

**ARE DIFFUSION COEFFICIENTS CALCULATED USING THE
STOKES-EINSTEIN EQUATION COMBINED WITH VISCOSITIES
CONSISTENT WITH MEASURED DIFFUSION COEFFICIENTS
OF TRACER ORGANICS WITHIN ORGANICS-WATER MEDIUMS?**

by

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B.Sc., The University of Waterloo, 2012

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Chemistry)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

June 2015

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Abstract

Recently, rates of molecular diffusion of organic species within organic-water particles of atmospheric relevance have become an area of intense research. This is because molecular diffusion rates are required for predicting rates of growth and reactivity of organic-water particles in the atmosphere. Due to the shortage of information on the topic, fluorescence recovery after photobleaching (FRAP) was used to measure the diffusion coefficients of three organic tracer dyes in sucrose-water aqueous solutions that serve as proxies for organic-water particles in the atmosphere. Organic tracer dyes used were fluorescein isothiocyanate (FITC)–dextran (molecular weight (MW) of 1.50×10^5 g/mol, hydrodynamic radius (R_H) of 83.1 Å), calcein (MW of 622 g/mol, R_H = 7.4 Å) and fluorescein sodium salt (fluorescein) (MW of 376 g/mol, R_H = 5.02 Å). For FITC-dextran, diffusion coefficients ranging from 12.6 – 1.53×10^{-2} $\mu\text{m}^2/\text{s}$ were measured for water activities (a_w) ranging from 0.99 to 0.75. For calcein, diffusion coefficients ranging from 4.10 – 1.65×10^{-3} $\mu\text{m}^2/\text{s}$ were measured for a_w from 0.88 to 0.65. For fluorescein, diffusion coefficients ranging from 7.09 – 2.51×10^{-4} $\mu\text{m}^2/\text{s}$ for a_w ranging from 0.88 to 0.50. The results in this dissertation showed that Stokes-Einstein equation is still valid for molecules at the size scale of fluorescein in sucrose-water mixtures when the $a_w \geq 0.50$. This corresponds to viscosities $\leq 10^4$ Pa·s and $T_g/T \leq 0.87$. This is consistent with the previous studies by Champion et al. (1997) who also observed consistency between the Stokes-Einstein equation and measurements when $T_g/T \leq 0.86$ when studying diffusion of fluorescein in sucrose- water mixtures. However, the results are inconsistent with the studies by Corti et al. (2008a) who showed decoupling between the Stokes-Einstein equation and viscosity measurements when $T_g/T > 0.65$.

Preface

Chapters 3 and 4 (to be prepared for submission):

- Identified research question with help from supervisor.
- Designed experimental setup and procedures.
- Prepared all sucrose-water films at various relative humidities.
- Performed all fluorescence recovery after photobleaching experiments.
- Conducted data analysis with Dr. Saeid Kamal.
- Prepared all figures for the manuscript.
- Shared manuscript preparation with my supervisor.

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List of Symbols

a_w	water activity
Ar	argon
Cl^-	chloride
D	diffusion coefficient
D_{water}	diffusion coefficient of water
erf	error function
F	force
f	frictional coefficient
F_0	intensity prior to photobleaching
$F(x, t)$	fluorescence recovery at a time t and position x after photobleaching
$F(x, y, t)$	fluorescence recovery at a time t and positions x and y after photobleaching
Hz	Hertz
K	Kelvin
k	Boltzmann constant
K_0	fraction of photobleached molecules
l_x	length of the photobleached square in the x direction
l_y	length of the photobleached square in the y direction
$M\Omega \cdot cm$	resistivity (measure of water purity)
N_2	nitrogen gas
NH_4^+	ammonium
NO_3^-	nitrate

P_{H_2O}	water vapour pressure
$P_{H_2O,sat}$	saturation water vapour pressure
$R_{droplet}$	radius of a spherical droplet
r	resolution parameter of the microscope
R_H	hydrodynamic radius
SO_4^{2-}	sulfate
T	temperature
t	elapsed time during recovery
T_g	glass transition temperature
$T^\ominus$	reference temperature of 298.15 K
v	velocity
wt %	weight percent
X_{H_2O}	mole fraction of water
π	pi
τ	time required for an aqueous spherical droplet to come to equilibration with the surrounding RH
γ_{H_2O}	activity coefficient of water
η	dynamic viscosity
$^\circ\text{C}$	Celsius

List of Abbreviations

AMS	atomic mass spectrometry
CGSS	chemistry graduate student society
CREATE-AAP	collaborative research and training experience - atmospheric aerosol program
FD150	fluorescein isothiocyanate-dextran, average molecular weight of 150 000 g/mol
FITC	fluorescein isothiocyanate
Fluorescein	fluorescein sodium salt
FRAP	fluorescence recovery after photobleaching
MW	molecular weight
MW _{FITC-dextran}	molecular weight of FITC-dextran
POM	primary organic material
RH	relative humidity
ROI	region of interest
SOM	secondary organic material
SVOC	semivolatile organic compound
VOC	volatile organic compound

Acknowledgements

I will start by thanking my supervisor, Dr. Allan Bertram, for accepting me into his group and CREATE-AAP, and letting me work on this very interesting project. Allan, thank you for all your hard work and support while I was performing experiments and writing my thesis. I had a great experience working for 2.5 years with you and learned a lot about physical, analytical and atmospheric chemistry. Thanks for everything!

I would also like to thank Dr. Saeid Kamal, for teaching me how to perform FRAP experiments and writing me a script for data analysis. Saeid, thank you for meeting with me on a regular basis and going through my data to ensure I was on the right track. Thank you for teaching me a lot about microscopy and always being so friendly and helpful. Thank you Saeid!

I would like to thank all the Bertram group members, past and present, you are: Ryan, Vickie, Dagny, Jason, Yuan, Donna, Meng, Mijung, Stephen, Lindsay, Michael, James, Kaitlin, Cédric, Sarah and all co-op and visiting students. Thank you all for creating such a stimulating and fun working environment in our lab, always there to give a hand if needed, and always there to have a laugh or two. Thanks guys!

Thanks to the faculty and staff of the Chemistry Department, for making our department such a great place for studying and doing research. Thanks to everyone in the mech shop and chem stores for being very helpful every time I was there. Thank you CGSS for organizing all the fun events. Also, thanks Maki from CREATE-AAP for always being very helpful. Thank you Dr. Jay Wickenden for nominating me to win the T.A. award.

I would especially like to thank my parents, Vladimir and Elena, for their love and support throughout my life. Thanks to my brother, Viktor, who could always make me laugh under any circumstances. Thanks for always saying that you are proud of me at the end of every

phone call. Also thanks to Nadia, Masha and Sasha for always being so friendly and kind every time I saw you, I am proud to call you my family.

I will end by thanking the love of my life and my one and only, Alexandra Sigouin, thank you for your never-ending love and great support in everything I do. Your genuine kindness, amazing smile, out of this world hugs – you are everything I ever wanted, and more – you are amazing in every kind of way. I will love you forever and ever!

To my parents, Vladimir and Elena, and to my brother, Viktor.

Chapter 1: Introduction

1.1 Introduction to atmospheric particles

Atmospheric particles, which are abundant in the atmosphere, range in size from 1 nm (size of a cluster of molecules) to about 20 μm . Concentrations of these particles range from 10^2 to 10^8 cm^{-3} . Based on the mechanism of production, atmospheric particles can be classified as primary or secondary. Primary particles are emitted directly into the atmosphere from a variety of natural sources (e.g. forest fires, dust storms and sea spray) and anthropogenic sources (e.g. stationary fossil fuel burning, traffic and agricultural activities). Secondary particles are formed in the atmosphere from gas-to-particle conversion of gas-phase species, such as volatile organic compounds (VOCs), that were emitted from natural (e.g. forest fires), biological (e.g. vegetation) and anthropogenic sources (e.g. fossil fuel burning) (Finlayson-Pitts and Pitts Jr, 2000; Seinfeld and Pandis, 2006).

1.2 Importance of atmospheric particles

Atmospheric particles have important implications on climate, visibility and health. Particles directly impact climate by scattering solar radiation or indirectly by acting as cloud condensation nuclei or ice nuclei (Boucher et al., 2013). In addition, particles lead to reduced visibility or “haze” in both polluted areas (e.g. large cities) and rural areas (e.g. national parks) (Gieré and Querol, 2010). Particles have also been shown to be linked with short and long term adverse health effects such as asthma and chronic obstructive pulmonary disease (Nel, 2005; Pope III, 2002; Smith et al., 2014). Furthermore, particles can influence the chemistry of the atmosphere, by providing a medium for reactions to occur (George and Abbatt, 2010).

1.3 Composition of atmospheric particles

Atmospheric particles are composed of inorganic or organic compounds or a combination of both. The number of inorganic constituents is relatively small, and NH_4^+ , SO_4^{2-} , NO_3^- and Cl^- are known to be important (Seinfeld and Pandis, 2006). On the other hand, the organic fraction of a submicron particle is much more complex and consists of thousands of different compounds. Only about 10% of organic compounds in atmospheric particles have been identified on a molecular level (Hallquist et al., 2009). Chemical characterization of the organic compounds has been a challenge due to the large amount of compounds and their large range of physical and chemical properties such as molecular weight and volatility (Decesari et al., 2006; Goldstein and Galbally, 2007; Hallquist et al., 2009; Hamilton et al., 2004; Jimenez et al., 2009).

Another important component of atmospheric particles is water. The relative humidity (RH) in the atmosphere is described with the following equation (Murphy and Koop, 2005a; Seinfeld and Pandis, 2006):

$$RH = \frac{P_{H_2O}}{P_{H_2O,sat}} \times 100 \quad (1.1)$$

where P_{H_2O} is water vapour pressure and $P_{H_2O,sat}$ is the saturation water vapour pressure. In addition, the water activity, a_w , in particles is described with the following equation (Murphy and Koop, 2005b; Seinfeld and Pandis, 2006):

$$a_w = \gamma_{H_2O} X_{H_2O} \quad (1.2)$$

where γ_{H_2O} is the activity coefficient of water and X_{H_2O} is the mole fraction of water in the particle phase. In the atmosphere the RH typically varies from 20% to 100% (Hamed et al., 2011; Held and Soden, 2000; Martin, 2000). As the RH changes, a_w in the particles adjusts to maintain equilibrium between the gas and particle phase. At equilibrium, a_w in the particles

equals $RH/100$ in the gas phase. As a result, in the atmosphere a_w in the particles typically varies from 0.2 to 1.

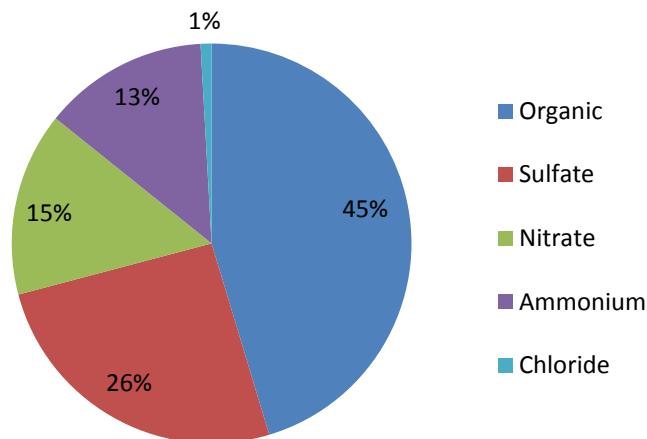


Figure 1.1 Average chemical compositions of submicron particles found in the atmosphere (not including the water content) determined from 30 field studies around the world. Data were taken from Jimenez et al. (2009).

Figure 1.1 summarizes the average chemical composition of submicron particles (not including the water content) from 30 field studies (urban and remote) around the world measured by aerosol mass spectrometer (AMS). Based on Figure 1.1, submicron particles found in the atmosphere on average consists of approximately 45% of organic material by mass (not including water content). The organic material within organic particles can be classified as primary organic material (POM) or secondary organic material (SOM). POM is directly emitted into the atmosphere in the particulate form, while SOM forms in the atmosphere from oxidation of volatile organic material and then gas-to-particle conversion of the oxidized material (Hallquist et al., 2009).

1.4 Thesis focus

This thesis focuses on properties of atmospherically relevant particles containing organics and water. More specifically this thesis focuses on diffusion rates of organic species within particles consisting of organics and water. Recently, rates of molecular diffusion of organic species within organic-water particles of atmospheric relevance have become an area of intense research. One reason this area has received intense focus is because the mechanism and growth rate of organic-water particles can depend on diffusion rates within these particles (see Figure 1.2), with implications for predictions of mass concentration, number concentration and mode diameter of particles in the atmosphere (Riipinen et al., 2011; Shiraiwa and Seinfeld, 2012). Organic-water particles grow by the uptake of oxidized semivolatile organic compounds. As illustrated in Figure 1.2, if diffusion rates of organics are fast within particles, particles may grow by an absorption type mechanism and reach larger sizes, while if diffusion rates are slow within the particles, particles may only grow by an adsorption type mechanism.

Another reason why rates of molecular diffusion of organic species within atmospheric particles containing organics and water have become an area of intense research is because diffusion rates within organic-water particles can influence reaction rates between organic species and oxidants within the particles. Hence, a better understanding of diffusion rates of organic species is needed for predicting oxidation rates within organic-water particles (Shiraiwa et al., 2011).

To estimate diffusion coefficients of organic species within organic-water particles of atmospheric relevance researchers have measured viscosities of organic-water particles and then calculated diffusion coefficients using the Stokes-Einstein equation (Hosny et al., 2013; Koop et al., 2011; Power et al., 2013; Renbaum-Wolff et al., 2013a, 2013b). In previous studies, it was

assumed that the Stokes-Einstein equation is accurate for predicting diffusion rates of organics in organic-water particles of atmospheric relevance; however, this assumption has not been thoroughly tested.

