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Analysis of Ripples on Icicles grown from Polyethylene Glycol Solutions

by

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Abstract

The aim of this thesis work is to observe how ripple patterns which form on icicles change as the molecular weight and concentration of their constituents are varied. Icicle ripple wavelengths and amplitudes are calculated from images taken from icicles grown from various solutions of distilled water and varying concentrations of solutes. This data is used to determine the behavior of the formation and properties of icicle ripples when the concentrations and molecular weights of the solvents in the water used to grow them changes.

Icicles were grown using the tabletop apparatus built by a previous student, and modified to grow icicles along a long stick to provide more useable data along the uniform radius of the stick. Polyethylene Glycol (PEG) solutions of varying molecular weights and concentrations were used to explore icicle ripples in this space. These icicles were grown under previously established conditions for icicle growth determined by previous students. Using Matlab routines to analyze the data, we obtain and discuss information pertaining to the ripples which form on icicles which contain solvents such as the PEG used in this study.

Acknowledgements

I would like to thank the department of physics at the University of Toronto for allowing me to conduct this master's research and for it's financial aid through TA positions. I would also like to thank my supervisor professor Stephen Morris for taking me on with this project and for his guidance throughout. I would also like to thank the other two readers of this report professor Mathew Wells and professor Sidhartha Goyal for taking the time to review this work. Finally, I would like to thank my parents for all of their help, both financially and emotionally, throughout the course of this project.

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Chapter 1

Introduction

Icicles are a common sight during cold winter weather and are the subject of interest to many scientists and artists alike. The process of formation of icicles and their properties are still not fully understood and is therefore still an active area of research. From engineering applications such as de-icing of power lines [1] and airplane wings [2] to applications for realistic icicle animation for use in film, knowledge of icicle formation is important to a wide range of fields.

Studies on how icicles form have been carried out previously by Chen [3]. From these studies, it is known that icicles grow from an overhanging support in sub-freezing conditions. The growth mechanism of icicles is also well documented [4]. As is shown in figure 1.1, an icicle grows from a single frozen drop, surrounded by a layer of water. At the ice-water interface the water is at its freezing point, whereas the air outside is below freezing. Thus the remainder of the water on the icicle surface is supercooled. As latent heat is removed from the ice-water interface the water freezes and the icicle grows laterally. The tip grows by a different process by which a column of water, maintained at the tip of the icicle by surface tension, freezes internally while the pendant drop beneath it periodically falls from the tip and is replaced by another as

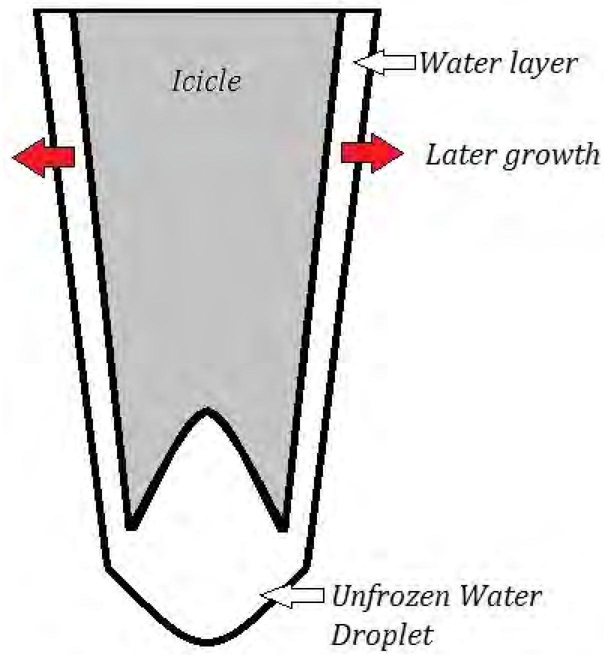

Figure 1.1: Drawing depicting the mechanism of icicle growth

more water runs over the icicle. As a result it is clear that in order for an icicle to grow it is necessary to have a constant flow of water over its surface. In nature this condition is often met by means of snow melting from rooftops. This natural scenario provides all the necessary conditions for icicle growth, namely subfreezing conditions, constant flow of water and an overhanging support.

Many models of the growth of icicles have been proposed, such as those of Makkonen [5], who used heat transfer arguments to justify the icicle growth rates vertically and horizontally. The work by K. Chung and E. Lozowski [6] uses a heat transfer model as well, but includes salinity as a parameter. According to their work, saline icicles grow more slowly and for a longer time than pure water icicles, and are also shorter and wider than their pure water counterparts. They also mention that the saline icicles tend to grow more pronounced ripples, or ribs as they call them, as opposed to the relatively smooth pure icicles. Although this is mentioned it is never fully explored, and indeed the exact mechanism for the growth of ripples in saline conditions remains largely unexplored. Attempts to approach the problem of icicle ripples from a theoretical point of view have been made [7] [8], however these theories do not include an analysis of icicles containing solutes such as salt. Experimental investigations on the formation of ripples have also been explored [9] however these experiments also neglect to use solutes, and indeed icicles grown from pure water often do not exhibit visible ripple patterns [10]. Icicles that grow in nature are typically ripply icicles, a consequence of the fact that the water from which they grow always contains some degree of impurities from their environment.

