larger particles, and therefore have short atmospheric lifetimes, on the order of tens of minutes. Aerosols with diameters of 100 nm – 2.5 µm will have lifetimes on the order of one week. Larger aerosols, with diameters > 2.5 µm, will typically remain in the atmosphere for a few hours to a few days (Seinfeld and Pandis, 2006). In addition to the loss through coagulation, aerosols are also removed from the atmosphere by dry deposition and wet deposition.
1.1.2 Effects of atmospheric aerosols

Atmospheric aerosols have effects on visibility, Earth’s climate, human health, and can facilitate the long-range transport of atmospheric pollutants.

Aerosols affect visibility by scattering and absorbing light. The loss in visibility due to these processes is called the extinction of light. The greater the concentration of aerosol at or near ground level, the greater the extent of the extinction of light, and the worse the visibility becomes.

Aerosols affect climate by modifying the radiative forcing of the atmosphere. Radiative forcing refers to the changes in energy fluxes of both incoming solar radiation and outgoing terrestrial radiation and is measured in Watts m$^{-2}$. Positive radiative forcings have a warming effect on Earth’s surface (e.g. absorption of terrestrial radiation by greenhouse gases, aerosols, or clouds), whereas negative radiative forcings have a cooling effect (e.g. scattering of solar radiation by aerosols or clouds). Aerosols’ effects on climate are classified as either direct or indirect. Direct effects are the result of aerosol particles themselves interacting with radiation, for example scattering or absorbing either solar or terrestrial radiation. Inorganic aerosols such as those containing large amounts of sulphate ($\text{SO}_4^{2-}$) scatter incoming solar radiation away from Earth’s surface and have a negative forcing, whereas black carbon absorbs incoming solar radiation, dissipating heat in the atmosphere and resulting in a positive forcing. The deposition of aerosols such as black carbon on snow and ice pack also has a positive radiative forcing.

The indirect effect of aerosols on radiative forcing is due to the influence of aerosols on cloud formation and properties (Stocker et al., 2013). For example, consider two liquid-phase clouds, which hold equivalent amounts of water, forming in two different regions of the atmosphere. The cloud which forms in the region of elevated aerosol concentration is likely to be composed of a greater total number of smaller droplets compared with the cloud formed in the region of lower aerosol concentration. The cloud formed in the region of elevated aerosol concentration, which contains a greater number of smaller droplets, will not only scatter a greater proportion of solar radiation, but will also have a longer lifetime as a result of the smaller droplets being less likely to precipitate.

The direct and indirect effects both have a net negative radiative forcing, although there are large uncertainties associated with the radiative forcings of aerosols. In fact, aerosols and clouds represent the largest uncertainty in radiative forcing among all known climate stressors.
(Stocker et al., 2013). An increased understanding of the physical and chemical properties of aerosols is required to constrain the uncertainty associated with the effects of aerosols on climate.

Increased concentrations of atmospheric aerosols, and particularly fine particulate matter (that is aerosol particles with a diameter of < 2.5 µm) are associated with negative human health effects including cardiovascular and respiratory diseases, as well as enhanced mortality. When inhaled, aerosols can travel through the respiratory tract before being deposited in the lungs, where they cause pulmonary inflammation. The smallest aerosols (with a diameter of < 0.1 µm), are able to penetrate the membranes of the respiratory tract and enter the blood circulation system, posing an increased hazard to human health. The World Health Organization attributed 4.2 million deaths to ambient air pollution in 2016. Ambient air pollution was responsible for 24% of the global burden of ischemic heart disease and 9% of the global burden of chronic obstructive pulmonary disease in 2012 (Prüss-Ustün et al., 2016).

Atmospheric aerosols can facilitate the long-range transportation of pollutants (Friedman et al., 2014; Mu et al., 2018; Shrivastava et al., 2017a; Vaden et al., 2011; Zelenyuk et al., 2012) including carcinogens such as polycyclic aromatic hydrocarbons (PAHs). When PAHs and precursors to secondary organic aerosol (Section 1.2.1) are co-emitted, for example during industrial activity or forest fires, the PAHs become embedded in the resulting atmospheric aerosol. Depending on the physical properties of the aerosol, the embedded PAHs may be protected from oxidants and other atmospheric constituents. In these cases, the atmospheric aerosol can be thought of as a protective vessel which contains PAHs. These aerosols, and the embedded PAHs, may be transported over long distances.

1.2 Secondary organic aerosol

1.2.1 Formation and properties of secondary organic aerosol (SOA)

Secondary organic aerosol (SOA) are particles that are formed in situ in the atmosphere, through gas-to-particle conversion processes in which gases react to form low-volatility products and subsequently condense to the particle phase (Ervens et al., 2011; Hallquist et al., 2009). SOA makes up approximately 20% to 70% of the mass of fine aerosol particles, depending on location (Hallquist et al., 2009; Jimenez et al., 2009; Kanakidou et al., 2005). This section considers the
formation as well as some physical and chemical properties of SOA. While the term “aerosol” specifically refers to a solid or liquid particle suspended in a gas phase, in the atmospheric chemistry community the term “aerosol” is commonly used to refer to only the particle phase and excludes the surrounding gas phase. Here the abbreviation SOA is used to refer to any secondary organic material, whether suspended in a gas phase or deposited on a surface. Note that some authors distinguish between material suspended in a gas phase and material deposited on a surface by using the terms secondary organic aerosol (SOA) and secondary organic material (SOM), respectively.

Secondary organic aerosol is formed following the emission of volatile organic compounds (VOCs) from the Earth’s surface. VOCs are produced by both natural and anthropogenic sources. Once in the atmosphere, VOCs react with oxidants including ozone (O$_3$) and the hydroxyl radical (·OH). The products of these oxidation reactions have lower volatilities than their precursors, and eventually the vapor pressure of the semi-volatile products can become low enough that those compounds partition to the particle phase.

VOCs are emitted from biogenic sources including the Earth’s forests and oceans. One important class of natural VOCs are terpenes, which are emitted by biogenic sources and are unsaturated hydrocarbons composed of repetitions of the base unit formula C$_5$H$_8$. Examples of common terpenes are the monoterpene α-pinene (C$_{10}$H$_{16}$) and the sesquiterpene β-caryophyllene (C$_{15}$H$_{24}$). One source of anthropogenic VOCs is the combustion of fossil fuels, which produces benzene and derivatives of benzene.

The large number of VOC precursors and many oxidation pathways result in SOA containing thousands of distinct chemical compounds, as observed by field studies using mass spectrometry techniques. While the exact chemical composition of SOA remains uncertain, research has shown that the compounds in SOA have average elemental oxygen-to-carbon (O:C) ratios of between 0.3 - 1.0 or even higher (Aiken et al., 2008; Cappa and Wilson, 2012; Chen et al., 2009; DeCarlo et al., 2008; Ditto et al., 2018; Hawkins et al., 2010; Heald et al., 2010; Jimenez et al., 2009; Laskin et al., 2018; Ng et al., 2010; Nozière et al., 2015; Takahama et al., 2011; Tsimpidi et al., 2018). SOA contains a range of functional groups including alcohols, carboxylic acids, and aromatics (Claeys et al., 2004, 2007; Edney et al., 2005; Fisseha et al., 2004; Glasius et al., 2000; Liu et al., 2011; Surratt et al., 2006, 2010a).
The physical properties of SOA vary due to the chemical diversity of its constituent compounds. For example, laboratory studies have shown that the hygroscopicity of SOA depends on the VOC precursors to the SOA (Varutbangkul et al., 2006). In the atmosphere, relative humidity (RH) is a parameter that affects the water content of SOA. SOA takes up or releases water so that the water activity \( (a_w = RH/100) \) of the particle-phase remains in equilibrium with that of the surrounding gas phase. Water is therefore an important component of SOA.

The viscosity of SOA depends on the chemical constituents, with the general trend that SOA containing compounds with a higher molecular weight and a higher O:C ratio have greater viscosities (DeRieux et al., 2018; Grayson et al., 2017; Rothfuss and Petters, 2017b). The viscosity of SOA is also a function of its water content, and therefore a function of the water activity within the SOA and the surrounding gas phase. Water is a plasticizer, meaning that as water activity of the SOA increases, the viscosity of the SOA will decrease.

The large number of competing pathways that lead to the formation and transformation of SOA in the atmosphere are computationally difficult to include in global atmospheric models. Further, the chemical complexity of SOA makes it difficult to attribute physical properties of SOA to specific chemical constituents. In field studies, the study of the properties of SOA is further complicated by the mixing of SOA with inorganic salts, dust, biological particles, and other constituents within atmospheric aerosol. It is therefore useful to perform laboratory experiments on model systems as simplified proxies for SOA as a first step towards understanding their physical properties.

### 1.2.2 Organic-water matrices as proxies for SOA

In research Chapters 2, 3, and 5, binary or ternary mixtures of organic solutes and water are used as proxies for SOA. The organic solutes that were chosen have similar properties (e.g. O:C ratios and functional groups) to some organic molecules found in lab generated and ambient SOA. The molecular weights, O:C ratios, and functional groups of the organic solute molecules used as proxies for SOA in this thesis are given in Table 1.1. These solutes have O:C ratios similar to the highest O:C ratios observed in molecules in SOA.
Table 1.1 Select physical properties of the organic solutes used as proxies for SOA in Chapters 2, 3 and 5.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Organic solute</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>O:C ratio</th>
<th>Functional group(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 3</td>
<td>Citric acid</td>
<td>192.12</td>
<td>1.16</td>
<td>Carboxylic acid, alcohol</td>
</tr>
<tr>
<td>2</td>
<td>Sorbitol</td>
<td>182.17</td>
<td>1.0</td>
<td>Alcohol</td>
</tr>
<tr>
<td>5</td>
<td>Erythritol</td>
<td>122.12</td>
<td>1.0</td>
<td>Alcohol</td>
</tr>
<tr>
<td>2, 3</td>
<td>Sucrose</td>
<td>342.3</td>
<td>0.92</td>
<td>Saccharide</td>
</tr>
<tr>
<td>3</td>
<td>Raffinose</td>
<td>504.42</td>
<td>0.88</td>
<td>Saccharide</td>
</tr>
</tbody>
</table>

While they are a useful starting point for controlled laboratory studies, binary or ternary organic-water mixtures such as those used in Chapters 2, 3, and 5 do not represent the full chemical complexity of SOA. In Chapter 4 we used two lab-generated aerosol samples which were more realistic and chemically complex. The first was SOA produced via ozonolysis of the biogenic VOC β-caryophyllene. The second was biomass burning aerosol (BBOA), which was generated through the pyrolysis of pine wood.

1.3 Diffusion

1.3.1 Molecular diffusion and diffusion coefficients

Molecular diffusion refers to the thermal motion of molecules. The diffusion coefficient is related to the flux of matter, $J$, which is the quantity of molecules passing through a unit area per unit time, given in units of molecules m⁻² s⁻¹. The flux parallel to an axis $x$, which we write as $J_x$, is related to the concentration gradient along that axis ($dc/dx$) and the diffusion coefficient ($D$) by the following equation:

$$J_x = -D \frac{dc}{dx} \quad \text{(Eq. 1.1)}$$

where $D$ is the coefficient of proportionality between the flux and the concentration gradient. Equation 1.1 is known as Fick’s first law and is valid when the concentration gradient is uniform.
with respect to time and position. If the concentration gradient is not uniform, a separate equation, known as Fick’s second law, must be used:

\[
\frac{dc}{dt} = D \frac{\partial^2 c}{dx^2}
\]  
(Eq. 1.2)

Fick’s second law as written above is valid when the diffusion coefficient is a constant. The diffusion coefficient will be constant when the diffusion of molecules through a fluid does not alter the physical properties of that fluid matrix, as is the case for the experiments performed in this thesis. However, there is an atmospherically relevant case where diffusion coefficients will not be constant. Section 1.2.1 has described that the viscosity of SOA depends on the water content of SOA. When water is the diffusing species in SOA or in a proxy for SOA, the viscosity of the fluid matrix will change as water diffuses through the matrix. This change in viscosity means that condensed phase diffusivities cannot be constant when water is the diffusing species.

1.3.2 The relationship between diffusion and viscosity

The relationship between diffusion of a spherical species within a continuous fluid and the viscosity of that fluid is quantified by the Stokes-Einstein relation:

\[
D = \frac{kT}{6\pi\eta R_H}
\]  
(Eq. 1.3)

where \( D \) is the diffusion coefficient, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \eta \) is the viscosity of the fluid, and \( R_H \) is the hydrodynamic radius of the diffusing species. The Stokes-Einstein relation as written above is for a spherical diffusing species. The factor of \( 6\pi \) assumes no-slip conditions at the boundary of the diffusing species. The no-slip condition means that the frictional coefficient \( (6\pi\eta R_H) \) acting on a diffusing sphere is the sum of two forces, as shown by Stokes: one is the pressure experienced by the front of the sphere \( (4\pi\eta R_H) \) and the other is the frictional force parallel to the direction of movement \( (2\pi\eta R_H) \).

The Stokes-Einstein relation was developed under assumption of specific conditions, namely that the diffusing species experiences the fluid as continuous and homogeneous. These
conditions may be satisfied when the fluid viscosity is low and the radius of the diffusing species \((R_{\text{diff}})\) is large relative to the radius of the molecules that make up the fluid \((R_{\text{matrix}})\). The Stokes-Einstein relation applies to Newtonian fluids. Newtonian fluids have a linear relationship between the viscosity of the fluid and the shear stress applied to the fluid. Many organic-water mixtures behave as Newtonian fluids. Fluids that are non-Newtonian, such as certain fluids with very large molecules, e.g. polymers, will have a non-linear relationship between viscosity and shear stress, and the Stokes-Einstein relation will not accurately describe diffusion coefficients in those fluids.

Previous work has shown that the Stokes-Einstein relation may not accurately represent the relationship between diffusion and viscosity in some cases, such as when the diffusing species are similar to or smaller in size that the molecules that make up the fluid \((R_{\text{diff}}/R_{\text{matrix}} \lesssim 1)\), as is often the case when organic molecules or oxidants are diffusing in organic-water mixtures or in SOA in the atmosphere. An alternative to the Stokes-Einstein relation is the fractional Stokes-Einstein relation. This relation states that diffusion is inversely proportional to viscosity to a fractional exponent:

\[
D \propto \frac{1}{\eta^{\zeta}}
\]  
(Eq. 1.4)

where \(\zeta\) is an empirical fit parameter, and \(0 < \zeta \leq 1\).

Both the Stokes-Einstein and fractional Stokes-Einstein relations have been evaluated for their ability to predict diffusion coefficients for some diffusing species in sucrose-water mixtures, as discussed in Section 1.3.4. However, whether or not these results can be extrapolated to other diffusing species or other organic-water mixtures has not been investigated. The ability of the fractional Stokes-Einstein relation to describe diffusion coefficients in organic-water mixtures is discussed in Section 1.3.4 and is the subject of Chapters 2 and 3 in this dissertation.

1.3.3 The importance of diffusion within SOA

The effects of atmospheric aerosols have been discussed generally in Section 1.1.2. Those effects depend on both the physical and the chemical properties of the aerosols themselves. Diffusion is one of the physical properties that affects aerosol particle growth, as well as mass and
size distributions (Zaveri et al., 2014), which subsequently impact visibility, human health, and
direct and indirect climate effects. Diffusion also affects the ability of an aerosol to participate in
ice cloud formation (Berkemeier et al., 2014; Knopf et al., 2018; Lienhard et al., 2015; Murray,
2008; Price et al., 2015), contributing to the indirect effect of aerosols on climate.

Diffusion affects the timescale for an SOA particle to come to equilibrium with semi-
volatile compounds (SVOCs) in the surrounding gas phase. When diffusion is fast, SOA comes to
equilibrium with the surrounding gas phase in a short period of time, and the distribution of SVOCs
taken up from the gas phase is homogeneous within an aerosol particle (Figure 1.1a). When
diffusion is slow, SOA will take a longer time to come to equilibrium with the surrounding gas
phase, and the result may be a core-shell morphology where SVOCs are limited to the outermost
region of the aerosol particle (Figure 1.1b). This will impact the growth rates and mass
concentrations of SOA in the atmosphere, which are important determinants of air quality (Perraud
et al., 2012; Shiraiwa and Seinfeld, 2012).

Throughout this thesis, the diffusion of molecules is assumed to be the only relevant
process when calculating the mixing times of atmospheric aerosols. Internal circulation is not
important for small particles in the atmosphere (e.g. for a $d_p$ of 200 nm, which is roughly the median
diameter in the volume distribution of ambient SOA (Martin et al., 2010; Pöschl et al., 2010;
Riipinen et al., 2011)). The movement of aerosol particles in the atmosphere due to the force of
gravity and due to Brownian motion are roughly equal, and so strong internal circulations are not
generated.
Figure 1.1 Distribution of semi-volatile organic compounds (SVOCs) and SOA molecules in an SOA particle when diffusion is a) fast, resulting in a homogeneous distribution of SVOCs and b) slow, resulting in SVOCs being limited to the outermost region of the aerosol particle.

Rates of diffusion also affect the lifetimes of SVOCs in atmospheric aerosol. For example, if SVOCs such as polycyclic aromatic hydrocarbons (PAHs) are present during the formation of SOA (e.g. if SOA precursors and PAHs are co-emitted), some PAH molecules will be distributed throughout the resulting SOA. Previous work has shown that the residence time of PAHs within SOA can be long in such cases. For example, Abramson et al. produced α-pinene SOA in the presence of the PAH pyrene, resulting in SOA with pyrene embedded throughout the particle (Abramson et al., 2013). They monitored the temporal loss of pyrene from the SOA using mass spectrometry and found that 50% of the initial pyrene remained embedded in the SOA after ~24 hours. The long residence time is due to slow diffusion of the PAH molecules inside the SOA under the experimental conditions. Zhou et al. showed that lifetimes of PAHs in SOA increase as the diffusion coefficient of the PAH decreases from $10^{-16}$ m$^2$s$^{-1}$ at a relative humidity of 50% to $10^{-18}$ m$^2$s$^{-1}$ under dry conditions (Zhou et al., 2019). Slow diffusion of PAHs in SOA as described in these examples can result in SOA acting as vessels which can contain and transport PAHs over long distances and lead to the deposition of PAHs in remote environments. However, the rate of diffusion is not the only factor determining the lifetime of PAHs in SOA. Other factors including rates of reaction with oxidants and concentrations of oxidants must be considered. A case study describing the lifetime of PAH molecules in SOA is included in Chapter 3.
While diffusion rates of organic molecules in SOA have been measured or inferred from experiments in some cases (Abramson et al., 2013; Liu et al., 2016; Perraud et al., 2012; Ullmann et al., 2019; Ye et al., 2016; Zhou et al., 2019), it is also common for researchers to predict diffusion rates of organic molecules within SOA using measured viscosities and the Stokes-Einstein relation (Eq. 1.3) (Booth et al., 2014; Hosny et al., 2013; Koop et al., 2011; Maclean et al., 2017; Power et al., 2013; Renbaum-Wolff et al., 2013b; Shiraiwa et al., 2011; Song et al., 2015, 2016a). This is due to the development and application of several techniques that can measure the viscosity of ambient aerosol or small volumes in the laboratory (Grayson et al., 2015; Pajunoja et al., 2014; Renbaum-Wolff et al., 2013a; Song et al., 2016b; Virtanen et al., 2010). It is therefore important to evaluate the ability of the Stokes-Einstein relation to accurately describe diffusion coefficients of molecules in SOA.

1.3.4 The importance of diffusion within organic-water mixtures

As discussed in Section 1.2.1 and 1.2.2, SOA is composed of mixtures of organic molecules and water, and simple binary or ternary organic-water mixtures can be used as proxies for SOA in a laboratory setting.

Organic-water mixtures are also important in industry, for example in the food sciences many products include organic molecules, such as saccharides, and water. The diffusion of both water and the organic molecules within a food product under specific conditions is important for storage times (Champion et al., 1997; Goff, 1992; Slade and Levine, 1991; van der Sman and Meinders, 2013).

Organic-water mixtures are also used for the storage of pharmaceutical agents, and the rates of diffusion within that matrix will influence the viability of a pharmaceutical formulation (Shamblin et al., 1999). Finally, organic-water mixtures are used in the cryopreservation of biomolecules (Cicerone and Douglas, 2012; Drummen et al., 2012; Fox, 1995; Imagi et al., 1992; Miller et al., 1998). In each of these cases, diffusion of molecules within these matrices can be one factor in determining whether a specific organic-water mixture is useful for a particular application.

Due in part to the importance of saccharide-water mixtures to the food industry, diffusion coefficients of several molecules, ranging from small species such as water, xenon, ferrocene
methanol, and polyethylene glycol, to large molecules including sucrose and fluorescent organic molecules have been measured in sucrose-water mixtures as a function of water activity (Bastelberger et al., 2017; Champion et al., 1997; Chenyakin et al., 2017; Davies and Wilson, 2016; Longinotti and Corti, 2007; Pollack, 1981; Price et al., 2014, 2016; Rampp et al., 2000). Some of those studies also evaluated the ability of the Stokes-Einstein relation to predict diffusion coefficients in sucrose-water mixtures (Bastelberger et al., 2017; Chenyakin et al., 2017; Price et al., 2016). This was possible due to the large quantity of viscosity data as a function of water activity available in the literature, including data from Power et al. who reported viscosities far outside the range of what had previously been reported (Först et al., 2002; Grayson et al., 2017; Green and Perry, 2007; Haynes, 2015; Lide, 2001; Migliori et al., 2007; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007). The Stokes-Einstein relation (Eq. 1.3) has been shown to under-predict diffusion coefficients in sucrose-water mixtures by several orders of magnitude when the diffusing species are small or the viscosity is high (Bastelberger et al., 2017; Chenyakin et al., 2017; Davies and Wilson, 2016; Price et al., 2016).

The fractional Stokes-Einstein relation (Eq. 1.4) has also been used to describe diffusion coefficients in organic-water mixtures by a few authors. Pollack showed that diffusion coefficients of xenon in sucrose-water mixtures can be described using the fractional Stokes-Einstein relation with \( \zeta = 0.63 \) (Pollack, 1981). Mallamace et al. showed that diffusion coefficients of water in concentrated glycerol-water mixtures can be described with \( \zeta = 0.85 \) (Mallamace et al., 2010). Price et al. showed that diffusion coefficients of water and sucrose in sucrose-water mixtures can be described with \( \zeta = 0.57 \) and \( \zeta = 0.90 \), respectively (Price et al., 2016). Whether or not these results can be extrapolated to other diffusing species or other organic-water mixtures, however, was not investigated. In addition, the relationship between the fractional exponent \( \zeta \) and \( R_{\text{diff}}/R_{\text{matrix}} \) was not explored for organic-water mixtures. There is currently no simple and accurate method to predict diffusion coefficients of small molecules in organic-water mixtures as a function of viscosity and \( R_{\text{diff}}/R_{\text{matrix}} \).

Measurements of diffusion of molecules in organic-water mixtures other than sucrose are limited, and the ability of the Stokes-Einstein relation and fractional Stokes-Einstein relation to predict diffusion coefficients in other organic-water mixtures has not been extensively studied. In one example, Davies and Wilson showed that the Stokes-Einstein relation under-predicts the
diffusion coefficients of water in a citric acid-water mixture by several orders of magnitude (Davies and Wilson, 2016). Recently, viscosity data as a function of water activity has become available for additional organic-water mixtures, such as citric acid-water (Song et al., 2016b), sorbitol-water (Song et al., 2016b), erythritol-water (Song et al., 2016b) raffinose-water (Grayson et al., 2017; Song et al., 2016b), and sucrose-citric acid-water mixtures (Rovelli et al., 2019), which allows for comparisons between measured diffusion coefficients and viscosity using the Stokes-Einstein and fractional Stokes-Einstein relations.

1.4 Overview of dissertation

Chapter 1 (this chapter) gives an introduction to the topics of atmospheric aerosols, secondary organic aerosol (SOA), and a brief overview of the physical phenomenon of diffusion as necessary to understand this thesis. It also provides the motivation for research Chapters 2-5. Chapter 2 describes the use of diffusion and viscosity data to develop a parameterization based on the Stokes-Einstein relation that relates the diffusion of large organic molecules \( \frac{R_{\text{diff}}}{R_{\text{matrix}}} \geq 1 \) to the viscosity of an organic-water mixture. Chapter 3 performs a similar function but describes a parameterization with universal application to both large and small molecules \( \left( \frac{R_{\text{diff}}}{R_{\text{matrix}}} \geq 1 \right) \) and \( \left( \frac{R_{\text{diff}}}{R_{\text{matrix}}} < 1 \right) \) diffusing in an organic-water mixture. Chapter 4 describes the relationship between diffusion and viscosity in lab-generated SOA produced via the ozonolysis of β-caryophyllene and in lab-generated BBOA produced via the pyrolysis of pine wood. Chapter 5 uses diffusion measurements of a large diffusing species to calculate the viscosity of an erythritol-water mixture and draws a comparison with viscosity measured using a separate technique, resolving a discrepancy between two published viscosity data sets for erythritol-water mixtures. Finally, Chapter 6 draws conclusions from each of the preceding chapters and suggests directions for future research into the relationship between diffusion and viscosity to support the field of atmospheric chemistry.
Chapter 2: Predictions of diffusion rates of large organic molecules in secondary organic aerosols using the Stokes-Einstein and fractional Stokes-Einstein relations

2.1 Introduction

This chapter presents measured diffusion coefficients of fluorescent organic molecules in organic-water mixtures as proxies for SOA (with $R_{diff}/R_{matrix} > 1$ in all cases). The organic solutes chosen have functional groups that have been observed in lab-generated and ambient SOA, namely alcohols and carboxylic acids (Claeys et al., 2004, 2007; Edney et al., 2005; Fisseha et al., 2004; Glasius et al., 2000; Liu et al., 2011; Surratt et al., 2006, 2010a).

As discussed in Chapter 1, information on the rate of diffusion of organic molecules within SOA is needed in order to accurately predict the impacts of SOA on climate, air quality, and the long-range transport of pollutants. In some cases, diffusion rates of organic molecules in SOA have been measured or inferred from experiments (Abramson et al., 2013; Liu et al., 2016; Perraud et al., 2012; Ullmann et al., 2019; Ye et al., 2016). However, in many cases researchers have predicted diffusion rates of organic molecules within SOA using measurements of viscosities and the Stokes-Einstein relation (Booth et al., 2014; Hosny et al., 2013; Koop et al., 2011; Maclean et al., 2017; Power et al., 2013; Renbaum-Wolff et al., 2013b; Shiraiwa et al., 2011; Song et al., 2015, 2016a).

Only a few studies have investigated the accuracy of the Stokes-Einstein relation for predicting diffusion coefficients of organic molecules in SOA, and almost all of these studies relied on sucrose as a proxy for SOA particles (Bastelberger et al., 2017; Chenyakin et al., 2017; Price et al., 2016). Sucrose was used as a proxy for SOA in these studies because 1) sucrose has an O:C ratio similar to that of highly oxidized components of SOA and 2) viscosity and diffusion data for sucrose exist in the literature (mainly from the food science literature, as well as from Power et al. (2013), who reported viscosities far outside the range of what had previously been reported). However, studies with other proxies of SOA are required to determine if the Stokes-Einstein relation can accurately represent the diffusion of organic molecules in SOA, and to more accurately...
predict the role of SOA in climate, air quality, and transport of pollutants (Reid et al., 2018; Shrivastava et al., 2017b).