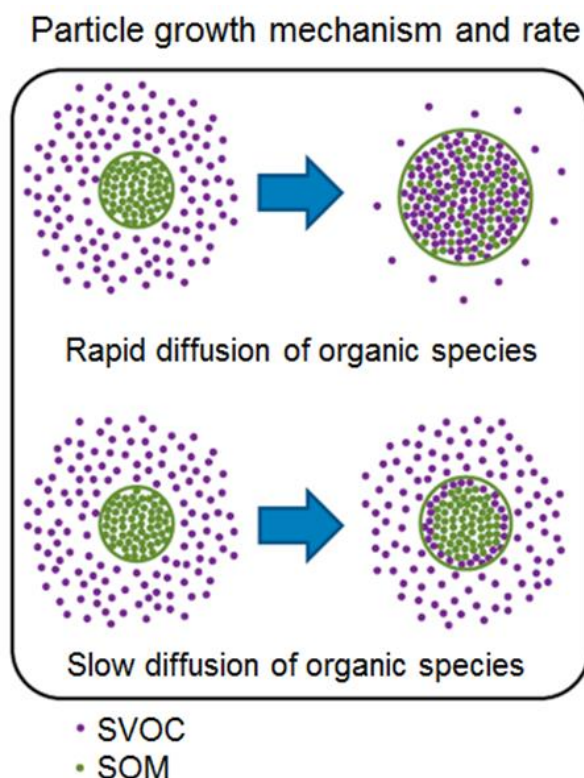


Figure 1.2 Effect of diffusion rates on the mechanism of growth of a particle by semivolatile organic compound (SVOC) uptake. Figure modified from Renbaum-Wolff et al. (2013a).

To test the applicability of the Stokes-Einstein equation to organic-water particles of atmospheric relevance, we measured directly diffusion rates of tracer organic molecules within proxies for organic-water particles found in the atmosphere and then compared the results with predictions of diffusion rates based on the Stokes-Einstein equation. As proxies of organic-water particles found in the atmosphere, we used mixtures of sucrose and water covering a range of water activities. Sucrose-water solutions were chosen because water activity dependent viscosities of these solutions are similar in some respects to the water activity dependent

viscosities of some secondary organic material (Bones et al., 2012; Renbaum-Wolff et al., 2013a). In addition, the viscosities of sucrose-water solutions are known for a wide range of water activities, allowing us to test the Stokes-Einstein equation over a wide range of water activities (see Figure 2.1). Since viscosity can depend strongly on water activity, it is important to test the Stokes-Einstein equation over a range of water activity values including water activities typically found in the atmosphere.

Chapter 2: Background Information

2.1 Derivation of the Stokes-Einstein equation

The Stokes-Einstein equation was first derived by Einstein to estimate the diffusion coefficient of a spherical particle suspended in a liquid or gas undergoing Brownian motion (random motion) at constant temperature and viscosity (Einstein, 1905). The Stokes-Einstein equation is derived as follows (Edward, 1970): Einstein showed that the drag force (F) of a colloid particle moving through a viscous medium with velocity v , due to Brownian motion can be described by the following equation:

$$F = vf \quad (2.1)$$

Where f is the frictional coefficient of the particle. Einstein then showed that the diffusion coefficient (D) of a particle can be described by:

$$D = kT/f \quad (2.2)$$

Where k is the Boltzmann constant, T is temperature and f is the frictional coefficient that impedes the diffusion. The Stokes part of the equation comes from the description that frictional coefficient f of a spherical particle of radius R_H moving with uniform velocity in a continuous medium of viscosity η is given by:

$$f = 6\pi\eta R_H \quad (2.3)$$

Einstein then combined his equation (2.2) with Stokes equation (2.3) to get the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\eta R_H} \quad (2.4)$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is temperature, η is the dynamic viscosity and R_H is the hydrodynamic radius (or Stokes radius) of the diffusing species. Equation 2.4, was derived for the motion of colloidal particles through a fluid. Hence, Equation 2.4 should be applicable for fluid cases where the diffusing molecules are much larger than the matrix molecules, and measurements of diffusion coefficients are consistent with this assumption (Braeckmans et al., 2003; Edward, 1970; Levine, 2008). Stokes' Equation 2.3 ($f = 6\pi\eta R_H$), was derived assuming that the movement of a spherical particle with uniform velocity is impeded by the interactions with fluid molecules in front of it ($f = 4\pi\eta R_H$) and parallel to its surface ($f = 2\pi\eta R_H$), and the addition of these two frictional coefficients gives Equation 2.3 ($f = 6\pi\eta R_H$) (Edward, 1970). Therefore, Stokes-Einstein equation (Equation 2.4) was derived assuming there is no slip at the surface of the diffusing particle (the diffusing particle is impeded by interactions with fluid molecules parallel to its surface). In cases where the fluid does not stick to the diffusing species, fluid mechanics suggests that the factor 6 should be replaced with a 4 in Equation 2.4 (Edward, 1970; Levine, 2008).

2.2 Previous tests of the Stokes-Einstein equation

Research has shown that the Stokes-Einstein equation gives accurate values of diffusion rates when the diffusing molecule is larger in size than the molecules that make up the solvent (Braeckmans et al., 2003; Edward, 1970; Levine, 2008). However, previous studies showed that when the size of the diffusing molecules are smaller than the matrix molecules they diffuse more rapidly than predicted by the Stokes-Einstein equation (Edward, 1970; Longinotti and Corti, 2007; Price et al., 2014; Rampp et al., 2000). It was also shown that the Stokes-Einstein equation deviates from measured diffusion coefficients when viscosity of the medium approaches that of a

glass ($\sim 10^{12}$ Pa·s – see Figure 2.1) (Champion et al., 1997; Corti et al., 2008b; Parker and Ring, 1995; Power et al., 2013; Rampp et al., 2000; Zhu et al., 2011). Shown in Table 2.1 is a summary of past studies that showed the break-down of the Stokes-Einstein equation as well as the T_g/T (T_g being the glass transition temperature of the matrix and T being the temperature at which the experiment was performed) value where break-down was observed.

Table 2.1 Summary of past studies that showed the break-down of the Stokes-Einstein equation.

Study	Matrix studied (and molecular weight of matrix)	Diffusing molecule (and molecular weight of diffusing molecules)	T_g/T where break-down of Stokes-Einstein was observed
Champion et al. (1997)	Sucrose-water (360 g/mol)	Fluorescein (376 g/mol)	>0.86
Corti et al. (2008a)	Sucrose-water (360 g/mol)	Fluorescein (376 g/mol)	>0.65
Corti et al. (2008b)	Trehalose-water (360 g/mol)	Fluorescein (376 g/mol)	>0.60
Longinotti and Corti (2007)	Sucrose-water (360 g/mol)	Ferrocenemethanol (216 g/mol)	>0.75
Price et al. (2014)	Sucrose-water (360 g/mol)	Water (18 g/mol)	>0.68
Rampp et al. (2000)	Sucrose/trehalose/ allosucrose/leucrose– water (360 g/mol)	Self-diffusion coefficient of water (18 g/mol) and sugar of matrix (sucrose, trehalose, allosucrose or leucrose) (molecular weight of each sugar = 342 g/mol)	>0.55 for both water and sugar

In this work organic dyes of different sizes were used to determine if the Stokes-Einstein equation is valid for a range of sizes and conditions that may be relevant and appropriate for the atmosphere.

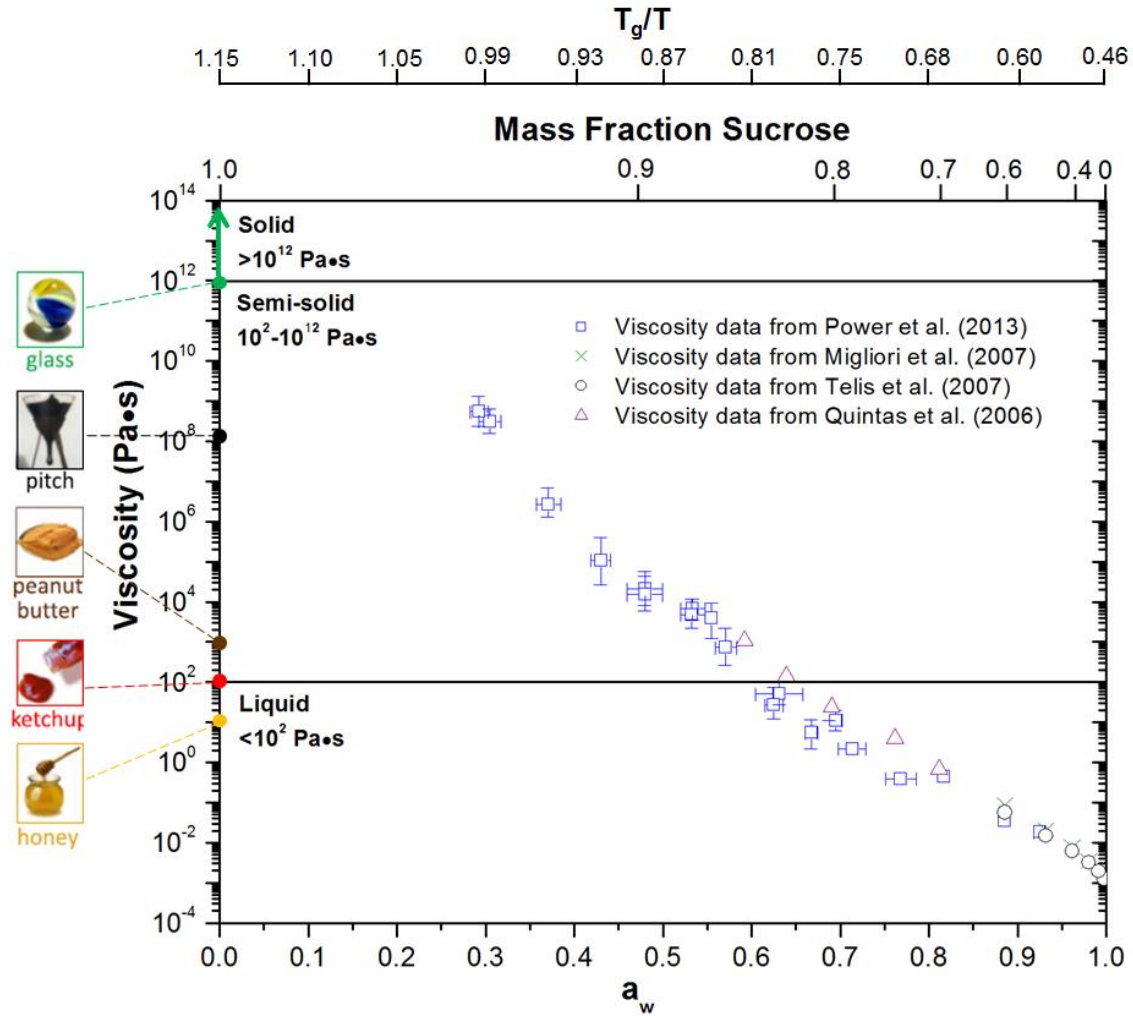


Figure 2.1 Viscosity measurements at 20 °C of aqueous sucrose solutions as a function of a_w obtained from Power et al. (2013) (blue squares), Migliori et al. (2007) (green crosses), Telis et al. (2007) (black circles) and Quintas et al. (2006) (purple triangles). Approximate viscosity values at 20 °C of common substances is also shown on the diagram to give a better understanding of viscosity values. Substances in the liquid state have viscosity values of $<10^2$ Pa·s, at the semi-solid state of 10^2 - 10^{12} Pa·s and the solid state of $>10^{12}$ Pa·s. The glass transition viscosity is at $\sim 10^{12}$ Pa·s. Figure obtained and modified from Renbaum-Wolff et al. (2013a).

Chapter 3: Experimental

To measure diffusion rates of organic tracer molecules within sucrose-water solutions we used fluorescence recovery after photobleaching (FRAP). The FRAP technique has often been utilized in the biological and materials science communities to measure diffusion coefficients in biological materials, single cells, and organic polymers (Braeckmans et al., 2003, 2007; Deschout et al., 2010; Hatzigrigoriou et al., 2011; Seksek et al., 1997; Smith and McConnell, 1978).

To utilize the FRAP technique, first a thin film (approximately 30-50 μm thick) of a sucrose-water solution with a known a_w and containing trace amounts of a fluorescent probe molecules (≤ 0.5 wt%) were generated (see Section 3.1). Then the FRAP technique was used to determine the rate of diffusion of the fluorescent probe molecules in the sucrose-water solutions (see Section 3.2).

3.1 Production of thin films of a sucrose-water solutions containing trace amounts of a fluorescence probe molecules

Three organic dyes (fluorescein isothiocyanate-dextran, calcein, and fluorescein sodium salt) were used in this study. Figure 3.1 shows the structures of the dyes used and Table 3.1 lists the dyes as well as their molecular weight (MW) and hydrodynamic radius (R_H). Although, there have been previous studies of diffusion of fluorescein sodium salt (fluorescein) in sucrose-water mixtures, fluorescein was chosen because there is discrepancy in the literature on the conditions at which deviations from the Stokes-Einstein equation occurs for this dye (see Table 2.1), and in addition this dye is similar in size to organic molecules found in secondary organic particles in

the atmosphere. Calcein was chosen for this study since there have been no previous studies of the diffusion of calcein in sucrose-water systems and this dye is also similar in size to some organic molecules found in atmospheric secondary organic particles. The dye fluorescein isothiocyanate (FITC)-dextran was chosen because it is a relative large molecule and hence diffusion rates for this dye in sucrose-water solutions should be consistent with the Stokes-Einstein equation, since in this case the FITC molecule is much larger than the matrix molecules (i.e. sucrose and water).

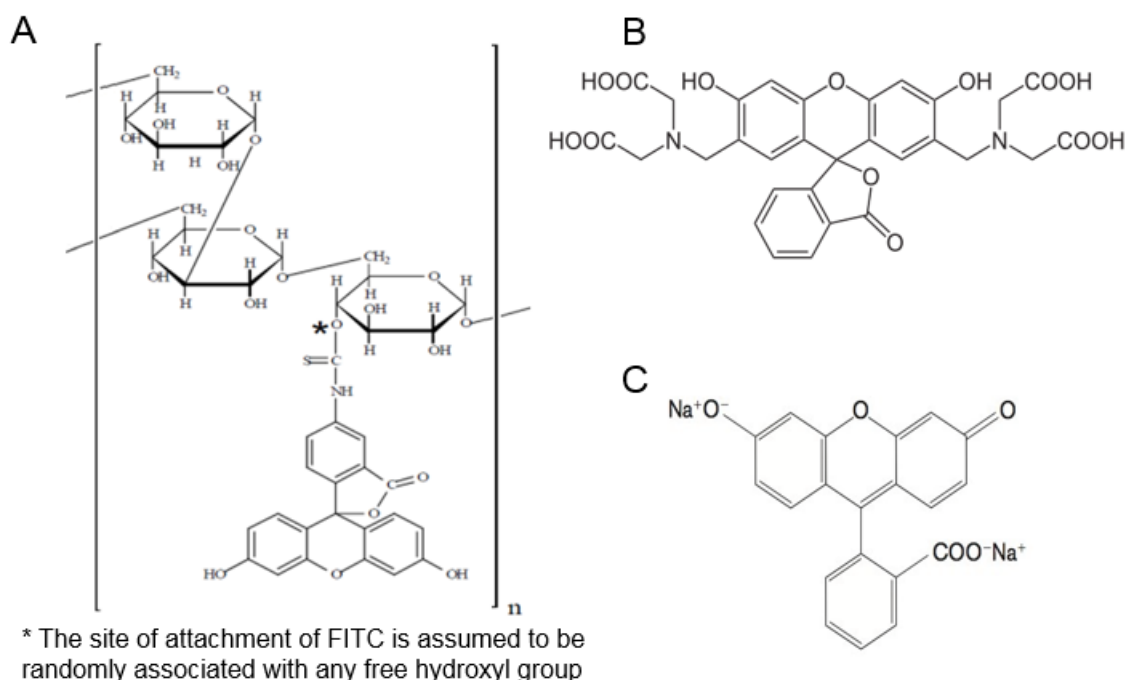


Figure 3.1 Organic dyes used in this work. A) Fluorescein isothiocyanate–dextran of average MW of 150, 000 g/mol (FD150). B) Calcein. C) Fluorescein sodium salt (fluorescein).