In this work experimental investigations on the effects of various solutes on the growth patterns of ripples will be investigated. Specifically, Polyethelyne Glycol (PEG) solutions of various molecular weights were used to observe the effects of the molecular weight on the occurrence and behavior of ripples. The icicles studied here were grown from solutions of varying concentrations of the various PEG's of different molecular weights. Thus, both the effect of solute concentration and molecular weight on the formation of icicle ripples will be observed. This will be done in order to verify if the ripples occur for all concentrations, or whether ripples have a certain onset concentration, and whether this is a general onset concentration or if it differs for different molecular weights. Finally, the wavelengths and amplitudes of the ripples themselves will be taken under consideration to determine if any changes in these parameters occurs at different concentrations or molecular weights.

Finally, it is well know that the presence of solutes in water can affect the freezing point of the solution [11]. This freezing point depression may also have an effect on the ripple growth. Therefore we will also explore the relationship between the freezing point depression and the parameters of the icicles, such as wavelength and amplitude, to determine if there is any trend in these parameters with respect to freezing point depression.

This work will begin with a discussion of the experiment in chapter two. This will include both a description of the apparatus and an overview of the experiment being performed. Along with this, the process of analyzing the icicle data will also be presented in chapter two. In chapter three the observations from the experiment will be presented and discussed, including discussions of the variations in wavelength and amplitude with respect to the three variables molecular weight, concentration and freezing point depression. Finally, the work will conclude with a discussion of the overall findings and implications of this work as well as suggestions for topics of future study.

Chapter 2

Experimental Methods

2.1 Apparatus

Icicles were grown on a modified version of the tabletop apparatus described in the thesis by Antony Chen [3]. The apparatus itself, pictured in figure 2.1, consists of an enclosed chamber for growing the icicles along with a variety of external attachments for cooling, drying and control of other growth conditions inside the chamber.

The apparatus pictured in figure 2.1 consists of a large insulated box (pictured on the left in a)). The box has an opening which is in line with a camera. When in use, a long piece of insulation is placed between the camera and the opening, with a hole just wide enough for the camera to acquire images from inside the box. Various power supply's (seen on the right in a)) control the variety of mechanisms at work inside the box, including the fans and the heated nozzle and funnel. In b) we see the mass balance (on the right) used to monitor the mass of solution during the experiment, and the peristaltic pump (left of the balance) used to pump the solution into the chamber. Left of the pump is the humidity regulator (Wilkerson X06-02-000 H14) which uses silica gel beads to absorb humidity from incoming air such that when the

a) b) c)

Figure 2.1: a) Image of the front of the icicle growth apparatus. b) Image of the side of the apparatus, including the peristaltic pump, mass balance and humidity regulator. c) Image of the back of the apparatus, including both of the cooling baths.

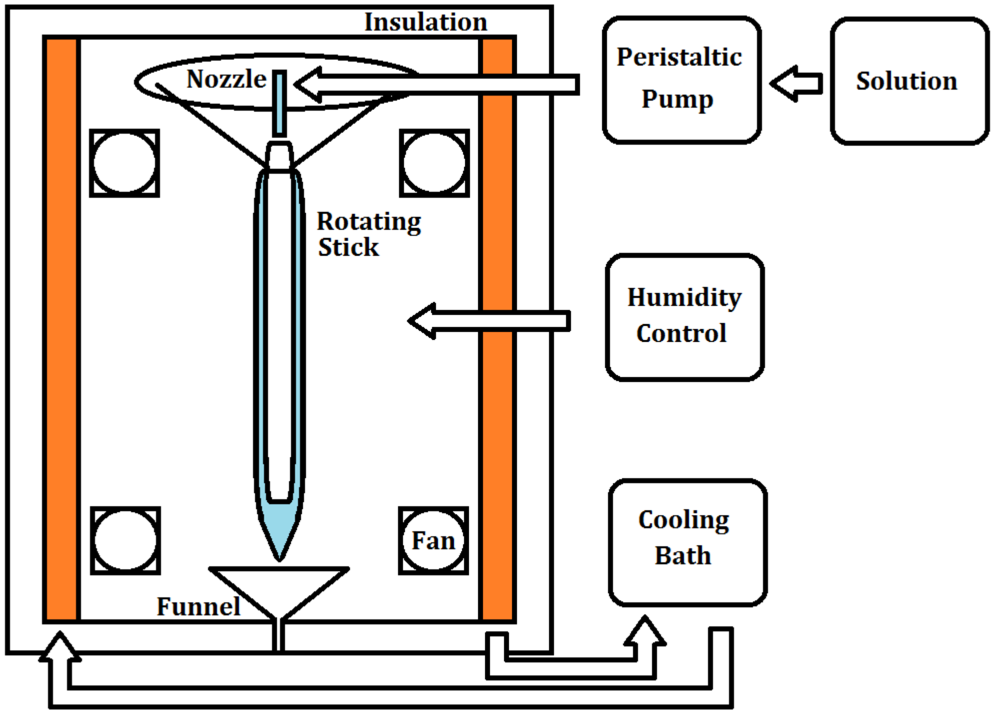

Figure 2.2: Schematic diagram of the apparatus, including the box in which icicles are grown along with external tools such as the peristaltic pump and humidity control.

air flows into the chamber it is dry, thus decreasing the humidity inside. Finally, in c) we see the two cooling baths which regulate the temperature of the inside of the chamber and the temperature of the incoming solution. The setup is also represented schematically in figure 2.2.