This chapter expands on literature studies with sucrose-water mixtures by testing the Stokes-Einstein relation in the following proxies for SOA: citric acid-water, sorbitol-water, and sucrose-citric acid-water. These proxies have functional groups that have been identified in SOA, and O:C ratios similar to those ratios found in the most highly oxidized components of SOA in the atmosphere (Table 1.1). To test the Stokes-Einstein relation, first diffusion coefficients of fluorescent organic molecules were determined as a function of water activity ($a_w$) in these SOA proxies using rectangular area fluorescence recovery after photobleaching (rFRAP; Section 2.2.4). The diffusing organic molecules studied in this work were the fluorescent organic molecules rhodamine 6G (R6G) and cresyl violet (Figure 2.1). The experimental diffusion coefficients are compared with predictions using literature viscosities (Rovelli et al., 2019; Song et al., 2016b) and the Stokes-Einstein relation. The results from the current study are then combined with literature diffusion (also limited to cases where $R_{\text{diff}}/R_{\text{matrix}} \geq 1$) (Champion et al., 1997; Chenyakin et al., 2017; Price et al., 2016; Rampp et al., 2000; Ullmann et al., 2019) and viscosity (Först et al., 2002; Grayson et al., 2017; Green and Perry, 2007; Haynes, 2015; Lide, 2001; Migliori et al., 2007; Power et al., 2013; Quintas et al., 2006; Rovelli et al., 2019; Swindells et al., 1958; Telis et al., 2007; Ullmann et al., 2019) data to assess the ability of the Stokes-Einstein relation to predict diffusion of organic molecules in atmospheric SOA. The ability of the fractional Stokes-Einstein relation to predict diffusion is also tested. This chapter only includes data for large diffusing species ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$), while both small and large diffusing species are included in Chapter 3.

2.2 Experimental methods

The experimental diffusion coefficients reported in this thesis were determined using rectangular area fluorescence recovery after photobleaching (rFRAP). This fluorescence microscopy technique enables the determination of diffusion coefficients of fluorescent molecules over eight orders of magnitude, from $10^{-19}$ to $10^{-11}$ m$^2$/s. Thin films of the sample of interest are required to perform experiments using the rFRAP technique. In this chapter, as well as Chapters 3 and 5, diffusion coefficients of fluorescent organic molecules were measured as a function of water activity ($a_w$) in thin films containing organic solutes, water, and fluorescent organic molecules.
The thin films were generated from bulk solutions. Both the preparation of thin films from bulk solutions and the rFRAP measurement technique are described in detail here, and these descriptions are referred to in relevant places in later chapters.

2.2.1 Materials

In this chapter, the organic solutes citric acid (> 99% purity, Sigma-Aldrich), sorbitol (> 98% purity, Sigma-Aldrich), and a mixture of sucrose (> 99% purity, Sigma-Aldrich) and citric acid (60:40 mass ratio) were used. Rhodamine 6G (R6G, > 99% purity, Acros Organics) and cresyl violet (> 75% purity, Santa Cruz Biotechnology) were used as the diffusing fluorescent organic molecules. All solutions were prepared using Millipore Milli-Q water. The chemical structures of R6G and cresyl violet are shown in Figure 2.1.

![Chemical structures (protonated form) of the fluorescent organic molecules used in this study: a) R6G and b) cresyl violet.](image)

2.2.2 Preparation of thin films containing organic solute, water, and fluorescent molecules from bulk solution

Solutions containing the organic solute molecules, water, and the fluorescent organic molecules were prepared gravimetrically. The concentrations of the organic solutes in the bulk solutions used in this chapter are given in Table 2.1. A mass ratio of 60:40 sucrose to citric acid
was used for the sucrose-citric acid mixtures. The concentrations of R6G and cresyl violet in the bulk solutions as well as the concentrations in the thin films conditioned to a specific \( d_w \) are also given in Table 2.1. At the chosen concentrations, the fluorescence intensity of the thin films was proportional to the concentration of the fluorescent organic molecules (Figures 2.2-2.5).

**Table 2.1** Concentrations of the organic solutes in the bulk solutions and concentrations of the fluorescent organic molecules in both the bulk solutions and the conditioned thin films used in this chapter.

<table>
<thead>
<tr>
<th>Solution identity</th>
<th>Organic solute concentration in bulk solution (mass fraction)</th>
<th>Fluorescent organic molecule concentration in bulk solution (mM)</th>
<th>Fluorescent organic molecule concentration after conditioning (mass fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R6G in citric acid-water</td>
<td>0.55</td>
<td>0.06</td>
<td>0.00332-0.00508</td>
</tr>
<tr>
<td>Cresyl violet in citric acid-water</td>
<td>0.55</td>
<td>0.08</td>
<td>0.00364-0.00454</td>
</tr>
<tr>
<td>R6G in sorbitol-water</td>
<td>0.30</td>
<td>0.06</td>
<td>0.00847-0.00913</td>
</tr>
<tr>
<td>R6G in sucrose-citric acid-water (60:40 mass ratio)</td>
<td>0.30</td>
<td>0.06</td>
<td>0.00672-0.00945</td>
</tr>
</tbody>
</table>
Figure 2.2 Average fluorescence intensity as a function of R6G mass fraction in citric acid-water thin films at $a_w = 0.800 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for R6G in citric acid-water thin films. rFRAP experiments were performed using R6G concentrations within the linear range indicated here.

Figure 2.3 Average fluorescence intensity as a function of cresyl violet mass fraction in citric acid-water thin films at $a_w = 0.800 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for cresyl violet in citric acid-water thin films. rFRAP experiments were performed using cresyl violet concentrations within the linear range indicated here.
Figure 2.4 Average fluorescence intensity as a function of R6G mass fraction in sorbitol-water thin films at $a_w = 0.800 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for R6G in sorbitol-water thin films. rFRAP experiments were performed using R6G concentrations within the linear range indicated here.

Figure 2.5 Average fluorescence intensity as a function of R6G mass fraction in sucrose-citric acid-water thin films at $a_w = 0.85 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for R6G in sucrose-citric acid-water thin films. rFRAP experiments were performed using R6G concentrations within the linear range indicated here.
Solutions were filtered to remove impurities by passing solutions through a 0.02 μm filter (Whatman™). Droplets of the filtered solutions were placed on cleaned siliconized hydrophobic slides (Hampton Research), by either nebulizing the bulk solution or using the tip of a sterilized needle (BD PrecisionGlide Needle). The generated droplets ranged in diameter from ~ 100 to ~ 1300 μm. After the droplets were located on the hydrophobic slides, the hydrophobic slides were placed inside sealed glass containers with a controlled water activity (aw). The aw was set by placing saturated inorganic salt solutions with known aw values within the sealed glass containers. The inorganic salts that were used to achieve each aw are given in Table 2.2.

**Table 2.2** Water activity (aw) of the headspace above each saturated salt solution used for conditioning droplets of fluorescent organic-water solutions. The aw was calculated from relative humidity (RH, aw = RH/100), which was measured using a handheld hygrometer with an uncertainty of ± 2.5%.

<table>
<thead>
<tr>
<th>Inorganic salt</th>
<th>Water activity (aw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium acetate (CH₃COOK) a</td>
<td>0.23</td>
</tr>
<tr>
<td>Potassium acetate (CH₃COOK) a</td>
<td>0.26</td>
</tr>
<tr>
<td>Potassium acetate (CH₃COOK) a</td>
<td>0.28</td>
</tr>
<tr>
<td>Magnesium chloride (MgCl₂·6H₂O)</td>
<td>0.33</td>
</tr>
<tr>
<td>Potassium carbonate (K₂CO₃)</td>
<td>0.43</td>
</tr>
<tr>
<td>Calcium nitrate Ca(NO₃)₂·4H₂O</td>
<td>0.51</td>
</tr>
<tr>
<td>Sodium bromide (NaBr)</td>
<td>0.57</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>0.75</td>
</tr>
<tr>
<td>Potassium chloride (KCl)</td>
<td>0.85</td>
</tr>
</tbody>
</table>

a Subsaturated solutions of potassium acetate were used to access water activities between 0.23 and 0.33.

The slides holding the droplets were left inside the sealed glass containers for an extended period of time to allow the droplets to equilibrate with the surrounding aw. The method used to calculate equilibration times is explained in Section 2.2.3.

After the droplets on the slides were conditioned to the aw of the airspace over the salt solution, the sealed glass containers holding the slides and conditioned droplets were brought into a Glove Bag™ (Glas-Col). The aw within the Glove Bag was controlled using a humidified flow.
of N₂ gas and monitored using a handheld hygrometer. The a_w within the Glove Bag™ was set to the same a_w used to condition the droplets, to prevent the droplets from being exposed to an unknown and uncontrolled a_w. To form a thin film, aluminum spacers were placed on the siliconized glass slide holding the droplets, followed by another siliconized glass slide, which sandwiched the droplets and the aluminum spacers. The thickness of the aluminum spacers (30-50 μm) determined the thickness of the thin film. The two slides were sealed together by vacuum grease spread around the perimeter of one slide before sandwiching. Figure 2.6 demonstrates this thin film preparation technique.

The organic-water matrices were often supersaturated with respect to crystalline organic solute. Nevertheless, crystallization was not observed in most cases until a_w values of 0.14 or 0.23, depending on the matrix. Solutions were passed through a filter and the glass slides used to make the thin films were covered with a hydrophobic coating. Filtration likely removed heterogeneous nuclei that could initiate crystallization and the hydrophobic coating reduced the ability of these surfaces to promote heterogeneous nucleation (Bodsworth et al., 2010; Pant et al., 2006; Price et al., 2014; Wheeler and Bertram, 2012). In the cases where crystallization was observed, determined using optical microscopy, the films were not used in rFRAP experiments. An image demonstrating the difference in appearance between crystallized and non-crystallized droplets is given in Figure 2.7. The lower experimental limit in a_w for a given organic solute was determined by crystallization of the samples, while the upper experimental limit in a_w was determined by the speed at which images could be collected with our experimental set-up, detailed in Section 2.2.4.

We did not condition droplets without fluorescent organic molecules to determine the effect of the fluorescent molecules on crystallization. However, previous studies have shown that droplets with the compositions and range of a_w values studied here can exist in the metastable liquid state if heterogeneous nucleation by surfaces is reduced. Furthermore, since the concentration of the fluorescent molecules in the droplets was so low, they are not expected to change the driving force for crystallization in the droplets.
Figure 2.6 Top view (a) and side view (b) of a thin film of an organic-water matrix containing trace amounts of the fluorescent organic molecules, sandwiched between two hydrophobic glass slides, for use in rFRAP experiments.
Figure 2.7 Image showing the difference between crystallized and non-crystallized droplets taken using an optical microscope. The sample was generated using a 0.08 mM solution of cresyl violet in a citric acid matrix, conditioned to \( a_w = 0.23 \). Slides with crystallized droplets were not used in rFRAP experiments.

2.2.3 Conditioning times for samples containing an organic solute, water, and fluorescent molecules

The time required for droplets to come to equilibrium with the surrounding \( a_w \) was calculated using the following equation (Seinfeld and Pandis, 2006):

\[
\tau_{\text{mix,H}2\text{O}} = \frac{d_p^2}{4\pi^2 D_{\text{H}2\text{O}}} \tag{Eq. 2.1}
\]

where \( \tau_{\text{mix,H}2\text{O}} \) is the characteristic mixing time of water due to molecular diffusion, \( d_p \) is the diameter of the droplet, and \( D_{\text{H}2\text{O}} \) is the diffusion coefficient of water in the matrix. A discussion of the values used for \( D_{\text{H}2\text{O}} \) in organic-water droplets follows. Diffusion coefficients of water in the organic-water mixtures studied here are assumed to equal the diffusion coefficients of water in a sucrose-water mixture when the viscosity of the two matrices are equal. Diffusion coefficients for water in a sucrose-water mixture at a given viscosity were calculated using a parametrization
for diffusion coefficients as a function of $a_w$ from Price et al. (2016) and a parameterization for sucrose viscosity as a function of $a_w$ from Grayson et al. (2017). The diffusion coefficients of water in sucrose were used as an estimate for diffusion coefficients of water in solutions of citric acid, sorbitol, and the sucrose-citric acid mixture at an equivalent viscosity. The expected viscosity of the organic-water matrices at each $a_w$ was calculated using viscosity-$a_w$ parameterizations for citric acid, sorbitol, and sucrose-citric acid (Appendix A, Figures A.1-A.3).

Conditioning times for all samples are given in Appendix A. Experimental conditioning times ($t_{exp}$) were a minimum of three times longer than calculated conditioning times ($\tau_{mix,H2O}$).

2.2.4 Rectangular area fluorescence recovery after photobleaching (rFRAP) technique and extraction of diffusion coefficients

Diffusion coefficients were determined using the rFRAP technique reported by Deschout et al. (2010). The technique uses a confocal laser scanning microscope to photobleach fluorescent molecules in a specified volume of an organic thin film containing fluorescent molecules. More information on confocal laser scanning microscopy is given in Section 2.2.5. The photobleaching event initially reduces the fluorescence intensity within the bleached volume. Afterward, the fluorescence intensity within the photobleached volume recovers due to the diffusion of fluorescent molecules from outside of the bleached region (e.g. Figure 2.8). From the time-dependent recovery of the fluorescence intensity, diffusion coefficients are determined. All diffusion experiments in this chapter were performed at 295 ± 1 K.

The rFRAP experiments were performed on a Zeiss Axio Observer LSM 510MP laser scanning microscope with a 10X, 0.3 NA objective and a pinhole setting between 80 and 120 μm. Photobleaching and the subsequent acquisition of recovery images were done using a 543 nm helium–neon (HeNe) laser. The bleach parameters (e.g. laser intensity, iterations, laser speed) were varied for each experiment so that the fraction of fluorescent molecules being photobleached in the bleach region was about 30%. A photobleaching of about 30% was suggested by Deschout et al. (2010), who report that diffusion coefficients determined using the rFRAP technique are independent of the extent of photobleaching up to a bleach depth of 50%. The energy absorbed by the thin film during photobleaching is not expected to affect experimental diffusion coefficients. Although local heating may occur during photobleaching, the thermal diffusivity in the samples is
orders of magnitude greater than the molecular diffusivity, and the heat resulting from photobleaching will dissipate to the surroundings on a timescale much faster than the diffusion of molecules will occur (Chenyakin et al., 2017). Measurements as a function of photobleaching size and power are consistent with this expectation (Chenyakin et al., 2017; Ullmann et al., 2019).

Bleached areas ranged from 20 µm² to 400 µm². The geometry of the photobleached region was a square with sides of length $l_x$ and $l_y$ ranging from 4.5 to 20 µm. Smaller bleach areas were used in experiments where diffusion was slower in order to shorten recovery times. Chenyakin et al. (2017) showed that experimental diffusion coefficients varied by less than the experimental uncertainty when the bleach area was varied from 1 µm² to 2500 µm² in sucrose-water films. Similarly, Deschout et al. (2010) demonstrated that diffusion coefficients varied by less than the experimental uncertainty when the bleach area was varied from approximately 4 µm² to 144 µm² in sucrose-water films. The images collected during a rFRAP experiment represent fluorescence intensities as a function of $x$ and $y$ coordinates and are taken at regular time intervals after photobleaching. Time intervals varied from a few seconds for the fastest diffusion coefficients, to one hour or more for the slowest diffusion coefficients. An example of images recorded during a rFRAP experiment are shown in Figure 2.8. Every image taken following the photobleaching event is normalized relative to an image taken before photobleaching. To reduce noise, all images are downsized by averaging from a resolution of 512x512 pixels to 128x128 pixels. Also included in Figure 2.8 is a schematic demonstrating the photobleaching and recovery processes. Figure 2.9 shows four additional examples of fluorescent images recorded during a rFRAP experiment, with one set of images taken in each organic-water mixture used in this chapter.
Figure 2.8 An example of fluorescent images recorded during an rFRAP experiment (a-d), and schematic representations of the rFRAP images (e-h). The data shown correspond to films at $a_w = 0.33$ containing citric acid, water, and trace amounts of R6G. Panel (a) shows an image taken prior to photobleaching and was used to normalize all images taken after photobleaching. Panel (b) shows an image taken immediately following photobleaching, and panels (c) and (d) were taken during the recovery period. Panels (e-h) are schematic representations of the fluorescent thin film at those same time intervals. The black dashed square in panels (a) and (e) indicates the region selected for photobleaching ($36 \, \mu m^2$), and the entire imaged area was $3600 \, \mu m^2$. 
Figure 2.9 An example of fluorescent images recorded during an rFRAP experiment using (a-d) films at $a_w = 0.33$ containing citric acid, water, and trace amounts of R6G, (e-h) films at $a_w = 0.23$ containing citric acid, water, and trace amounts of cresyl violet, (i-l) films at $a_w = 0.33$ containing sorbitol, water, and trace amounts of R6G, and (m-p) films at $a_w = 0.33$ containing sucrose, citric acid, water, and trace amounts of R6G. Panels (a, e, i, and m) show images taken prior to photobleaching and was used to normalize all images taken after photobleaching. Panels (b, f, j, and n) show images taken immediately following photobleaching. Panels (c-d), (g-h), (k-l) and (o-p) were taken during the recovery period. The black dashed square in panels (a, e, i, and m) indicates the region selected for photobleaching (20 – 36 µm$^2$), and the entire imaged area was 2000 - 3600 µm$^2$.

The mathematical description of the fluorescence intensity as a function of position ($x$ and $y$) and time ($t$) after photobleaching a rectangular area in a thin film, was given by Deschout et al. (2010):

$$
\frac{F(x,y,t)}{F_0(x,y)} = \left[ 1 - \frac{K_o}{4} \left( \text{erf} \left( \frac{x + \frac{1}{2} L_x}{\sqrt{t^2 + 4Dt}} \right) - \text{erf} \left( \frac{x - \frac{1}{2} L_x}{\sqrt{t^2 + 4Dt}} \right) \right) \cdot \left( \text{erf} \left( \frac{y + \frac{1}{2} L_y}{\sqrt{t^2 + 4Dt}} \right) - \text{erf} \left( \frac{y - \frac{1}{2} L_y}{\sqrt{t^2 + 4Dt}} \right) \right) \right] \quad \text{(Eq. 2.2)}
$$
where \( F(x,y,t) \) is the fluorescence intensity at position \( x \) and \( y \) after a time \( t \), \( F_0(x,y) \) corresponds to the initial intensity at position \( x \) and \( y \) before photobleaching, \( K_0 \) is related to the initial fraction of photobleached molecules in the bleach region, and \( l_x \) and \( l_y \) correspond to the size (length) of the bleach region in the \( x \) and \( y \) directions. The parameter \( r \) represents the resolution of the microscope, \( t \) is the time after photobleaching, and \( D \) is the diffusion coefficient.

The full images (128x128 pixels following downsizing) collected during a rFRAP experiment were fit to Eq. 2.2 using a Matlab script (The Mathworks, Natick, MA, USA), with the terms \( K_0 \), and \( r^2 + 4Dt \) left as free parameters. An additional normalization factor was also left as a free parameter, and returned a value close to 1, since images recorded after photobleaching were normalized to the pre-bleach image before fitting. To determine the bleach width \((l_x, l_y)\), Eq. 2.2 was fit to the first five images recorded after photobleaching a film with the bleach width \((l_x, l_y)\) left as a free parameter. The bleach width determined by the fit to the first five frames was then used as input in Eq. 2.2 to analyze the full set of images.

From the fitting procedure, a value for \( r^2 + 4Dt \) was determined for each image and was plotted as a function of time after photobleaching. A straight line was then fit to the \( r^2 + 4Dt \) vs. \( t \) plot, and from the slope of the line \( D \) was calculated. Examples are shown in Figures 2.10-2.13.

As the fluorescence intensity in the bleached region recovered, the noise in the data became large relative to the difference in fluorescence intensity between the bleached and non-bleached regions (i.e. signal). To ensure only data with a reasonable signal to noise were used, images were not used if this signal was less than 3x the standard deviation of the noise.
Figure 2.10 A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of R6G in a citric acid matrix at $a_w = 0.33$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

Figure 2.11 A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of cresyl violet in a citric acid matrix at $a_w = 0.23$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.
Figure 2.12 A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of R6G in a sorbitol matrix at $a_w = 0.33$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

Figure 2.13 A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of R6G in a sucrose-citric acid matrix at $a_w = 0.33$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.
Figure 2.14 shows a cross section of the fluorescence intensity along the x direction from the images in Figure 2.8 and is given only to visualize the fit of the equation to the data. The cross-sectional fit in Figure 2.14 was not used to determine diffusion coefficients. As mentioned above, the full images (128x128 pixels following downsizing) were used to determine diffusion coefficients. To generate the cross-sectional view, at each position x, the measured fluorescence intensity is averaged over the width of the photobleached region in the y direction (black squares). Also included in Figure 2.14 are cross-sectional views of the calculated fluorescence intensity along the x direction generated from the fitting procedure (solid red lines). To generate the line, Eq. 2.2 was first fit to the images. The resulting fit was then averaged over the width of the photobleached region in the y direction. The good agreement between the measured cross section and the predicted cross section illustrates that Eq. 2.2 describes the rFRAP data well.

Equation 2.2 assumes that there is no net diffusion in the axial direction (i.e. z-direction). Deschout et al. (2010) have shown that Eq. 2.2 gives accurate diffusion coefficients when the numerical aperture of the microscope is low (≤ 0.45) and the thickness of the fluorescent films is small (≤ 120 µm), which is consistent with the numerical aperture of 0.30 and film thickness of 30–50 µm used here.
Figure 2.14 Cross-sectional view of the fluorescence intensity along the $x$ direction for the fluorescence images shown in Figure 2.8. To generate these plots, at each $x$ position the fluorescence intensity is averaged over the width of the photobleached region in the $y$ direction. The black squares represent measured fluorescence intensities, while the red line represents the calculated fit to the data. (a) shows the cross-sectional view immediately following the photobleaching event ($t = 0$ s), while (b-d) show the cross-sectional views during fluorescence recovery, at $t = 180$, 540, and 840 s.

2.2.5 Confocal laser scanning microscopy

Experiments in this thesis are performed using a confocal laser scanning microscope (CLSM). The CLSM is similar in design to a conventional optical microscope, however a laser beam is used in place of a lamp. The laser beam, which passes through an objective lens, is focused on the sample. The beam can be moved precisely and quickly over the sample in two dimensions (e.g. $x$ and $y$) using two scanning mirrors, which direct the laser beam in the $x$ and $y$ directions,
respectively. The laser beam is scanned in a raster pattern across the sample. When the sample is fluorescent, the light emitted from the sample will pass back into the objective lens, travelling backwards through the light path that the laser followed. The simplified schematic of a CLSM in Figure 2.15 demonstrates the path taken by the light from the laser to the sample and taken by the light emitted from the sample to the detector. As the laser beam is scanned across a fluorescent sample, an image is built up pixel by pixel.

An advantage of CLSM is the ability to eliminate out-of-focus light so that the image produced is representative of only the part of the sample in the immediate plane of focus. That is, in a sample of some thickness, we can observe the sample at a specific depth, referred to here as a specific z-position within the sample. The out-of-focus light is excluded from reaching the detector of a CLSM by two pinholes in the path that the light travels between the sample and the detector.

![Figure 2.15 A schematic showing the path taken by light in a confocal laser scanning microscope, from the source of the laser to the detector.](image)

2.3 Results and discussion

2.3.1 Diffusion coefficients of fluorescent organic molecules in citric acid, sorbitol, and sucrose-citric acid matrices

The experimental diffusion coefficients of organic molecules in matrices of citric acid, sorbitol, and sucrose-citric acid as a function of water activity ($a_w$) are shown in Figure 2.16 (and listed in Tables A.1-A.4). The experimental diffusion coefficients depend strongly on $a_w$ for all three proxies of SOA. As $a_w$ increases from 0.23 (0.14 in one case) to 0.86, diffusion coefficients
increase by between five and eight orders of magnitude. This dependence on $a_w$ arises from the plasticizing influence of water on these matrices; as $a_w$ increases (and hence the water content increases) the viscosity decreases (Koop et al., 2011). In addition, the experimental diffusion coefficients varied significantly from matrix to matrix at the same $a_w$ (Figure 2.16). As an example, at $a_w = 0.23$ the diffusion coefficient of R6G is about four orders of magnitude larger in citric acid compared to the sucrose-citric acid mixture.

**Figure 2.16** Experimental diffusion coefficients of fluorescent organic molecules in various organic matrices as a function of water activity ($a_w$). X-error bars represent the uncertainty in the measured $a_w$ ($\pm 0.025$) and y-error bars correspond to two times the standard deviation in the diffusion measurements. Each data point is the average of a minimum of four measurements. Indicated in the legend are the fluorescent organic molecules studied and the corresponding matrices.

Figure 2.17 considers the relationship between $\log(D) - \log(kT/6\pi R_H)$ and $\log(\eta)$, a comparison that allows for the identification of deviations from the Stokes-Einstein relation. By plotting $\log(D) - \log(kT/6\pi R_H)$, differences in the hydrodynamic radii of diffusing species (Table 2.3), as well as small differences in temperature (within a range of 6 K), are accounted for. The viscosity corresponding to each diffusion coefficient was determined from relationships between
\(a_w\) and viscosity developed from literature data (Figures A.1-A.3). The solid line in Figure 2.17 corresponds to the relationship between \(\log(D) - \log(kT/6\pi R_H)\) and \(\log(\eta)\) if the Stokes-Einstein relation is obeyed. Figure 2.17 shows that the diffusion coefficients of the fluorescent organic molecules depend strongly on viscosity, with the diffusion coefficients varying by approximately eight orders of magnitude as viscosity varied by eight orders of magnitude. If the uncertainties of the measurements are considered, all the data points except three (89% of the data) are consistent with predictions from the Stokes-Einstein relation (meaning that the error bars on the measurements overlap with the solid line in Figure 2.17) over eight orders of magnitude change in diffusion coefficients. This finding is remarkable considering the assumptions inherent in the Stokes-Einstein relation (e.g. the diffusing species is a hard sphere that experiences the fluid as a homogeneous continuum and no slip at the boundary of the diffusing species).

Table 2.3 Hydrodynamic radii of diffusing organic molecules and matrix molecules used in this study including data sets taken from the literature.

<table>
<thead>
<tr>
<th>Diffusing or matrix species</th>
<th>Organic Molecule</th>
<th>Radius (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusing</td>
<td>Fluorescein</td>
<td>5.02</td>
<td>(Mustafa et al., 1993)</td>
</tr>
<tr>
<td></td>
<td>Rhodamine 6G</td>
<td>5.89</td>
<td>(Müller and Loman, 2008)</td>
</tr>
<tr>
<td></td>
<td>Calcein</td>
<td>7.4</td>
<td>(Tamba et al., 2010)</td>
</tr>
<tr>
<td></td>
<td>Cresyl violet</td>
<td>3.7</td>
<td>Molecular radius calculated using Van der Waals theory of atomic increments (Edward, 1970)</td>
</tr>
<tr>
<td>Diffusing and matrix</td>
<td>Sucrose</td>
<td>4.5</td>
<td>Based on the density of amorphous sucrose (Chenyakin et al., 2017)</td>
</tr>
<tr>
<td>Brown limonene SOA components</td>
<td>5.4 ± 0.9</td>
<td></td>
<td>(Ullmann et al., 2019)</td>
</tr>
<tr>
<td>Matrix</td>
<td>Citric acid</td>
<td>3.7</td>
<td>(Müller and Stokes, 1956)</td>
</tr>
<tr>
<td></td>
<td>Sorbitol</td>
<td>3.6</td>
<td>(Comper, 1996)</td>
</tr>
</tbody>
</table>
2.3.2 Comparison with relevant literature data

Previous studies have used sucrose to evaluate the ability of the Stokes-Einstein relation to predict diffusion coefficients of organic molecules in SOA (Bastelberger et al., 2017; Chenyakin et al., 2017; Price et al., 2016). In Figure 2.18a, the results from the current study (i.e. the results from Figure 2.17) are combined with results from previous studies of diffusion and viscosity in
sucrose and brown limonene SOA (Champion et al., 1997; Chenyakin et al., 2017; Price et al., 2016; Rampp et al., 2000; Ullmann et al., 2019). To be consistent with the new measurements, diffusion coefficients and viscosities that were measured at, or calculated using, temperatures outside the range of 292 – 298 K have not been included in Figure 2.18a. Further, Figure 2.18a only includes diffusion measurements where the radius of the diffusing molecules is equal to or greater than radius of the molecules in the fluid matrix ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$). Cases where $R_{\text{diff}}/R_{\text{matrix}} < 1$ are outside the scope of this chapter but are included in Chapter 3. Additional details for the literature data shown in Figure 2.18a are included in Appendix A and the radii of the diffusing and matrix molecules are given in Table 2.3.