The concentrations of the dyes used in the FRAP experiments are listed in Table 3.1. Values were chosen so that the concentrations were small enough to not influence significantly the properties (e.g. viscosity) of the sucrose-water solutions, and the fluorescence signal was large enough to detect in the FRAP experiments, and the fluorescence signal was also linear with

concentration of the fluorescence dyes. To determine the values at which the fluorescence signal was linear with concentration and the signal was large enough for the FRAP experiments, we carried out a series of measurements where we determined the fluorescence signal as a function of the dye concentration in pure water films (see Figures 3.2-3.4). To dissolve calcein in water and the sucrose-water solutions small amounts of NaOH was required (<0.5 wt%). For the other cases the dyes dissolved completely at the concentrations studied.

Table 3.1 Organic dyes, their molecular weight (MW), hydrodynamic radius (R_H) and concentration that were used in this work.

Organic dye (acronym used in this work)	MW (g/mol)	R_H (Å)	Concentration (mM)
Fluorescein isothiocyanate– dextran (FD150)	1.50×10^5	83.1 (error range of 65.4-105.4) (Smedt et al., 1994)	0.02
Calcein	622	7.4 (error range of 6.0- 8.0) (value reported by Tamba et al., (2010) and range reported by Edwards et al., (1995))	0.3
Fluorescein sodium salt (fluorescein)	376	5.02 ± 0.14 (Mustafa et al., 1993)	0.8

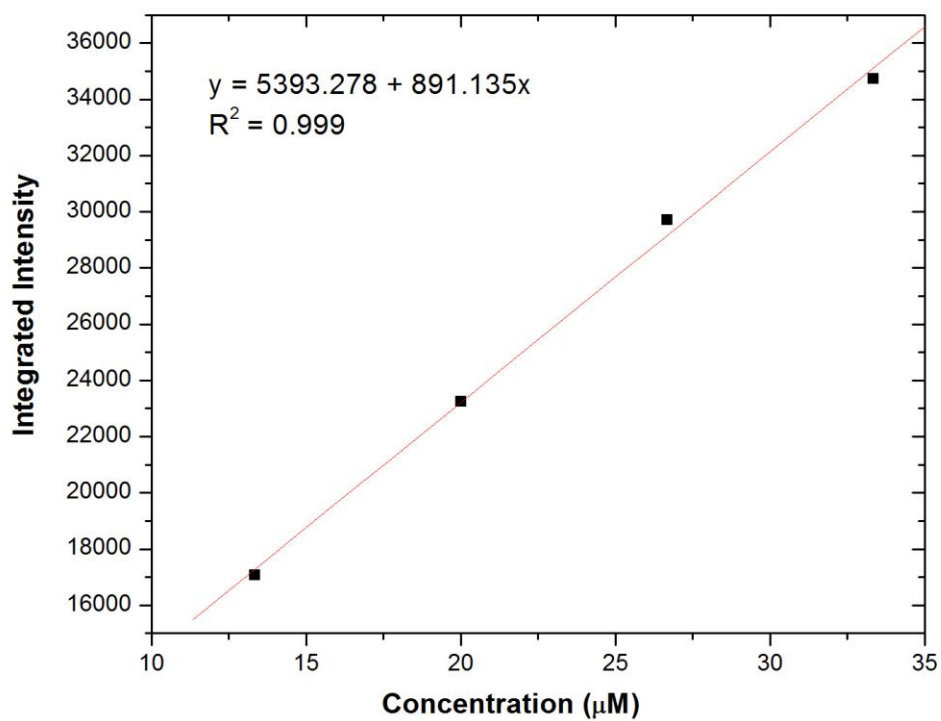


Figure 3.2 Shown in this figure is the linearity of FD150 fluorescence as a function of concentration (aqueous solutions composed of just FD150 and pure water). 20 μM FD150 concentration was chosen for the FRAP experiments in this work.

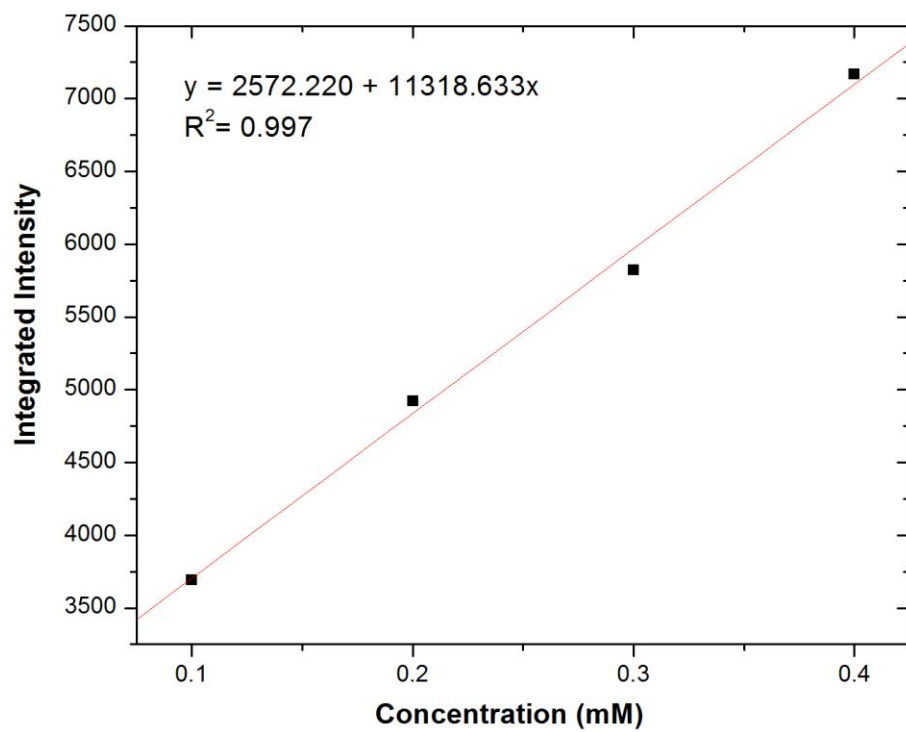


Figure 3.3 Shown in this figure is the linearity of calcein fluorescence as a function of concentration (aqueous solutions composed of just calcein and pure water). 0.3 mM calcein concentration was chosen for the FRAP experiments in this work.

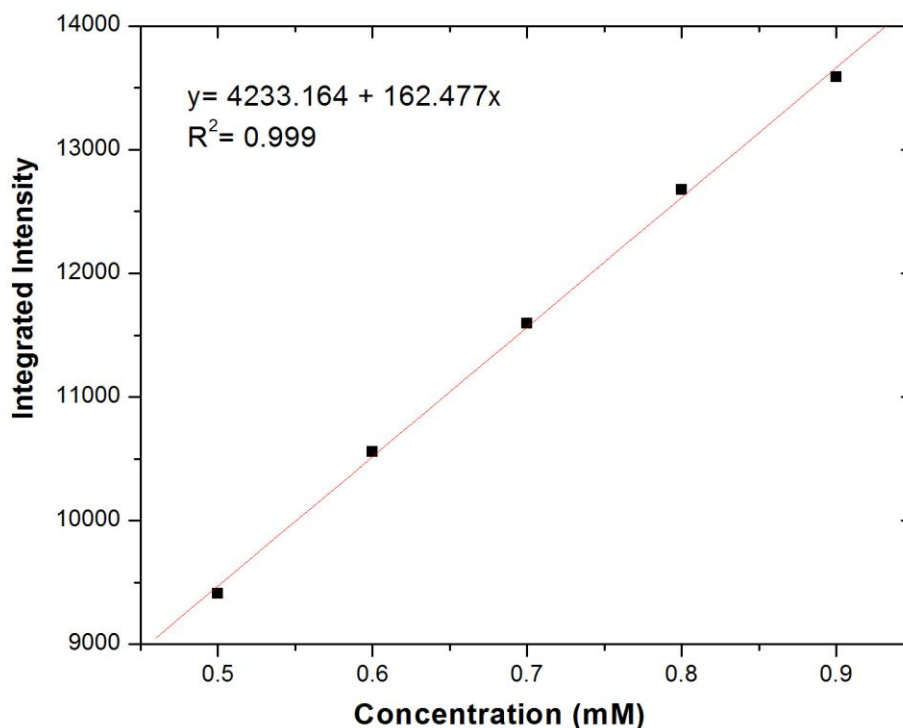


Figure 3.4 Shown in this figure is the linearity of fluorescein fluorescence as a function of concentration (aqueous solutions composed of just fluorescein and pure water). 0.8 mM fluorescein concentration was chosen for the FRAP experiments in this work.

To prepare thin films of sucrose and water containing trace amounts of the fluorescent dye molecules, two different approaches were used depending on the concentration (or water activity) that was desired. For concentrations < 60 wt % sucrose (near the solubility limit of sucrose in water) the approach was rather straightforward, while a more detailed approach was needed for concentrations > 60 wt % sucrose, since these concentrations correspond to supersaturated solutions with respect to sucrose.

The following is the method used to prepare films with concentrations < 60 wt % sucrose (which corresponds to water activities (a_w) > 0.88): First a solution of sucrose in water with a known sucrose wt % was prepared with the dye included using a mass balance. Then a 0.5 μ L

droplet of the solution was pipetted onto a siliconized hydrophobic glass slide (Hampton Research). Next an additional hydrophobic slide was placed on top. The two slides were pushed together forming an aqueous film with a thickness determined by aluminum spacers (thickness = 24 μm). High-vacuum grease provided a seal between the two slides to ensure the composition of the solution did not change after film preparation (see Figure 3.5). The water activity (a_w) of the solutions were calculated from the concentrations of the sucrose solution, wt (wt = wt % sucrose / 100) using the parameterization described in Zobrist et al., 2011:

$$a_w(T, wt) = \left[\frac{1 + awt}{1 + bwt + cwt^2} + (T - T^\theta)(dwt + ewt^2 + fwt^3 + gwt^4) \right] \quad (3.1)$$

Where T is the temperature at which the experiment was performed (293.15 K in this work), T^θ is a reference temperature of 298.15 K, and a to g are constants: a=-1, b=-0.99721, c=0.13599, d=0.001688, e=-0.005151, f=0.009607 and g=-0.006142. The uncertainty in a_w using this parameterization is ± 0.03 . Note that all experiments in this work were performed at room temperature that ranges from 20-22 $^\circ\text{C}$. Since a_w calculations are not sensitive to minor temperature changes within the range of 20-22 $^\circ\text{C}$, for ease of data analysis, all a_w calculations in this work were performed at a temperature of 20 $^\circ\text{C}$ (293.15 K).

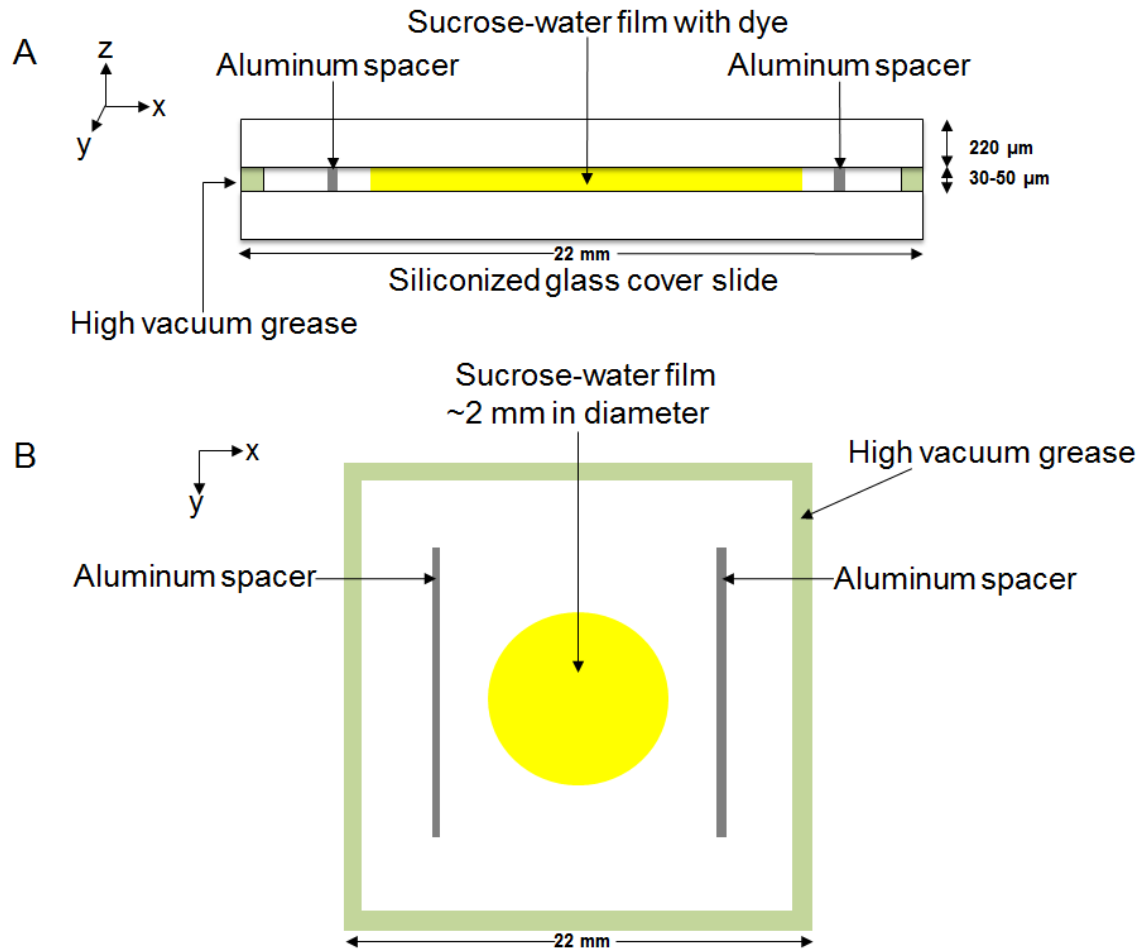


Figure 3.5 Panel A is a side view and Panel B is a top view of a thin film sandwiched between two glass slides that was used in FRAP experiments.