The chamber was outfitted with four aluminum walls lined with copper piping and was further insulated with 10 cm of foam. The box's internal copper piping was connected to a cooling bath (ThermoScientific Haake A40/AC200) which circulated antifreeze throughout the pipes. Computer case fans (Vantec TF8025) inside the chamber helped to circulate the air inside and thermocouples were used to monitor the temperature at the bottom, top and center of the chamber. A humidity sensor(RH-USB) was used to monitor the relative humidity inside the chamber during icicle

a) b) c)

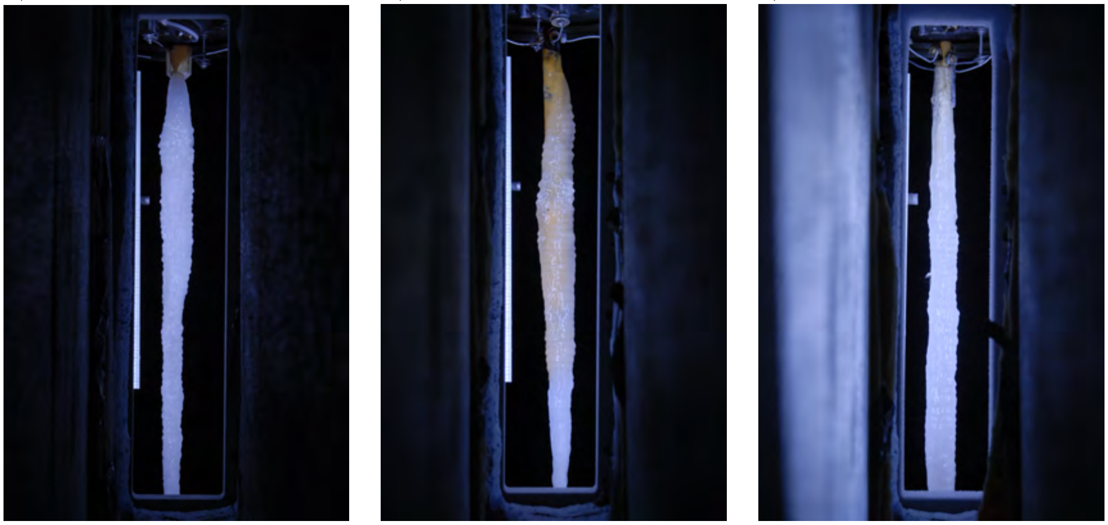

Figure 2.3: Examples of Icicles grown on a) the small conical support, b) the sham-wow stick, and c) the wool stick)

growth.

Icicles grown previously by Chen [3] were grown on small conical supports. In this study longer stick supports covered in absorbent material (sham-wow or wool) were used to allow for uniform coverage and soaking of the stick before freezing. Examples of icicles grown on all three of these growth mediums can be seen in figure 2.3. These supports were bound to a ring connected to a stepper motor which allowed the ring to rotate the supports. The ring was fashioned with notches and a photo-interrupter was placed in line with the notches to allow for precise control of the timing of image acquisition. Using LabVIEW and the interrupter, a LabVIEW VI precisely timed the rotation of the supports and then controlled the timing of the picture acquisition of the camera, a digital single-lens reflex (DSLR) camera (NikonD200). The rotational period of the supports was set to 6 minutes per revolution with 16 images being taken per rotation. This is double the number of images per rotation reported in the previous work [3] in order to allow for more data per rotation.

Aqueous solutions of PEG were prepared prior to the experiment. These solutions were pumped from a beaker into the chamber via a peristaltic pump (Gilson Minipuls 3), which uses a rotor whose surface contains several 'bumps'. The flexible tygon tubing through which the water was pumped is thus compressed and uncompressed, forcing the fluid to flow through. A section of this tubing was cooled via a separate cooling bath connected to neighboring copper tubes (ThermoScientific Digital Plus) before reaching the nozzle, which was kept near 0°C, and dripped water onto the supports for icicle growth. As water dripped from the supports it fell into a copper funnel, which was heated to prevent freezing. The water in this funnel was then removed from the apparatus, preventing a buildup of water and/or humidity.

The entire apparatus as described was automated via four LabVIEW VI's, one for controlling the peristaltic pump, one for control of the stepper motor and thus the rotation of the supports, one for the monitoring of temperatures inside the box (top, bottom, center and nozzle) and one for the camera control. The humidity inside the chamber was also monitored using an RH-USB and the program TRH Central.

2.2 Icicle preparation and growth

Icicles were grown from solutions of distilled water and a variety of solutes. While the previous work [3] focussed on salt solutions(NaCl) in this work we use Polyethelyne Glycol (PEG) of various molecular weights (ie. PEG 600, PEG 3350 and PEG 8000). The concentrations of these solutions were measured in weight percent as shown in equation 1.1:

$$wt.\% = \frac{wt.Solute}{wt.solvent + wt.Solute} * 100 \tag{2.1}$$

Solutions of 0.1, 0.5, 1.0 and 2.0 weight percent of each of the solutes were used to grow the icicles. The peristaltic pump was used to pump the solutions into the chamber, while the weight of the solutions was measured with a mass balance (Scout Pro). The total remaining weight of the solution was monitored, via the balance,in the labVIEW VI for the peristaltic pump.