Based on Figure 2.18a the diffusion coefficients of the organic molecules in sucrose matrices and matrices consisting of SOA generated in the laboratory depend strongly on viscosity, similar to the results shown in Figure 2.17. In addition, almost all the data agree with the Stokes-Einstein relation (solid line in Figure 2.18a) within a factor of ten. This finding is in stark contrast with the diffusion of water in organic-water mixtures ($R_{\text{diff}}/R_{\text{matrix}} < 1$), where much larger deviations between experimental and predicted diffusion coefficients were observed over the same viscosity range (Davies and Wilson, 2016; Marshall et al., 2016; Price et al., 2016).

Figure 2.18b shows the differences between the experimental values and the solid line in Figure 2.18a as a function of viscosity. If the Stokes-Einstein relation describes the data well, these differences (i.e. residuals) should be scattered symmetrically about zero, while the magnitude of the residuals should be less than or equal to the uncertainty in the measurements. However, the residuals are skewed to be positive, especially as viscosity increases, with experimental diffusion faster than expected based on the Stokes-Einstein relation. Figure 2.18b suggests that the Stokes-Einstein relation may not be the optimal model for predicting diffusion coefficients in SOA, particularly at high viscosities.
Figure 2.18 a) Plot of log ($D$) – log ($kT/6\pi R_H$) as a function of log ($\eta$) for experimental diffusion coefficients reported in this work and literature data. Indicated in the legend are the diffusing organic molecules studied and the corresponding matrices. The symbols represent experimental data points. The solid line represents the relationship between log ($D$) – log ($kT/6\pi R_H$) and log ($\eta$) predicted by the Stokes-Einstein relation, while the dashed line represents the relationship between log ($D$) – log ($kT/6\pi R_H$) and log ($\eta$) predicted by a fractional Stokes-Einstein relation with slope = -0.93 and $\eta_0$ of $10^{-3}$ Pa s. Panels b) and c) are plots of the differences (i.e. residuals) between experimental and predicted values of log ($D$) – log($kT/6\pi R_H$) using the Stokes-Einstein relation and the fractional Stokes-Einstein relation, respectively. The sum-of-squared residuals for the Stokes-Einstein relation is 19.7 and the sum-of-squared residuals for the fractional Stokes-Einstein relation is 10.8.
2.3.3 Fractional Stokes-Einstein relation

When deviation from the Stokes-Einstein relation has been observed in the past, a fractional Stokes-Einstein relation \( (D \propto 1/\eta^{\xi} \), where \( \xi \) is an empirical fit parameter) has often been used to quantify the relationship between diffusion and viscosity. The data in Figure 2.18a were fit to the following version of the fractional Stokes-Einstein relation (Easteal, 1990):

\[
D = D_0 \left( \frac{\eta_0}{\eta} \right)^\xi
\]

(Eq. 2.3)

where \( \xi \) is an empirical fit parameter, \( \eta_0 \) is 1x10\(^{-3}\) Pa s, and \( D_0 \) is the diffusion coefficient at 1x10\(^{-3}\) Pa s, calculated using the Stokes-Einstein relation. This approach assumes that the Stokes-Einstein relation is valid for predicting the diffusion coefficients at 1x10\(^{-3}\) Pa s, which is consistent with the experimental data (e.g. the data in Figures 2.17 and 2.18). The best fit to the data (represented by the dashed line in Figure 2.18a) resulted in a \( \xi \) value of 0.93. Each data point was weighted equally when performing the fitting.

Figure 2.18c shows the plotted difference between the experimental values shown in Figure 2.18a and the predicted values using the fractional Stokes-Einstein relation (dashed line in Figure 2.18a). These residuals are more symmetrically scattered about zero compared to the residuals plotted in Figure 2.18b. In addition, the sum-of-squared residuals (r\(^2\)) in Figure 2.18c was less than the sum-of-squared residuals in Figure 2.18b (r\(^2\) = 10.8 compared to 19.7). Beyond the sum-of-squared residuals test, a reduced chi-squared (\( \chi^2 \)) test was performed, which takes into account the extra fitting variable present in the fractional Stokes-Einstein relation. Assuming a variance of 0.25, the reduced \( \chi^2 \) value is 1.24 for the Stokes-Einstein relation and is 0.67 for the fractional Stokes-Einstein relation. This information suggests that the fractional Stokes-Einstein relation with an exponent value of \( \xi = 0.93 \) may be the better model for predicting diffusion coefficients of organic molecules in SOA compared to the traditional Stokes-Einstein relation. This is in close agreement with the findings of Price et al. (2016) who showed that the diffusion of sucrose in a sucrose-water matrix could be modelled using a fractional Stokes-Einstein relation with \( \xi = 0.90 \) over a large range in viscosity. The new fractional Stokes-Einstein relation, which builds on the work of Price et al. (2016), was derived using diffusion data of several large organic molecules in
several types of organic water-matrices, and thus demonstrates a broader utility of the fractional
Stokes-Einstein relation.

For the case of large diffusing molecules such as those included in this chapter ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$), a strong dependence of $\zeta$ on the size or nature of the diffusing molecule is not observed. For smaller molecules, $\zeta$ is expected to change significantly. For example, Price et al., (2016) showed that $\zeta = 0.57$ for the diffusion of water in a sucrose-water matrix. The development of a relationship between $\zeta$ and the size of the diffusing molecules is the subject of Chapter 3.

2.3.4 Implications for atmospheric mixing times

To investigate the atmospheric implications of these results, the mixing times of organic
molecules within SOA in the atmosphere as a function of viscosity have been calculated using
both the Stokes-Einstein relation (Eq. 1.3) and the fractional Stokes-Einstein relation (Eq. 2.3 with
$\zeta = 0.93$). Mixing times were calculated with the following equation (Seinfeld and Pandis, 2006):

$$\tau_{\text{mix}} = \frac{d_p^2 \zeta}{4\pi^2 D} \quad \text{(Eq. 2.4)}$$

where $\tau_{\text{mix}}$ is the characteristic mixing time, $d_p$ is the SOA particle diameter, and $D$ is the diffusion
coefficient. $\tau_{\text{mix}}$ corresponds to the time at which the concentration of the diffusing molecules at
the centre of the particle deviates by less than a factor of 1/e from the equilibrium concentration.
A $d_p$ of 200 nm is assumed here, which is roughly the median diameter in the volume distribution
of ambient SOA (Martin et al., 2010; Pöschl et al., 2010; Riipinen et al., 2011). A value of 0.38
nm is used for $R_H$ based on literature values for molecular weight (175 g mol$^{-1}$; Huff Hartz et al.,
2005) and the density of SOA molecules (1.3 g cm$^{-3}$; Chen and Hopke, 2009; Saathoff et al., 2009),
and assuming a spherical symmetry of the diffusing species.

Figure 2.19 shows the calculated mixing times of 200 nm particles as a function of the
viscosity of the matrix. The mixing time of 1 hour is highlighted, since when calculating the growth
and evaporation of SOA and the long-range transport of pollutants using chemical transport
models, a mixing times of $< 1$ hour for organic molecules within SOA is often assumed (Hallquist
et al., 2009). At a viscosity of $5 \times 10^6$ Pa s, the mixing time is $> 1$ hour based on the Stokes-Einstein
relation, but remains $< 1$ hour based on the fractional Stokes-Einstein relation. Furthermore, at
high viscosities > 5 x 10^6 Pa s, the mixing times predicted with the traditional Stokes-Einstein relation are at least a factor of 5 greater than those predicted with the fractional Stokes-Einstein relation.

Shiraiwa et al. (2017) estimated mixing times of organic molecules in SOA particles in the global atmosphere using the global chemistry climate model EMAC (Jöckel et al., 2006) and the organic module ORACLE (Tsimpidi et al., 2014). Glass transition temperatures of SOA compounds were predicted based on molar mass and the O:C ratio of SOA components, followed by predictions of viscosity. Diffusion coefficients and mixing times were predicted using the Stokes-Einstein relation. To further explore the implications of the results of this chapter, mixing times of organic molecules in SOA globally were calculated using the same approach as Shiraiwa et al. (2017) and compared with predictions using the Stokes-Einstein relation and predictions using the fractional Stokes-Einstein relation with ξ = 0.93. Shown in Figure 2.20 are results from these calculations. At all latitudes at the surface, the mixing times are well below the 1 hour often assumed in chemical transport models, regardless if the Stokes-Einstein relation or the fractional Stokes-Einstein relation is used (Figure 2.20a). On the other hand, at an altitude of approximately 1.4 km, the latitudes where the mixing times exceed 1 hour will depend on whether the Stokes-Einstein relation or fractional Stokes-Einstein relation is used (Figure 2.20b). At an altitude of 3.2 km the mixing times are well above the 1-hour cut-off regardless of what relation is used, and the Stokes-Einstein relation can over predict mixing times of SOA particles by as much as one order of magnitude compared to the fractional Stokes-Einstein relation (Figure 2.20c). A caveat is that the predictions at 3.2 km are based on viscosities higher than the viscosities studied in the current work. Hence, at 3.2 km the Stokes-Einstein and fractional Stokes-Einstein relations are being used outside the viscosity range tested here. Although experimentally challenging, additional studies are recommended to determine if the fractional Stokes-Einstein relation with ξ = 0.93 is able to accurately predict diffusion coefficients of organic molecules in proxies of SOA at viscosities higher than investigated in the current study.
Figure 2.19 Mixing times of organic molecules within a 200 nm particle as a function of viscosity using the Stokes-Einstein relation (black line) and a fractional Stokes-Einstein relation (red line). The dashed lines indicate that the relations were extrapolated to viscosities beyond the tested range of viscosities ($\geq 4 \times 10^6$ Pa s).

Figure 2.20 Mixing times (in hours) of organic molecules in 200 nm SOA particles at a) the surface, b) 850 hPa or $\sim$1.4 km altitude, and c) 700 hPa or $\sim$3.2 km altitude, using diffusion coefficients calculated with the Stokes-Einstein relation (solid black lines) and the fractional Stokes-Einstein relation (dashed black lines). A one-hour mixing time, which is often assumed in chemical transport models, is also indicated in each figure with a horizontal dotted line.
2.4 Summary and conclusions

The diffusion coefficients of fluorescent organic molecules in a variety of SOA proxies have been measured. The reported experimental diffusion coefficients varied by about eight orders of magnitude as the water activity in the SOA proxies varied from 0.23 (0.14 in one case) to 0.86. By combining the new diffusion coefficients with literature data, it is shown that, in almost all cases, the Stokes-Einstein relation correctly predicts diffusion coefficients of organic molecules in SOA proxies within a factor of ten (when $R_{\text{diff}}/R_{\text{matrix}} \geq 1$). This finding is in stark contrast with the diffusion of water in SOA proxies ($R_{\text{diff}}/R_{\text{matrix}} < 1$), where much larger deviations between experimental and predicted diffusion coefficients have been observed over the same viscosity range. Even though the Stokes-Einstein relation correctly predicts diffusion of organic molecules in the majority of cases within a factor of ten, a sum-of-squared residuals analysis shows that a fractional Stokes-Einstein relation with an exponent of $\xi = 0.93$ is a better model for predicting diffusion coefficients in SOA proxies, for the range of viscosities included in this study. This is consistent with earlier work that showed the fractional Stokes-Einstein relation is able to reproduce experimental diffusion coefficients of sucrose in sucrose-water matrices. The fractional Stokes-Einstein relation predicts faster diffusion coefficients and therefore shorter mixing times of SOA particles in the atmosphere. At an altitude of ~3.2 km, the difference in mixing times predicted by the two relations is as much as one order of magnitude.
Chapter 3: A unified description of diffusion coefficients from small to large molecules in organic-water mixtures

3.1 Introduction

As described in Chapter 1, organic-water mixtures are ubiquitous and important in the natural and technological world. For example, in the Earth’s atmosphere, suspended aerosol particles consisting of organic-water mixtures affect air quality and climate (Hallquist et al., 2009; Shrivastava et al., 2017b). Organic-water mixtures, particularly saccharide-water mixtures, are important constituents affecting the properties of many foods (Champion et al., 1997, 2000; van der Sman and Meinders, 2013). Organic-water mixtures are also used in the cryopreservation of biomolecules such as proteins (Cicerone and Douglas, 2012; Fox, 1995; Manning et al., 2010; Miller et al., 1998) and the storage of pharmaceutical agents (Shamblin et al., 1999). In all of these cases, knowledge of diffusion coefficients in organic-water mixtures are needed.

Often, the Stokes-Einstein relation, expressed as \( D \propto 1/\eta \) where \( D \) is the diffusion coefficient and \( \eta \) is the viscosity, is used to predict diffusion coefficients in organic-water mixtures (Booth et al., 2014; Koop et al., 2011; Maclean et al., 2017; Renbaum-Wolff et al., 2013b; Song et al., 2015, 2016a). Chapter 2 showed that this relationship can describe the diffusion coefficients of large organic molecules \( (R_{\text{diff}}/R_{\text{matrix}} \geq 1) \) within a factor of 10, in most cases, in organic-water mixtures with viscosities ranging from \( 10^{-3} \) to \( 10^6 \) Pa s. In contrast, for small diffusing molecules \( (R_{\text{diff}}/R_{\text{matrix}} < 1) \), the Stokes-Einstein relation greatly under-predicts diffusion coefficients in organic-water mixtures by several orders of magnitude (Bastelberger et al., 2017; Davies and Wilson, 2016; Marshall et al., 2016; Price et al., 2015, 2016). Alternative approaches to the Stokes-Einstein relation for predicting diffusion coefficients of small molecules in organic-water mixtures are percolation theory (Shiraiwa et al., 2011; Stauffer and Aharony, 1994) and free volume theory (Perdana et al., 2014; Vrentas and Duda, 1977). However, a practical limitation of both theories is the requirement of numerous parameters, which are often not available in the literature.

Another alternative to the Stokes-Einstein relation, the fractional Stokes-Einstein relation, was described in Chapters 1 and 2. The fractional Stokes-Einstein relation includes \( \xi \) as a fractional exponent \( (D \propto 1/\eta^\xi) \). For single component organic matrices, the fractional Stokes-Einstein
relation has been used successfully to parameterize diffusion coefficients of small molecules as a function of viscosity (Funazukuri et al., 2008; Harris, 2009; Heuberger and Sillescu, 1996; Hiss and Cussler, 1973). For single component organic matrices, the fractional exponent $\xi$ has also been shown to depend on $R_{diff}$ (Chen et al., 1982; Kowert and Watson, 2011) and $R_{diff}/R_{matrix}$ (Heuberger and Sillescu, 1996). The fractional Stokes Einstein relation has also been used to describe diffusion coefficients in organic-water mixtures, for example for xenon in sucrose-water mixtures ($\xi = 0.63$, Pollack, 1981), for water in concentrated glycerol-water mixtures ($\xi = 0.85$, Mallamace et al., 2016), and for both water and sucrose in sucrose-water mixtures ($\xi = 0.57$ and 0.90 respectively, Price et al., 2016). Whether or not these results can be extrapolated to other diffusing species or other organic-water mixtures, however, was not investigated. In addition, the relationship between the fractional exponent $\xi$ and $R_{diff}/R_{matrix}$ was not explored for organic-water mixtures. There is currently no simple and accurate method to predict diffusion coefficients of small molecules in organic-water mixtures as a function of viscosity and $R_{diff}/R_{matrix}$.

This chapter reports diffusion coefficients of a fluorescent organic molecule, cresyl violet, in two organic-water mixtures, raffinose-water and sucrose-citric acid-water at a temperature of 295 ± 1 K. These new data add to the limited number of measurements of diffusion coefficients in organic-water mixtures with $R_{diff}/R_{matrix} < 1$. The new data, as well as literature data, are used to investigate the relationship between the exponent $\xi$ in the fractional Stokes-Einstein relation and $R_{diff}/R_{matrix}$ for organic-water mixtures at temperatures of 292-298 K.

The analysis shows that the fractional Stokes-Einstein relation with $\xi$ expressed only as a monotonic function of $R_{diff}/R_{matrix}$ is able to describe 98% of the observed diffusion coefficients roughly within the uncertainties of the measurements. As a case study of these findings, the fractional Stokes-Einstein relation with $\xi$ expressed as a monotonic function of $R_{diff}/R_{matrix}$ is used to quantify the degradation of polycyclic aromatic hydrocarbons (PAHs) by O$_3$ within organic-water particles in the planetary boundary layer, the region of the atmosphere ranging from the Earth’s surface to approximately 1 km in altitude (Wallace and Hobbs, 2006).
3.2 Experimental methods

3.2.1 Materials

In this chapter, the organic solutes raffinose (> 99% purity, Sigma-Aldrich), and a mixture of sucrose (> 99% purity, Sigma-Aldrich) and citric acid (> 99% purity, Sigma-Aldrich), in a mass ratio of 60:40 sucrose to citric acid, were used. Cresyl violet (> 75% purity, Santa Cruz Biotechnology) was used as the diffusing fluorescent organic molecule. All solutions were prepared using Millipore Milli-Q water.

The $R_{\text{diff}}/R_{\text{matrix}}$ values for cresyl violet in raffinose-water and sucrose-citric acid-water mixtures are 0.711 and 0.91 ± 0.09, respectively. These $R_{\text{diff}}/R_{\text{matrix}}$ values were calculated using a $R_{\text{diff}}$ for cresyl violet of 3.7 Å and a $R_{\text{matrix}}$ for raffinose, sucrose, and citric acid of 5.2, 4.5, and 3.7 Å, respectively. The viscosity of each organic-water mixture was calculated from the $a_w$ of the organic-water mixture using literature viscosity measurements (Rovelli et al., 2019; Song et al., 2016b) and relationships between these viscosities and $a_w$. The viscosity-$a_w$ relationships are given in Figure B.1 in Appendix B for raffinose-water mixtures and Figure A.3 in Appendix A for sucrose-citric acid-water mixtures. Raffinose-water and sucrose-citric acid-water mixtures were chosen for these experiments in part because their viscosities have been measured over a wide range of $a_w$ values (Grayson et al., 2017; Rovelli et al., 2019; Song et al., 2016b).

3.2.2 Preparation of fluorescent organic-water films

The procedure for the preparation of thin films containing an organic solute, water, and trace amounts of the diffusing fluorescent molecules from a bulk solution is detailed in Section 2.2.2. Details relevant to this chapter are included here. Bulk solutions were prepared gravimetrically. The concentrations of the organic solutes in the bulk solutions, the concentrations of cresyl violet in the bulk solutions, and the concentrations of cresyl violet in the thin films conditioned to a specific $a_w$ are also given in Table 3.1. At the chosen concentrations, the fluorescence intensity of the thin films was proportional to the concentration of the fluorescent organic molecules (Figures 3.1 and 3.2).
Figure 3.1 Average fluorescence intensity as a function of cresyl violet mass fraction in sucrose-citric acid-water thin films at $a_w = 0.85 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \, \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for cresyl violet in sucrose-citric acid-water thin films. rFRAP experiments were performed using cresyl violet concentrations within the linear range indicated here.

Figure 3.2 Average fluorescence intensity as a function of cresyl violet mass fraction in raffinose-water thin films at $a_w = 0.90 \pm 0.025$. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately $30 \times 30 \, \mu m^2$. The laser scanning microscope settings used were identical to those used in the rFRAP experiments for cresyl violet in raffinose-water thin films. rFRAP experiments were performed using cresyl violet concentrations within the linear range indicated here.
The bulk solutions were filtered to remove impurities by passing solutions through a 0.02 μm filter (Whatman™). Droplets of the filtered solutions were placed on cleaned siliconized hydrophobic slides (Hampton Research) using the tip of a sterilized needle (BD PrecisionGlide Needle). The droplets ranged in diameter from ~ 200 to ~ 700 μm and are given in Tables B.1 and B.2. After the droplets were located on the hydrophobic slides, the hydrophobic slides were placed inside sealed glass containers with a controlled water activity (a_w). The a_w was set by placing saturated inorganic salt solutions with known a_w values within the sealed glass containers. The a_w values used ranged from 0.51 to 0.75 for raffinose solutions and from 0.14 to 0.57 for sucrose-citric acid solutions. The inorganic salts that were used to achieve each a_w are given in Table 2.2. When the a_w values were higher than 0.75 (raffinose-water mixture), or 0.57 (sucrose-citric acid-water mixture) recovery times were too fast to measure with the rFRAP setup. When the a_w values were lower than 0.51 (raffinose-water mixture) or 0.14 (sucrose-citric acid-water mixture), solution droplets often crystallized.

The method used to calculate conditioning times is explained in Section 2.2.3. As in Chapter 2, diffusion coefficients of water in the organic-water mixtures were required to calculate equilibrium times. Diffusion coefficients of water in raffinose-water and sucrose-citric acid-water mixtures are assumed to equal the diffusion coefficients of water in a sucrose-water mixture when the viscosity of the two matrices are equal. Diffusion coefficients for water in a sucrose-water mixture at a given viscosity were calculated using a parametrization for diffusion coefficients as a function of a_w from Price et al. (2016) and a parameterization for sucrose viscosity as a function of a_w from Grayson et al. (2017). The diffusion coefficients of water in sucrose were used as an estimate for diffusion coefficients of water in solutions of the sucrose-citric acid mixture and raffinose at an equivalent viscosity. The expected viscosity of the organic-water matrices at each a_w was calculated using viscosity-a_w parameterizations for sucrose-citric acid (Appendix A, Figure A.3), and raffinose (Appendix B, Figure B.1). These D_{H2O} values were used with Eq. 2.1 to calculate equilibration times. Experimental conditioning times (t_{exp}) were a minimum of three times longer than calculated conditioning times (t_{mix,H2O}), and are given in Tables B.1 and B.2.

After the droplets on the slides were conditioned to the a_w of the airspace over the salt solution, thin films were formed by sandwiching the glass slide holding the droplets with a second
hydrophobic glass slide inside a Glove Bag™ (Glas-Col) following the procedure described in Section 2.2.2.

Table 3.1 Concentrations of the organic solutes in the bulk solutions and concentrations of the fluorescent organic molecules in both the bulk solutions and the conditioned thin films used in this chapter.

<table>
<thead>
<tr>
<th>Solution identity</th>
<th>Organic solute concentration in bulk solution (mass fraction)</th>
<th>Fluorescent organic molecule concentration in bulk solution (mM)</th>
<th>Fluorescent organic molecule concentration after conditioning (mass fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cresyl violet in sucrose-citric acid-water (60:40 mass ratio)</td>
<td>0.30</td>
<td>0.08</td>
<td>0.00784-0.00845</td>
</tr>
<tr>
<td>Cresyl violet in raffinose-water</td>
<td>0.10</td>
<td>0.08</td>
<td>0.0231-0.0248</td>
</tr>
</tbody>
</table>

3.2.3 Rectangular area fluorescence recovery after photobleaching (rFRAP) technique and extraction of diffusion coefficients

The procedure for the rFRAP experiments and the extraction of diffusion coefficients is detailed in Section 2.2.4. All diffusion experiments in this chapter were performed at 295 ± 1 K. In all experiments the bleached area was 4.5 µm x 4.5 µm, in contrast to Chapter 2, where bleached areas ranged from 4.5 µm x 4.5 µm to 20 µm x 20 µm. A smaller bleach size was used in the current studies since experiments with a smaller bleach size allow smaller diffusion coefficients to be measured in shorter times. When a small bleach size is used, the spot size of the laser beam becomes similar to the size of the bleached area, and as a result the margins of the bleached area are not sharply defined. Nevertheless, previous work has shown that diffusion coefficients determined with rFRAP are independent of bleached areas ranging from 1 µm x 1 µm to 50 µm x 50 µm, even if the rectangles are less well defined using smaller bleached areas (Chenyakin et al., 2017). Figure 3.3 shows two examples of fluorescent images recorded during a rFRAP experiment. Examples of $r^2+4Dt$ vs. $t$ plots are given in Figures 3.4 and 3.5 (see Chapter 2 for details).
Figure 3.3 An example of fluorescent images recorded during an rFRAP experiment using (a-d) films at $a_w = 0.75$ containing raffinose, water, and trace amounts of cresyl violet and (e-h) films at $a_w = 0.43$ containing sucrose, citric acid, water, and trace amounts of cresyl violet. Panels (a and e) show images taken prior to photobleaching and was used to normalize all images taken after photobleaching. Panels (b and f) show images taken immediately following photobleaching. Panels (c-d) and (g-h) were taken during the recovery period. The black dashed square in panels (a) and (e) indicates the region selected for photobleaching (20 $\mu$m$^2$), and the entire imaged area was 2000 $\mu$m$^2$. 
Figure 3.4 A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of cresyl violet in a raffinose matrix at $a_w = 0.75$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

Figure 3.5 A plot of $r^2 + 4Dt$ as a function of time after photobleaching in a sample of cresyl violet in a sucrose-citric acid matrix at $a_w = 0.43$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.
3.3 Results and discussion

3.3.1 Diffusion as a function of viscosity

The experimental diffusion coefficients are plotted in Figure 3.6a (closed squares) and listed in Tables B.1 and B.2 in Appendix B as a function of the viscosity of the organic-water mixtures. Diffusion coefficients of small and large molecules within organic-water mixtures, as reported in the literature, are also plotted in Figure 3.6a (open squares), and listed in Table B.3 in Appendix B (Bastelberger et al., 2017; Champion et al., 1997; Chenyakin et al., 2017; Davies and Wilson, 2016; Evoy et al., 2019; Longinotti and Corti, 2007; Pollack, 1981; Price et al., 2014, 2016; Rampp et al., 2000). In most cases, the viscosity of the organic-water mixture was calculated using relationships between viscosity and $a_w$ developed using literature data (Appendix B, Section B1). The plotted data sets include only diffusion coefficients measured between 292-298 K and for which viscosity information was available in the same temperature range. The combined data set in Figure 3.6a covers a range of diffusing species (water, xenon, polyethylene glycol, ferrocene methanol, and several large fluorescent organic molecules) and a range of organic-water mixtures (raffinose-water, sucrose-citric acid-water, sorbitol-water, citric acid-water, sucrose-water). There are 10 data points from the new measurements and 128 data points from the literature data sets included in this study. A total of 15 unique combinations of diffusing species and organic-water mixtures are included. These 15 unique combinations are listed in Table 3.3.

Figure 3.6a shows that the diffusion coefficients are a strong function of viscosity, decreasing by six to nine orders of magnitude as viscosity increases by ten orders of magnitude. Furthermore, diffusion coefficients increase as $R_{diff}/R_{matrix}$ decreases for a fixed viscosity.
Table 3.2 Radii of diffusing molecules and organic solute molecules used in this study.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Radius (Å)</th>
<th>Additional details</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>4.5</td>
<td>Based on amorphous density</td>
<td>(Hancock and Zografi, 1997)</td>
</tr>
<tr>
<td>Citric acid</td>
<td>3.7</td>
<td>Measured hydrodynamic radius in water (^a)</td>
<td>(Müller and Stokes, 1956)</td>
</tr>
<tr>
<td>Raffinose</td>
<td>5.2</td>
<td>3D structural model of hydrated molecule</td>
<td>(Liesche and Schulz, 2013)</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>3.36</td>
<td>Calculated Van der Waals radius</td>
<td>(Edward, 1970)</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>5.89</td>
<td>Measured hydrodynamic radius in water (^a)</td>
<td>(Müller and Loman, 2008)</td>
</tr>
<tr>
<td>Cresyl violet</td>
<td>3.7</td>
<td>Calculated Van der Waals radius</td>
<td>(Edward, 1970)</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>5.02</td>
<td>Measured hydrodynamic radius in water (^a)</td>
<td>(Mustafa et al., 1993)</td>
</tr>
<tr>
<td>Calcein</td>
<td>4.9</td>
<td>Calculated Van der Waals radius</td>
<td>(Edward, 1970)</td>
</tr>
<tr>
<td>PEG-4</td>
<td>4.0</td>
<td>Measured hydrodynamic radius in water using gel permeation chromatography</td>
<td>(Kuga, 1981)</td>
</tr>
<tr>
<td>Ferrocene methanol</td>
<td>2.8-3.4 (^b)</td>
<td>Measured hydrodynamic radius in water (^a)</td>
<td>(Longinotti and Corti, 2007)</td>
</tr>
<tr>
<td>Water</td>
<td>1.41</td>
<td>Calculated Van der Waals radius</td>
<td>(Pang, 2014)</td>
</tr>
<tr>
<td>Xenon</td>
<td>2.16</td>
<td>Calculated Van der Waals radius</td>
<td>(Bondi, 1964)</td>
</tr>
</tbody>
</table>

\(^a\) In the cases where the hydrodynamic radii are solved for using diffusion measurements and the Stokes-Einstein relation, the measurements were performed in water. In those cases the Stokes-Einstein relation is expected to hold as \(R_{\text{diff}}/R_{\text{matrix}} \geq 2\) and viscosity is low \((8.9 \times 10^{-4} \text{ Pa s})\) (Rampp et al., 2000).