The following is the method used to prepare films with concentrations > 60 wt% sucrose (which corresponds to $a_w < 0.88$): First a solution of sucrose with a concentration of 60% sucrose w/w was prepared. The mixture was then passed through a $0.02\ \mu\text{m}$ filter (Whatman™) to eliminate any impurities (e.g. dust). A $0.5\ \mu\text{L}$ droplet of the prepared solution was placed on a siliconized hydrophobic slide (Hampton Research) using a micropipette. This resulted in a droplet of approximately $350\ \mu\text{m}$ in radius on the hydrophobic slide. Next, the hydrophobic slide containing the droplet was put into a flow cell with temperature and RH control (see Figure 3.6A). The RH in the flow cell was set to values ranging from 85 to 50%. The slide containing

the droplet was left inside the flow cell and allowed to come into equilibrium, with the surrounding RH of the gas, by evaporating water. After equilibrium was reached, the chemical potential of water in the gas phase and condensed phases should be equal, therefore the a_w in the droplet was equal to $RH/100$. By varying the RH used in the flow cell from 85% to 50%, we were able to generate droplets with a_w values ranging from 0.85 to 0.50. In most cases, we did not observe crystallization of the droplets even though the droplets were supersaturated with respect to sucrose. This was likely because we were using glass slides that were coated with a hydrophobic material which has been shown previously not to induce crystallization, and the solutions were first passed through filters to remove any heterogeneous nuclei, such as dust in the solutions (Bodsworth et al., 2010; Pant et al., 2004, 2006; Wheeler and Bertram, 2012). In a few cases crystallization was observed when viewing the films under the microscope and these films were not analyzed.

The time (τ) required for the aqueous spherical droplet to come to equilibration with the surrounding RH, was estimated using the following expression (Seinfeld and Pandis, 2006; Shiraiwa et al., 2011):

$$\tau = \frac{R_{droplet}^2 \cdot e}{\pi^2 D_{water}} \quad (3.2)$$

Where $R_{droplet}$ is the radius of the spherical droplet and D_{water} is the diffusion coefficient of water molecules at constant a_w . Diffusion coefficients of water in aqueous sucrose solutions as a function of a_w were obtained from Price et al. (2014). Three slides were conditioned at a specific RH, the first slide was conditioned for τ (using Equation 3.2), the second slide was conditioned for $1.5 \times \tau$ and the third for $2 \times \tau$. The equilibration time varied between minutes at high RH to days at low RH. The measured diffusion coefficients for all slides agreed within uncertainties.

After the droplet on the slide was conditioned to a known a_w , the conditioned droplet was sandwiched between another siliconized hydrophobic slide producing a film of approximately 30-50 μm in thickness and 2 mm in diameter as shown in Figure 3.5. Once slides were conditioned, they were kept over various saturated inorganic salt solutions (in a sealed container) to ensure that the prepared slides were stored in an environment of the same RH as used to prepare the films.

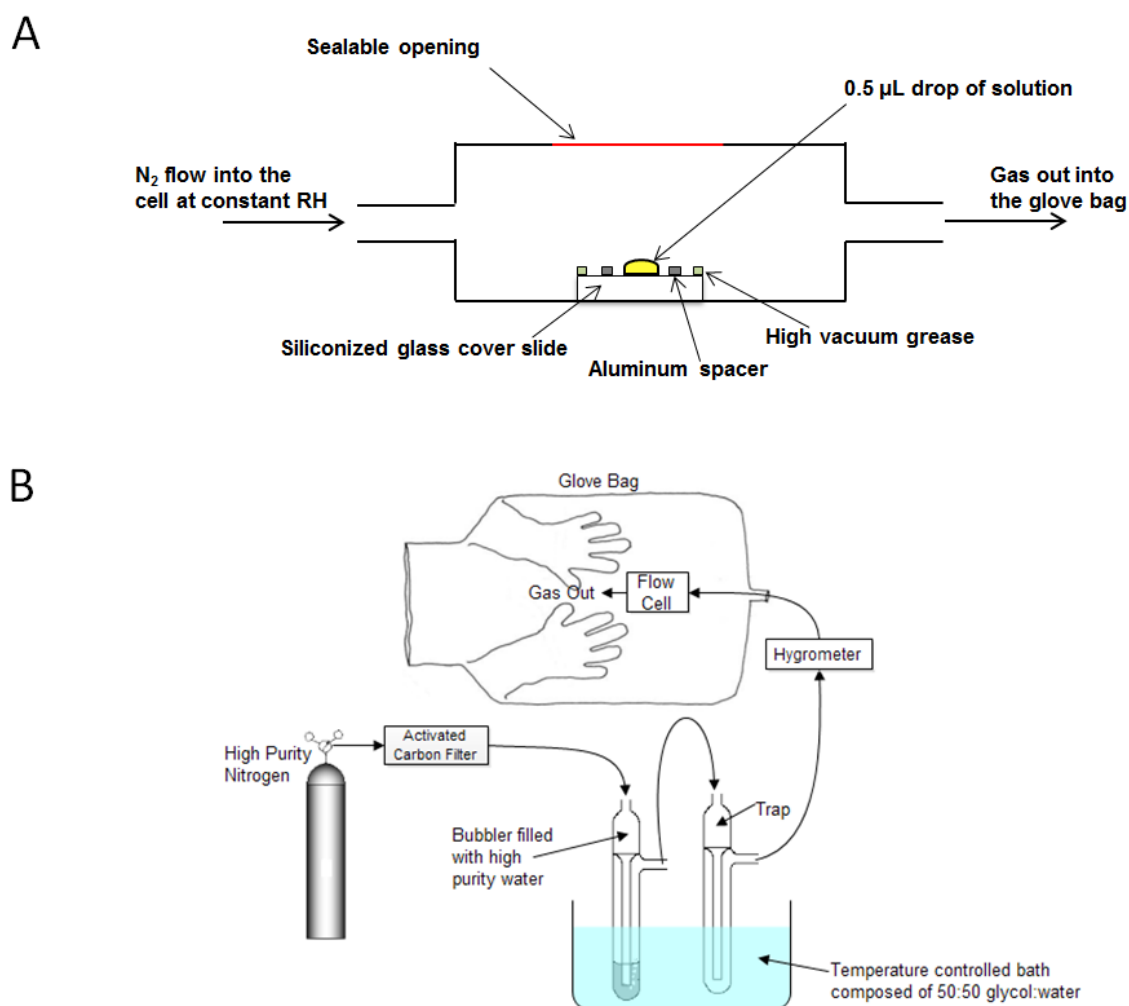


Figure 3.6 Panel A shows the experimental set up that was used to condition films with a_w values < 0.88 . Panel B shows the detailed view of the flow cell in which a drop of solution is conditioned to specific a_w .

As discussed above, after the droplet on the slide was conditioned to a known RH, the conditioned droplet was sandwiched between another siliconized hydrophobic slide. In order to do this, the flow cell shown in Figure 3.6A needed to be opened. To prevent the surrounding air with a different RH from getting inside the flow cell and possibly changing the RH exposed to the droplet, the flow cell was put inside a Glove Bag™ of size 17” length x 17” width x 11” height (Glas-Col), and was inflated with the humidified flow from the flow cell as shown in Figure 3.6B. The sandwiching of the conditioned droplet was carried out within the Glove Bag™, preventing the droplet from being exposed to an unknown and uncontrolled RH.

The RH inside the flow cell discussed above was controlled by using a humidified flow of N₂ gas. High purity N₂ is first passed through a bubbler filled with high purity water (18 MΩ•cm) immersed in a temperature controlled bath. The nitrogen gas exiting the bubble is passed through the flow cell to control the RH in the flow cell. The RH of the N₂ gas could be adjusted by adjusting the temperature of the bath containing the bubbler. The RH of the N₂ gas we determined with a hygrometer (General Eastern Model D-2). The uncertainty in a_w measurements is ± 0.025 based on the uncertainty of the hygrometer.

3.2 FRAP technique

In the FRAP experiment, a small volume of the thin film was photobleached with a laser beam (Figure 3.7, Panel A), deactivating/destroying the organic fluorescent probe molecules in the photobleached volume irreversibly (Figure 3.7, Panel B). The fluorescence in this region was then monitored as a function of time. Due to molecular diffusion of organic fluorescent probe molecules, the fluorescence in the photobleached region recovered over a given time period

(Figure 3.7, Panels C-D). From the time dependent recovery of the fluorescence signal, the diffusion coefficient was determined.

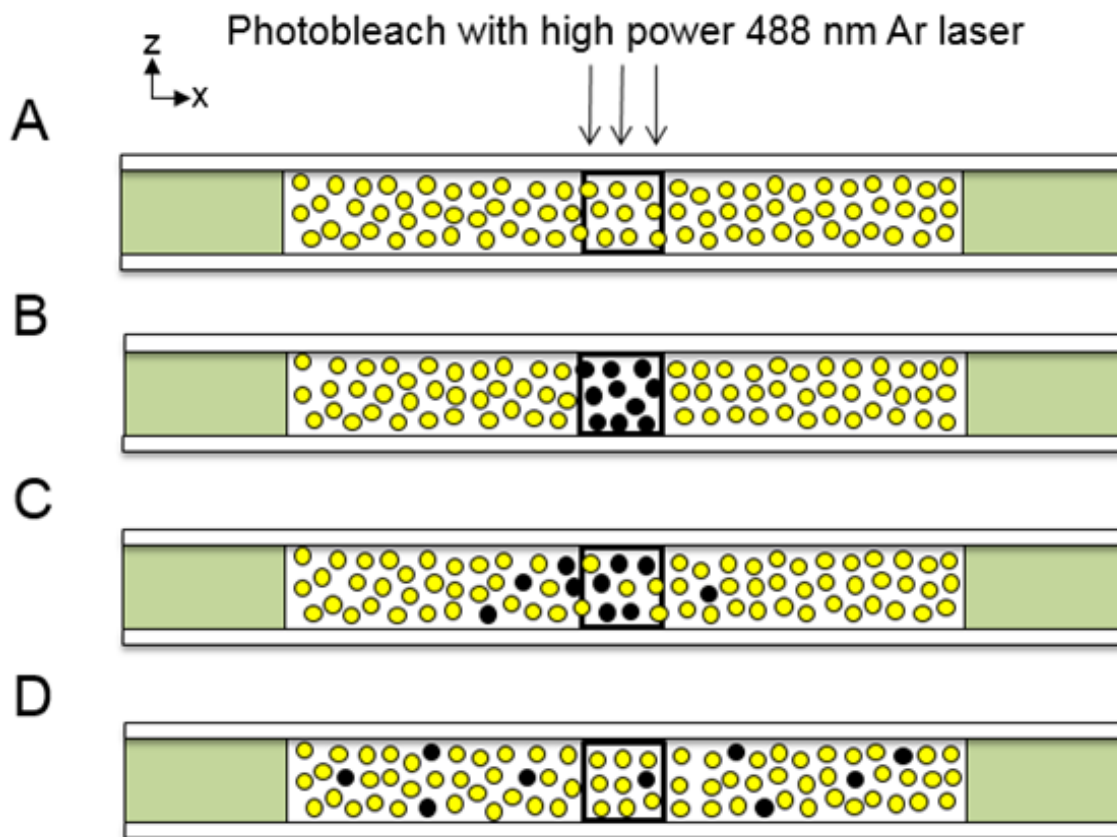


Figure 3.7 FRAP experiment schematic. Shown are the dye tracer molecules in a thin film of sucrose-water film. The region of interest (ROI) is denoted by a black box. Panel A shows tracer fluorescent molecules before photobleaching the ROI. Shortly after photobleaching is shown in panel B, where a drastic decrease in intensity takes place due to the irreversible photobleaching of the dye molecules in the ROI. Panels C and D show the diffusion of non-photobleached dye molecules into the ROI and diffusion of photobleached dye molecules out of the ROI.

All the FRAP experiments were performed on Leica TCS SP5 II confocal laser scanning microscope with a 10x 0.4 NA objective at about 20 °C (room temperature), with a scanning frequency of 540 Hz, bi-directional scanning, a resolution of 512x512 pixels and a pinhole set to

53.07 μm . Based on these settings the image scan time was 0.498 seconds. Photobleaching was performed using a 488 nm Ar laser set at 80% (1.18 mW) and images were acquired with the same laser line at 2% (2.2 μW) of the Ar laser power. All FRAP experiments were performed using Leica FRAP Wizard software, using “Zoom-In” bleach mode. The time for photobleaching was chosen such that it resulted in approximately 30% of the fluorescence molecules in being photobleached in the ROI, in other words, 30% reduction in image intensity.

In all experiments, the geometry of the photobleached region was a square in the x and y direction (see Figure 3.9). The area of the square was chosen based on how fast the fluorescence signal recovered in the photobleached region. Larger sizes were used in cases when the recovery was faster. For slides at $a_w > 0.80$, 30x30 μm and 15x15 μm bleach sizes were used. Fluorescence recovery for slides conditioned at $a_w < 0.80$ was on the time scale of days when using 30x30 μm and 15x15 μm bleach sizes, therefore to shorten the fluorescence recovery time smaller bleach sizes of 5x5 μm and 1x1 μm were used. In a separate set of experiments, we measured the diffusion coefficient as a function of bleach size using a sucrose-water solution with a_w of 0.8 and calcein as the fluorescent dye. The results show that the diffusion coefficients varied by less than the uncertainty in the measurements when the bleach size was varied from 50x50 to 1x1 μm (Figure 3.8). This finding is consistent with previous FRAP experiments (Deschout et al., 2010).