The solutions were dripped onto the support (one of the two sticks covered in sham-wow or wool) at a rate of 5 g/min initially, to ensure uniform wetting of the support before growth. The supports were rotated initially at a rotational period of 1 minute per rotation by the stepper motor and controlled in labVIEW. This was done to allow uniform soaking of the entire surface of the growth medium. Once the supports were sufficiently soaked, the water supply rate and rotational period were set to 0.7 g/min and 6 minutes per rotation respectively, and were kept at those values for the remainder of the icicle growth.

The temperature inside the chamber was maintained at around $-10°$C and was monitored and recorded via LabVIEW in three different locations inside the chamber, to ensure uniform cooling. The temperature of the nozzle was kept slightly above freezing to avoid ice blocking the nozzle, and likewise the funnel at the base of the chamber, used to collect drops of falling solution, was also kept above freezing to prevent buildup of ice. The humidity was also monitored and recorded for the duration of the experiment.

The apparatus was set to run overnight, while the camera control LabVIEW VI took pictures periodically according to the rotation rate of the support. The camera was programed to take a picture every time the interrupter entered or exited one of the tabs on the supporting ring (pictured in figure 2.4). This resulted in a collection of images (between 2000 and 3000 images per run) documenting the growth of the icicle over time. These images were then analyzed via Matlab to determine properties

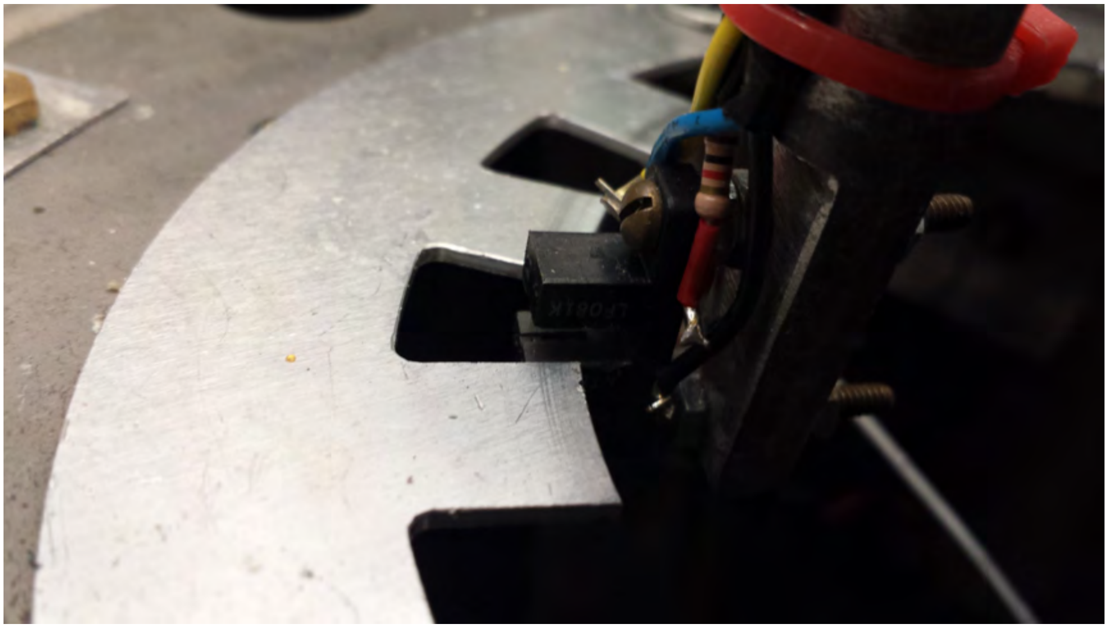

Figure 2.4: Image of the interrupter as it passes through a tab on the rotating ring, blocking the interrupter beam. When the beam is interrupted the LabVIEW VI is programed to take a picture.

of the icicles such as ripple wavelength and amplitude.

2.3 Icicle Analysis

Icicle images were analyzed using a modified version of Matlab codes created by a previous student [3]. The process for any given run, which contains between 2500 and 3500 icicle images, will be outlined in this section.

Firstly, the images are loaded and cropped to contain only the region of interest (i.e. where the icicle is growing). This simple process is done by loading all images in the run, and defining a crop window for the set of images. The crop window is chosen such that the icicle is at the center of the image and the remainder of the image is the dark background.

The cropped images are then converted to simple binary black and white images through a series of steps. The first step is converting the image to gray-scale and obtaining a threshold value of the gray-scale image to determine which pixels can be considered black and which are white. Pixels below this threshold value are considered black (binary 0) and those above are considered white (binary 1) Holes in the image are then filled in as a part of the background (black or binary 0). Thus, after these steps the image has been converted into a grid of binary numbers, the zeros corresponding to the background and the ones corresponding to the icicle. The angle at which the icicle hangs in each image is then obtained and used to rotate all images to a common center. Once the images are all lined up, the first 16 images are used as background images, one for each rotational position, and are subtracted from all future images. The edge of the icicle is then identified using the built in Matlab function bwtraceboundary along with information such as the first edge pixel and last edge pixel.