\(^b\) Longinotti and Corti (2007) have reported two values for the radius of ferrocene methanol based on diffusion measurements in water. The average of the two measured values (3.1 Å) is used in this work and error bars are included to represent the uncertainty in the radius.
Table 3.3 Diffusing species and matrix organic species in which diffusion coefficients were measured, including current and literature data sets. There 15 total unique combinations of diffusing and matrix organic species.

<table>
<thead>
<tr>
<th>Diffusing species</th>
<th>Matrix organic species</th>
<th>Literature source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cresyl violet</td>
<td>Raffinose</td>
<td>Current chapter</td>
</tr>
<tr>
<td>Cresyl violet</td>
<td>Sucrose-citric acid</td>
<td>Current chapter</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>Sorbitol</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>Citric acid</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>Sucrose-citric acid</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>Sucrose</td>
<td>(Chenyakin et al., 2017)</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>Sucrose</td>
<td>(Champion et al., 1997; Chenyakin et al., 2017)</td>
</tr>
<tr>
<td>Calcein</td>
<td>Sucrose</td>
<td>(Chenyakin et al., 2017)</td>
</tr>
<tr>
<td>Cresyl violet</td>
<td>Citric acid</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Sucrose</td>
<td>(Price et al., 2016; Rampp et al., 2000)</td>
</tr>
<tr>
<td>Poly-ethylene glycol-4</td>
<td>Sucrose</td>
<td>(Bastelberger et al., 2017)</td>
</tr>
<tr>
<td>Ferrocene methanol</td>
<td>Sucrose</td>
<td>(Longinotti and Corti, 2007)</td>
</tr>
<tr>
<td>Xenon</td>
<td>Sucrose</td>
<td>(Pollack, 1981)</td>
</tr>
<tr>
<td>Water</td>
<td>Citric acid</td>
<td>(Davies and Wilson, 2016)</td>
</tr>
<tr>
<td>Water</td>
<td>Sucrose</td>
<td>(Davies and Wilson, 2016; Price et al., 2014)</td>
</tr>
</tbody>
</table>

3.3.2 The Stokes-Einstein relation

Based on the classic Stokes-Einstein relation, a plot of log $D$ – log ($kT/6\pi R_{\text{diff}}$) vs log $\eta$ should give a straight line with a slope of -1 and an intercept of 0 (solid line in Figure 3.6b). The data from Figure 3.6a are plotted in Figure 3.6b within this framework using $R_{\text{diff}}$ values listed in Table 3.2 for the diffusing species. Deviations from the line represent the residual error in the Stokes-Einstein relation. For relatively large diffusing species characterized by $R_{\text{diff}}/R_{\text{matrix}} \geq 1$, the measured diffusion coefficients largely agree within a factor of 10 with the Stokes-Einstein relation.
(dashed lines in Figure 3.6b). A factor of 10 roughly corresponds to the uncertainties in the viscosity measurements (Appendix B, Section B3). In contrast, for relatively small diffusing species characterized by $R_{\text{diff}}/R_{\text{matrix}} < 1$, there is a significant underestimation of measured diffusion coefficients by up to a factor of $10^6$ with the Stokes-Einstein relation, especially for the highest viscosities.

![Image](image.png)

**Figure 3.6** Double log plots of (a) log $D$ versus log $\eta$ and (b) log $D - \log (kT/6\pi R_{\text{diff}})$ versus log $\eta$. Closed symbols indicate diffusion coefficients measured in this work, and open symbols represent diffusion coefficients taken from the literature (Table B.3 and Appendix B, Section B1). The solid line in (b) represents the Stokes-Einstein relation and the dashed lines represent an order of magnitude uncertainty in the Stokes-Einstein relation (an order of magnitude uncertainty corresponds to roughly the uncertainty in the original viscosity measurements). In both panels the colour of the data points corresponds to $R_{\text{diff}}/R_{\text{matrix}}$, where $R_{\text{diff}}$ is the radius of the diffusing molecules and $R_{\text{matrix}}$ is the radius of the organic molecules in the organic-water mixture. $R_{\text{diff}}/R_{\text{matrix}}$ was determined using the values listed in Table 3.2.
3.3.3 The fractional Stokes-Einstein relation

For a constant temperature, the fractional Stokes-Einstein relation can be written in the following form (Easteal, 1990):

$$\frac{D}{D_0} = \left(\frac{\eta_0}{\eta}\right)^\eta$$

(Eq. 3.1)

where $\eta$ is the fractional exponent, $\eta_0$ is the viscosity of pure water ($8.9 \times 10^{-4}$ Pa s), and $D_0$ is the diffusion coefficient in pure water. This is the same version of the fractional relation that was given in Chapter 2. The individual data sets included in Figure 3.6b are plotted in Figures B2-B19 in the form log ($D/D_0$) as a function of log ($\eta_0/\eta$) with $D_0$ calculated with the Stokes-Einstein relation. Equation 3.1 is applied to those data with the intercept forced to 0 to obtain a $\xi$ value for each data set. This approach assumes that the Stokes-Einstein relation is valid for predicting the diffusion coefficients in pure water, which is consistent with the experimental data (i.e., in Figure 3.6b, at $\eta \approx 10^{-3}$ Pa s all the data are consistent with the Stokes-Einstein relation within the uncertainty of the measurements).

For 17 of 18 data sets, Eq. 3.1, with $\xi$ as the only free parameter, describes each data set within a factor of 10 (Figures B2-B19). Again, a factor of 10 corresponds to roughly the uncertainty in the original viscosity measurements. This illustrates that the fractional Stokes-Einstein relation is proficient at describing diffusion coefficients in organic-water mixtures with viscosities ranging from $10^{-3}$ up to $10^{10}$ Pa s and $R_{diff}/R_{matrix}$ values ranging from 0.31 to 1.75. The only data set that did not fit within the factor of 10 was cresyl violet in raffinose-water, possibly due to errors in the diffusion measurements or the viscosity measurements.

Importantly, a relationship can be established between the obtained $\xi$-values and the corresponding $R_{diff}/R_{matrix}$ values of each data set. The $\xi$-values determined from the fits in Figures B2-B19 are listed in Table B.3 and plotted in Figure 3.7. Based on an exponential fit to the data (solid line in Figure 3.7), $\xi$ can be represented as a monotonic function of $R_{diff}/R_{matrix}$:

$$\xi = 1 - \left[A exp\left(-B \frac{R_{diff}}{R_{matrix}}\right)\right]$$

(Eq. 3.2)
where $A = 0.73$ and $B = 1.79$. The standard error in $A$ is 0.12 and the standard error in $B$ is 0.29.

As $R_{\text{diff}}/R_{\text{matrix}}$ increases, the exponential equation, and hence $\xi$, approaches 1, which is a necessary requirement to be consistent with the classical Stokes-Einstein equation when $R_{\text{diff}}/R_{\text{matrix}} \gg 1$ (i.e. diffusion in a continuum). Other equations that gave $\xi$ values approaching 1 at high $R_{\text{diff}}/R_{\text{matrix}}$ values were also fit to the data, but Eq. 3.2 gave the best fit based on a sum of least squares analysis.

**Figure 3.7** The exponent value to be used in the fractional Stokes-Einstein relation, $\xi$, plotted as a function of $R_{\text{diff}}/R_{\text{matrix}}$ (black squares) and an exponential best fit to that data (red line). The equation of the exponential best fit line is Eq. 3.2 with $A = 0.73$ and $B = 1.79$. Closed symbols correspond to $\xi$ values based on diffusion data sets measured in this work, and open symbols correspond to $\xi$ values based on diffusion data sets from the literature. $R_{\text{diff}}/R_{\text{matrix}}$ was determined using the values listed in Table 3.2. X-axis error bars represent the uncertainty in $R_{\text{diff}}/R_{\text{matrix}}$ determined from the uncertainty in reported $R_{\text{diff}}$ values and the range of $R_{\text{matrix}}$ values if two organic molecules were used in the organic-water mixture. Y-axis error bars represent 95% confidence intervals (1.96 times the standard error) for the $\xi$ values determined in Figures B2-B19. The red shaded region represents the 95% confidence band to the fitted equation. The uncertainty in $\xi$ from the 95% confidence bands is between ± 0.025 and 0.08. The standard error in $A$ is 0.12 and the standard error in $B$ is 0.29.

In Figure 3.8, the measured diffusion coefficients shown in Figure 3.6a are compared with diffusion coefficients calculated using both the Stokes-Einstein relation (panel a) and the fractional Stokes-Einstein relation (panel b) with the $\xi$-value in the fractional Stokes-Einstein relation described with Eq. 3.2. Figure 3.8a shows that the Stokes-Einstein relation correctly describes only
75% of the measured diffusion coefficients within a factor of ten. In comparison, Figure 3.8b shows that the fractional Stokes-Einstein relation, with $\zeta$ calculated using Eq. 3.2, correctly describes 98% of the data (135 out of 138 data points) within a factor of ten. The three data points not correctly described by the fractional Stokes-Einstein relation correspond to the diffusion of water in citric acid (one data point), the diffusion of cresyl violet in sucrose-citric acid (one data point), and the diffusion of cresyl violet in raffinose (one data point).
Figure 3.8 Double log plots of measured and calculated $D$ using (a) the Stokes-Einstein relation and (b) the fractional Stokes-Einstein relation, with $\zeta$ calculated using Eq. 3.2. Closed symbols indicate diffusion coefficients measured in this work and open symbols represent diffusion coefficients taken from the literature. The colours of the data points correspond to $R_{\text{diff}}/R_{\text{matrix}}$, where $R_{\text{diff}}$ is the radius of the diffusing molecules and $R_{\text{matrix}}$ is the radius of the organic molecules in the organic-water mixture. $R_{\text{diff}}/R_{\text{matrix}}$ was determined using the values listed in Table 3.2. The solid black line in each panel is a 1-to-1 line. The dashed lines represent an order of magnitude uncertainty, corresponding to roughly the uncertainty in the viscosity data used to calculate the diffusion coefficients (Appendix B, Section B2). There is also uncertainty in the predicted diffusion coefficients in panel (b) due to the uncertainty in the $\zeta$ values calculated using Eq. 3.2. This uncertainty is not included in the figure for the sake of clarity.
A physical explanation of the fractional Stokes-Einstein relation has been put forward by Voronel et al. (1998). If diffusion and viscosity have activation energies \( E_D \) and \( E_\eta \), respectively, and obey Arrhenius type equations, then \( D \propto e^{-E_D/RT} \) and \( \eta^{-1} \propto e^{-E_\eta/RT} \), where \( R \) is the gas constant and \( T \) is temperature. By algebraic manipulation one obtains \( D \propto (1/\eta)^\xi \), where \( \xi = E_D/E_\eta \). At a fixed temperature, this relationship leads to Eq. 3.1. When both activation energies are equal, as might be expected for diffusion in a continuum, \( \xi = 1 \) and the classical Stokes-Einstein relationship holds. However, when \( E_D/E_\eta < 1 \), \( \xi < 1 \). Put another way, \( \xi \)-values < 1 imply that \( E_D/E_\eta < 1 \). Figure 3.7, together with this physical explanation of the fractional Stokes-Einstein relation, suggests that \( E_D/E_\eta < 1 \) when \( R_{\text{diff}}/R_{\text{matrix}} \lesssim 1.5 \). Figure 3.7 also suggests that \( E_D/E_\eta \) decreases as \( R_{\text{diff}}/R_{\text{matrix}} \) decreases. Consistent with this suggestion, molecular dynamics simulations have shown that the dynamics of diffusing molecules and matrix molecules, and hence \( E_D \) and \( E_\eta \), become increasingly decoupled as \( R_{\text{diff}}/R_{\text{matrix}} \) decreases (Ould-Kaddour and Barrat, 1992).

The above discussion implies that \( \xi \) will be independent of temperature if diffusion and viscosity follow Arrhenius-type equations. At temperatures approaching the glass transition temperature (\( T_g \)), organic-water mixtures often have a super-Arrhenius behavior, which can be described by Vogel-Fulcher-Tammann (VFT) equations, \( D \propto \frac{B_D}{T-T_{0,D}} \) and \( \eta^{-1} \propto \frac{B_\eta}{T-T_{0,\eta}} \), where \( B_D, B_\eta, T_{0,D}, \) and \( T_{0,\eta} \) are fitting parameters. The values \( T_{0,D} \) and \( T_{0,\eta} \) correspond to the temperatures at which diffusion approaches zero, and viscosity approaches infinity, respectively. By algebraic manipulation of these expressions, one obtains \( D \propto 1/\eta^{\xi} \), where \( \xi \) is represented by the following equation:

\[
\xi = \left( \frac{B_D}{B_\eta} \right) \frac{T-T_{0,\eta}}{T-T_{0,D}} \quad \text{(Eq. 3.3)}
\]

According to Eq. 3.3, if \( T_{0,\eta} = T_{0,D} \) then \( \xi = B_D/B_\eta \), again implying that \( \xi \) is independent of temperature. Even if \( T_{0,\eta} \neq T_{0,D} \), \( \xi \) will only weakly depend on temperature when \( T \) is significantly larger than \( T_{0,\eta} \) and \( T_{0,D} \).

Based on the discussion above, \( \xi \) may depend on temperature as \( T-T_g \) approaches 0 (i.e. as the temperature approaches the glass transition temperature). Even though the current analysis was based only on data collected between 292-298 K, the data set used covered a wide range of \( T-T_g \).
values. The following section describes the calculation of \( T-T_g \) values in a sucrose-water matrix as an example.

### 3.3.4 Calculations of \( T-T_g \) values for sucrose-water mixtures

\( T_g \) values for the sucrose-water mixtures can be calculated using the Gordon-Taylor equation:

\[
T_{g,mix} = \frac{1}{K_{GT}} \frac{w_1 T_{g,1} + w_2 T_{g,2}}{w_1 + w_2}
\]  
(Eq. 3.4)

where \( T_{g,mix} \) is the glass transition temperature of the sucrose-water mixture, \( w_1 \) is the weight fraction of sucrose and \( w_2 \) is the weight fraction of water, \( T_{g,1} \) and \( T_{g,2} \) are the glass transition temperatures of sucrose and water, respectively, and \( K_{GT} \) is the Gordon-Taylor constant. Based on Rothfuss and Petters (2017a) \( T_{g,1} = 341 \text{ K}, T_{g,2} = 136 \text{ K}, \) and \( K_{GT} = 5.25. \)

The viscosities of the sucrose-water solutions used in the current analysis ranged from \( 10^{-2} \) to \( 10^{6} \) Pa s in many cases, and so \( T_{g,mix} \) values were calculated for sucrose-water mixtures with viscosities of \( 10^{-2} \) and \( 10^{6} \) Pa s at 295 K. First, \( a_w \) values for sucrose-water mixtures with viscosities of \( 10^{-2} \) and \( 10^{6} \) Pa s at 295 K were calculated using the viscosity vs. \( a_w \) parameterization from Grayson et al. (Grayson et al., 2017; Figure S1) for sucrose solutions. Then \( a_w \) values were converted into weight fractions using the relationship between \( a_w \) and weight fractions (Zobrist et al., 2011). Weight fractions were used in Eq. 3.4, together with the \( T_{g,1}, T_{g,2}, \) and \( K_{GT} \) values (Rothfuss and Petters, 2017a), to calculate \( T_{g,mix} \) values. Finally, \( T-T_g \) values were calculated from the \( T_{g,mix} \) values for \( T = 295 \text{ K}. \)

The resulting \( T-T_g \) values range from 130 K to 17 K. It can be speculated that \( \zeta \) determined in the current analysis can be applied at other temperatures as long as viscosities are \( \lesssim 10^{6} \) Pa s, and \( T-T_g \) values are \( \gtrsim 20. \) Nevertheless, this speculation needs to be tested.

### 3.3.5 Degradation of polycyclic aromatic hydrocarbons within organic-water particles in the planetary boundary layer

As a case study, the findings of this chapter are used to predict the degradation of polycyclic aromatic hydrocarbons (PAHs) within organic-water particles in the planetary boundary layer.
The main source of PAHs to the planetary boundary layer is the incomplete combustion of organic material such as coal, oil, and wood. Exposure to PAHs is associated with cancer and other negative health outcomes (Kim et al., 2013). In the atmosphere, PAHs can be incorporated into organic-water particles by gas-to-particle partitioning. PAHs can then be degraded by O$_3$ either at the surface or within the bulk of the organic-water particles (Keyte et al., 2013; Lammel et al., 2009). Here, the focus is on degradation within the bulk of the particles. To predict degradation rates of PAHs within the bulk of organic-water particles, both diffusion coefficients of PAHs and O$_3$, as well as reaction rates between PAHs and O$_3$ within organic-water particles are needed (Finlayson-Pitts and Pitts Jr, 2000). However, diffusion coefficients of O$_3$ and PAHs within organic-water particles remain highly uncertain.

The fractional Stokes-Einstein relation and Eq. 3.2 were used to predict diffusion coefficients of O$_3$ and PAHs as a function of viscosity in organic-water particles. These diffusion coefficients, together with a resistor model and mass-balance calculations (Finlayson-Pitts and Pitts Jr, 2000; Kolb et al., 2010; Robinson et al., 2006; Smith et al., 2002; Worsnop et al., 2002), were then used to calculate the time needed to degrade PAHs by reaction with O$_3$ within a 200 nm diameter organic-water particle.

To calculate the degradation time of PAHs by O$_3$, first the net uptake coefficient of O$_3$ into a 200 nm diameter organic-water particle ($\gamma_{net}$) was calculated using a resistor model (Finlayson-Pitts and Pitts Jr, 2000; Robinson et al., 2006; Smith et al., 2002; Worsnop et al., 2002). Assuming that reactions between O$_3$ and PAHs occur within the bulk of the particle, $\gamma_{net}$ can be described by the following equation:

$$\frac{1}{\gamma_{net}} = \frac{1}{\alpha} + \frac{4HR}{c_{avg}}\sqrt{D_{O3}k_b[PAH]}\left(\coth\left(\frac{a}{T}\right) - \left(\frac{1}{a}\right)\right) + \frac{1}{n_{O3}c_{avg}a}$$

(Eq. 3.5)

where $\alpha$ is the mass accommodation coefficient, $H$ is the Henry’s law coefficient for ozone, $R$ is the ideal gas constant, $T$ is the temperature, $c_{avg}$ is the average thermal speed of ozone in the gas phase, $D_{O3}$ is the diffusion coefficient of ozone in the particle bulk calculated using the Stokes-Einstein or fractional Stokes-Einstein relation, $k_b$ is the bulk rate constant for the reaction between ozone and PAHs, [PAH] is the concentration of PAHs in the particle phase, $a$ is the particle radius.
$D_{PAH}$ is the diffusion coefficient of PAHs in the particle bulk calculated using the Stokes Einstein or fractional Stokes-Einstein relation, $n_{O3}$ is the concentration of ozone in the gas phase, and $l$ is the reacto-diffusive length. In Eq. 3.5, each term is a “conductance” representing, respectively, the mass accommodation of O$_3$, bulk phase reactions, and diffusion limited mixing of PAHs within the particle.

The reacto-diffusion length, which represents the distance a molecule of ozone travels into the particle bulk before reacting with a PAH molecule, can be described by the following equation:

$$l = \frac{D_{O3}}{k_b[PAH]}$$  \hspace{1cm} (Eq. 3.6)

Parameters used in Eqs. 3.5 and 3.6, not including diffusion coefficients, are listed in Table 3.4. These values are based on benzo[a]pyrene, an atmospherically relevant PAH. To determine the diffusion coefficients of O$_3$ and benzo[a]pyrene needed for Eqs. 3.5 and 3.6, both the Stokes-Einstein relation and the fractional Stokes-Einstein relation were used, with $\xi$ calculated using Eq. 3.2. $R_{diff}$ values of $1.98 \times 10^{-10}$ m and $3.77 \times 10^{-10}$ m were used for O$_3$ and benzo[a]pyrene, respectively, to calculate $\xi$ using Eq. 3.2. These $R_{diff}$ values are calculated van der Waals radii using atomic increments from Edward et al. (1970). A $R_{matrix}$ equal to the radius of benzo[a]pyrene was assumed when calculating $\xi$ using Eq. 3.2. This assumes the matrix molecules were equal in size to benzo[a]pyrene, with the result that $\xi = 1$ for benzo[a]pyrene as a diffusing species.

Once $\gamma_{net}$ was calculated using Eqs. 3.5 and 3.6, the following equation was used to estimate the degradation time of PAHs within a 200 nm diameter particle by the bulk-phase reaction between O$_3$ and PAHs (Robinson et al., 2006):

$$\tau_{degradation} = \frac{4\pi a^3[PAH]}{\frac{4}{3} \pi a^3 c_{avg} 4 \pi a^2 \gamma_{net}}$$  \hspace{1cm} (Eq. 3.7)

where the numerator represents the number of molecules of PAH in the particle and the denominator represents the net flux of ozone molecules into the particle. Equation 3.7 is based on a mass balance between the uptake of O$_3$ and the loss of PAHs within a particle (Robinson et al., 2006).
The result of these calculations (Figure 3.9) show that the time needed to degrade PAHs (i.e., degradation time) within the bulk of a 200 nm diameter organic-water particle in the planetary boundary layer is relatively short ($\lesssim 1$ day) when the viscosity of the particle is $\lesssim 10^2 \text{ Pa s}$. Aerosol particles with viscosities $\lesssim 10^2 \text{ Pa s}$ are common within the planetary boundary layer since high relative humidities and warm temperatures occur regularly in this region of the atmosphere (Shiraiwa et al., 2017). On the other hand, in dry regions of the planetary boundary layer, viscosities can reach $10^6 \text{ Pa s}$ or greater (Shiraiwa et al., 2017). For these cases the time needed to degrade PAHs will be relatively long ($\geq 10$ days).

For comparison, the classical Stokes-Einstein relation was also used to predict diffusion coefficients of $O_3$ and PAHs in organic-water particles, and those diffusion coefficients were then used to calculate the time needed to degrade PAHs by reaction with $O_3$ within a 200 nm diameter organic-water particle. The degradation times calculated using the Stokes-Einstein relation were a factor of $\sim 10$ larger than the degradation times calculated using the fractional Stokes-Einstein relation at a viscosity $\gtrsim 10^4 \text{ Pa s}$ (Figure 3.9). This difference illustrates the importance of using the fractional Stokes-Einstein relation compared to the Stokes-Einstein relation when predicting degradation times.

In addition to this analysis, additional fates of PAHs should be considered, such as reactions between $O_3$ and PAHs at the surfaces of organic-water particles, which can be a dominant degradation process (Kahan et al., 2006; Zhou et al., 2013), or reactions between PAHs and other oxidants such as the OH radical at the surface or in the bulk of the organic-water particles (Jariyasopit et al., 2014; Keyte et al., 2013).
Table 3.4 Parameters used in Eqs. 3.5 and 3.6 to calculate the net uptake coefficient of O\textsubscript{3} into a 200 nm diameter organic-water particle. Values are based on benzo[a]pyrene, an atmospherically relevant PAH.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Numerical value</th>
<th>Unit</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>298</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>n\textsubscript{O3}</td>
<td>1.23 x 10\textsuperscript{-6}</td>
<td>mol m\textsuperscript{-3}</td>
<td>Concentration of ozone in the gas phase (Vingarzan, 2004) \textsuperscript{a}</td>
</tr>
<tr>
<td>[PAH]</td>
<td>1 x 10\textsuperscript{3}</td>
<td>mol m\textsuperscript{-3}</td>
<td>Concentration of PAH (benzo[a]pyrene) in the particle phase</td>
</tr>
<tr>
<td>k\textsubscript{b}</td>
<td>3.01</td>
<td>m\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}</td>
<td>Reaction rate of ozone with benzo[a]pyrene at 296 K (Mu et al., 2018)</td>
</tr>
<tr>
<td>a</td>
<td>100 x 10\textsuperscript{-9}</td>
<td>m</td>
<td>Particle radius</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>1</td>
<td>Unitless</td>
<td>Mass accommodation coefficient (Mu et al., 2018)</td>
</tr>
<tr>
<td>c\textsubscript{avg}</td>
<td>362.5</td>
<td>m/s</td>
<td>Average molecular speed of O\textsubscript{3} in the gas phase at 298 K (Finlayson-Pitts and Pitts Jr, 2000), page 159</td>
</tr>
<tr>
<td>H</td>
<td>600</td>
<td>mol m\textsuperscript{-3} atm\textsuperscript{-1}</td>
<td>Henry’s law coefficient of ozone at 296 K (Zhou et al., 2019)</td>
</tr>
<tr>
<td>R</td>
<td>8.205 x 10\textsuperscript{-5}</td>
<td>m\textsuperscript{3} atm K\textsuperscript{-1} mol\textsuperscript{-1}</td>
<td>Ideal gas constant</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ozone concentration corresponds to typical surface-level annual average background concentrations (Vingarzan, 2004).
Figure 3.9 Degradation time of PAHs due to the bulk-phase reaction between PAHs and O₃ within a 200 nm diameter organic-water particle. Black squares indicate degradation times calculated using diffusion coefficients of O₃ and PAHs based on the Stokes-Einstein relation, while red circles indicate diffusion coefficients based on the fractional Stokes-Einstein relation. The dashed red lines indicate the upper and lower limits for degradation times calculated using the fractional Stokes-Einstein relation when the 95% confidence band in Figure 3.7 is used to calculate upper and lower limits for the exponent (the uncertainty in $\xi$ from the 95% confidence bands is $\pm 0.046$ for an $R_{\text{diff}}/R_{\text{matrix}} = 0.53$).

3.4 Summary and conclusions

Here, diffusion coefficients for the fluorescent organic molecule cresyl violet in mixtures of raffinose and sucrose-citric acid with water have been reported. These new experimental data were combined with literature measurements of diffusion and viscosity in organic-water mixtures. A fractional Stokes-Einstein relation, $D \propto 1/\eta^{\xi}$, where $\xi$ is a fractional exponent expressed only as a function of $R_{\text{diff}}/R_{\text{matrix}}$, describes 98% of the experimental diffusion coefficients within a factor of 10, while the Stokes-Einstein relation describes only 75% of that data within a factor of 10. The fractional Stokes-Einstein relation with $\xi$ expressed only as a function of $R_{\text{diff}}/R_{\text{matrix}}$ holds for a wide range of $R_{\text{diff}}/R_{\text{matrix}}$ values (0.31 to 1.75), viscosities ($10^{-3}$ up to $10^{10}$ Pa s), and intermolecular interactions (e.g. hydrogen bonding, dipole-dipole, dipole-induced dipole). These results also suggest that the activation energy for diffusion, $E_D$, is less than the activation energy for viscosity, $E_\eta$, when $R_{\text{diff}}/R_{\text{matrix}} \lesssim 1.5$, and $E_D/E_\eta$ decreases as $R_{\text{diff}}/R_{\text{matrix}}$ decreases in organic-water mixtures.
when $R_{diff}/R_{matrix} \lesssim 1.5$. The fractional Stokes-Einstein relation developed here can be useful in many applications within the atmospheric, food, biological, and pharmaceutical sciences.
Chapter 4: Predictions of diffusion rates in lab-generated SOA and BBOA using the Stokes-Einstein and fractional Stokes-Einstein relations

4.1 Introduction

Previous work, including Chapters 2 and 3 in this thesis, have evaluated the Stokes-Einstein relation to determine whether it can correctly predict the diffusion coefficients of large and small molecules in proxies for atmospheric organic aerosol. Chapter 2 showed that the Stokes-Einstein relation can accurately predict diffusion coefficients of large organic molecules diffusing in organic-water mixtures within a factor of ten in most cases, when the radius of the diffusing molecule is greater than or equal to the radius of the organic solute molecules ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$) and the viscosity of the matrix is $\lesssim 10^6$ Pa s. Nevertheless, both a sum of squared residuals analysis and a reduced chi-squared test show that a fractional Stokes-Einstein relation with an exponent of 0.93 does a better job describing diffusion coefficients of large organic molecules diffusing in organic-water matrices. Chapter 3 evaluated the ability of both the Stokes-Einstein relation and the fractional Stokes-Einstein relation to describe diffusion coefficients of large and small molecules ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and $R_{\text{diff}}/R_{\text{matrix}} < 1$) diffusing in organic-water mixtures. The Stokes-Einstein relation was able to describe only 75% of the measured diffusion coefficients within a factor of 10, and under-predicted diffusion coefficients by up to six orders of magnitude. In comparison, a fractional Stokes-Einstein relation, $D/D_0 = (\eta_0/\eta)^{\xi}$, with $\xi = 1-[0.73*\exp(-1.79*(R_{\text{diff}}/R_{\text{matrix}}))]$ was able to describe 98% of the measured diffusion coefficients within a factor of 10.