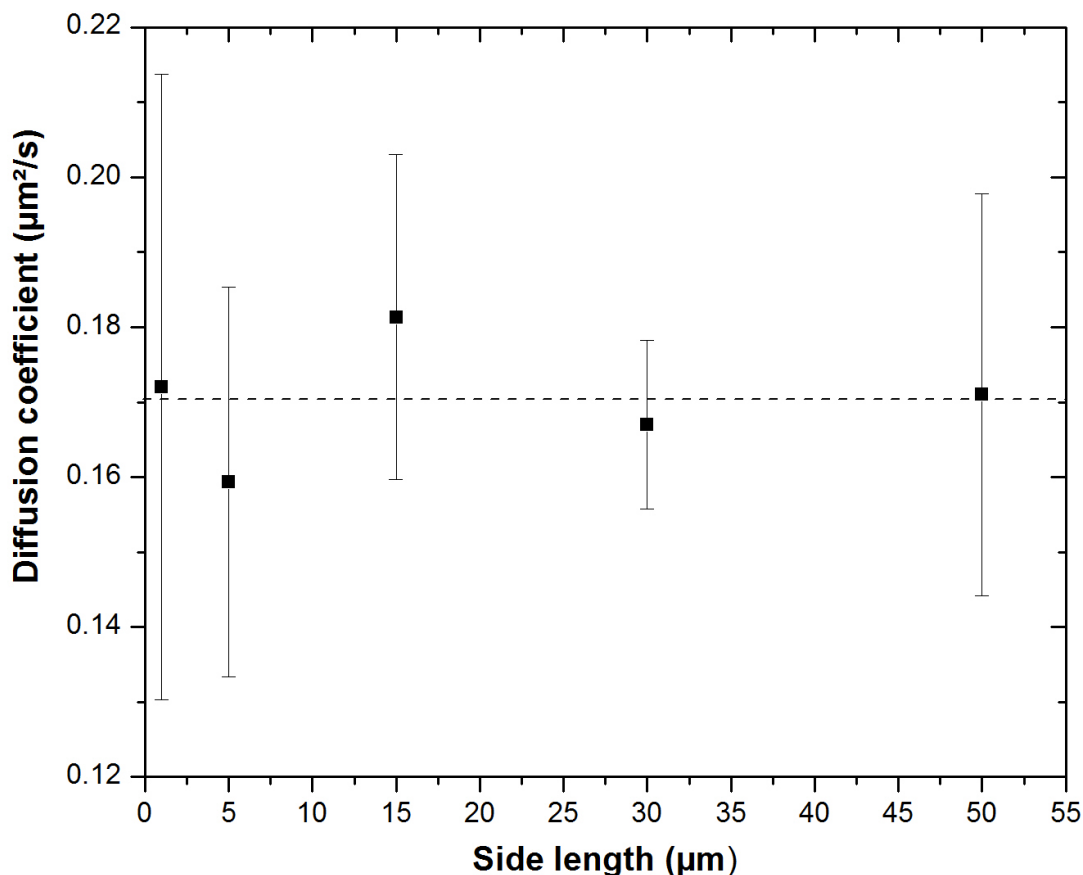


Figure 3.8 A comparison of measured diffusion coefficients of calcein in sucrose-water films conditioned at a_w of 0.80 using bleach sizes of 1x1 μm, 5x5 μm, 15x15 μm, 30x30 μm and 50x50 μm. The dashed line represents the average value of the data points (black squares).

Shown in Figure 3.9 are examples of data recorded from a FRAP experiments. Panel A shows an image prior to photobleaching, panel B shows the area photobleached (white area) and panels C-E show images after photobleaching at different times. All the images during recovery phase are normalized by dividing each image by an image prior to photobleaching. This proved to be a sufficient normalization since no additional photobleaching was observed during image acquisitions which is evident from the background level of the profiles in Figure 3.10. Next, for ease of data analysis, the intensities as a function of x and y are converted into intensities as a function of just x , by averaging (integrating) the intensities over all pixels in the y position (over

the entire region imaged) for a given x position. Examples of plots of intensities as a function of x generated by averaging over all pixels in the y direction are shown in Figure 3.10. This averaging (integrating) was also incorporated into the analysis in order to obtain the appropriate fit model. Furthermore, to reduce noise, all images were averaged down from 512x512 to 128x128 pixels.

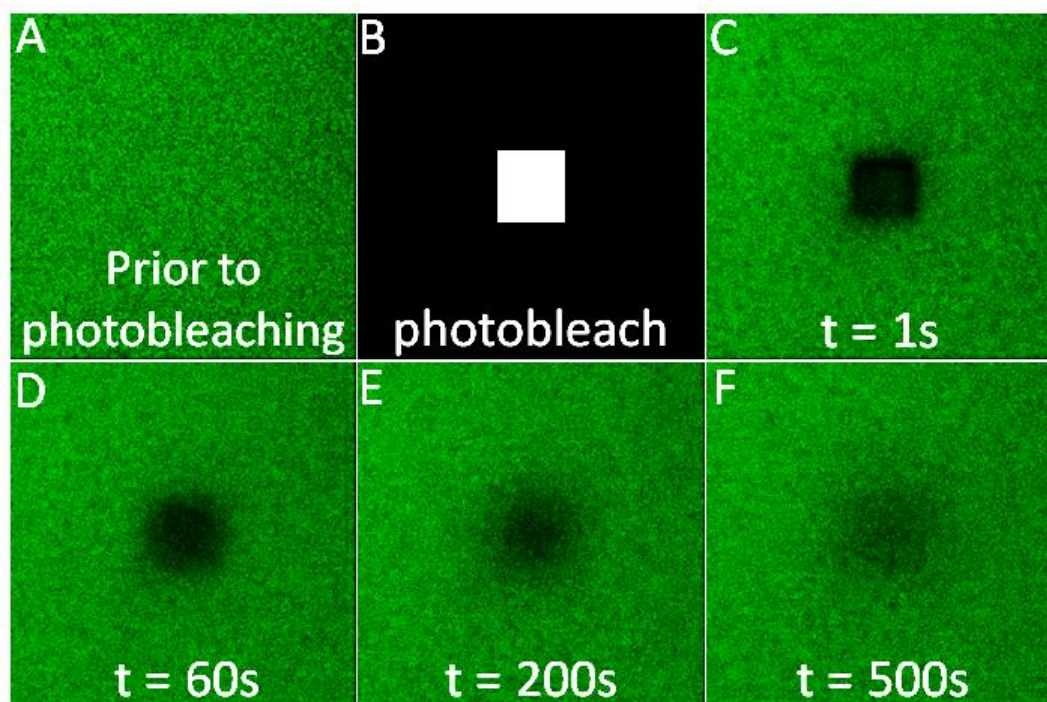


Figure 3.9 Panel A shows a fluorescent film composed of a 60% sucrose-water ($a_w = 0.88$) and 20 μM FD150 solution viewed with a confocal laser scanning microscope before photobleaching. In Panel B the white square indicates the area of the film that was bleached (30x30 μm). Panel C shows the film shortly after photobleaching a 30x30 μm region. Panels D, E and F show the same film at a time (t) for 60, 200 and 500 seconds, respectively, after photobleaching.

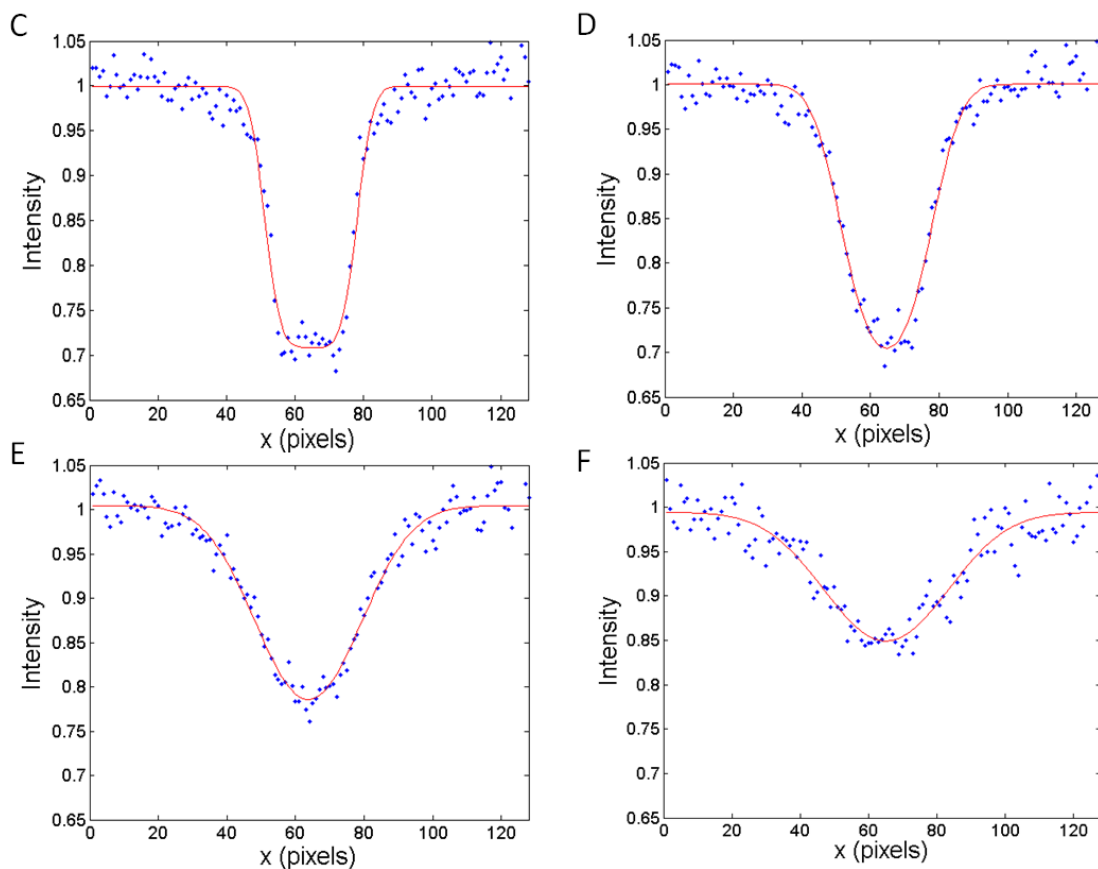


Figure 3.10 Intensities of panels C, D, E and F from Figure 3.9 were averaged over all pixels in the y direction (over the entire region imaged) for a given x position to obtain intensity profile as a function of x. The blue dots show the data points and the red line shows the fit to the data using Equation 3.5. Prior to fitting all intensities in panels C, D, E and F have been normalized using the image shown in Figure 3.9 panel A (prior to photobleaching).

3.2.1 Data analysis

The mathematical description for the intensity of fluorescence as a function of x , y and t after photobleaching a square profile was determined by solving Fick's second law equation and previously described by Deschout et al. (2010):

$$\frac{F(x,y,t)}{F_0} = 1 - \frac{K_0}{4} \left(\operatorname{erf} \left(\frac{x + \frac{l_x}{2}}{\sqrt{w(D,t,r)}} \right) - \operatorname{erf} \left(\frac{x - \frac{l_x}{2}}{\sqrt{w(D,t,r)}} \right) \right) \cdot \left(\operatorname{erf} \left(\frac{y + \frac{l_y}{2}}{\sqrt{w(D,t,r)}} \right) - \operatorname{erf} \left(\frac{y - \frac{l_y}{2}}{\sqrt{w(D,t,r)}} \right) \right) \quad (3.3)$$

Where $F(x,y,t)$ describes the fluorescence recovery at a time t and positions x and y after photobleaching, F_0 is the intensity prior to photobleaching, K_0 is related to the fraction of molecules photobleached in the square of rectangle and l_x and l_y are the lengths of the photobleached square in our case in the x and y direction, respectively, and erf is the error function (Andrews, 1992). The function $w(D,t,r) = r^2 + 4 \cdot D \cdot t$, where r is the resolution parameter of the microscope, t is the elapsed time during recovery and D is the diffusion coefficient of the dye.

The following assumptions, which are valid for our experiments, were made when deriving this analytical solution (Braeckmans et al., 2003, 2007; Deschout et al., 2010):

1. The degree of photobleaching is assumed to be independent of the z -direction (i.e. the depth of the film), which is a reasonable approximation in our experiments since we used very thin films (30-50 μm), and a 10x objective lens/numerical aperture 0.4, which gives a near cylindrical geometry of the photobleach over a distance of 30-50 μm .

2. During fluorescence recovery the diffusion front of the dye should not propagate outside of region imaged. Also, in our experiments, the diameter of the film was about 2 mm, which was much larger than the photobleached regions which ranged in size from 30x30 to 1x1 μm .

In our work the intensities as a function of x and y are converted into intensities as a function of just x by averaging (integrating) the intensities over all pixels in the y direction (over the entire region imaged) for a given x position, as a result Equation 3.3 is converted to the following expression:

$$\frac{F(x, y, t)}{F_0} = 1 - \frac{K_0}{4} \left(\text{erf} \left(\frac{x + \frac{l_x}{2}}{\sqrt{w(D, t, r)}} \right) - \text{erf} \left(\frac{x - \frac{l_x}{2}}{\sqrt{w(D, t, r)}} \right) \right) \cdot \int_{-\infty}^{+\infty} \left(\text{erf} \left(\frac{y + \frac{l_y}{2}}{\sqrt{w(D, t, r)}} \right) - \text{erf} \left(\frac{y - \frac{l_y}{2}}{\sqrt{w(D, t, r)}} \right) \right) \cdot dy \quad (3.4)$$

The integral in Equation 3.4 can be solved to give the following simplified expression:

$$\frac{F(x, t)}{F_0} = 1 - \frac{K_0}{4} \left(\text{erf} \left(\frac{x + \frac{l_x}{2}}{\sqrt{w(D, t, r)}} \right) - \text{erf} \left(\frac{x - \frac{l_x}{2}}{\sqrt{w(D, t, r)}} \right) \right) \cdot 4 \frac{l_y}{2} \quad (3.5)$$

Where $F(x, t)$ describes the fluorescence recovery at a time t and position x after photobleaching.

The method for determining diffusion coefficients from our experiments consisted of the following:

- 1) For a given experiment (i.e. FRAP measurements for one concentration of sucrose-water), the plots similar to what is shown in Figure 3.9, were fitted to Equation 3.5 to determine a $\frac{1}{4}w(D, t, r)$ value for each time an image was recorded. This was done using a

MATLAB script, and K_0 and $\frac{1}{4}w(D,t,r)$ were left as free parameters during the fitting.

There was also an overall normalization factor in the fit, usually with a value pretty close to 1 since the images were normalized in advance.