The ripple data is then extracted by subtracting the edge shape by smoothing the edge to make a background trace of the edge which lacks ripples. This is then subtracted from the actual edge, to give data that is simply the ripples along the edges of the icicle. This is done for both the left and right edges of each image in a given run.

In order to obtain wavelengths, amplitudes and other information from the data, the picture times must be analyzed. Since there are sixteen pictures per rotation, the picture times previously recorded in seconds are modified into a periodic set of sixteen times. Each time is generated by adding the average change in time from the previous time value to the current time value. These delta t values are generated from the original time file, thus making the new time file only semi-periodic. Thus what is obtained in the end is a set of sixteen repeating times plus an added amount of time which is calculated from the change in time between the two previous times.

Finally, the wavelengths and amplitudes are determined from the images. Both the left and right edges of an image are subjected to the condition that any edge value greater than 10cm is removed. A fast fourier transform (fft) is applied to the edges, from which the wavelengths and amplitudes are determined. These values are determined using a gaussian fit to the largest peak in the fft. The wavelength and it's uncertainty are determined from the position of this peak, and the amplitude is found from the intensity. After these wavelength values are obtained they are averaged over the lifetime of the icicle, and the uncertainty is determined from the uncertainties of the individual wavelengths, as shown in equation 2.2.

$$d\overline{\lambda} = \sqrt{\frac{\sum (d\lambda)^2}{n^2}} \tag{2.2}$$

where $d\overline{\lambda}$ is the error in the average wavelength, $d\lambda$ is the error in a single wavelength, and n is the number of wavelengths used in the average (ie. the number of images). The sum is thus over all wavelengths determined from each individual image.

The average amplitude for each icicle was determined in a similar way, however because the individual amplitudes had no associated errors, the errors in the amplitudes were determined from the statistics of the amplitudes instead (ie. standard deviation).

After all of the images were processed and the data was obtained these wavelengths and amplitudes were analyzed for the range of concentrations and molecular weights studied, as well as the freezing point depression. The analysis and discussion of these results will be carried out in the next section.

Chapter 3

Results and Discussion

3.1 Icicle Data

In this section data for a typical icicle will be presented and observations over the full range of icicles grown during this study will be conducted. Specifically, the wavelength and amplitude of icicle ripples will be analyzed with respect to concentration, molecular weight and freezing point depression. The icicles considered for analysis in this study were grown from solutions of various concentrations of PEG's with different molecular weights.

Eight icicles were made from each solution, four of different concentrations grown on the sham-wow covered stick and four of these same concentrations grown on the wool covered stick. Based on a simple observation of a succession of images of different concentrations, like the images shown in figure 3.1, it is clear that the ripples on the icicles become more pronounced at higher concentrations.

Based on the images alone (such as the images in figure 3.1) it seems that the ripples become more pronounced at higher concentrations, and indeed it appears as though there are little or no ripples for the low concentration icicles by eye. To