An important caveat when applying the results of those previous studies to atmospheric organic aerosol is that those experiments were done in simple proxies for atmospheric aerosol, composed of binary or ternary mixtures containing one or two organic solutes and water, while atmospheric organic aerosol contain thousands of different organic molecules and water. The fractional Stokes-Einstein relation from Chapter 3, as well as the Stokes-Einstein relation, should therefore be evaluated in more realistic and chemically complex organic aerosol samples.
Examples of more realistic and chemically complex organic aerosol samples include lab-generated secondary organic aerosol (SOA) and lab-generated biomass burning organic aerosol (BBOA).

SOA can be generated in a lab by injecting volatile organic compounds (VOCs) and an oxidant (i.e. OH radicals or O₃) into an environmental chamber. The VOCs are chemical species that are commonly emitted from either biogenic or anthropogenic sources to the ambient environment. Inside the environmental chamber, the VOCs and the oxidants react to generate thousands of products, some of which condense to the particle phase to form SOA particles. Biogenic VOC emissions exceed anthropogenic VOC emissions on a global scale (Kanakidou et al., 2005), and include isoprene (C₅H₈), monoterpenes (C₁₀H₁₆), and sesquiterpenes (C₁₅H₂₄). While sesquiterpernes are emitted in smaller amounts than either isoprene or monoterpenes, they are important due to their large aerosol formation potential (Griffin et al., 1999). β-caryophyllene is one of the most abundant sesquiterpenes (Helmig et al., 2007). We have therefore chosen to study SOA produced within an environmental chamber by the ozonolysis of β-caryophyllene. Experimental details are given in Section 4.2.1.

BBOA particles can also be generated in a lab by pyrolysis of a biomass sample within a tube furnace. Pyrolysis generates hundreds to thousands of organic compounds, some of which condense to the particle phase to form BBOA particles. Here, we have chosen pine wood as the biomass sample to produce BBOA. Experimental details are given in Section 4.2.4.

While several previous studies have measured or inferred diffusion coefficients in more realistic and chemically complex organic aerosol (e.g. Abramson et al. (2013), Liu et al. (2016) and Ye et al. (2016)), only a few studies have evaluated the Stokes-Einstein relation for predicting diffusion in these types of organic samples, and none have evaluated a fractional Stokes-Einstein relation in this context. Ullmann et al. (2019) measured diffusion coefficients of an intrinsic fluorescent molecule in SOA generated by the ozonolysis of limonene. Ullmann et al. also reported viscosities for the limonene SOA and compared their measured diffusion coefficients to viscosities using the Stokes-Einstein relation, and found that the Stokes-Einstein relation was able to predict diffusion coefficients within the uncertainty of the measurements under all conditions studied (viscosity of \(\lesssim 10^4\) Pa s). Marshall et al. (2016) compared measured diffusion coefficients of both water (Price et al., 2015) and pyrene (Abramson et al., 2013) with Stokes-Einstein predicted diffusion coefficients within SOA produced by the ozonolysis of α-pinene (Renbaum-Wolff et al.,
The Stokes-Einstein relation under-predicted diffusion coefficients of water in all cases (viscosity of $3 \times 10^6 - 5 \times 10^7$ Pa s) by 2 orders of magnitude or more. For pyrene as a diffusing species, Marshall et al. (2016) found that the measured diffusion coefficients agreed with Stokes-Einstein predicted diffusion coefficients within one order of magnitude when the lower limit of α-pinene SOA viscosity was used in the predictions.

Despite these recent contributions, additional studies are still needed to test the Stokes-Einstein relation as well as the fractional Stokes-Einstein relation given in Chapter 3, using realistic and chemically complex organic aerosol samples, such as SOA and BBOA generated in the laboratory.

Here we have measured diffusion coefficients of organic molecules in SOA and BBOA generated in the laboratory as a function of water activity ($a_w$) at a temperature of $295 \pm 1$ K. The SOA was produced via the ozonolysis of β-caryophyllene in an environmental chamber. The BBOA was produced via the pyrolysis of pine wood in a tube furnace. Experimental details are given in the following section. These two systems were chosen in part because viscosity data are available for both the β-caryophyllene SOA (manuscript in preparation by Maclean et al.) and the BBOA (manuscript in preparation by Schnitzler et al.), which are need to make comparisons between the measured diffusion coefficients, the Stokes-Einstein relation, and the fractional Stokes-Einstein relation. The fractional Stokes-Einstein relation used in this chapter is the same version as used in Chapters 2 and 3, an approach which assumes that the Stokes-Einstein relation is valid for predicting the diffusion coefficients in pure water.

4.2 Experimental

4.2.1 β-caryophyllene SOA production

β-caryophyllene SOA was produced at the University of British Columbia in a continuous flow, constant temperature environmental chamber (1.8 m$^3$ Teflon bag) by dark ozonolysis of β-caryophyllene. A pure air generator (Aadco 737) was used to produce clean, dry (< 1% relative humidity) air for the inlet flow of the chamber. At the inlet, a 2-weight percent mixture of β-caryophyllene in 2-butanol was vaporized and injected continuously into the chamber. The 2-butanol acted as a scavenger for hydroxyl radicals that may have been produced (Kroll et al., 2002). Additionally, ozone generated by passing clean air through an ozone generator (Jelight Ozone
Generator 600) was injected into the chamber at the inlet. Prior to reaction, ozone and β-caryophyllene concentrations in the chamber were 400-1200 ppb and 40 ppb, respectively. The ozone concentration in the chamber was in excess to the amount needed to react with β-caryophyllene, determined by monitoring the ozone concentration at the outlet of the chamber. The mass concentration of SOA in the chamber was 16-20 µg m$^{-3}$. SOA particles were collected at the exit of the chamber on a glass slide previously coated with the fluorescent organic dye rhodamine 6G (R6G). The method of coating the glass slides with the fluorescent organic dye is described in the following section. Collection of SOA on the glass slide was accomplished with a multi-orifice two-stage impactor (model 100–180nm–10lpm; MSP Corp., Shoreview, MN, USA) with a flow rate of 15 L/min at the chamber outlet. The sample collection time was 48 hours.

4.2.2 Preparation of R6G coated slides and fluorescent thin films containing SOA, water, and R6G

Prior to collecting the SOA, 12 mm circular plain glass slides were rinsed with Milli-Q water followed by methanol and dried in an oven at a minimum temperature of 60 °C for at least 12 hours. The clean, dry slides were then placed on a spin coater (Laurell Technologies Corporation WS-400-6NPP), and 10 µL of 4 mM R6G in ethanol was deposited on the centre of the slide. The slides were spun at 6100 rpm for 1 minute, resulting in a slide coated with a uniform layer of fluorescent organic molecules, determined with confocal laser scanning microscopy. β-caryophyllene SOA particles from an environmental chamber were then deposited directly on those fluorescent slides as discussed above.

4.2.3 Conditioning times for β-caryophyllene SOA samples

After collection, the SOA particles were conditioned to a particular $a_w$ using two conditioning steps. First, all β-caryophyllene SOA samples were placed in a sealed glass jar with an airspace at $a_w = 0.85$, set by placing a saturated potassium chloride (KCl) solution within the sealed glass jars. At this high $a_w$, the β-caryophyllene SOA had a relatively lower viscosity (manuscript in preparation by Maclean et al.), facilitating rapid mixing of the R6G molecules from the surface of the glass slide throughout the β-caryophyllene SOA sample. Samples were left in the jars with $a_w = 0.85$ for 24 hours. After this time, the fluorescent molecules were well mixed.
throughout the sample, determined with confocal laser scanning microscopy. Specifically, after the conditioning time, the fluorescence intensity within the samples was measured as a function of distance from the glass slide, by taking planar images at different heights (z-levels), and the fluorescence intensity was found to be the same at each z-level.

After conditioning at $a_w = 0.85$, the slides containing the $\beta$-caryophyllene SOA samples were moved to a second sealed glass jar containing a saturated inorganic salt solution with known $a_w$ (values ranging from 0.23 to 0.85). The inorganic salts that were used to achieve this range of $a_w$-values are given in Table 2.2. The slides holding the samples were left inside the sealed glass jars for an extended period of time to allow the samples to equilibrate with the surrounding $a_w$. Unlike the samples described in Chapter 2, 3 and 5, the $\beta$-caryophyllene SOA were thin films rather than droplets after deposition, determined with confocal laser scanning microscopy. The difference in morphology was due to the difference in the hydrophobic nature of the slides used to collect the SOA. In Chapters 2, 3 and 5, hydrophobic glass slides were used resulting in high contact angles with organic-water particles. In the current cases, hydrophilic glass slides were used resulting in very low contact angles with organic-water particles, and hence, thin films. The time required for thin films to come to equilibrium with the surrounding $a_w$ was calculated using the following equation (Atkins and de Paula, 2010):

$$\tau_{\text{mix,H2O}} = \left(\frac{x}{2}\right)^2 \frac{\pi}{D_{\text{H2O}}}$$  (Eq. 4.1)

where $\tau_{\text{mix,H2O}}$ is the time it takes for water molecules to diffuse an average distance of $x$, $x$ is the thickness of the thin film, and $D_{\text{H2O}}$ is the diffusion coefficient of water in the thin film. A discussion of the values used for $D_{\text{H2O}}$ in $\beta$-caryophyllene SOA follows.

$D_{\text{H2O}}$ values in the $\beta$-caryophyllene SOA matrix are assumed to be equal to $D_{\text{H2O}}$ values in a sucrose matrix when the viscosity of the two matrices are equal. $D_{\text{H2O}}$ in a sucrose matrix at a given viscosity was calculated using a parametrization for diffusion coefficients as a function of $a_w$ from Price et al. (2016) and a parameterization for sucrose viscosity as a function of $a_w$ from Grayson et al. (2017). Those diffusion coefficients in sucrose were used as an estimate for diffusion coefficients of water in $\beta$-caryophyllene SOA at an equivalent viscosity. The expected viscosity values of the $\beta$-caryophyllene SOA matrices at the $a_w$ values inside the sealed glass jars were
calculated using a viscosity-\(a_w\) parameterization. To generate this parameterization, the upper limits for viscosity determined using the poke-flow technique (Grayson et al., 2015; Renbaum-Wolff et al., 2013b) were plotted as a function of \(a_w\) and a straight line was fit to the data (Figure 4.1). The poke-flow viscosity values are given in Table 4.1. Conditioning times based on the viscosity-\(a_w\) parameterization for all samples are given in Table 4.2. Experimental times for conditioning (\(t_{exp}\)) were between 4.3 and 56.9 times longer than calculated equilibration times.

Figure 4.1 Upper and lower limits of \(\beta\)-caryophyllene SOA viscosity measured using the poke-flow technique (Table 4.1) and a linear best fit to the upper limits of viscosity, used to calculate the time required for thin films containing the SOA to come to equilibrium with the surrounding \(a_w\) as described in Section 4.2.3.

Table 4.1 \(\beta\)-caryophyllene SOA viscosity measured as a function of \(a_w\) using the poke-flow technique (manuscript in preparation by Maclean et al.). The upper limits of viscosity are used to generate a viscosity-\(a_w\) parameterization that is used to calculate the time required for the SOA thin films to come to equilibrium with the surrounding \(a_w\) as described in Section 4.2.3.

<table>
<thead>
<tr>
<th>(a_w)</th>
<th>Lower limit log ((\eta), Pa s)</th>
<th>Upper limit log ((\eta), Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 ± 0.025</td>
<td>5.79</td>
<td>7.86</td>
</tr>
<tr>
<td>0.15 ± 0.025</td>
<td>4.62</td>
<td>7.98</td>
</tr>
<tr>
<td>0.28 ± 0.025</td>
<td>3.65</td>
<td>6.25</td>
</tr>
<tr>
<td>0.48 ± 0.025</td>
<td>3.10</td>
<td>5.43</td>
</tr>
</tbody>
</table>
Table 4.2 Conditioning times and diffusion coefficients for R6G in β-caryophyllene SOA. The error in the diffusion coefficients represents two standard deviations. \( \tau_{\text{mix,H2O}} \) is the calculated characteristic mixing time for molecular diffusion of water in the thin films (see 4.2.3 and Eq. 4.1). \( t_{\text{exp}} \) is the experimental time used for conditioning the thin films at a given \( a_w \).

<table>
<thead>
<tr>
<th>( a_w ) in glass jar used to condition rFRAP sample</th>
<th>Log (( \eta ), Pa s) used to calculate conditioning time</th>
<th>Thickness of film for conditioning (µm)</th>
<th>( \tau_{\text{mix,H2O}} ) (hours)</th>
<th>( t_{\text{exp}} ) (hours)</th>
<th>Ratio of ( t_{\text{exp}} / \tau_{\text{mix,H2O}} )</th>
<th>Measured diffusion coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>6.88 (^b)</td>
<td>20 µm</td>
<td>26.9</td>
<td>120</td>
<td>4.46</td>
<td>1.10 \times 10^{-16} \pm 2.14 \times 10^{-17}</td>
</tr>
<tr>
<td>0.33</td>
<td>6.32 (^b)</td>
<td>20 µm</td>
<td>14.2</td>
<td>65</td>
<td>4.58</td>
<td>6.35 \times 10^{-17} \pm 5.94 \times 10^{-17}</td>
</tr>
<tr>
<td>0.43</td>
<td>5.75 (^b)</td>
<td>20 µm</td>
<td>7.59</td>
<td>432</td>
<td>56.9</td>
<td>3.57 \times 10^{-16} \pm 4.54 \times 10^{-17}</td>
</tr>
<tr>
<td>0.57</td>
<td>5.47 (^c)</td>
<td>20 µm</td>
<td>5.56</td>
<td>52</td>
<td>9.35</td>
<td>1.67 \times 10^{-15} \pm 1.01 \times 10^{-15}</td>
</tr>
<tr>
<td>0.75</td>
<td>5.47 (^c)</td>
<td>20 µm</td>
<td>5.56</td>
<td>24</td>
<td>4.3</td>
<td>3.50 \times 10^{-15} \pm 8.57 \times 10^{-16}</td>
</tr>
<tr>
<td>0.85</td>
<td>5.47 (^c)</td>
<td>20 µm</td>
<td>5.56</td>
<td>50</td>
<td>8.99</td>
<td>1.27 \times 10^{-14} \pm 3.25 \times 10^{-15}</td>
</tr>
</tbody>
</table>

\(^a\) Thickness was determined by using the confocal laser scanning microscope. Planar images were taken at different heights (z-levels) within the film to capture a full height profile.

\(^b\) Based on the viscosity of β-caryophyllene SOA at the conditioning \( a_w \) determined using the viscosity-\( a_w \) parameterization in Figure 4.1.

\(^c\) Based on the viscosity of β-caryophyllene SOA at \( a_w = 0.48 \), the highest \( a_w \) included in the viscosity-\( a_w \) parameterization in Figure 4.1 and used as an upper limit for viscosities at \( a_w > 0.48 \).

After the films on the slides were conditioned to the \( a_w \) of the airspace over the salt solution, the sealed glass jars holding the slides and conditioned films were brought into a Glove Bag™ (Glas-Col). The \( a_w \) within the Glove Bag was controlled using a humidified flow of N\(_2\) gas and monitored using a handheld hygrometer. The \( a_w \) within the Glove Bag was set to the same \( a_w \) as used to condition the films, to prevent the films from being exposed to an unknown and uncontrolled \( a_w \). To seal β-caryophyllene SOA thin films, a second 12 mm circular glass slide was placed on top of the slide holding the film. This second circular glass slide had a hydrophobic coating. Then, the two 12 mm circular slides were sealed in between two larger, 22 mm square
slides, with a layer of vacuum grease between them. This sandwiching procedure was carried out within the Glove Bag. Figure 4.2 illustrates the configuration of the glass slides holding the fluorescent SOA thin films.

![Diagram of glass slides holding fluorescent SOA thin films](image)

**Figure 4.2** Configuration of the glass slides holding the fluorescent SOA thin films. Top view (panel A) and side view (panel B) of a thin film of a lab-generated SOA sample deposited on a plain glass slide previously coated with a uniform layer of R6G molecules. The sample is sandwiched with a hydrophobic glass slide and contained within two hydrophobic glass slides sealed with vacuum grease, for use in rFRAP experiments.

### 4.2.4 Production and collection of BBOA and preparation of fluorescent thin films containing BBOA and water

The BBOA samples were produced at the University of Toronto via the pyrolysis of pine wood (similar to the method used by Trofimova et al. (2019)). The pine wood used was untreated lumber purchased from a hardware store in Toronto. Approximately 2 g of pine was placed in a flow tube inside a tube furnace heated to a temperature of 400 °C. Clean air was flowed through
the flow tube at a rate of 2 L min\(^{-1}\). A 47 mm polytetrafluoroethylene (PTFE) filter was placed in a filter holder at the exit of the flow tube and particles were collected with a filter for 15 minutes.

After collection, filters holding the BBOA were wrapped in aluminum foil to avoid exposure to ambient light and shipped from the University of Toronto to the University of British Columbia (UBC). At UBC, filters were extracted using 10 mL of water in a Falcon tube, with gentle shaking over a period of 10 minutes. The water extract was then filtered through a 0.22 µm PES membrane filter (Millipore Millex™). The extract was then transferred to a glass vial coated in aluminum foil to avoid exposure of the solution to ambient light and then stored in a 4 °C fridge until used. From here on “BBOA” is used in the context of our experiments to refer only to the water-soluble fraction of material in the original BBOA sample.

Thin films of BBOA were prepared using the following method. First 1 µL droplets of the extract were deposited onto a clean hydrophobic glass slide. These droplets were allowed to equilibrate at room RH for 1-2 hours, after which time their diameter had decreased from 1800 µm to 250-400 µm. At that time, the glass slides holding the droplets were placed in sealed glass jars containing a saturated inorganic salt solution with known \(a_w\) (values ranging from 0.23 to 0.43). The inorganic salts that were used to achieve this range of \(a_w\)-values are given in Table 2.2. The slides holding the droplets were left inside the sealed glass jars for an extended period of time to allow the droplets to equilibrate with the surrounding \(a_w\). The time required for droplets to come to equilibrium with the surrounding \(a_w\) was calculated using Eq. 2.1. \(D_{H2O}\) values in the BBOA matrix are assumed to be equal to \(D_{H2O}\) values in a sucrose matrix when the viscosity of the two matrices are equal. \(D_{H2O}\) in a sucrose matrix at a given viscosity was calculated using a parametrization for diffusion coefficients as a function of \(a_w\) from Price et al. (2016) and a parameterization for sucrose viscosity as a function of \(a_w\) from Grayson et al. (2017). Those diffusion coefficients in sucrose were used as an estimate for diffusion coefficients of water in BBOA at an equivalent viscosity. The expected viscosity values of the BBOA matrices were based on a viscosity-\(a_w\) parameterization. The viscosity-\(a_w\) parameterization was developed by plotting the upper limits for viscosity determined using the poke-flow technique and fitting a straight line to the data (Figure 4.3). The poke-flow viscosity values are given in Table 4.3. The poke-flow experiments were also performed on water extracts, and so the viscosity data represent only the water soluble-fraction of material in the original BBOA sample and are therefore comparable to
the diffusion measurements. Calculated conditioning times ($\tau_{\text{mix}, H2O}$) for all samples are given in Table 4.4. Experimental times for conditioning ($t_{\text{exp}}$) were between 3.9 and 9.8 times longer than calculated equilibration times (Table 4.4).

After the droplets on the slides were conditioned to the $a_w$ of the airspace over the salt solution, the samples were sealed in a Glove Bag™ (Glas-Col) as in Section 2.2.2, resulting in thin films of thickness 30-50 μm.

There were no fluorescent organic molecules added to the BBOA samples. Rather, the BBOA contained intrinsic fluorescent molecules that absorb and emit light when irradiated with a 543 nm laser, as used in the rFRAP experiments. The molecular identity of these intrinsic fluorescent molecules is not known. Based on the literature we estimated the range of average molecular weight of these molecules (Section 4.3.2).

Table 4.3 BBOA viscosity measured as a function of $a_w$ using the poke-flow technique (manuscript in preparation by Schnitzler et al.). The upper limits of viscosity are used to generate a viscosity-$a_w$ parameterization that is used to calculate equilibration times for BBOA droplets as described in Section 4.2.4.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Lower limit log (η, Pa s)</th>
<th>Upper limit log (η, Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 ± 0.025</td>
<td>4.87</td>
<td>6.64</td>
</tr>
<tr>
<td>0.10 ± 0.025</td>
<td>4.65</td>
<td>6.41</td>
</tr>
<tr>
<td>0.15 ± 0.025</td>
<td>3.81</td>
<td>5.79</td>
</tr>
<tr>
<td>0.25 ± 0.025</td>
<td>3.09</td>
<td>5.02</td>
</tr>
<tr>
<td>0.40 ± 0.025</td>
<td>2.54</td>
<td>4.31</td>
</tr>
</tbody>
</table>
Figure 4.3 Upper and lower limits of BBOA viscosity measured using the poke-flow technique and a linear best fit to the upper limits of viscosity, used to calculate the conditioning times given in Table 4.4.

Table 4.4 Conditioning times and diffusion coefficients for intrinsic fluorescent molecules in BBOA. The error in the diffusion coefficients represents two standard deviations. $\tau_{\text{mix},H2O}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the experimental the time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$ used to condition sample</th>
<th>Log ($\eta$, Pa s) used to calculate $\tau_{\text{mix},H2O}$</th>
<th>Diameter of particle for conditioning (µm)</th>
<th>$\tau_{\text{mix},H2O}$ (h)</th>
<th>$t_{\text{exp}}$ (h)</th>
<th>Ratio of $t_{\text{exp}}/\tau_{\text{mix},H2O}$</th>
<th>Measured diffusion coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>5.34 $^a$</td>
<td>250</td>
<td>24.2</td>
<td>236.5</td>
<td>9.8</td>
<td>$7.27 \times 10^{-17} \pm 3.59 \times 10^{-17}$</td>
</tr>
<tr>
<td>0.33</td>
<td>4.71 $^a$</td>
<td>250</td>
<td>12.2</td>
<td>48</td>
<td>3.9</td>
<td>$1.78 \times 10^{-16} \pm 4.95 \times 10^{-17}$</td>
</tr>
<tr>
<td>0.43</td>
<td>4.09 $^a$</td>
<td>400</td>
<td>15.6</td>
<td>89</td>
<td>5.7</td>
<td>$6.57 \times 10^{-16} \pm 4.19 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

$^a$ Based on the viscosity of BBOA at the conditioning $a_w$ determined using the viscosity-$a_w$ parameterization in Figure 4.3.
4.2.5 rFRAP technique and extraction of diffusion coefficients

rFRAP experiments were performed on the thin films containing either β-caryophyllene SOA or BBOA, and diffusion coefficients were determined from those experiments. The rFRAP technique is described in detail in Chapter 2, Section 2.2.4.

Examples of images collected using the confocal laser scanning microscope during an rFRAP experiment are given in Figures 4.4 and 4.5, depicting β-caryophyllene SOA and BBOA films, respectively. All bleached areas in this chapter were 20 µm². Examples of $r^2 + 4Dt$ vs. $t$ plots are given in Figures 4.6 and 4.7, corresponding to β-caryophyllene SOA and BBOA films, respectively.

**Figure 4.4** Fluorescence images of films containing R6G, β-caryophyllene SOA, and water, at $a_w = 0.85 \pm 0.025$ (a-d) and at $a_w = 0.23 \pm 0.025$ (e-h), collected using a confocal laser scanning microscope during a rFRAP experiment. Images (a) and (e) were taken prior to photobleaching and used to normalize all images after photobleaching. Images (b) and (f) were taken immediately following the photobleaching event and images (c-d) and (g-h) were taken during the recovery period. The white square in images (a) and (e) represents a 20 µm² region for photobleaching, while the size of the imaged region is 2000 µm².
Figure 4.5 Fluorescence images of films containing BBOA including an intrinsic fluorescent molecule, and water, at $a_w = 0.43 \pm 0.025$ (a-d) and at $a_w = 0.23 \pm 0.025$ (e-h), collected using a confocal laser scanning microscope during a rFRAP experiment. Images (a) and (e) were taken prior to photobleaching and used to normalize all images after photobleaching. Images (b) and (f) were taken immediately following the photobleaching event and images (c-d) and (g-h) were taken during the recovery period. The white square in images (a) and (e) represents a 20 μm$^2$ region for photobleaching, while the size of the imaged region is 2000 μm$^2$.

Figure 4.6 A plot of $r^2 + 4Dt$ as a function of time after photobleaching R6G in a sample of β-caryophyllene SOA at $a_w = 0.85 \pm 0.025$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.
Figure 4.7 A plot of $r^2 + 4Dt$ as a function of time after photobleaching intrinsic fluorescent molecules in a sample of biomass burning aerosol at $a_w = 0.43 \pm 0.025$. Each black square represents a value of $r^2 + 4Dt$ from the fit of Eq. 2.2 to an image recorded after photobleaching. The red line is a linear best fit to the data.

4.3 Results and Discussion

4.3.1 Diffusion of R6G in β-caryophyllene SOA

The diffusion coefficients of R6G as a function of $a_w$ in β-caryophyllene SOA are plotted in Figure 4.8 and given in Table 4.2. All measurements were performed at a temperature of 295 ± 1 K. The experimental diffusion coefficients increased by more than two orders of magnitude as $a_w$ increased from 0.23 to 0.86, indicating a plasticizing effect of water on the matrix.

Also included in Figure 4.8 are diffusion coefficients predicted using both the Stokes-Einstein and fractional Stokes-Einstein relations. Viscosities measured using the poke-flow technique are used in these predictions (Table 4.2, manuscript in preparation by Maclean et al.). The hydrodynamic radius of the diffusing molecule, R6G, is needed for both the Stokes-Einstein (Eq. 1.3) and fractional Stokes-Einstein (Eq. 3.1) relations. The hydrodynamic radius of the molecules that make up the matrix are also required for the fractional Stokes-Einstein relation calculations. The hydrodynamic radius of R6G is 5.89 Å (Müller and Loman, 2008). The hydrodynamic radius of β-caryophyllene SOA molecules is assumed to be between 4.41 and 5.17...
Å, based an average molar mass between 214 and 345 g mol\(^{-1}\) determined using electrospray ionization (ESI), nano-electrospray ionization (nESI) and nano-desorption electrospray ionization (nDESI) mass spectrometry (manuscript in preparation by Maclean et al.). Each ionization technique was run using both positive and negative modes, resulting in six values for the average molar mass of β-caryophyllene SOA. The lowest average molar mass (214 g mol\(^{-1}\)) came from the negative mode ESI and the highest average molar mass (345 g mol\(^{-1}\)) came from the negative mode nDESI. This range of average molar masses is generally consistent with molar masses for first- and second-generation products from β-caryophyllene ozonolysis, which have been observed to range between 198 and 302 g mol\(^{-1}\) (Li et al., 2011). The average molar mass was converted to average radii for molecules in β-caryophyllene SOA assuming a spherical geometry and a density of 0.99 (Tasoglou and Pandis, 2015). \(R_{\text{diff}}/R_{\text{matrix}}\) values are between 1.14 and 1.34 based on the hydrodynamic radius of R6G and the average radii of molecules in β-caryophyllene SOA based on mass spectrometry data described above, resulting in \(\xi\) values between 0.905 and 0.933 in the fractional Stokes-Einstein relation.