- 2) For a give concentration of sucrose-water, $\frac{1}{4}w(D,t,r)$ was plotted as a function of t . See Figures 3.11 and 3.12 as examples.
- 3) The data of $w(D,t,r)$ as a function of t were fit to $r^2 + 4 \cdot D \cdot t$, and the slope was used to calculate the diffusion coefficient for a given concentration of sucrose-water and for a given dye, since the slope was equal to $4 \cdot D$, based on the solution developed by Deschout et al. (2010). In Figures 3.11 and 3.12, plots of $\frac{1}{4}w(D,t,r)$ as a function of t are shown.

In Figure 3.8, the diffusion coefficient was determined 3 times (3 different slides were used and 1 measurement carried out on each slide). In Figures 4.1-4.6, at each RH the diffusion coefficient was determined 9 times (3 different slides were used and 3 measurements were carried out on each slide). In Figures 3.8 and 4.1-4.6 the mean of the measurements are reported as well as the 95% confidence interval.

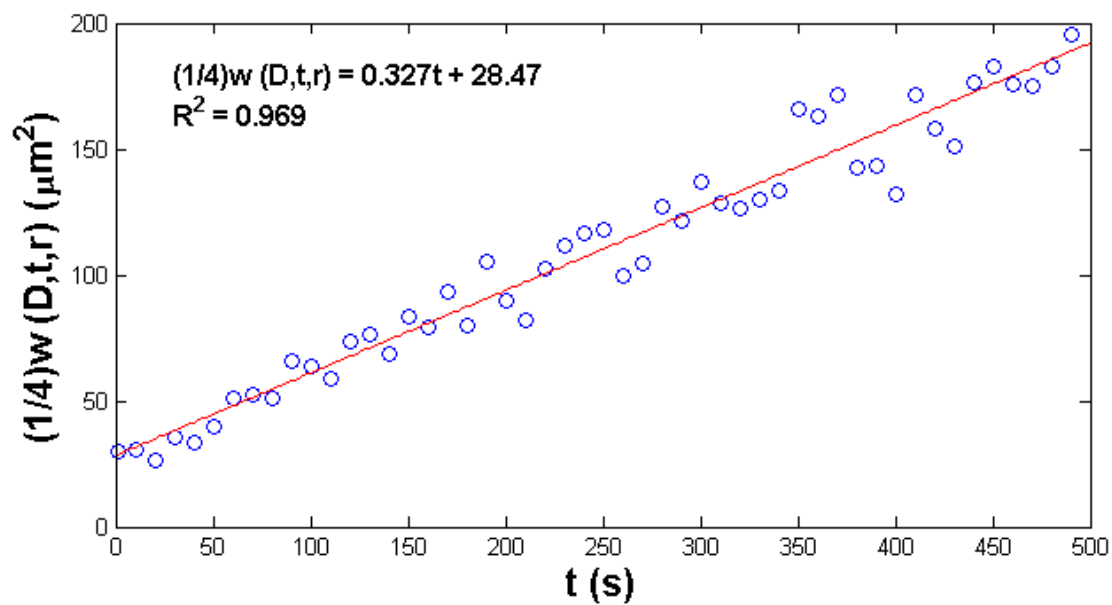


Figure 3.11 Plot of $\frac{1}{4}w(D,t,r)$ as a function of time for FD150 in 60% w/w sucrose-water ($a_w = 0.88$) film. The blue symbols represent data obtained from Figures 3.10, and the red line is a linear fit to the data. From the slope of the line, the diffusion coefficient was determined. In this case the diffusion coefficient was found to be $0.327 \mu\text{m}^2/\text{s}$.

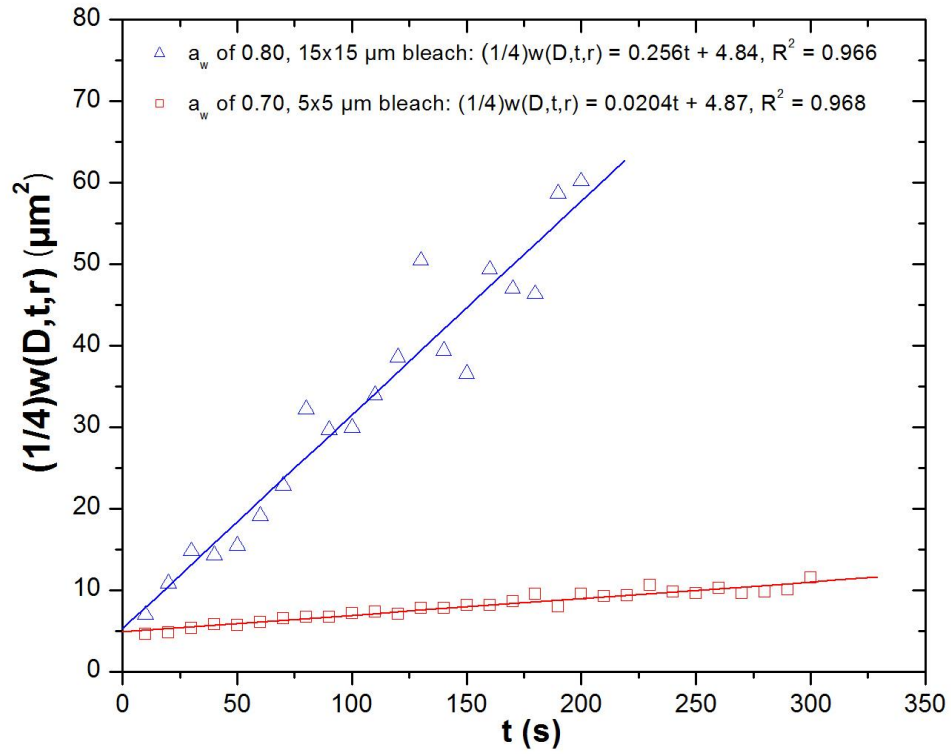


Figure 3.12 $\frac{1}{4}w(D,t,r)$ as a function of time plot for calcein diffusion in sucrose-water films conditioned at a_w of 0.80 and 0.70. The slope decreases (smaller/slower diffusion coefficient) as sucrose-water film becomes more viscous. From the slopes, diffusion coefficients of calcein were determined to be $0.256 \mu\text{m}^2/\text{s}$ and $0.0204 \mu\text{m}^2/\text{s}$ for a_w vales of 0.80 and 0.70, respectively.

Chapter 4: Results and Discussions

4.1 Diffusion of FD150 in sucrose-water

Shown in Figure 4.1 are diffusion coefficients as a function a_w for FD150 in sucrose-water solutions. These experiments were performed to validate our approach, since diffusion coefficients of FD150 in sucrose-water solutions exist in the literature. Diffusion coefficients ranging from 12.6 to $1.53 \times 10^{-2} \mu\text{m}^2/\text{s}$ were measured at water activities (a_w) values ranging from 0.99 to 0.75 , respectively. Diffusion coefficients at a_w lower than 0.75 were not measured since the fluorescence recovery is on time scale of weeks and not possible to record with our experimental setup at these water activities for FD150. Also included in Figure 4.1 for comparison purposes are the diffusion coefficients for FD150 in sucrose-water films measured by Xiong et al. (2014) using FRAP. Figure 4.1 illustrates that our results are consistent with previous measurements of the diffusion coefficients of FD150 in sucrose-water films.

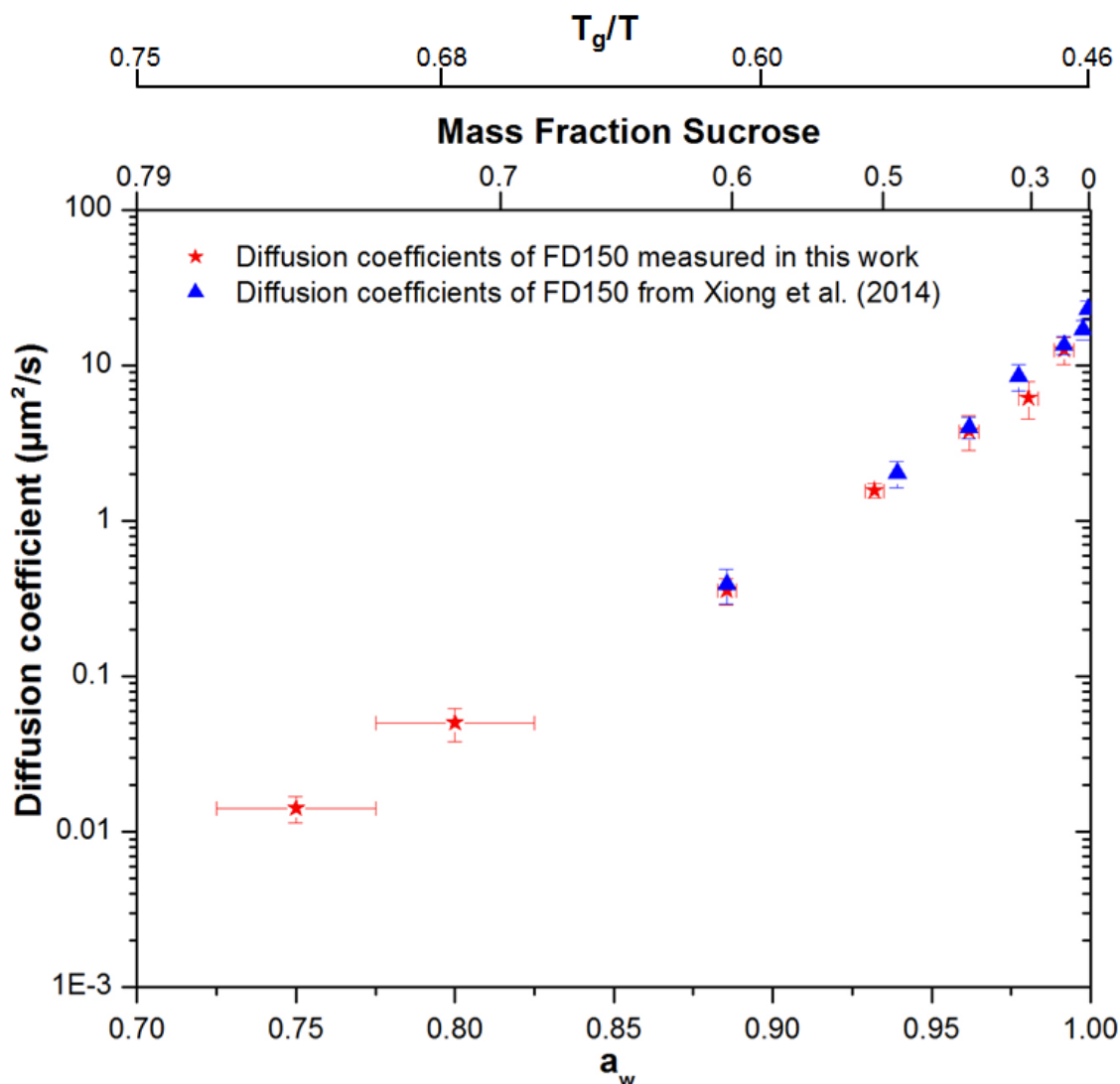


Figure 4.1 A comparison of measured diffusion coefficients of FD150 from this work (red stars) with measured diffusion coefficients of FD150 from Xiong et al. 2014 (blue triangles) in sucrose-water films.

Shown in Figure 4.2 are diffusion coefficients measured in this work for FD150 and diffusion coefficients predicted based on the Stokes-Einstein equation and viscosities of sucrose-water solutions reported in the literature. The hydrodynamic radius (R_H) for FD150 used in the Stokes-Einstein equation was estimated using an equation proposed by Smedt et al. (1994) based on previous diffusion measurements of FITC-dextran molecules in pure water with molecular

weight (MW) of 71 200, 148 000, and 487 000 g/mol and the Stokes-Einstein equation (units for R_H using this equation is in nm):

$$R_H = 0.018(MW_{\text{FITC-dextran}})^{0.53 \pm 0.02} \quad (4.1)$$

Where MW is molecular weight of FITC-dextran expressed in g/mol. Figure 4.2 shows a good agreement between the measurements of diffusion coefficients of FD150 and predictions of diffusion coefficients based on the Stokes-Einstein equation down to a_w of 0.75. This finding is consistent with previous studies by Braeckmans et al. (2003), who showed good agreement between diffusion coefficients and predictions with the Stokes-Einstein equation when studying diffusion of FITC-dextran molecules in sugar-water solutions down to a_w of 0.88. The good agreement in our work between diffusion measurements of FD150 and the Stokes-Einstein equation is not surprising since FD150 is much larger in size ($R_H = 83.1 \text{ \AA}$) than the molecules in the sucrose-water matrix (R_H of sucrose = $4.9 \text{ \AA}$ (Champion et al., 1995) and R_H of water = $1 \text{ \AA}$ (Price et al., 2014)), which is one of the assumptions used when deriving the Stokes-Einstein equation. In addition, the a_w studied for the FITC-dextran dyes (0.99 to 0.75) are well outside the a_w range where sucrose-water solutions form a glass ($a_w < 0.2$, see Figure 2.1).