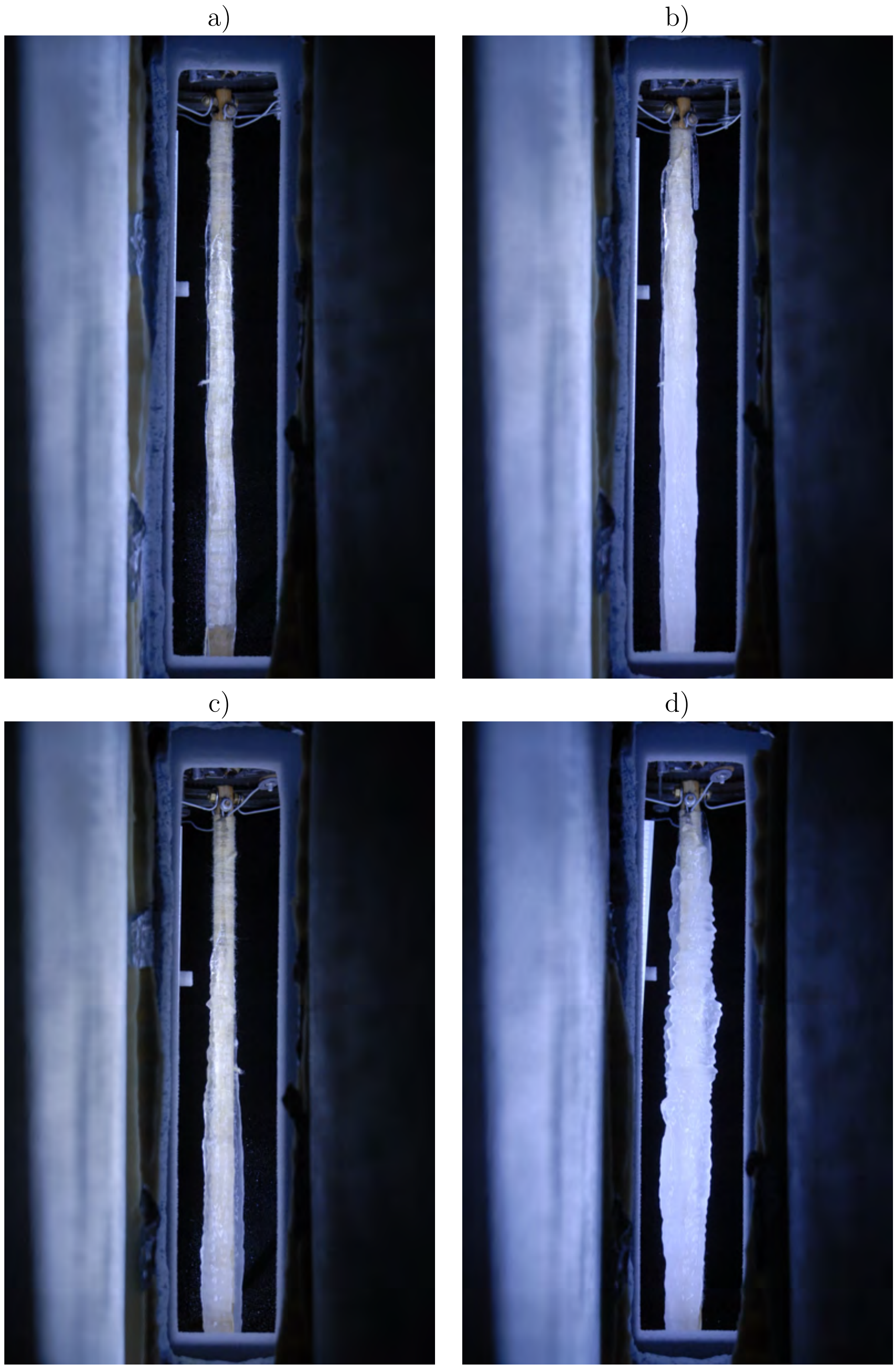

Figure 3.1: Icicle images obtained from a) 0.1wt%, b) 0.5wt% c) 1.0wt%, and d) 2.0wt% PEG3350

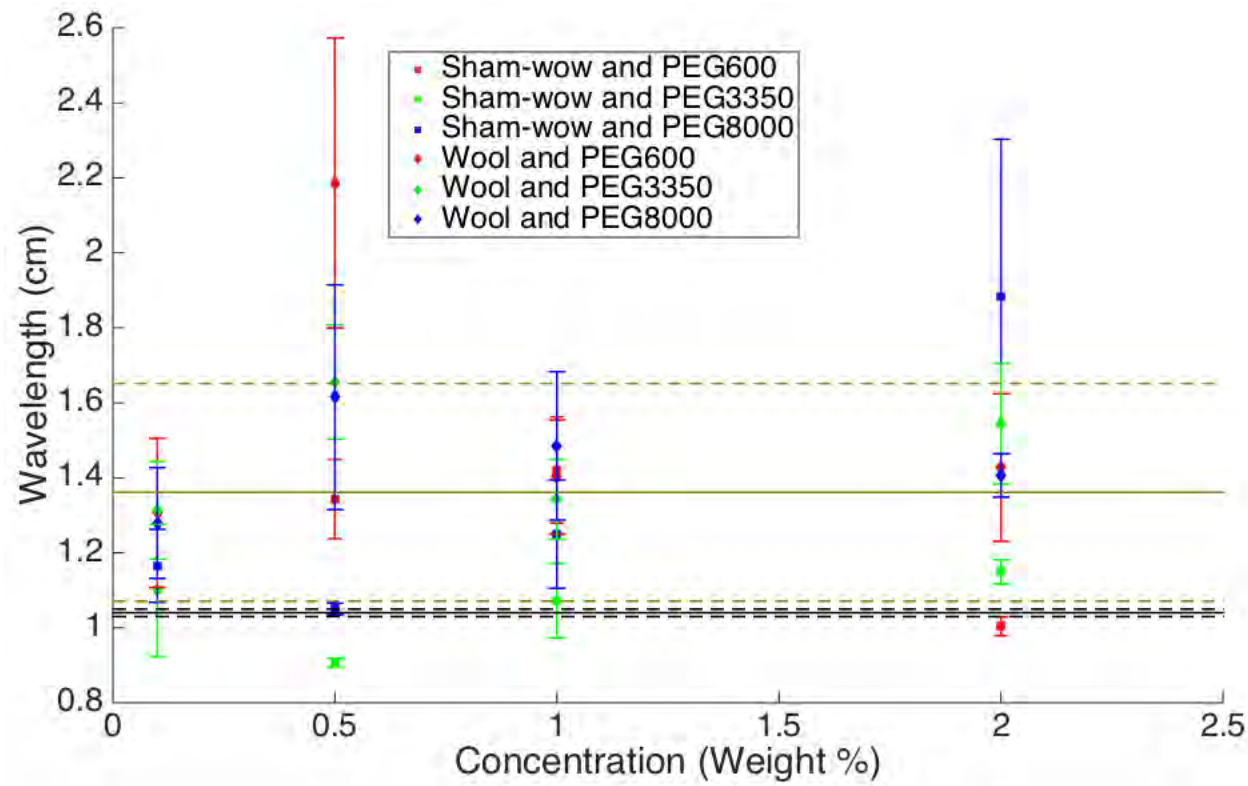

Figure 3.2: Plots of average ripple wavelength over a single run for various solutions of PEG600, PEG3350 and PEG8000, plotted as a function of concentration. The average wavelength of icicles previously grown is shown as a black solid line, with one standard deviation represented as a black dashed line. Likewise, the mean and standard deviation for the present analysis is represented by gold solid and dashed lines respectively.

determine whether ripples were present and how they behave, the ripple wavelengths and amplitudes were obtained.