Figure 4.8 allows for a comparison between measured and predicted diffusion coefficients of R6G in β-caryophyllene SOA. A linear best fit to the measured diffusion coefficients, including 95% confidence bands, is shown in Figure 4.8. The diffusion coefficients predicted using viscosity data and the Stokes-Einstein relation do not overlap with the 95% confidence bands. In contrast, the diffusion coefficients predicted using the fractional Stokes-Einstein relation do overlap with the 95% confidence bands. This indicates that for diffusion coefficients between \(\sim 10^{-16} - 10^{-15} \text{ m}^2 \text{ s}^{-1}\) (the range when the data sets overlap) the Stokes-Einstein relation under-predicts diffusion coefficients, while the fractional Stokes-Einstein relation is consistent with measured diffusion coefficients of R6G in β-caryophyllene SOA.

The results of Figure 4.8 are consistent with the results of Chapter 3, where the fractional Stokes-Einstein relation was able to predict diffusion coefficients in systems with both \(R_{\text{diff}}/R_{\text{matrix}} < 1\) and \(R_{\text{diff}}/R_{\text{matrix}} \geq 1\) in 98% of cases.
Figure 4.8 Diffusion coefficients of R6G in β-caryophyllene SOA as a function of water activity ($a_w$). The x error bars represent the uncertainty in the measured $a_w$ and the y error bars are equal to 2 times the standard deviation of the measured diffusion coefficients. Each data point represents the average of a minimum of 4 measurements. For diffusion coefficients predicted using the Stokes-Einstein relation, the lower limit was calculated using the upper limit in viscosity and the upper limit was calculated using the lower limit in viscosity. For diffusion coefficients predicted using the fractional Stokes-Einstein relation, the lower limit was calculated using the upper limit in viscosity and the lower limit of the hydrodynamic radius of β-caryophyllene SOA molecules, while the upper limit in diffusion was calculated using the lower limit in viscosity and the upper limit of the hydrodynamic radius of β-caryophyllene SOA molecules. The secondary y axis shows mixing times for R6G in a 200 nm β-caryophyllene SOA particle.

4.3.2 Diffusion of an intrinsic fluorescent molecule within BBOA as a function of $a_w$

The diffusion coefficients of intrinsic fluorescent molecules measured as a function of $a_w$ in BBOA are plotted in Figure 4.9 and given in Table 4.4. All measurements were performed at a temperature of 295 ± 1 K. The experimental diffusion coefficients increased approximately one order of magnitude as $a_w$ increased from 0.23 to 0.43, indicating a plasticizing effect of increased water content on the matrix. Also included in Figure 4.9 are diffusion coefficients predicted using the Stokes-Einstein relation. Viscosities measured using the poke-flow technique are used in these predictions. The hydrodynamic radius of the diffusing intrinsic fluorescent molecules is needed.
for the Stokes-Einstein relation. We have used 3.8 and 5.2 Å as lower and upper limits for the radii of the intrinsic fluorescent molecules. These radii are calculated using the lowest and highest molar masses (138 and 358 g mol$^{-1}$) for individual chromophores observed in pine BBOA (Fleming et al., 2020), a density of 1 g cm$^{-3}$ (Reid et al., 2005), and a spherical geometry. This range of molar masses is also consistent with Di Lorenzo et al. (2017) who observed an abundance of absorbing molecules in the range of 200-300 g mol$^{-1}$ in “less-aged” BBOA collected in the atmosphere.

Figure 4.9 allows for a comparison between measured and predicted diffusion coefficients of intrinsic fluorescent molecules in BBOA. A linear best fit to the measured diffusion coefficients, including 95% confidence bands, is shown in Figure 4.9. The diffusion coefficients predicted using the Stokes-Einstein relation overlap with the 95% confidence bands. This indicates that the Stokes-Einstein relation accurately predicts diffusion coefficients of intrinsic fluorescent molecules in BBOA for diffusion coefficients within the range of 5x10$^{-17}$ - 1x10$^{15}$ m$^2$ s$^{-1}$. Without knowledge of the radii of the molecules that make up the BBOA matrix, we cannot compare our measured diffusion coefficients with predictions using the fractional Stokes-Einstein relation.
Figure 4.9 Diffusion coefficients of an intrinsic fluorescent molecule in BBOA as a function of water activity ($a_w$). The x error bars represent the uncertainty in the measured $a_w$ and the y error bars are equal to 2 times the standard deviation of the measured diffusion coefficients. Each data point represents the average of a minimum of 5 measurements. For diffusion coefficients predicted using the Stokes-Einstein relation, the lower limit was calculated using the upper limit in viscosity and the upper limit for the hydrodynamic radius of the diffusing intrinsic fluorescent molecule. The upper limit of diffusion was calculated using the lower limit in viscosity and the lower limit for the hydrodynamic radius of the diffusing intrinsic fluorescent molecules. The secondary y axis shows mixing times for the intrinsic fluorescent molecules in a 200 nm BBOA particle.

4.3.3 Atmospheric implications

To understand the atmospheric implications of these results, we consider mixing times of R6G, a proxy for large organic molecules that may be found in the atmosphere in 200 nm β-caryophyllene SOA particles. We also consider the mixing times for intrinsic fluorescent molecules in 200 nm BBOA particles. Mixing times in β-caryophyllene SOA particles and BBOA particles are plotted on the secondary y axes in Figures 4.8 and 4.9 respectively. The mixing time axes were calculated with the following equation (Seinfeld and Pandis, 2006):

$$\tau_{mix} = \frac{d_p^2}{4\pi^2 D} \quad \text{(Eq. 4.2)}$$
where $\tau_{mix}$ is the characteristic mixing time, $d_p$ is the particle diameter, and $D$ is the diffusion coefficient of an organic molecule (taken from the primary y axis in Figure 4.8 or 4.9).

Based on the measured diffusion coefficients, at $a_w \geq 0.23$, the mixing times of large organic molecules in 200 nm β-caryophyllene SOA particles are $\leq 10$ seconds. In the planetary boundary layer, $a_w$ is often $\geq 0.23$ (Maclean et al., 2017), and so mixing times within the β-caryophyllene SOA studied here will often be short for conditions found in the planetary boundary layer. At $a_w = 0$, diffusion coefficients predicted using the fractional Stokes-Einstein relation range from $3 \times 10^{-20}$ to $4 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$, corresponding to mixing times as long as 8 hours.

Based on the diffusion coefficients of intrinsic fluorescent molecules, at $a_w \geq 0.23$, mixing times in 200 nm BBOA particles are $\leq 30$ seconds. Again, in the planetary boundary layer $a_w$ is often $\geq 0.23$, and so mixing times within the BBOA studied here will often be short for conditions found in the planetary boundary layer. At $a_w = 0$, diffusion coefficients predicted using the Stokes-Einstein relation range from $1 \times 10^{-19}$ to $8 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$, corresponding to mixing times greater than 2 hours.

In the planetary boundary layer, $a_w$ values $< 0.1$ are not common (Maclean et al., 2017). Nonetheless, knowledge of diffusion coefficients and $\tau_{mix}$ times at these low $a_w$ values are important in laboratory experiments, as lab-generated organic aerosol is often generated under low $a_w$ conditions. The slow diffusion and long $\tau_{mix}$ times predicted using the Stokes-Einstein and fractional Stokes-Einstein relations here should be considered when generating and studying lab-generated organic aerosol at $a_w$ approaching 0.

### 4.4 Conclusions

The parameters for the fractional Stokes-Einstein relation given in Chapters 2 and 3 were developed using diffusion measurements and viscosity data for relatively simple binary and ternary organic-water mixtures. It was necessary to test that relation in a more realistic and chemically complex organic aerosol sample, to determine whether the results of Chapters 2 and 3 could be applied to atmospheric organic aerosol. The ability of the Stokes-Einstein and fractional Stokes-Einstein relations to accurately describe diffusion coefficients in more realistic and chemically complex aerosol has been tested here. The results demonstrate that the Stokes-Einstein relation was able to accurately describe diffusion coefficients in the pine wood BBOA sample, but not in
the β-caryophyllene SOA sample. The fractional Stokes-Einstein relation with ζ described as a function of $R_{diff}/R_{matrix}$ was able to describe diffusion coefficients in one type of lab-generated SOA, β-caryophyllene SOA, though this relation should be tested in additional types of SOA. This chapter also demonstrates the need for further characterization of the molecules in organic aerosol, including the chemical composition, structure, and size of the constituent molecules, in order to place better constraints on $R_{diff}$ and $R_{matrix}$ values for components of atmospheric organic aerosol.
Chapter 5: Viscosity of erythritol and erythritol-water particles as a function of water activity: new results and an intercomparison of techniques for measuring the viscosity of particles

5.1 Introduction

The atmospheric importance of SOA, as well as the importance of diffusion within SOA particles, was outlined in Chapter 1. Chapters 2-4 have furthered our understanding of and ability to quantify diffusion within SOA, by demonstrating that the Stokes-Einstein relation accurately predicts diffusion coefficients of diffusing species when \( R_{\text{diff}} \gg R_{\text{matrix}} \), while a fractional Stokes-Einstein relation is necessary when \( R_{\text{diff}} \) is similar in size or smaller than \( R_{\text{matrix}} \). This is demonstrated in Chapter 3, Figure 3.7, where the \( \xi \) value depends on \( R_{\text{diff}}/R_{\text{matrix}} \), and \( \xi \) approaches 1 (approaches a Stokes-Einstein relation) as \( R_{\text{diff}}/R_{\text{matrix}} \) increases. Those results indicate that if \( R_{\text{diff}}/R_{\text{matrix}} \) is sufficiently large, then the Stokes-Einstein relation can be used to convert between diffusion and viscosity in organic-water mixtures.

Previously, researchers have investigated the viscosity of SOA in the atmosphere (Bateman et al., 2016; Bateman et al., 2017; O’Brien et al., 2014; Pajunoja et al., 2016; Virtanen et al., 2010), the viscosity of SOA material generated in environmental chambers (Grayson et al., 2016; Pajunoja et al., 2014; Renbaum-Wolff et al., 2013b; Song et al., 2015, 2016a; Virtanen et al., 2011), the viscosity of compounds identified in SOA particles (Abramson et al., 2013; Bateman et al., 2015; Hosny et al., 2015), and the viscosity of simple proxies of SOA material (Chenyakin et al., 2017; Marshall et al., 2016; Power et al., 2013). In addition, researchers have investigated the dependence of viscosity on molar mass and the number and type of functional groups (Grayson et al., 2017; Rothfuss and Petters, 2017b; Song et al., 2016b). For example, Grayson et al. (2017) investigated the dependence of viscosity on the number of hydroxyl (OH) functional groups on a carbon backbone and found that viscosity increased, on average, by a factor of 22 – 45 following the addition of an OH functional group to linear C\(_3\), linear C\(_4\), branched C\(_5\), and linear C\(_6\) carbon backbones. However, the study by Grayson et al. revealed a large discrepancy between the viscosity of erythritol (1,2,3,4-butanetetrol) measured with the bead-mobility technique (Grayson et al., 2017) and measured with the aerosol optical tweezers technique (Song et al., 2016b) at ≤
25% relative humidity (RH). This led to uncertainties when predicting the effect of adding OH functional groups to a linear C₄ carbon backbone on viscosity. This also led to uncertainties regarding the viscosity of tetrots, which have been observed in ambient SOA particles and SOA particles generated in environmental chambers (Claeys et al., 2004; Edney et al., 2005; Surratt et al., 2006, 2010b). An important formation pathway for tetrots is the hydrolysis of isoprene epoxidiol (IEPOX). IEPOX has been identified as a key intermediate during the oxidation of isoprene, an SOA precursor (Guenther et al., 2006; Surratt et al., 2010b).

To help reduce the uncertainty in the viscosity of erythritol-water particles, we measured the diffusion coefficients of a large organic dye (rhodamine B isothiocyanate-dextran, referred to as RBID in the following, average molecular weight ~ 70,000 g mol⁻¹) in erythritol-water matrices as a function of water activity (a_w) using the rectangular area fluorescence recovery after photobleaching (rFRAP) technique, described in Chapter 2. The diffusion coefficients were then converted to viscosities using the Stokes-Einstein relation (Eq. 1.3). RBID has a hydrodynamic radius that is more than 16 times larger than that of erythritol (Table 5.1 and Figure 5.1). It should be possible to accurately calculate the viscosity of an erythritol-water particle from the diffusion coefficient of RBID and the Stokes-Einstein relation since when \( R_{\text{diff}}/R_{\text{matrix}} = 16 \), the \( \xi \) value to be used in a fractional Stokes-Einstein relation is \( \approx 1 \) based on Eq. 3.2 from Chapter 3 and therefore the Stokes-Einstein relation applies. A caveat is that this is extrapolating Eq. 3.2 far beyond the range of \( R_{\text{diff}}/R_{\text{matrix}} \) values used to parameterize Eq. 3.2.

In addition to determining viscosities from the rFRAP diffusion measurements, we carried out new viscosity measurements for erythritol-water particles at \( a_w < 0.1 \) using the aerosol optical tweezers technique. The new viscosity results from the rFRAP experiments and the aerosol optical tweezers technique were then used to update our understanding of the viscosity of erythritol-water particles and the effect of adding OH functional groups to a linear C₄ carbon backbone on viscosity. The new results also allowed us to perform an intercomparison between three techniques (rFRAP, aerosol optical tweezers, and bead-mobility) used for measuring the viscosity of organic-water particles.
Figure 5.1 Molecular structures of (a) erythritol and (b) rhodamine B isothiocyanate – dextran (RBID) in neutral form. On average, $n \approx 429$.

Table 5.1 The molar masses ($M_w$) and hydrodynamic radii ($R_H$) of erythritol and rhodamine B isothiocyanate-dextran (RBID), which are used as the organic matrix species and diffusing fluorescent organic molecule in this work, respectively.

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

5.2 Experimental Methods

5.2.1 Materials

In this chapter the organic solute erythritol (> 99 % purity, Sigma Aldrich) was used. Rhodamine B isothiocyanate-dextran (RBID, average MW ~ 70000 g mol$^{-1}$, Sigma-Aldrich) was
used as the diffusing fluorescent organic molecule. All solutions were prepared using Millipore Milli-Q water.

5.2.2 Preparation of fluorescent organic-water films

The procedure for the preparation of thin films containing an organic solute, water, and trace amounts of the diffusing fluorescent molecules is detailed in Section 2.2.2. Details specific to this chapter are given here. A bulk solution containing 20 weight percent erythritol in water and 0.056 weight percent (0.01 mmol L⁻¹) RBID was prepared gravimetrically. The concentration of RBID in the thin films after conditioning was between 0.302 - 0.348 weight percent. Within that concentration range, the fluorescence intensity of the thin films was proportional to the concentration of the fluorescent organic molecules (Figure 5.2).

![Graph showing fluorescence intensity as a function of RBID mass fraction in erythritol-water thin films at α_w = 0.630 ± 0.025. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately 30×30 μm². The laser scanning microscope settings used were identical to those used in the rFRAP experiments for RBID in erythritol-water thin films. rFRAP experiments were performed using RBID concentrations within the linear range indicated here.]

**Figure 5.2** Average fluorescence intensity as a function of RBID mass fraction in erythritol-water thin films at α_w = 0.630 ± 0.025. The red line is a linear fit to the data. The fluorescence intensity was averaged over an area of approximately 30×30 μm². The laser scanning microscope settings used were identical to those used in the rFRAP experiments for RBID in erythritol-water thin films. rFRAP experiments were performed using RBID concentrations within the linear range indicated here.
The prepared bulk solution was then filtered using a 0.45μm Millex®-HV syringe filter unit (Millipore Sigma Ltd.) to eliminate solid impurities. The solution was nebulized onto clean a siliconized hydrophobic glass slide, resulting in droplets with radii ranging from 100 to 185 μm on the hydrophobic glass slide. For most of the experiments, the slide holding the droplets was then transferred into a flow cell in an inflatable Glove Bag™ (Glas-Col) for conditioning at a particular \(a_w\). For some of the experiments, the slide holding the droplets was placed in a sealed container above a saturated inorganic salt solution with a known \(a_w\). A handheld hygrometer (OMEGA) with an accuracy of ±2.5 % was used to measure the RH at the flow cell outlet and in the glove bag or above the bulk solutions.

The method used to calculate conditioning times is explained in Section 2.2.3. As in Chapter 2, diffusion coefficients of water in the erythritol-water mixture was required to calculate equilibrium times. Diffusion coefficients of water in the erythritol-water mixture are assumed to equal the diffusion coefficients of water in a sucrose-water mixture when the viscosity of the two matrices are equal. Diffusion coefficients for water in a sucrose-water mixture at a given viscosity were calculated using a parametrization for diffusion coefficients as a function of \(a_w\) from Price et al. (2016) and a parameterization for sucrose viscosity as a function of \(a_w\) from Grayson et al. (2017). The diffusion coefficients of water in sucrose were used as an estimate for diffusion coefficients of water in erythritol-water solutions at an equivalent viscosity. The expected viscosity of the erythritol-water matrix at each \(a_w\) was calculated using upper limit of the viscosity of erythritol droplets given in Table SI.22 in Song et al. (2016). These \(D_{\text{H}_2\text{O}}\) values were used with Eq. 2.1 to calculate equilibration times. Experimental times for conditioning (\(t_{\text{exp}}\)) were a minimum of 6.5 times longer than calculated equilibration times (Appendix C, Table C.1). Section 5.3.1 shows that this duration is sufficient for particles to equilibrate with the corresponding relative humidity in the surrounding gas phase.

After the droplets on the slides were conditioned to the \(a_w\) of the airspace over the salt solution, thin films were formed by sandwiching the glass slide holding the droplets with a second hydrophobic glass slide inside a Glove Bag™ (Glas-Col) following the procedure described in Section 2.2.2.
5.2.3 Rectangular area fluorescence recovery after photobleaching (rFRAP) technique and extraction of diffusion coefficients

The procedure for the rFRAP experiments and the extraction of diffusion coefficients is detailed in Section 2.2.4. All diffusion experiments in this chapter were performed at 292–294 K. Examples of images collected using the confocal laser scanning microscope are given in Figure 5.3. An example of an $r^2 + 4Dt$ vs. $t$ plot is given in Figure 5.4.

![Images](image.png)

**Figure 5.3** Images captured during an rFRAP experiment for erythritol-water thin films conditioned at $a_w = 0.023 \pm 0.023$. RBID concentration in the films was approximately 0.3 weight percent. The red square in (a) indicates the region selected for photobleaching. Images (b–f) were recorded at 0, 360, 720, 1080 and 1440 s after photobleaching. Dimensions of the images and the red square are $60 \times 60 \ \mu m^2$ and $6 \times 6 \ \mu m^2$, respectively.
Figure 5.4 $r^2 + 4Dt$ as a function of $t$ for the diffusion of RBID in erythritol-water matrix with $a_w = 0.023 \pm 0.023$. RBID concentration in the conditioned films was approximately 0.3 weight percent. The red line represents a linear fit to the data.

The mathematical description of the fluorescence intensity used to model fluorescence recovery, and hence diffusion (Eq. 2.2), as described in Chapter 2, Section 2.2.4, assumes that the only mechanism for recovery in the photobleached region is diffusion. An additional possible mechanism is reversible photobleaching (or photoswitching), where the fluorescent molecules convert between a fluorescent and a non-fluorescent state without being permanently photobleached (Fukaminato, 2011; Long et al., 2011; Sinnecker et al., 2005). To determine if reversible photobleaching was responsible for the recovery of fluorescence in the photobleached region, experiments with small droplets (10–30 μm in diameter) containing erythritol, water, and trace amount of RBID (approximately 0.3 weight percent) were carried out. In these experiments, we uniformly photobleached the entire droplet, resulting in ~ 30% reduction in fluorescence intensity. Uniform bleaching ensures that the diffusion of fluorescent RBID molecules will not result in a change in fluorescence intensity. After bleaching, the average fluorescence intensity of the entire droplet was monitored over time, as shown in Figure 5.5. The fluorescence intensity remained constant within the uncertainty of the measurements, indicating that reversible photobleaching was not an important mechanism in our rFRAP experiments.
Figure 5.5 Average fluorescence intensity as a function of time following the uniform photobleaching of an entire droplet. The average fluorescence intensities after photobleaching were normalized against an image taken prior to photobleaching. The RBID mass fraction within the conditioned droplets was approximately 0.3 weight percent. P0 represents a non-photobleached reference droplet. P1 and P2 represent two droplets chosen for the experiments.

5.2.4 Aerosol optical tweezers

The application of the aerosol optical tweezers technique to measure the viscosity of aerosol particles has been discussed in detail in previous publications (Bzdek et al., 2017; Song et al., 2016b) and will only be briefly reviewed here. Two optical traps are formed using a holographic optical tweezers instrument equipped with a laser at 532 nm (Laser Quantum Opus 3W). The holographic arrangement uses a spatial light modulator (Hamamatsu, X10468) to encode phase information into the expanded laser-light wavefront, creating an interference pattern in the trapping plane that resembles two tightly focused beams. Aerosol droplets are captured from a cloud of aerosol generated from a medical nebulizer and introduced into a RH-controlled trapping cell with the RH recorded by a capacitance probe (Honeywell, HIH-4202A). Typical particle diameters are 9–16 μm. Experiments were performed at room temperature of 293 K. Droplet sizes and refractive indices are inferred from the discrete wavelengths commensurate with whispering gallery modes (WGMs) that are observed in the Raman scattering fingerprints recorded from the two droplets. Particle size and refractive index are estimated from comparison with calculated WGM wavelengths using Mie scattering theory and can be determined with an accuracy of < ±2 nm and < ±0.0005, respectively (Preston and Reid, 2013).

Following a conditioning period of many hours, identified by a steady droplet size over a period of tens of minutes, the particles are coalesced by manipulating the optical trap positions.
Once brought into contact, the shape of the composite particle relaxes over a timescale of microseconds to hours, dependent on the viscosity. One of three methods is then chosen to infer particle viscosity from the shape relaxation based on the relaxation timescale:

1) For relaxation timescales of < 1 ms (equivalent to viscosities < 10 Pa s) (Power and Reid, 2014), the time-dependence of the backscattered light intensity can be used to monitor the change in shape using a silicon photodetector (Thorlabs, DET 110) and oscilloscope (LeCroy, HDO 6034-MS). At timescales longer than this, the movement of the trapped particle relative to the laser beam focus (i.e. the relaxation in trapped position) contributes to the change in light scattering signal and becomes convoluted with the change arising from the relaxation in shape. Thus, light scattering measurements cannot be used for viscosities > 10 Pa s (Bzdek et al., 2017).

2) For longer timescales, the relaxation in shape can be directly viewed from brightfield microscopy over a period spanning from 5 – 10 ms (equivalent to viscosities > 10 Pa s) to as long as 10³ s (equivalent to viscosities ~ 10⁷ Pa s) (Bzdek et al., 2017). Images are recorded by a camera (Dalsa Genie HM 640, CMOS) with 5 – 10 ms time resolution. The change in aspect ratio for the relaxing particle is determined and used to determine the relaxation time constant (Song et al., 2016b).

3) The disappearance followed by the reappearance of WGMs from the Raman spectrum from the coalesced dimer (recorded with 1 s time resolution) can be used to infer the slow disappearance of a spherical cavity on one side of the dimer and reemergence of a single spherical particle at the end of the relaxation process (Power et al., 2013). With a coarse time resolution of 1 s, this method should only be used to infer the viscosity when higher than 10⁴ Pa s (Power and Reid, 2014).

With three analysis methods, viscosity measurement can cover a wide range, from 10⁻³ Pa s to > 10⁹ Pa s. However, it should be noted that there are ranges where two techniques may overlap but with varying accuracy (e.g. brightfield imaging and Raman for viscosities 10⁴ – 10⁵ Pa s with relaxation times of 1 – 10 s). Examples of brightfield images captured during an optical tweezers experiment are given in Figure 5.6.
Figure 5.6 An example of the captured brightfield images as a function of time after the coalescence of two erythritol particles in optical tweezers at $a_w = 0.04 \pm 0.02$. The relaxation to a spherical particle occurred within 56 milliseconds.

5.3 Results and discussion

5.3.1 Diffusion coefficients of RBID in and viscosities of erythritol-water matrices measured by the rFRAP technique

Shown in Figure 5.7(a) and listed in Table C.1 (Appendix C) are the measured diffusion coefficients of RBID in erythritol-water matrices as a function of $a_w$. The diffusion coefficient decreased by 2–3 orders of magnitude as $a_w$ decreased from approximately 0.5 to 0. This decrease in the diffusion coefficients with a decrease in $a_w$ is due to the plasticizing effect of water (Koop et al., 2011; Power et al., 2013).

The Stokes-Einstein relation (Eq. 1.3) and measured diffusion coefficients were used to calculate the viscosity of erythritol-water particles. The Stokes-Einstein relation significantly underestimates the diffusion coefficients of small molecules such as water and ozone within a matrix containing larger molecules ($R_{\text{diff}}/R_{\text{matrix}} < 1$), as shown in Chapter 3 and the following references (Bastelberger et al., 2017; Davies and Wilson, 2016; Li et al., 2015; Marshall et al., 2016; Price et al., 2014; Shiraiwa et al., 2011). On the other hand, as discussed in Section 5.1, the
Stokes-Einstein relation is expected to accurately relate diffusion and viscosity when the diffusing species is large relative to the matrix molecules ($R_{\text{diff}} \gg R_{\text{matrix}}$), as is the case here, where $R_{\text{diff}}$ (RBID) is over 16 times larger than $R_{\text{matrix}}$ (erythritol). Chenyakin et al. and Price et al. also showed that the Stokes-Einstein relation accurately predicts diffusion coefficients when $R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and the matrix viscosity is $\lesssim 10^4$ Pa s (Chenyakin et al., 2017; Price et al., 2016), as is the case in this chapter. Hence, in this study, we assume that the viscosity of erythritol-water particles can be accurately calculated using the measured RBID diffusion coefficient and the Stokes-Einstein relation, because RBID is much larger than the matrix molecules (Table 5.1) and the highest reported viscosity of erythritol in the literature is on the order of $10^4$ Pa s (Grayson et al., 2017; Song et al., 2016b).

Figure 5.7(b) and Table C.1 show the viscosity of erythritol-water particles (calculated using diffusion coefficients from Figure 5.7(a) and the Stokes-Einstein relation) as a function of $a_w$. As $a_w$ decreased from approximately 0.5 to 0, the viscosity increased from approximately $1 \times 10^{-1}$ to $5 \times 10^1$ Pa s. The symbols in Figure 5.7 are color-coded by the time allowed to condition the samples to a particular $a_w$ value before measuring the diffusion coefficient. The color scale in the top left corner applies to both panels (a) and (b). No clear trend is observed between the conditioning time and diffusion coefficient or particle viscosity.
Figure 5.7 (a) The measured diffusion coefficients of RBID as a function of $a_w$. (b) The viscosity of erythritol-water particles as a function of $a_w$ based on the measured RBID diffusion coefficients and the Stokes-Einstein relation. Results from rFRAP measurements are color-coded by the sample conditioning time prior to the rFRAP experiments. The color scale applies to both panel (a) and (b). Horizontal error bars indicate the upper and lower limits of $a_w$. Vertical error bars correspond to two standard deviations of diffusion coefficient (in panel a) and log (viscosity) (in panel b).