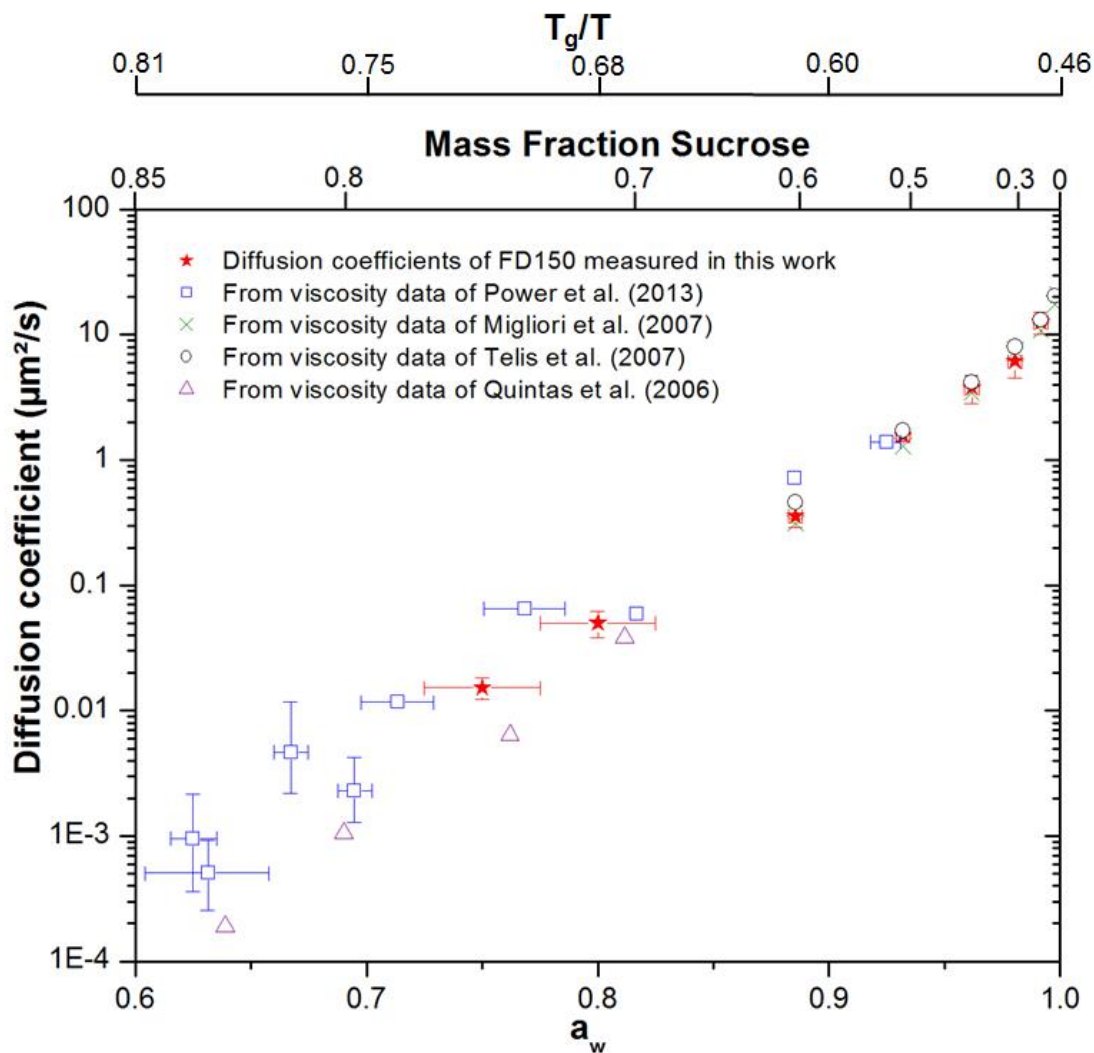


Figure 4.2 A comparison of measured diffusion coefficients of FD150 in sucrose-water films from this work (red stars) with predicted diffusion coefficients based on measured viscosity coefficients of sucrose-water solutions and the Stokes-Einstein equation from Power et al. (2013) (blue squares), Migliori et al. (2007) (green crosses), Telis et al. (2007) (black circles) and Quintas et al. (2006) (purple triangles). RH of 83.1 Å was used for FD150 (RH value for FD150 was obtained from Smedt et al. (1994)).

4.2 Diffusion of calcein in sucrose-water

Shown in Figure 4.3 are diffusion coefficients as a function a_w for calcein in sucrose-water solutions. Diffusion coefficients ranging from 4.10 to $1.65 \times 10^{-3} \mu\text{m}^2/\text{s}$ were measured at a_w values ranging from 0.88 to 0.60, respectively. Diffusion coefficients at a_w lower than 0.60 were not measured since the fluorescence recovery for calcein is on time scale of weeks and not possible to record with our experimental setup at these a_w values. Also included in Figure 4.3 are diffusion coefficients predicted based on the Stokes-Einstein equation and viscosities of sucrose-water solutions reported in the literature. The R_H of calcein ($R_H = 7.4 \text{ \AA}$) used in this work was estimated by Tamba et al., (2010) and is based on diffusion measurements of calcein in water and the Stokes-Einstein equation. Figure 4.3 shows that measured diffusion coefficients were consistent with Stokes-Einstein equation and viscosity measurements for calcein. In this case the size of calcein ($R_H = 7.4 \text{ \AA}$) was still larger than the molecules in the sucrose-water matrix (R_H of sucrose = $4.9 \text{ \AA}$ (Champion et al., 1995) and R_H of water = $1 \text{ \AA}$ (Price et al., 2014)). Although calcein is not as large in size as FD150 ($R_H = 83.1 \text{ \AA}$), the Stokes-Einstein equation was shown to be valid for this relative difference in size between the diffusing molecule and matrix molecules. In addition, the a_w studied for calcein (0.99 to 0.60) was also well outside the a_w range where sucrose-water solutions form a glass ($a_w < 0.2$, see Figure 2.1).

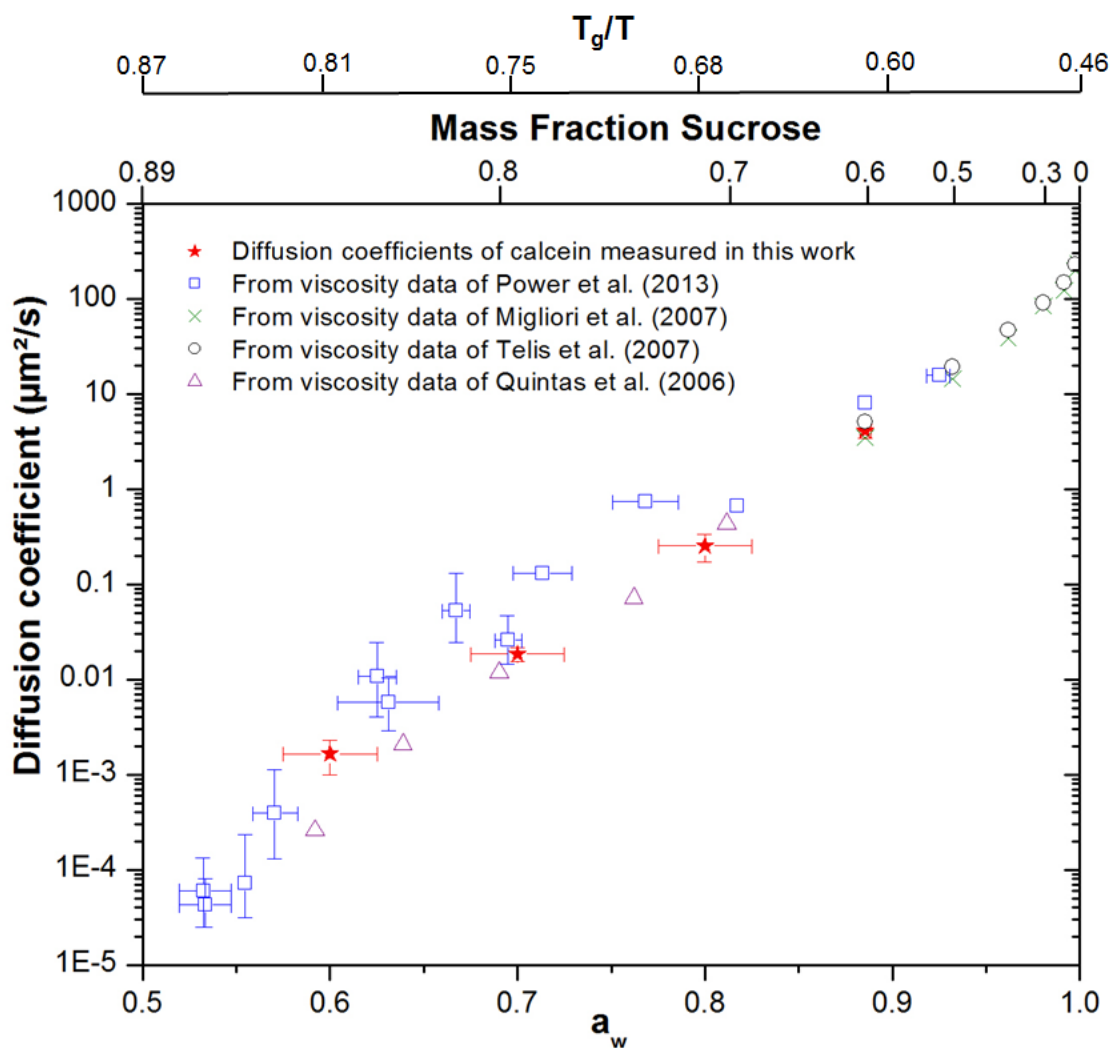


Figure 4.3 A comparison of measured diffusion coefficients of calcein in sucrose-water films from this work (red stars) with predicted diffusion coefficients based on measured viscosity coefficients of sucrose-water solutions and the Stokes-Einstein equation from Power et al. (2013) (blue squares), Migliori et al. (2007) (green crosses), Telis et al. (2007) (black circles) and Quintas et al. (2006) (purple triangles). R_H of $7.4 \text{ \AA}$ was used for calcein (R_H value for calcein was obtained from Tamba et al. (2010)).

4.3 Diffusion of fluorescein in sucrose-water

Shown in Figure 4.4 are diffusion coefficients as a function a_w for fluorescein in sucrose-water solutions. Diffusion coefficients ranging from 7.09 to $2.51 \times 10^{-4} \mu\text{m}^2/\text{s}$ were measured at a_w values ranging from 0.88 to 0.50, respectively. Diffusion coefficients at a_w lower than 0.50 were not measured since the fluorescence recovery for fluorescein was on time scale of weeks at these lower a_w values and not possible to record with our experimental setup. Also included in Figure 4.4 are the predictions of diffusion coefficients based on the Stokes-Einstein equation and previous viscosity measurements. The R_H of fluorescein ($R_H = 5.02 \text{ \AA}$) used in this work was estimated by Mustafa et al. (1993) and is based on diffusion measurements of fluorescein in pure water and the Stokes-Einstein equation. Figure 4.4 shows that the measured diffusion coefficients of fluorescein at a_w range of 0.88-0.50, within the uncertainty of the measurements, agree with the Stokes-Einstein equation and viscosity measurements. Figure 4.4 also shows that we did not observe a difference (i.e. decoupling) between the diffusion coefficient measurements and predictions based on the Stokes-Einstein equations and viscosity measurements at T_g/T values ≤ 0.87 .

Champion et al. (1997) and Corti et al. (2008a) also measured diffusion coefficients of fluorescein in sucrose-water solutions using FRAP. While we performed the measurements at a temperature of about 20 °C (room temperature) as a function a_w ranging from 0.88 to 0.50, Champion et al. (1997) measured diffusion coefficients of fluorescein as a function of glass transition temperature and temperature (T_g/T) of aqueous sucrose, where the temperature ranged from 20 °C to -15 °C. Our results were consistent with the results of Champion et al. (1997), who did not observe a clear decoupling between the diffusion coefficient measurements and the Stokes-Einstein equation and viscosity measurements at $T_g/T \leq 0.86$ (see Figure 4.4).

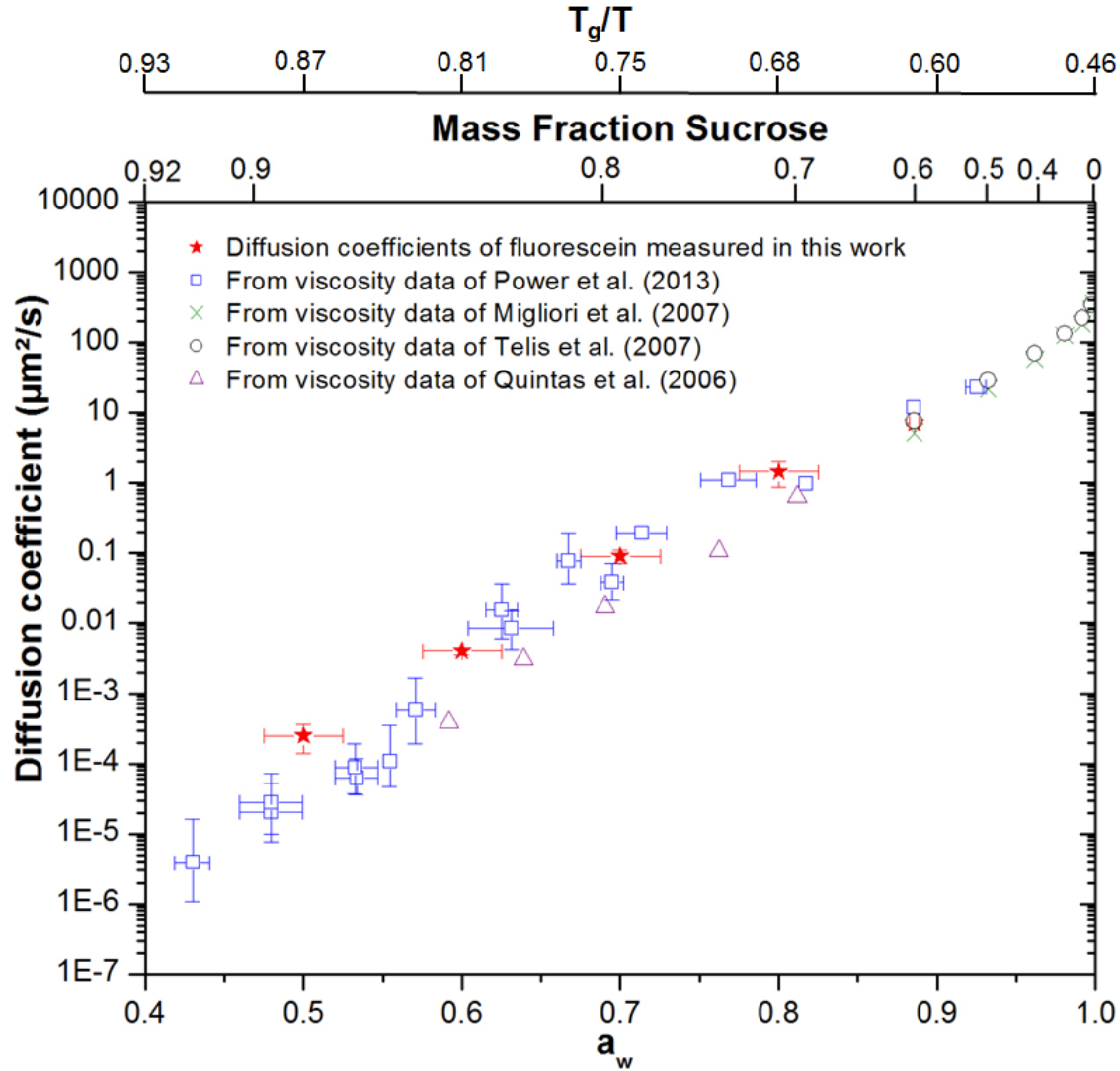


Figure 4.4 A comparison of measured diffusion coefficients of fluorescein in sucrose-water films from this work (red stars) with predicted diffusion coefficients based on measured viscosity coefficients of sucrose-water solutions and the Stokes-Einstein equation from Power et al. (2013) (blue squares), Migliori et al. (2007) (green crosses), Telis et al. (2007) (black circles) and Quintas et al. (2006) (purple triangles). R_H of 5.02 Å was used for fluorescein (R_H value for fluorescein was obtained from Mustafa et al. (1993)).