The code used to find the wavelengths and amplitudes uses a ripple profile determined from a previous step. To determine how the icicle ripples scale with concentration, the ripple wavelength was plotted as a function of the concentration for three different solutions. Each of these solutions was made from PEG of one of three different molecular weights. A plot of the wavelengths and uncertainties of the resulting icicles is shown in figure 3.2, plotted as a function of the solution concentration.

As can be seen from figure 3.2, the average wavelengths for all of the icicles grown in this study is higher than the average wavelengths reported previously[3]. It is also clear from this plot that there is no definite trend in ripple wavelength with increasing concentration. While there sometimes seems to be a trend of increasing wavelength, this appears to be negligible within uncertainties. More data would need to be obtained to definitively determine if this increase is significant. This possible increase is easier to see in the data. Table 3.1 shows a summary of the runs performed in this study, along with the calculated average wavelengths and their uncertainties.

Table 3.1: Table of runs showing what the icicle was grown on, the solute used, its concentration, the wavelength of the resultant icicle and its uncertainty.

Growth Medium	Solute	Concentration	Wavelength (cm)	Uncertainty (cm)
Sham-Wow Stick	PEG600	0.5%	1.3433	0.1058
Sham-Wow Stick	PEG600	1.0%	1.4207	0.1413
Sham-Wow Stick	PEG600	2.0%	1.0038	0.0250
Sham-Wow Stick	PEG3350	0.1%	1.0999	0.1759
Sham-Wow Stick	PEG3350	0.5%	0.9073	0.0115
Sham-Wow Stick	PEG3350	1.0%	1.0724	0.0989
Sham-Wow Stick	PEG3350	2.0%	1.1492	0.0325
Sham-Wow Stick	PEG8000	0.1%	1.1652	0.0974
Sham-Wow Stick	PEG8000	0.5%	1.0498	0.0155
Sham-Wow Stick	PEG8000	2.0%	1.8833	0.4196
Wool Stick	PEG600	0.1%	1.3063	0.1987
Wool Stick	PEG600	0.5%	2.1864	0.3866
Wool Stick	PEG600	1.0%	1.4020	0.1522
Wool Stick	PEG600	2.0%	1.4271	0.1967
Wool Stick	PEG3350	0.1%	1.3135	0.1304
Wool Stick	PEG3350	0.5%	1.6552	0.1523
Wool Stick	PEG3350	1.0%	1.3426	0.1053
Wool Stick	PEG3350	2.0%	1.5435	0.1601
Wool Stick	PEG8000	0.1%	1.2796	0.1480
Wool Stick	PEG8000	0.5%	1.6149	0.2996
Wool Stick	PEG8000	1.0%	1.4582	0.1978
Wool Stick	PEG8000	2.0%	1.4063	0.0579