To further investigate the effect of the time used to condition the samples to a particular $a_w$ value, in Figure 5.8 the measured RBID diffusion coefficients in erythritol-water matrices are plotted as a function of conditioning time at $a_w \leq 0.105$. The data shown in Figure 5.8 were taken from the data shown in Figure 5.7(a). Included as a secondary x-axis is the sample conditioning time in multiples of $\tau_{mix,H2O}$, where $\tau_{mix,H2O}$ is the characteristic time for water diffusion within the sample droplets used in the conditioning experiments (see Chapter 2, Section 2.2.3). Consistent with Figure 5.7(a), Figure 5.8 illustrates that there is no clear trend between diffusion coefficient and the time allowed for conditioning the samples prior to the diffusion measurements. Figure 5.8
also suggests that a sample conditioning time of $\geq 21.5$ hours, or $\geq 6.5 \tau_{\text{mix,H}_2\text{O}}$ was sufficient to reach near equilibrium between the RH used for conditioning and the $a_w$ in particles.

**Figure 5.8** The diffusion coefficient of RBID as a function of the time allowed for conditioning erythritol-water particles at $a_w = 0 - 0.046$ (open squares) and $0 - 0.105$ (filled squares). The secondary (top) x-axis represents the conditioning time expressed in multiples of $\tau_{\text{mix,H}_2\text{O}}$ (characteristic time for the diffusion of water molecules within the erythritol-water droplets). For the calculation of $\tau_{\text{mix,H}_2\text{O}}$, the lower limit of $a_w$ (i.e., 0) was taken, leading to maximum $\tau_{\text{mix,H}_2\text{O}}$ values of 3.3 h for droplets with a radius of 100 μm. Error bars represent two standard deviations of RBID diffusion coefficients.

### 5.3.2 Viscosity of erythritol-water matrices measured by the aerosol optical tweezers technique

Erythritol viscosity measurements using the aerosol optical tweezers technique are shown in Figure 5.9. The viscosity of pure water at 293 K (Korson et al., 1969) is also included for comparison. The red circles represent the new aerosol optical tweezers measurements obtained in this work (also listed in Table C.2, Appendix C), based solely on brightfield images. The gray circles represent the viscosities reported in Song et al. (2016b). The new averaged viscosities reported here based on the aerosol optical tweezers technique are lower than those reported by Song et al. (2016b) at $a_w < 0.1$, although the error bars (representing two standard deviations) overlap.
In the previous aerosol optical tweezers measurements at $a_w < 0.1$ (Song et al., 2016b), the timescale for relaxation to a sphere was estimated from two methods: the change in coalesced particle shape as recorded by the brightfield images and the reappearance of WGMs in the Raman spectrum. Figure 5.6 shows an example of captured brightfield images as a function of time after the coalescence of two erythritol particles at $a_w = 0.04 \pm 0.02$. The relaxation to a spherical particle occurred within 56 milliseconds, a timescale that is too short to be resolved by Raman spectral measurements (time resolution of 1 s, see Section 5.2.4). Therefore, previous erythritol viscosity measurements under dry conditions using the Raman spectral measurements (Song et al., 2016b) were compromised by the limited time resolution (1 s, equivalent to $\sim 10^4$ Pa s) and higher than those estimated from brightfield imaging, yielding an overestimate of the viscosity. Since the new aerosol optical tweezers measurements in this work are based solely on the brightfield images, they are more accurate than the previous results at $a_w < 0.1$ as a consequence of the higher time resolution of the brightfield imaging measurements compared to the Raman spectroscopy measurements. The viscosity at $a_w = 0.22 \pm 0.02$ reported by Song et al. (2016b) was based on brightfield images alone and those at $a_w \geq 0.43$ were based on back-scattered light intensity (where viscosities were $< 10$ Pa s, see Section 5.2.4).

![Figure 5.9](image)

**Figure 5.9** Viscosity of erythritol-water particles as a function of $a_w$, determined using the aerosol optical tweezers technique. Red circles represent experimental results from this study. Gray circles represent experimental results from Song et al. (2016b). The green circle represents the viscosity...
of pure water at 293 K (Korson et al., 1969). Horizontal error bars indicate the upper and lower limits of $a_w$. Vertical error bars represent two standard deviations of log (viscosity).

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

In Figure 5.10, we have summarized the previous and current measurements of the viscosity of erythritol-water particles as a function of $a_w$. The black triangles represent measurements by Grayson et al. (2017) using the bead-mobility technique. The blue squares represent the rFRAP results from this work, where experimental data at similar $a_w$ have been binned together so as not to give extra weight to the rFRAP data. The red circles indicate aerosol optical tweezers measurements from Song et al. (2016b) (open circles) and this study (solid circles). The previous measurements at $a_w \leq 0.1$ by Song et al. (2016b) were excluded from Figure 5.10, because the new aerosol optical tweezers measurements reported in this study at $a_w \leq 0.1$ are thought to be more accurate. At $a_w > 0.4$, the viscosity measurements from the bead-mobility, rFRAP, and optical tweezers techniques are in reasonable agreement, if the experimental uncertainties are considered. At $a_w < 0.4$, the mean viscosity values determined using optical tweezers are higher than those from rFRAP and bead-mobility measurements by 1 – 2 orders of magnitude. The error bars (two standard deviations) overlap in some, but not all, cases. Nevertheless, the disagreement in viscosity measured using multiple techniques seen here is smaller than reported previously.

To determine the viscosity of pure erythritol under dry conditions (at $a_w = 0$), a straight line was fit to the data in Figure 5.10 based on the orthogonal distance regression-fitting algorithm using IGOR Pro 6 and then extrapolated to $a_w = 0$. This algorithm weighted the fit based on the x and y uncertainties of each data point. The viscosity of pure water ($a_w = 1$) is well constrained (Korson et al., 1969), giving it a larger weighting than data points at $a_w < 1$. The intercept on the y-axis was $2.27 \pm 0.22$ (two standard deviations), corresponding to a viscosity of pure erythritol of $184^{+122}_{-111}$ Pa s.
5.3.4 Effect of the addition of OH functional groups to a linear C$_4$ carbon backbone

Grayson et al. (2017) previously estimated the effect of adding OH functional groups on the viscosity of a linear C$_4$ compound. Here we repeat this analysis (Figure 5.11) based on the updated viscosity of pure erythritol ($184_{-111}^{+122}$ Pa s) determined above. For those compounds with the same number but different positions of OH functional groups, the average of their viscosities was taken from the literature (Grayson et al., 2017; Rothfuss and Petters, 2017b; Song et al., 2016b). Table C.3 (Appendix C) lists the values and sources of literature data used. The data in Figure 5.11 were fit to a linear equation, resulting in a slope of $1.43 \pm 0.08$ (two standard
deviations), which indicates that the viscosity of a linear C₄ molecule increases on average by a factor of $27^{\pm 6}$ per addition of an OH functional group. The increase in viscosity with the addition of an OH functional group to a linear C₄ backbone is attributed to the increased number of hydrogen bonds (H–O⋯H) formed between adjacent molecules, as discussed previously (Rothfuss and Petters, 2017b). Similarly, the addition of carboxyl groups (–COOH) leads to an increase in viscosity due to enhanced formation of intermolecular hydrogen bonds (Rothfuss and Petters, 2017b).

The increase in viscosity from the addition of OH functional groups to a carbon backbone may depend on the level of prior functionalization. To investigate this aspect further, we calculated the viscosity sensitivity parameter ($S_\eta$) for a linear C₄ carbon backbone using the viscosity data presented in Figure 5.11 and the following equation (Rothfuss and Petters, 2017):

$$S_\eta = \Delta \log (\eta) / \Delta N$$  \hspace{1cm} (Eq. 5.1)

where $\Delta \log (\eta)$ is the change in viscosity on a log₁₀ scale, and $\Delta N$ is the change in the number of OH functional groups. $S_\eta$ was estimated based on the addition of one OH functional group ($\Delta N = 1$), starting from n-butane. The relationship between $S_\eta$ and $N$ is shown in Figure 5.12 for a linear C₄ carbon backbone. $S_\eta$ is between 0.7 and 1.9 for $N = 1 – 3$. On the other hand, $S_\eta$ is between 1.6 and 2.5 for $N = 4$, suggesting $S_\eta$ likely increases with the addition of the fourth OH functional group to the linear C₄ carbon backbone. However, additional studies are needed in order to reduce the uncertainties of the measurements and make stronger conclusions.
Figure 5.11 Viscosities of compounds with a linear C₄ carbon backbone at 292 – 295 K plotted against the number of OH functional groups. Black circles represent viscosities of the compounds with 0 – 3 OH functional groups (i.e., n-butane, 1-butanol, 2-butanol, 1,2-butanediol, 1,4-butanediol, 2,3-butanediol, 1,2,3-butanetriol and 1,2,4-butanetriol) taken from literature (Grayson et al., 2017; Rothfuss and Petters, 2017b; Song et al., 2016b). For the literature data points, the error bars are two standard deviations of log (viscosity) of multiple compounds. The blue circle represents the viscosity of pure erythritol, with error bars of two standard deviations, based on the linear fit in Figure 5.10. The red line is a linear fit to the data, which is weighted based on the uncertainties in viscosity data. The slope and regression coefficient ($R^2$) are shown in the annotation. The uncertainty in the slope corresponds to two standard deviations.
Figure 5.12 The viscosity sensitivity parameter at 292 – 295 K plotted against the number of OH functional groups for linear C₄ compounds (alkane, alcohol and polyols). Black circles represent values estimated using literature data alone (Grayson et al., 2017; Rothfuss and Petters, 2017b; Song et al., 2016b); the blue circle represents the value estimated using experimental results from this work and literature data (Grayson et al., 2017; Song et al., 2016b). The error bars are propagated from the uncertainties shown in Figure 5.11.

5.4 Summary and conclusions

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

In general, at $a_w > 0.4$, the viscosity measurements from the bead-mobility, rFRAP, and optical tweezers techniques are in reasonable agreement, if the experimental uncertainties are considered. At $a_w < 0.4$, the mean viscosity values determined using optical tweezers are higher than those using the bead-mobility and rFRAP techniques by 1 – 2 orders of magnitude. Nevertheless, the disagreement in viscosity measured using multiple techniques seen here is smaller than reported previously. A linear fit was performed for the experimentally determined
viscosities of erythritol-water particles against $a_w$ and extrapolated to $a_w = 0$. Based on the extrapolation, the viscosity of pure erythritol at 292 – 295 K is estimated at $184^{+122}_{-111}$ Pa s (two standard deviations). Based on these results, the addition of an OH functional group to a linear C$_4$ carbon backbone increases the viscosity by a factor of $27^{+6}_{-5}$ (two standard deviations), on average. In comparison, Grayson et al. (2017) reported a factor of $41^{+27}_{-16}$ based on previous measurements.

The viscosity sensitivity parameter was calculated to determine the dependency of viscosity on the degree of prior functionalization for a linear C$_4$ carbon backbone. Based on the viscosity sensitivity parameter analysis, the increase in viscosity due to the addition of one OH functional group to a linear C$_4$ carbon backbone is not a strong function of the number of OH groups already present in the molecule, up to the addition of three OH functional groups. On the other hand, the degree of increase in viscosity is likely larger when the linear C$_4$ carbon backbone already contains three OH groups. These results should help improve the understanding of the viscosity of SOA particles in the atmosphere.
Chapter 6: Conclusions and future work

6.1 Conclusions

6.1.1 Testing the ability of the Stokes-Einstein and fractional Stokes-Einstein relations to predict diffusion rates of large and small molecules in organic-water mixtures

Chapters 2 and 3 tested the ability of the Stokes-Einstein relation to accurately predict diffusion coefficients from viscosity in organic-water mixtures. Additionally, parameters for a fractional Stokes-Einstein relation were developed to predict diffusion coefficients of both large and small molecules ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and $R_{\text{diff}}/R_{\text{matrix}} < 1$) from viscosity. Mixtures containing one or two organic solutes and water are useful proxies for atmospheric organic aerosol, and are also widely used in food products, pharmaceutical formulations, and in the cryopreservation of biomolecules.

Chapter 2 showed that the Stokes-Einstein relation accurately predicts diffusion coefficients for $R_{\text{diff}}/R_{\text{matrix}} \geq 1$ within a factor of 10 in most cases, for viscosities up to about $10^6$ Pa s. However, a fractional Stokes-Einstein relation with a single $\xi$ value does a better job than the Stokes-Einstein relation for describing diffusion coefficients for $R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and for the range of viscosities studied in that chapter, based on a sum-of-squared residuals analysis. Those results were used to model mixing times of SOA in the atmosphere. The fractional Stokes-Einstein relation predicts faster diffusion coefficients and therefore shorter mixing times of SOA particles in the atmosphere. The difference in mixing times predicted by the two relations is as much as one order of magnitude at an altitude of 3.2 km.

Chapter 3 showed that for a data set including diffusion coefficients of large and small molecules ($R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and $R_{\text{diff}}/R_{\text{matrix}} < 1$) in mixtures containing one or two organic solutes and water, the Stokes-Einstein relation accurately describes only 75% of diffusion coefficients in organic-water mixtures. In contrast, a fractional Stokes-Einstein relation with $\xi$ expressed as a function of $R_{\text{diff}}/R_{\text{matrix}}$ accurately describes 98% of the diffusion coefficients in that data set. The fractional Stokes-Einstein relation given in Chapter 3, with $\xi$ expressed as a function of $R_{\text{diff}}/R_{\text{matrix}}$, holds for a wide range of $R_{\text{diff}}/R_{\text{matrix}}$ values (0.31 to 1.75), viscosities ($10^{-3}$ up to $10^{10}$ Pa s), and
intermolecular interactions (e.g. hydrogen bonding, dipole-dipole, dipole-induced dipole). The result is a unified description of diffusion coefficients of large and small molecules in organic-water mixtures. A modeling study used the Stokes-Einstein and fractional Stokes-Einstein relations to calculate degradation times of PAHs within organic-water particles in the planetary boundary layer of the atmosphere. The degradation times calculated using the Stokes-Einstein relation were a factor of ~10 larger than the degradation times calculated using the fractional Stokes-Einstein relation at a viscosity $\geq 10^4$ Pa s.

6.1.2 Application of the fractional Stokes-Einstein relation in atmospherically realistic and chemically complex lab-generated organic aerosol

While the organic-water mixtures used in Chapters 2 and 3 are good proxies for use in lab studies, they are less chemically complex than atmospheric organic aerosol. Chapter 4 tests the ability of the Stokes-Einstein and fractional Stokes-Einstein relations to accurately describe diffusion coefficients in more atmospherically realistic and chemically complex lab-generated organic aerosol samples. This was done by measuring diffusion coefficients in two lab-generated organic aerosol samples for which viscosity data was also available. The Stokes-Einstein relation was able to accurately describe diffusion coefficients in one sample (with an unknown $R_{\text{diff}}/R_{\text{matrix}}$), while the fractional Stokes-Einstein relation, with $\xi$ determined using the parameterization for $\xi$ as a function of $R_{\text{diff}}/R_{\text{matrix}}$ given in Chapter 3, was required to describe diffusion coefficients in the second lab-generated organic aerosol sample (with $R_{\text{diff}}/R_{\text{matrix}} > 1$).

6.1.3 An intercomparison of techniques used to measure the viscosity of a binary organic-water mixture

In Chapter 5, diffusion coefficients of a very large organic molecule, RBID, were used in combination with the Stokes-Einstein relation to determine the viscosity of an erythritol-water mixture ($R_{\text{diff}}/R_{\text{matrix}} > 16$). The use of the Stokes-Einstein relation in this case is supported by the results of Chapter 3. This work was done to resolve a discrepancy in the literature, as two disagreeing data sets for the viscosity of erythritol-water mixtures had been published. Additional measurements were also performed using the optical tweezers technique, which was used to
measure viscosity in one of the original literature data sets. The new measurements obtained using the rFRAP and optical tweezers techniques resulted in viscosity data in agreement within the uncertainty of the measurement techniques.

6.2 Directions for future work

A unified description for diffusion coefficients of large and small molecules in mixtures containing one or two organic solutes and water has been presented here. As noted, these mixtures are less chemically complex than atmospheric organic aerosol. The ability of the Stokes-Einstein and fractional Stokes-Einstein relations to describe diffusion coefficients in two types of lab-generated organic aerosol (SOA generated from the oxidation of the VOC β-caryophyllene and BBOA generated from the pyrolysis of pine wood) was also assessed. However, there are numerous VOC precursors to SOA and numerous fuel precursors to BBOA, and we have tested only one of each. Further measurements are necessary to determine whether the fractional Stokes-Einstein relation is the best relation to use to relate diffusion and viscosity in lab-generated and ambient atmospheric organic aerosol. In addition to more diffusion and viscosity measurements, this will require further characterization of the molecules in organic aerosol, including the chemical composition, structure, and size of the constituent molecules. This data may be obtained through mass spectrometry experiments and will place better constraints on $R_{\text{diff}}$ and $R_{\text{matrix}}$ values for components of atmospheric organic aerosol.

As seen in the data sets used in Chapters 2 and 3, the majority of diffusion coefficients for both $R_{\text{diff}}/R_{\text{matrix}} \geq 1$ and $R_{\text{diff}}/R_{\text{matrix}} < 1$ have been measured in matrices with viscosities $\leq 10^6$ Pa s. Additional diffusion measurements in organic-water mixtures at viscosities $> 10^6$ Pa s are needed to further evaluate the relationship between diffusion and viscosity in highly viscous matrices. Additional measurements of diffusing species with $R_{\text{diff}}/R_{\text{matrix}} < 1$ are also needed, particularly in matrices other than sucrose-water mixtures. Those measurements are needed to better understand the variability in $\zeta$ values observed for small diffusing species in Chapter 3.
All diffusion and viscosity data included in this work were collected between 292-298 K. Temperatures below this range are atmospherically relevant, particularly in the free troposphere, where the temperature may be as low as 217 K (Seinfeld and Pandis, 2006). As described in Chapter 3, the data set used does cover a wide range of $T-T_g$ values, and it is speculated that the results of the current analysis can be applied at other temperatures as long as viscosities are $\leq 10^6$ Pa s, and $T-T_g$ values are $\geq 20$. Nevertheless, this speculation needs to be tested. Low-temperature diffusion measurements are now possible using the rFRAP technique (Kiland et al., 2019), and low-temperature diffusion measurements should be made in additional organic-water mixtures as well as in lab-generated organic aerosol samples. Low-temperature diffusion measurements in combination with low-temperature viscosity measurements will allow for the Stokes-Einstein and fractional Stokes-Einstein relations to be evaluated at low temperatures.
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Appendices

Appendix A  Appendix to Chapter 2

A.1  Diffusion coefficients and viscosity data from literature sources

Figure 2.18a in Chapter 2 includes \( \log(D) - \log(kT/6\pi R_H) \) plotted as a function of \( \log(\eta) \) for organics diffusing in sucrose and brown limonene SOA matrices. The following gives additional details on this data.

In Price et al. (2016) and Chenyakin et al. (2017), diffusion coefficients were reported as a function of \( a_w \). The \( a_w \) was converted to viscosity using the viscosity vs. \( a_w \) parameterization from Figure S1 in Grayson et al. (2017) for sucrose solutions. The experiments of Chenyakin et al. (2017) were performed at 294.5 K, and the experiments of Price et al. (2016) were performed at 296 K.

The diffusion coefficients of Champion et al. (1997) were reported as a function of experimental temperature (\( T \)) minus the glass transition temperature (\( T_g \)). Those data were digitized using Origin software. The sucrose mass fraction of the solution used for each measurement was also given. The \( T_g \) at each sucrose mass fraction was calculated, using the Gordon-Taylor equation and parameters provided by Champion et al. (1997). Next, the experimental temperature for each measurement was calculated using the reported \( T-T_g \) values and the calculated \( T_g \). Only diffusion coefficients measured at temperatures of 292 – 298 K were used. The sucrose mass fraction was converted to \( a_w \) using the relation between sucrose mass fraction and \( a_w \) given in Zobrist et al. (2011). Finally, viscosity was calculated using the viscosity-\( a_w \) parametrization given in Grayson et al. (2017) for sucrose solutions.

Rampp et al. (2000) measured diffusion coefficients of sucrose as a function of temperature, but reported their results for sucrose-water solutions in terms of parameters for the Vogel-Tammann-Fulcher (VTF) equation:

\[
D = D_0 e^{-\frac{T_0 e}{T-T_0}}
\]  

(A1)
where $D$ is the diffusion coefficient ($m^2/s$), and $D_0$, $T_0$, and $C$ are free parameters. $D_0$ represents the expected diffusion at some value $T_0$, and $C$ is the fragility parameter. The VTF parameters were reported as a function of mass fraction sucrose. Using the VTF equation and the reported VTF parameters, a diffusion coefficient was calculated at a temperature of 295 K for each mass fraction sucrose studied by Rampp et al. (2000). Sucrose mass fraction was then converted to viscosity using the relation between sucrose mass fraction and $a_w$ of Zobrist et al. (2011) and the viscosity-$a_w$ parametrization given in Grayson et al. (2017) for sucrose solutions.

Diffusion coefficients of the fluorescent organic molecule fluorescein in a sucrose matrix have also been measured by Corti et al. (2008) in the temperature range of 292-298 K. However, diffusion coefficients measured by Corti et al. (2008) are not included in Figure 2.18 of the main text because Price et al. (2016) has shown that these measurements are inconsistent with other literature measurements of large organics in sucrose matrices.

As mentioned above, the viscosity-$a_w$ parameterization provided in Figure S1 in Grayson et al. (2017) was used to convert water activities to viscosities in sucrose-water matrices. Sucrose-water viscosity data in that parameterization come from several viscosity measurements (Först et al., 2002; Green and Perry, 2007; Haynes, 2015; Lide, 2001; Migliori et al., 2007; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007). All viscosity measurements were made at a temperature of 293 K.

Diffusion coefficients in brown limonene SOA are reported as a function of $a_w$ in Ullmann et al. (2019). The viscosity of brown limonene SOA matrices as a function of $a_w$ were also reported in that work. Both diffusion and viscosity measurements were performed at 294.5 K.
Table A.1 Selected parameters used in preparing droplets containing rhodamine 6G in a citric acid matrix for rFRAP experiments and experimental diffusion coefficients. $\tau_{\text{mix,H2O}}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the experimental time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Max diameter (µm)</th>
<th>$\tau_{\text{mix,H2O}}$</th>
<th>$t_{\text{exp}}$</th>
<th>Log ($\eta$, Pa s) $^a$</th>
<th>Diffusion coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 ± 0.025</td>
<td>228</td>
<td>1 h</td>
<td>4.2 days</td>
<td>2.92 ± 0.61</td>
<td>2.99 E-15 ± 2.55E-15</td>
</tr>
<tr>
<td>0.331 ± 0.025</td>
<td>628</td>
<td>2.89 h</td>
<td>20 h</td>
<td>1.82 ± 0.56</td>
<td>1.73E-14 ± 7.83 E-15</td>
</tr>
<tr>
<td>0.432 ± 0.025</td>
<td>656</td>
<td>0.75 h</td>
<td>20 h</td>
<td>0.85 ± 0.54</td>
<td>1.30 E-13 ± 2.53 E-14</td>
</tr>
<tr>
<td>0.514 ± 0.025</td>
<td>542</td>
<td>0.15 h</td>
<td>15 h</td>
<td>0.16 ± 0.51</td>
<td>5.53 E-13 ± 1.26E-13</td>
</tr>
<tr>
<td>0.571 ± 0.025</td>
<td>828</td>
<td>0.14 h</td>
<td>15 h</td>
<td>-0.30 ± 0.50</td>
<td>1.05 E-12 ± 1.13 E-13</td>
</tr>
<tr>
<td>0.732 ± 0.025</td>
<td>914</td>
<td>38 s</td>
<td>20 h</td>
<td>-1.31 ± 0.47</td>
<td>1.07 E-11 ± 1.44 E-12</td>
</tr>
<tr>
<td>0.863 ± 0.025</td>
<td>1128</td>
<td>6 s</td>
<td>15 h</td>
<td>-1.89 ± 0.47</td>
<td>3.14 E-11 ± 3.72 E-12</td>
</tr>
</tbody>
</table>

$^a$ The lower limit of viscosity was calculated using the upper limit of $a_w$ with the lower 95% confidence band in Figure A.1, while upper limit of viscosity was calculated using the lower limit of $a_w$ with the upper 95% confidence band in Figure A.1.

Table A.2 Selected parameters used in preparing droplets containing cresyl violet in a citric acid matrix for rFRAP experiments and experimental diffusion coefficients. $\tau_{\text{mix,H2O}}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the experimental time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Max diameter (µm)</th>
<th>$\tau_{\text{mix,H2O}}$</th>
<th>$t_{\text{exp}}$</th>
<th>Log ($\eta$, Pa s) $^a$</th>
<th>Diffusion coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 ± 0.025</td>
<td>171</td>
<td>0.58 h</td>
<td>16 days</td>
<td>2.92 ± 0.61</td>
<td>8.59 E-16 ± 3.60 E-16</td>
</tr>
<tr>
<td>0.331 ± 0.025</td>
<td>100</td>
<td>246 s</td>
<td>17 h</td>
<td>1.82 ± 0.56</td>
<td>3.80 E-14 ± 1.30 E-14</td>
</tr>
<tr>
<td>0.432 ± 0.025</td>
<td>100</td>
<td>62 s</td>
<td>17 h</td>
<td>0.85 ± 0.54</td>
<td>2.63 E-13 ± 1.41 E-13</td>
</tr>
<tr>
<td>0.514 ± 0.025</td>
<td>1286</td>
<td>0.85 h</td>
<td>116 h</td>
<td>0.16 ± 0.51</td>
<td>3.98 E-13 ± 2.87 E-13</td>
</tr>
<tr>
<td>0.571 ± 0.025</td>
<td>1170</td>
<td>0.28 h</td>
<td>18 h</td>
<td>-0.30 ± 0.50</td>
<td>1.10 E-12 ± 6.87 E-13</td>
</tr>
<tr>
<td>0.732 ± 0.025</td>
<td>671</td>
<td>20 s</td>
<td>15 days</td>
<td>-1.31 ± 0.47</td>
<td>6.17 E-12 ± 3.49 E-12</td>
</tr>
</tbody>
</table>

$^a$ The lower limit of viscosity was calculated using the upper limit of $a_w$ with the lower 95% confidence band in Figure A.1, while upper limit of viscosity was calculated using the lower limit of $a_w$ with the upper 95% confidence band in Figure A.1.
Table A.3 Selected parameters used in preparing droplets containing rhodamine 6G in a sorbitol matrix for rFRAP experiments and experimental diffusion coefficients. $\tau_{\text{mix,H2O}}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the experimental time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Max diameter (µm)</th>
<th>$\tau_{\text{mix,H2O}}$</th>
<th>$t_{\text{exp}}$</th>
<th>Log (η, Pa s)</th>
<th>Diffusion coefficient (µm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 ± 0.025</td>
<td>742</td>
<td>63.5 h</td>
<td>8 days</td>
<td>4.24 ± 0.78</td>
<td>1.65 E-17 ± 1.44 E-17</td>
</tr>
<tr>
<td>0.331 ± 0.025</td>
<td>770</td>
<td>20.1 h</td>
<td>7 days</td>
<td>3.31 ± 0.63</td>
<td>9.62 E-17 ± 2.55 E-17</td>
</tr>
<tr>
<td>0.432 ± 0.025</td>
<td>828</td>
<td>7.7 h</td>
<td>4 days</td>
<td>2.36 ± 0.53</td>
<td>1.96 E-14 ± 4.52E-15</td>
</tr>
<tr>
<td>0.514 ± 0.025</td>
<td>1142</td>
<td>5.7 h</td>
<td>4 days</td>
<td>1.61 ± 0.50</td>
<td>1.15 E-13 ± 3.24 E-14</td>
</tr>
<tr>
<td>0.571 ± 0.025</td>
<td>1000</td>
<td>2.2 h</td>
<td>18 h</td>
<td>1.05 ± 0.51</td>
<td>1.88E-13 + 2.17 E-14</td>
</tr>
</tbody>
</table>

* The lower limit of viscosity was calculated using the upper limit of $a_w$ with the lower 95% confidence band in Figure A.2, while upper limit of viscosity was calculated using the lower limit of $a_w$ with the upper 95% confidence band in Figure A.2.