Meanwhile, Corti et al. (2008a) measured diffusion coefficients of fluorescein in sucrose-water solutions as a function of T_g/T with similar temperature conditions as we used of about 20 °C. However, they observed decoupling between diffusion coefficient measurements and the

Stokes-Einstein equation and viscosity measurements at $T_g/T > 0.65$. The reason for the discrepancy between the work by Corti et al. (2008a), on one hand, and our work and the work by Champion et al. (1997), on the other hand, is not clear.

In our work, the measured diffusion coefficients of fluorescein was consistent with the Stokes-Einstein equation and viscosity measurements at a_w range of 0.88-0.50. On the other hand, Price et al. (2014) showed that the diffusion coefficient of water in sucrose-water solutions was inconsistent with the Stokes-Einstein equation over this a_w range. In Figures 4.5 we have replotted the data from Price et al. (2014) and also included the predicted diffusion coefficients based on the Stokes-Einstein equation and viscosity measurements. For the predictions, a R_H of 1 Å was used based on diffusion measurements of water in pure water and the Stokes-Einstein equation (Price et al., 2014).

Based on Figure 4.5, the diffusion coefficients of water measured by Price et al. (2014) using Raman isotope tracer method start to deviate at approximately $a_w < 0.8$ or $T_g/T > 0.68$. Similar deviations from the Stokes-Einstein equation have been observed by others when the size of the diffusing molecule is less than the size of the matrix molecules (Longinotti and Corti, 2007; Rampp et al., 2000) (see Table 2.1), indicating, that the other theories, such as percolation theory, should be used when trying to predict the diffusion of molecules with sizes less than the size of the matrix molecules. Percolation theory is a mathematical model that can describe the penetration of molecule through a porous medium (Essam, 1980; Murata et al., 1999). As the sucrose-water matrix is dominated by sucrose molecules, small water molecules are able to percolate between the sucrose molecules, resulting in a more rapid (larger) diffusion rate than the diffusion rate based on the Stokes-Einstein equation and viscosity measurements (Molinero et al., 2003).

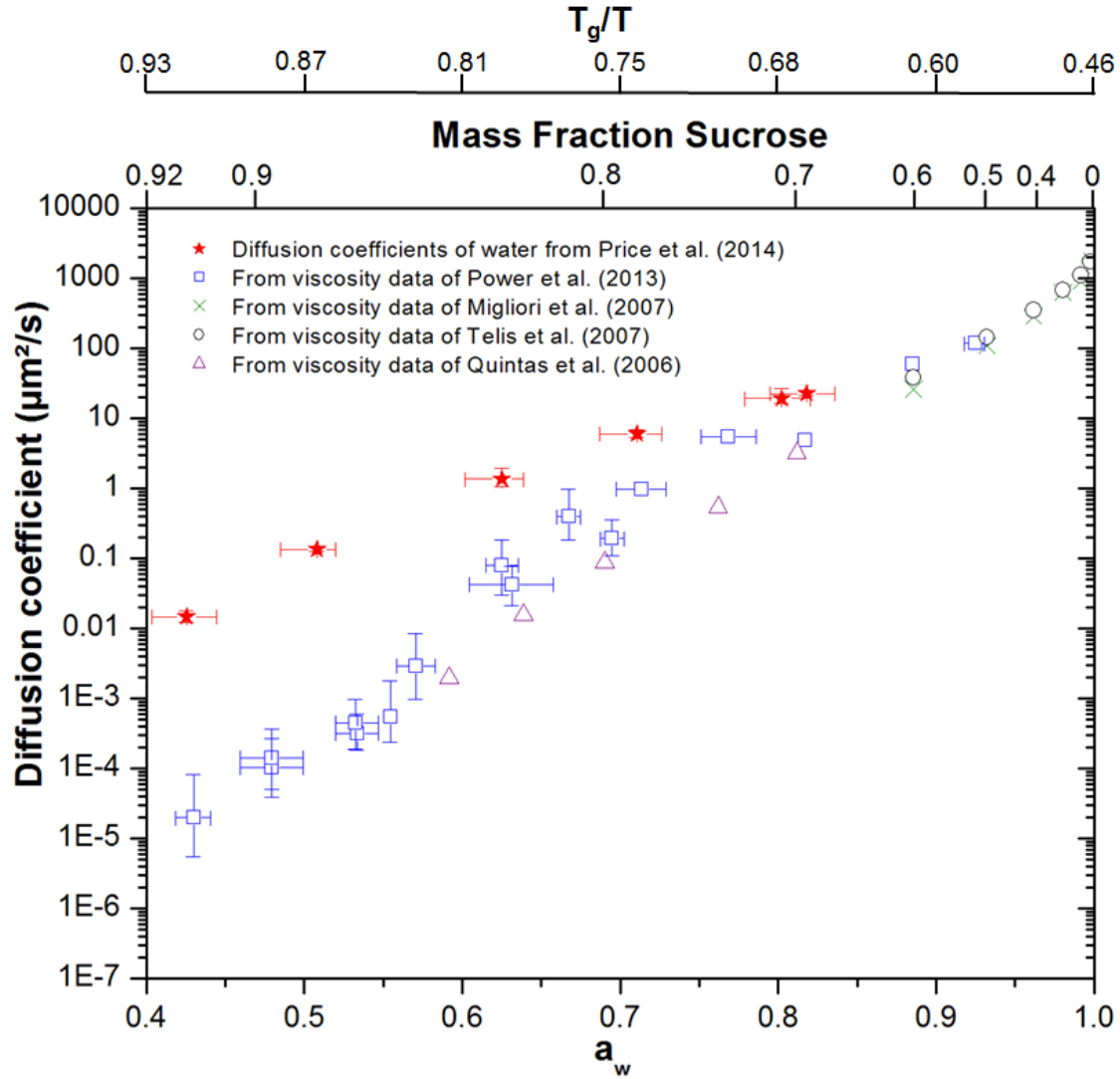


Figure 4.5 A comparison of measured diffusion coefficients of water in sucrose-water films from Price et al. (2014) (red stars) with predicted diffusion coefficients based on measured viscosity coefficients of sucrose-water solutions and the Stokes-Einstein equation from Power et al. (2013) (blue squares) Migliori et al. (2007) (green crosses), Telis et al. (2007) (black circles) and Quintas et al. (2006) (purple triangles). R_H of 1 Å was used for water (R_H value for water was obtained from Price et al. (2014)).

4.4 Linear relationship between log (diffusion coefficient) and water activity

Shown in Figure 4.6 is a comparison of measured diffusion coefficients as a function of a_w for FD150, calcein and fluorescein from this work. As expected and consistent with the Stokes-Einstein equation, the diffusion coefficient is inversely dependent on the size of the diffusing molecule. Measured diffusion coefficients for all dyes showed a roughly linear dependence between log diffusion coefficient and a_w . In the graph, the mass fraction sucrose in the aqueous solution is shown as a secondary x-axis. Diffusion coefficients scale much better with a_w than mass fraction of sucrose. The linear dependence between log diffusion coefficient and a_w can be explained by the linear relationship expected between log diffusion and log viscosity (based on the Stokes-Einstein equation), and the linear relationship between log viscosity and a_w for sucrose-water solutions, as shown in Figure 2.1.

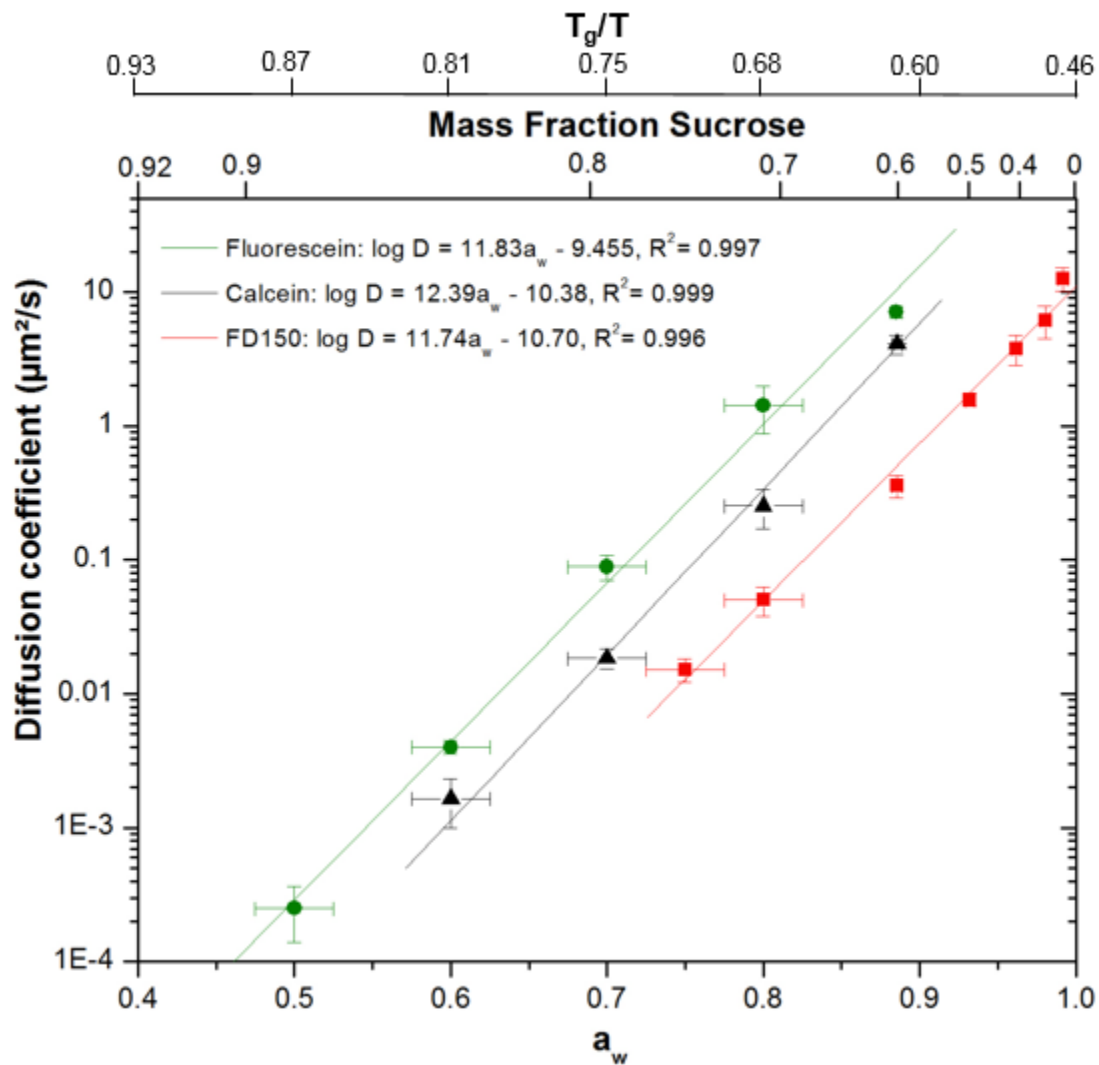


Figure 4.6 A comparison of measured diffusion coefficients at 20 °C of fluorescein (green circles), calcein (black triangles) and FD150 (red squares) in sucrose-water films from this work. Also included in the figure is a linear fit for fluorescein, calcein and FD150 data points.

Chapter 5: Conclusions

5.1 Summary of work

The overall goal of this thesis was to test whether or not the Stokes-Einstein equation combined with viscosities give accurate value of diffusion coefficients under atmospheric relevant conditions. This was achieved by measuring diffusion coefficients of organic dyes within aqueous sucrose-water solutions that act as proxies for organic-water atmospheric particles. The measured diffusion coefficients were then compared to estimated diffusion coefficients using Stokes-Einstein equation and viscosity measurements of sucrose-water aqueous solutions. The results from the measurements and the comparisons with Stokes-Einstein are summarized in the Table 5.1.

Table 5.1 Summary of results.

Compound used	Molecular weight (g/mol)	Hydrodynamic radius, R_H (Å)	Diffusion coefficient range measured ($\mu\text{m}^2/\text{s}$)	Water activity (a_w) range	viscosity range (Pa·s)	Consistent with Stokes-Einstein equation
FD150	1.50×10^5	83.1 (error range of 65.4-105.4) (Smedt et al., 1994)	$12.6\text{-}1.53 \times 10^{-2}$	0.99-0.75	0.002-2	Yes
Calcein	622	7.4 (error range of 6.0-8.0) (Edwards et al., 1995; Tamba et al., 2010)	$4.10\text{-}1.65 \times 10^{-3}$	0.88-0.60	0.05-200	Yes
Fluorescein	376	5.02 ± 0.14 (Mustafa et al., 1993)	$7.09\text{-}2.51 \times 10^{-4}$	0.88-0.50	$0.05\text{-}10^4$	Yes

In short, measured diffusion coefficients of FD150, calcein and fluorescein were consistent with the Stokes-Einstein equation and viscosity measurements. These results indicate that the Stokes-Einstein equation for molecules at size scale of fluorescein ($R_H = 5.02$ Å) at $a_w \geq 0.50$ (or viscosities $< 10^4$ Pa·s) is still valid.

5.2 Consideration of future work

Measurements of diffusion coefficients at lower $a_w < 0.5$ or viscosity values of $> 10^4$ Pa·s for fluorescein are needed to see if the diffusion is decoupled from viscosity for this dye and at these lower water activities and higher viscosities. Fluorescence recoveries at these viscosities would be on time scale of weeks. Experiments carried out over the time period of weeks may be possible by photobleaching a spot in a film and then weekly record the fluorescence profile of the film. In between imaging, the films could be stored in a jar above a salt solution with a RH equal to the RH at which the droplet was conditioned.

Furthermore, diffusion measurements with a dye molecules smaller than fluorescein, such as coumarin (MW = 146 g/mol, $R_H = 3-4$ Å), it would be interesting to see if or at what viscosity range the Stokes-Einstein equation is not valid. In our case, the Stokes-Einstein equation was still valid for fluorescein ($R_H = 5.02$ Å) at a_w of 0.50 (viscosity of $\sim 10^4$ Pa·s).

Also, to further test the Stokes-Einstein equation, performing diffusion measurements as a function of temperature at constant a_w , such as -20-80 °C, would be very interesting. To do this, a cell would have to be designed with temperature control that holds a slide with the conditioned film, and this cell will be placed directly on the microscope stage to perform FRAP experiments.

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