Table A.4 Selected parameters used in preparing droplets containing rhodamine 6G in a sucrose-citric acid matrix for rFRAP experiments and experimental diffusion coefficients. $\tau_{\text{mix,H2O}}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Max diameter (µm)</th>
<th>$\tau_{\text{mix,H2O}}$</th>
<th>$t_{\text{exp}}$</th>
<th>Log (η, Pa s)</th>
<th>Diffusion coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14 ± 0.025</td>
<td>243</td>
<td>60 h</td>
<td>216 h</td>
<td>6.60 ± 1.15</td>
<td>3.79E-19 ± 2.75 E-19</td>
</tr>
<tr>
<td>0.23 ± 0.025</td>
<td>685</td>
<td>60 h</td>
<td>168 h</td>
<td>4.92 ± 0.98</td>
<td>1.17 E-18 ± 9.72 E-19</td>
</tr>
<tr>
<td>0.26 ± 0.025</td>
<td>257</td>
<td>8.8 h</td>
<td>72 h</td>
<td>4.38 ± 0.93</td>
<td>6.23 E-17 ± 5.83 E-17</td>
</tr>
<tr>
<td>0.282 ± 0.025</td>
<td>385</td>
<td>13.7 h</td>
<td>87 h</td>
<td>4.03 ± 0.89</td>
<td>1.22 E-16 ± 6.49 E-17</td>
</tr>
<tr>
<td>0.331 ± 0.025</td>
<td>600</td>
<td>13.4 h</td>
<td>576 h</td>
<td>3.26 ± 0.82</td>
<td>4.78 E-16 ± 2.31 E-16</td>
</tr>
<tr>
<td>0.432 ± 0.025</td>
<td>571</td>
<td>2.2 h</td>
<td>601 h</td>
<td>1.82 ± 0.71</td>
<td>4.08 E-15 ± 1.15 E-15</td>
</tr>
<tr>
<td>0.514 ± 0.025</td>
<td>514</td>
<td>0.46 h</td>
<td>19 h</td>
<td>0.82 ± 0.64</td>
<td>4.84 E-14 ± 1.52 E-14</td>
</tr>
<tr>
<td>0.571 ± 0.025</td>
<td>714</td>
<td>0.34 h</td>
<td>19 h</td>
<td>0.16 ± 0.60</td>
<td>1.61 E-13 ± 1.24 E-14</td>
</tr>
<tr>
<td>0.732 ± 0.025</td>
<td>657</td>
<td>52 s</td>
<td>19 h</td>
<td>-1.22 ± 0.60</td>
<td>2.85 E-12 ± 3.88 E-13</td>
</tr>
<tr>
<td>0.863 ± 0.025</td>
<td>685</td>
<td>13 s</td>
<td>19 h</td>
<td>-1.94 ± 0.67</td>
<td>1.90 E-11 ± 2.00 E-12</td>
</tr>
</tbody>
</table>

* The lower limit of viscosity was calculated using the upper limit of $a_w$ with the lower 95% confidence band in Figure A.3, while upper limit of viscosity was calculated using the lower limit of $a_w$ with the upper 95% confidence band in Figure A.3.
Figure A.1 Parameterization between viscosity and water activity for citric acid solutions. Data come from Song et al. (2016) and include measurements on particles using the optical tweezers technique and measurements in the bulk phase using a rheometer. Measurements were performed at 293 ± 2 K. The equation of the second order polynomial line (red line) is \( \log(\eta) = 5.9232 \pm 0.3772 - 14.508 \pm 0.3124(a_w) + 6.30235 \pm 0.3605(a_w^2) \). X-error bars on the data points represent the ± 0.02 \( a_w \) and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.
Figure A.2 Parameterization between viscosity and water activity for sorbitol solutions. Data come from Song et al. (2016) and include measurements on particles using the optical tweezers technique. Measurements were performed at 293 ± 2 K. The equation of the line (red line) is log ($\eta$) = 6.4134 ± 1.021 – 9.4175 ± 2.871(a_w) + 0 ± 2.708(a_w^2). X-error bars on the data points represent the ± 0.02 a_w and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.
Figure A.3 Parameterization between viscosity and water activity for sucrose-citric acid solutions. Data come from Rovelli et al. (2019) and only include measurements on particles using the optical tweezers technique. Measurements performed using the poke-and-flow technique were not included due to the larger uncertainty in viscosity measurements using that technique. Measurements were performed at 293 ± 2 K. The equation of the line (red line) is \( \log(\eta) = 9.55 \pm 0.857 - 22.62 \pm 1.97(a_w) + 10.76 \pm 1.87(a_w^2) \). X-error bars on the data points represent the ± 0.02 \( a_w \) and y-error bars represent one standard deviation calculated based on multiple viscosity measurements. Uncertainty in the parameterization (red shaded region) represent 95% confidence intervals.
Appendix B  Appendix to Chapter 3

B.1 Diffusion coefficients and viscosity data from literature sources and Chapter 3

Table B.3 lists diffusion coefficients of small and large molecules within organic-water matrices reported in the literature and included in Figures 3.6 and 3.8. Also included are the viscosities of the matrices. The following gives additional details on these diffusion coefficients and how the viscosities corresponding to the diffusion measurements were determined.

Chapter 3 reported diffusion coefficients of R6G in citric acid, sorbitol, and sucrose-citric acid solutions, and of cresyl violet in citric acid solution. Diffusion coefficients were measured at 295 ± 1 K and were reported as a function of $a_w$. The $a_w$ values were converted to viscosities using viscosity vs. $a_w$ parameterizations given in Appendix A, Figures A.1-A.3, based on viscosity data from Song et al. (2016) for citric acid and sorbitol, and based on viscosity data from Rovelli et al. (2019) for the sucrose-citric acid mixture. The citric acid, sorbitol, and sucrose-citric acid viscosity measurements were all performed at 293 ± 2 K.

Chenyakin et al. (2017) reported diffusion coefficients of fluorescein, R6G, and calcein in sucrose solutions as a function of $a_w$. The diffusion measurements were performed at 294.5 ± 1 K. The $a_w$ values were converted to viscosities using the viscosity vs. $a_w$ parameterization from Grayson et al. (2017, Figure S1) for sucrose solutions. The sucrose viscosity vs. $a_w$ parameterization given in Grayson et al. (2017) uses literature viscosity data (Först et al., 2002; Green and Perry, 2007; Haynes, 2001; Migliori et al., 2007; Power et al., 2013; Quintas et al., 2006; Swindells et al., 1958; Telis et al., 2007). The viscosity measurements were performed at 293 ± 2 K.

Price et al. (2014, 2016) reported diffusion coefficients of both water and sucrose in sucrose solutions as a function of $a_w$. The sucrose diffusion measurements were performed at 296 K. The water diffusion measurements were performed at 296.65 ± 0.3 K. In both cases the $a_w$ values were converted to viscosities using the viscosity vs. $a_w$ parameterization from Grayson et al. (2017) for sucrose solutions. The viscosity measurements were performed at 293 ± 2 K.

Bastelberger et al. (2017) reported diffusion coefficients of PEG-4 in sucrose-PEG-4-water mixtures as a function of both $a_w$ and mole fraction sucrose. PEG-4 is a polyethylene glycol
polymer with four repeat units. Only the diffusion measurements made at 292.65 K were included here. There are no measurements of the viscosity of sucrose-PEG-4-water solutions. Bastelberger et al. (2017) suggest using mole fractions to calculate viscosity for the system. They state that due to the very high viscosity of pure sucrose, the viscosity of the mixture will be dominated by sucrose, and the contribution of PEG-4 to the solution viscosity can be treated as water, to a first approximation. Following the suggestion of Bastelberger et al. (2017), the sucrose mole fraction values reported by Bastelberger et al. (2017) were used to calculate sucrose mass fraction values, and subsequently converted mass fraction sucrose to \(a_w\) using the parameterization given by Zobrist et al. (2011), assuming that the remainder of the solution is made up of water. Finally, viscosity was calculated using the viscosity vs. \(a_w\) parameterization from Grayson et al. (2017) for sucrose solutions. The viscosity measurements were performed at 293 ± 2 K.

Champion et al. (1997) reported diffusion coefficients of sucrose in sucrose solutions as a function of experimental temperature (\(T\)) minus the glass transition temperature (\(T_g\)). Champion et al. (1997) also reported the sucrose mass fraction of the solution used for each diffusion measurement. The \(T_g\) at each sucrose mass fraction was calculated using the Gordon-Taylor equation with parameters provided by Champion et al. (1997). The experimental temperature for each diffusion measurement was calculated using the reported \(T-T_g\) values and the calculated \(T_g\). The sucrose mass fraction was converted to \(a_w\) using the relation between sucrose mass fraction and \(a_w\) given in Zobrist (2011). Viscosity was calculated using the relation between viscosity and \(a_w\) given in Grayson et al. (2017) for sucrose solutions. The viscosity measurements were performed at 293 ± 2 K. Only diffusion coefficients measured between 292 – 298 K were taken from Champion et al. (1997).

Rampp et al. (2000) measured diffusion coefficients of sucrose in sucrose solutions as a function of temperature, and reported their results as parameters for the Vogel-Tammann-Fulcher (VTF) equation:

\[
D = D_0 e^{(-\frac{T_0C}{T-T_0})} 
\]  

where \(D\) is the diffusion coefficient (m\(^2\)/s), and \(D_0, T_0,\) and \(C\) are free parameters. \(D_0\) represents the expected diffusion at some value \(T_0\), and \(C\) is a fragility parameter. The VTF parameters were reported as a function of mass fraction sucrose. Diffusion coefficients were calculated using the
VTF equation and the reported VTF parameters for each mass fraction sucrose studied by Rampp et al. at 295 K. The sucrose mass fraction was then converted to $a_w$ using the parameterization given by Zobrist et al. (2011). Subsequently, $a_w$ was converted to viscosity using the relation between viscosity and $a_w$ in sucrose solutions given in Grayson et al. (2017). The viscosity measurements were performed at 293 ± 2 K.

Longinotti and Corti (2007) measured diffusion coefficients of ferrocene methanol in sucrose solutions and reported them as a function of mass fraction sucrose. Only measurements made at $T = 298.15$ K from Longinotti and Corti (2007) were used here. Mass fraction sucrose was converted to $a_w$ using the parameterization from Zobrist et al. (2011), and viscosity was calculated using the viscosity vs. $a_w$ parameterization of Grayson et al. (2017) for sucrose solutions. The viscosity measurements were performed at 293 ± 2 K.

Davies and Wilson (2016) reported diffusion coefficients of water in sucrose and citric acid solutions as a function of $a_w$, measured at 293 ± 2 K. The $a_w$ was converted to viscosity using the viscosity vs. $a_w$ parameterization of Grayson et al. (2017) for sucrose solutions, and using a viscosity vs. $a_w$ parameterization given in Appendix A (Figure A 1) for citric acid solutions, using viscosity data from Song et al. (2016). Both the sucrose and the citric acid viscosity measurements were performed at 293 ± 2 K.

Pollack (1981) reported diffusion coefficients of xenon in sucrose solutions (measured at 293.15 K) as a function of viscosity. This data was used directly in the current study.

Corti et al. (2008) measured diffusion coefficients of the fluorescent organic molecule fluorescein in sucrose solutions in the temperature range 292-298 K. Those measurements are not included here as they have been shown to be inconsistent with other literature measurements of large diffusing molecules in sucrose solutions (Price et al., 2016).

B.2 Discussion of uncertainty of literature viscosities

As mentioned in Chapter 3, the uncertainty in the viscosity data included in Figures 3.6 and 3.8 is approximately a factor of 10. In most cases, the viscosity was calculated from measured $a_w$ values and relationships between viscosity and $a_w$. The uncertainty in the viscosity is therefore a combination of the uncertainty in the viscosity-$a_w$ parameterization as well as an uncertainty in the $a_w$. When reported, the uncertainty in $a_w$ is either ± 0.02 or 0.025, and uncertainty in the
viscosity vs \(a_w\) parameterizations ranges from a factor of about ± 0.2 orders of magnitude (sucrose-water) to about ± 0.5 orders of magnitude (sucrose-citric acid) in viscosity at a given \(a_w\) (95% confidence bands). Combining these two uncertainties results in an average uncertainty in viscosity of approximately ± 1 order of magnitude. In the sucrose matrices the uncertainties in the viscosities range from about 0.4 orders of magnitude at low viscosity \((\eta = 10^0 \text{ Pa s})\) to about 1 order of magnitude at high viscosity \((\eta = 10^{10} \text{ Pa s})\). The specific uncertainties in the viscosities of the raffinose and sucrose-citric acid matrices in which measured diffusion coefficients were measured in Chapter 3 are given in Tables B1 and B2, and range from 0.63 to 1.15 orders of magnitude (sucrose-citric acid-water mixture) and 0.84 to 1.04 orders of magnitude (raffinose-water mixture).

In addition to the uncertainty in viscosity data shown in Figures 3.6 and 3.8, there is uncertainty associated with the measured diffusion coefficients. The new diffusion coefficients measured in this work are reported as the average of a minimum of five repeated measurements plus or minus two standard deviations. Those values are given in Tables B1 and B2. For other diffusion coefficients measured using FRAP (Chapter 2, Champion et al., 1997; Chenyakin et al., 2017) standard deviations are roughly between 10 to 100% of the measured values.
Table B.1 Measured diffusion coefficients and selected parameters used in preparing droplets containing cresyl violet in a raffinose-water mixture for rFRAP experiments. $\tau_{mix, H2O}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see Section 2.2.3 and Eq. 2.1). $t_{exp}$ is the experimental time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Max diameter (µm)</th>
<th>$\tau_{mix, H2O}$</th>
<th>$t_{exp}$</th>
<th>Log ($\eta$, Pa s) $^a$</th>
<th>Diffusion coefficient (m²/s) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51 ± 0.025</td>
<td>257</td>
<td>6 days</td>
<td>35 days</td>
<td>6.91 ± 1.04</td>
<td>2.63E-16 ± 2.24E-16</td>
</tr>
<tr>
<td>0.57 ± 0.025</td>
<td>500</td>
<td>4.5 days</td>
<td>19 days</td>
<td>5.42 ± 0.97</td>
<td>1.60E-15 ± 2.23E-16</td>
</tr>
<tr>
<td>0.70 ± 0.025</td>
<td>500</td>
<td>4 h</td>
<td>16 days</td>
<td>2.42 ± 0.87</td>
<td>2.54E-14 ± 2.81E-14 $^c$</td>
</tr>
<tr>
<td>0.75 ± 0.025</td>
<td>571</td>
<td>1.25 h</td>
<td>16 days</td>
<td>1.34 ± 0.84</td>
<td>3.95E-14 ± 4.16E-14</td>
</tr>
</tbody>
</table>

$^a$ The viscosity of raffinose was calculated using the viscosity-$a_w$ parameterization in Appendix B (Figure B.1). The uncertainty takes into account the uncertainty in $a_w$ and the uncertainty in the parameterization shown in Figure B.1 (95% confidence bands).

$^b$ The uncertainty in the measured diffusion coefficient corresponds to two times the standard deviation of a minimum of 5 diffusion measurements.

$^c$ In this case, the error (two times the standard deviation of the measurements) was larger than the average diffusion coefficient. 16 repeated measurements were performed at this condition. While most of the measurements agreed within a factor of two, one outlier was three times larger than the average diffusion coefficient.
**Table B.2** Measured diffusion coefficients and selected parameters used in preparing droplets containing cresyl violet in a sucrose-citric acid-water mixture for rFRAP experiments. $\tau_{\text{mix,H}_2\text{O}}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (see Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the experimental time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>Max diameter (µm)</th>
<th>$\tau_{\text{mix,H}_2\text{O}}$</th>
<th>$t_{\text{exp}}$</th>
<th>Log (η, Pa s)</th>
<th>Diffusion coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14 ± 0.025</td>
<td>242</td>
<td>78 h</td>
<td>19 days</td>
<td>6.60 ± 1.15</td>
<td>2.75E-18 ± 2.06E-18</td>
</tr>
<tr>
<td>0.23 ± 0.025</td>
<td>457</td>
<td>50 h</td>
<td>23 days</td>
<td>4.91 ± 1.00</td>
<td>1.61E-17 ± 7.60E-18</td>
</tr>
<tr>
<td>0.33 ± 0.025</td>
<td>457</td>
<td>8 h</td>
<td>1 day</td>
<td>3.24 ± 0.85</td>
<td>5.02E-16 ± 3.28E-16</td>
</tr>
<tr>
<td>0.43 ± 0.025</td>
<td>542</td>
<td>2 h</td>
<td>5 days</td>
<td>1.79 ± 0.73</td>
<td>3.27E-15 ± 8.85E-16</td>
</tr>
<tr>
<td>0.51 ± 0.025</td>
<td>714</td>
<td>1 h</td>
<td>5 days</td>
<td>0.79 ± 0.67</td>
<td>2.23E-14 ± 1.93E-14</td>
</tr>
<tr>
<td>0.57 ± 0.025</td>
<td>571</td>
<td>0.22 h</td>
<td>5 days</td>
<td>0.13 ± 0.63</td>
<td>6.49E-14 ± 4.29E-14</td>
</tr>
</tbody>
</table>

*The viscosity of sucrose-citric acid was calculated using the viscosity-$a_w$ parameterization in Appendix A (Figure A.3). The uncertainty takes into account the uncertainty in $a_w$ and the uncertainty in the viscosity-$a_w$ parameterization (95% confidence bands).*

*The uncertainty in the measured diffusion coefficient corresponds to two times the standard deviation of a minimum of 5 diffusion measurements.*
### Table B.3 Diffusion coefficients of small and large molecules within organic-water matrices reported in the literature, Chapter 2 of this thesis, and included in Figures 3.6 and 3.8. Also included are the viscosities of the organic-water mixtures and the $\xi$ values from the fits shown in Figures B2-B19. Entries are listed in order of decreasing $R_{\text{diff}}/R_{\text{matrix}}$.

<table>
<thead>
<tr>
<th>Reference for diffusion measurements</th>
<th>Diffusing molecule/organic solute</th>
<th>$R_{\text{diff}}/R_{\text{matrix}}$</th>
<th>Log (η)</th>
<th>Log (D$_{\text{meas}}$)</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 2</td>
<td>R6G/sorbitol</td>
<td>1.75</td>
<td>4.25</td>
<td>-16.78</td>
<td>0.927</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.31</td>
<td>-16.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.36</td>
<td>-13.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.61</td>
<td>-12.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.04</td>
<td>-12.70</td>
<td></td>
</tr>
<tr>
<td>Chapter 2</td>
<td>R6G/citric acid</td>
<td>1.59</td>
<td>2.92</td>
<td>-14.50</td>
<td>0.888</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.82</td>
<td>-13.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.85</td>
<td>-12.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.16</td>
<td>-12.25</td>
<td></td>
</tr>
<tr>
<td></td>
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Figure B.1 Viscosity of raffinose-water solutions as a function of $a_w$. Viscosity data come from Grayson et al. (2017) and Song et al. (2016). A second order polynomial was fit to the data, with the resulting equation $\log(\eta, \text{Pa s}) = 22.15 - (34.42 \times a_w) + (8.907 \times a_w^2)$. X-error bars correspond to the uncertainty in the $a_w$ (0.025 for Grayson et al. (2017) and 0.02 for Song et al. (2016)). Y-error bars represent deviations between multiple measurements at the same $a_w$. The y-error bars for Grayson et al. (2017) represent two standard deviations, and the y-error bars for Song et al. (2016) represent one standard deviation. Viscosity measurements from Song et al. (2016) were made at a temperature of 293 ± 2 K, and viscosity measurements from Grayson et al. (2017) were made at a temperature of 294-295 K.
Figure B.2 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system cresyl violet in raffinose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.

Figure B.3 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system cresyl violet in sucrose-citric acid. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.
Figure B.4 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system R6G in sorbitol. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.

Figure B.5 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system R6G in citric acid. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.
Figure B.6 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system R6G in sucrose-citric acid. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\zeta\) value is the standard error of the slope.

Figure B.7 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system R6G in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\zeta\) value is the standard error of the slope.
Figure B.8 Log \((D/D_0)\) as a function of log \((\eta/\eta_0)\) for the system fluorescein in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\zeta\) value is the standard error of the slope.

Figure B.9 Log \((D/D_0)\) as a function of log \((\eta/\eta_0)\) for the system fluorescein in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\zeta\) value is the standard error of the slope.
Figure B.10 Log \( (D/D_0) \) as a function of log \( (\eta_0/\eta) \) for the system calcein in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \( \xi \) value is the standard error of the slope.

Figure B.11 Log \( (D/D_0) \) as a function of log \( (\eta_0/\eta) \) for the system cresyl violet in citric acid. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \( \xi \) value is the standard error of the slope.
Figure B.12 Log ($D/D_0$) as a function of log ($\eta_0/\eta$) for the system sucrose in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the $\xi$ value is the standard error of the slope.

Figure B.13 Log ($D/D_0$) as a function of log ($\eta_0/\eta$) for the system sucrose in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the $\xi$ value is the standard error of the slope.
Figure B.14 Log \( \frac{D}{D_0} \) as a function of log \( \frac{\eta_0}{\eta} \) for the system PEG-4 in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \( \xi \) value is the standard error of the slope.

Figure B.15 Log \( \frac{D}{D_0} \) as a function of log \( \frac{\eta_0}{\eta} \) for the system ferrocene methanol in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \( \xi \) value is the standard error of the slope.
Figure B.16 Log \( (D/D_0) \) as a function of log \( (\eta_0/\eta) \) for the system xenon in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \( \zeta \) value is the standard error of the slope.

Figure B.17 Log \( (D/D_0) \) as a function of log \( (\eta_0/\eta) \) for the system water in citric acid. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point (0,0). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \( \zeta \) value is the standard error of the slope.
Figure B.18 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system water in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.

Figure B.19 Log \((D/D_0)\) as a function of log \((\eta_0/\eta)\) for the system water in sucrose. The black squares represent measured diffusion coefficients, while the solid line represents a linear best fit to the data, with the constraint that the line passes through the point \((0,0)\). The dashed lines indicate an order of magnitude uncertainty. The factor of ten was chosen as it approximates the average uncertainty in the viscosity measurements (Section B2). The reported uncertainty in the \(\xi\) value is the standard error of the slope.
Appendix C  Appendix to Chapter 5

Table C.1 Selected parameters used in preparing droplets containing RBID in an erythritol-water mixture for rFRAP experiments and measured diffusion coefficients. $\tau_{\text{mix,H2O}}$ is the calculated characteristic mixing time for molecular diffusion of water in the droplets (Section 2.2.3 and Eq. 2.1). $t_{\text{exp}}$ is the time used for conditioning the droplets at a given relative humidity.

<table>
<thead>
<tr>
<th>$a_w$ (±)</th>
<th>Max diameter (µm)</th>
<th>$\tau_{\text{mix,H2O}}$ (calculated) at $a_w$ lower limit $^a$</th>
<th>$t_{\text{exp}}$</th>
<th>Diffusion coefficient (m$^2$/s) $^b$</th>
<th>Viscosity (Pa s) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\tau_{\text{mix,H2O}}$ at $a_w$ lower limit $^a$</td>
<td>$t_{\text{exp}}$</td>
<td>Mean</td>
<td>Upper limit</td>
</tr>
<tr>
<td>0.019 ± 0.019</td>
<td>200</td>
<td>3.3 h</td>
<td>80 h</td>
<td>1.19 x 10$^{-15}$</td>
<td>1.63 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.023 ± 0.023</td>
<td>200</td>
<td>3.3 h</td>
<td>24 h</td>
<td>3.35 x 10$^{-15}$</td>
<td>4.17 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.047 ± 0.047</td>
<td>200</td>
<td>3.3 h</td>
<td>21.5 h</td>
<td>1.47 x 10$^{-15}$</td>
<td>3.43 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.053 ± 0.053</td>
<td>200</td>
<td>3.3 h</td>
<td>48 h</td>
<td>2.76 x 10$^{-15}$</td>
<td>4.81 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.050 ± 0.050</td>
<td>200</td>
<td>3.3 h</td>
<td>72 h</td>
<td>2.36 x 10$^{-15}$</td>
<td>4.12 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.048 ± 0.048</td>
<td>200</td>
<td>3.3 h</td>
<td>96 h</td>
<td>6.36 x 10$^{-15}$</td>
<td>1.00 x 10$^{-14}$</td>
</tr>
<tr>
<td>0.153 ± 0.025</td>
<td>370</td>
<td>3.6 h</td>
<td>65 h</td>
<td>5.02 x 10$^{-15}$</td>
<td>7.73 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.261 ± 0.025</td>
<td>300</td>
<td>1.7 h</td>
<td>48 h</td>
<td>1.67 x 10$^{-14}$</td>
<td>2.21 x 10$^{-14}$</td>
</tr>
<tr>
<td>0.514 ± 0.025</td>
<td>340</td>
<td>0.41 h</td>
<td>68 h</td>
<td>2.86 x 10$^{-13}$</td>
<td>3.52 x 10$^{-13}$</td>
</tr>
</tbody>
</table>

$^a$ $\tau_{\text{mix,H2O}}$ is the calculated characteristic time for water molecules to diffuse within erythritol-water droplets of specified radii at the lower limit of $a_w$, corresponding to the upper limit of droplet viscosity.

$^b$ The reported RBID diffusion coefficients are the result of a minimum of four repeated measurements on separate thin films.

$^c$ The reported viscosities are calculated using the measured diffusion coefficients and the Stokes-Einstein relation.
Table C.2 Viscosity of erythritol at $a_w < 0.1$ measured using the optical tweezers technique in this study.

<table>
<thead>
<tr>
<th>$a_w$</th>
<th>log (viscosity, Pa s)</th>
<th>Viscosity (Pa s)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Upper limit</td>
</tr>
<tr>
<td>0.040 ± 0.020</td>
<td>3.04 ± 0.92</td>
<td>1.10 x $10^3$</td>
<td>9.12 x $10^3$</td>
</tr>
<tr>
<td>0.085 ± 0.020</td>
<td>2.32 ± 1.68</td>
<td>2.09 x $10^2$</td>
<td>1.00 x $10^4$</td>
</tr>
</tbody>
</table>

Table C.3 Literature viscosity data included in Figure 5.11 in Chapter 5.

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Viscosity (Pa s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane</td>
<td>n-butane</td>
<td>$1.8 \times 10^{-4}$ $^a$</td>
<td>Rothfuss and Petters (2017)</td>
</tr>
<tr>
<td>Alcohol</td>
<td>1-butanol</td>
<td>$2.9 \times 10^{-3}$ $^a$</td>
<td>Rothfuss and Petters (2017)</td>
</tr>
<tr>
<td>Alcohol</td>
<td>2-butanol</td>
<td>$3.7 \times 10^{-3}$ $^a$</td>
<td>Rothfuss and Petters (2017)</td>
</tr>
<tr>
<td>Diol</td>
<td>1,2-butanediol</td>
<td>$6.6 \times 10^{-2}$ $^a$</td>
<td>Rothfuss and Petters (2017)</td>
</tr>
<tr>
<td>Diol</td>
<td>1,4-butanediol</td>
<td>$9.1 \times 10^{-2}$ $^a$</td>
<td>Rothfuss and Petters (2017)</td>
</tr>
<tr>
<td>Diol</td>
<td>2,3-butanediol</td>
<td>$1.3 \times 10^{-1}$ $^a$</td>
<td>Rothfuss and Petters (2017)</td>
</tr>
<tr>
<td>Triol</td>
<td>1,2,3-butanetriol</td>
<td>$1.6 \times 10^{0}$ $(1.5 \times 10^{0} - 1.7 \times 10^{0})$ $^b$</td>
<td>Grayson et al. (2017)</td>
</tr>
<tr>
<td>Triol</td>
<td>1,2,4-butanetriol</td>
<td>$1.8 \times 10^{0}$ $(1.0 \times 10^{0} - 3.1 \times 10^{0})$ $^a$</td>
<td>Song et al. (2016)</td>
</tr>
</tbody>
</table>

$^a$ Viscosity data at 293 K were estimated using the parameterization of viscosity as a function of temperature given in specified references.

$^b$ Measurement was performed at 295 K using a rotational rheometer.