We see, for example in the wool stick runs of PEG 600, an increase between 0.1%,

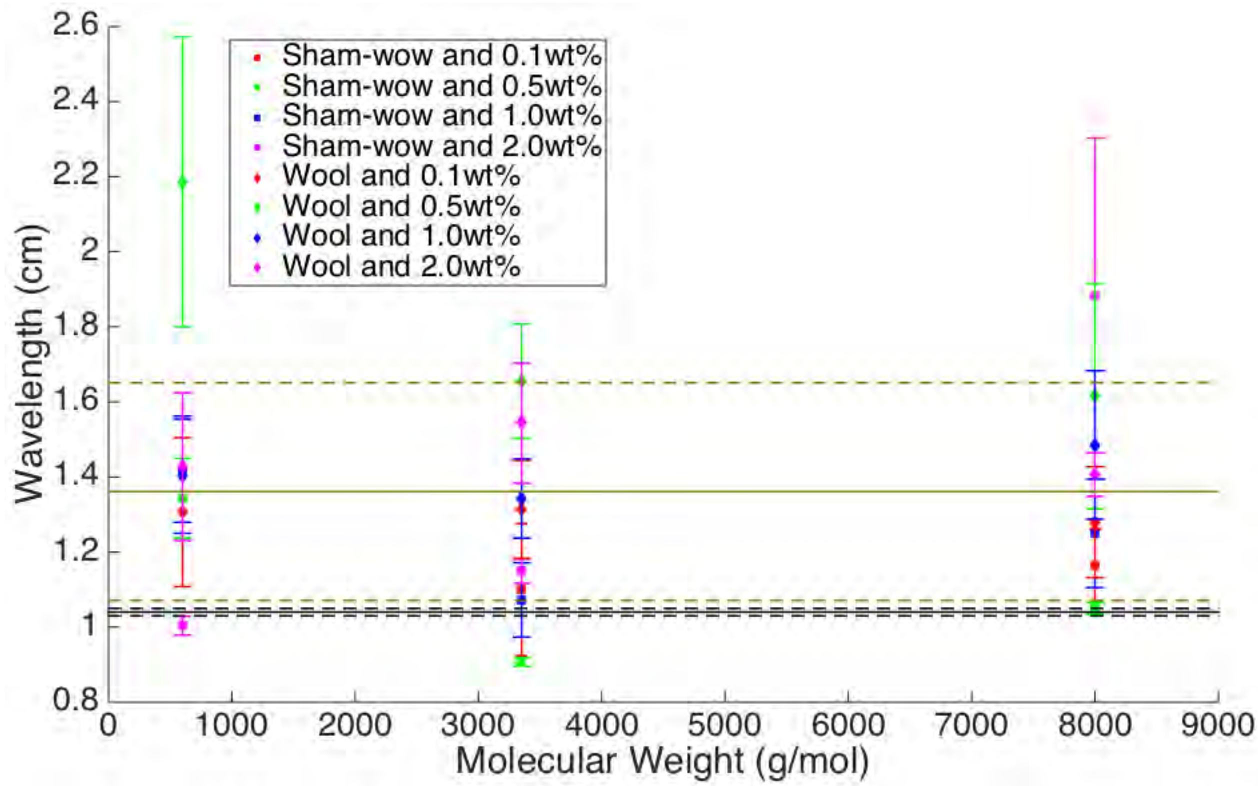

Figure 3.3: Plots of average ripple wavelength over a single run for various solutions of PEG600, PEG3350 and PEG8000 plotted as a function of molecular weight. The average wavelength of icicles previously grown is shown as a black solid line, with one standard deviation represented as a black dashed line. Likewise, the mean and standard deviation for the present analysis is represented by gold solid and dashed lines respectively

1.0% and 2.0% runs. There is however a marked increase at 0.5% which cannot be explained. This change in wavelength at 0.5% seems to occur a few times in the data, but it is not a significant change within uncertainty.

We can also observe trends in the wavelength with respect to the molecular weight, using the three molecular weights of PEG. This result is shown in figure 3.3.

As with the previous figure, there is no clear trend in wavelength with molecular weight. As such we can only say that there is no clear trend in the data, and that more data would be needed in order to make a definite statement on the effect of the molecular weight of the solute on the wavelength of the ripples. Although inconclusive, there is an observed possible trend in the data with respect to concentration, whereas the spread of the data for molecular weight seems relatively uniform indicating that there may not be any trend with molecular weight. Further experimental data for a wider range of both molecular weights and concentrations would help clarify if such trends exist.

Also of note is the average and standard deviation of the two experiments. The averages of the two data sets, that of the previous work [3] and that of the current work are different within one standard deviation. The two data sets lie within two standard deviations of each other, and to definitively state that the two data sets are fundamentally separate we would expect them to be significantly different to within three standard deviations. While the means of the two sets of data are significantly different, the problem arises because of the relatively large standard deviation obtained in the current work. Thus, while we can say that it appears that the PEG solutions create icicles whose wavelengths are generally larger, in order to make this statement more definitive would require a larger set of data, thereby potentially reducing the standard deviation. In the case of the previous work, a much larger amount of data over a wider range of concentrations was obtained, thus leading to an overall lower standard deviation. It is thus necessary for future studies into this topic to require more data to be obtained on icicles grown from PEG solutions. It would also be of interest to obtain more data over a greater spread of concentrations and molecular weights, to see if the wavelengths deviate from the mean obtained here over a larger range of solution parameters.

Another avenue that can be explored is that of the freezing point depression. A general rule for the reduction of the freezing point of a substance with the addition of a solute is known [11], and is shown in equation 3.1,

$$\Delta T = K_f m_B \tag{3.1}$$

where ΔT is the freezing point depression, K_f is the cryoscopic constant of the solvent and m_B is the molality of the solution in mol/g. The cryoscopic constant for water is $1.86KKg/mol$ and the molality was obtained using the molecular weight and the total mass of the solution as per equation 3.2,

$$molality = \frac{\frac{m_{solute}}{M_{solute}}}{m_{solvent}} \tag{3.2}$$

where m_{solute} is the mass of solute added to the solution, M_{solute} is the molecular weight of the solute and $m_{solvent}$ is the mass of the solevnt, in this case water. By calculating the molality for each of the solutions in this study, the behavior of the wavelength as a function of the freezing point depression was observed and can be seen in figure 3.4.

Figure 3.4 shows that in general, the icicles with lower weight percents, and thus lower freezing points (the red points in figure 3.4) all lie below the average value (with the exception of some of the error bars). The icicles whose weight percents were either 0.5wt% or 1.0wt%, and thus have freezing point depression values in the medium range of the plot, appear to have an equal number of points above and below the average wavelength. Finally, the icicles grown with the highest freezing point depression values (those shown in magenta in the figure) almost all lie above the average value. Although this trend isn't always apparent, and indeed as stated previously a larger quantity of data would be necessary to further support this trend, it seems that there is a general tendency for icicles grown from solutions with overall higher freezing point depressions will in fact have longer wavelength ripples.

It is important to note that equation 3.1 was obtained by assuming that the

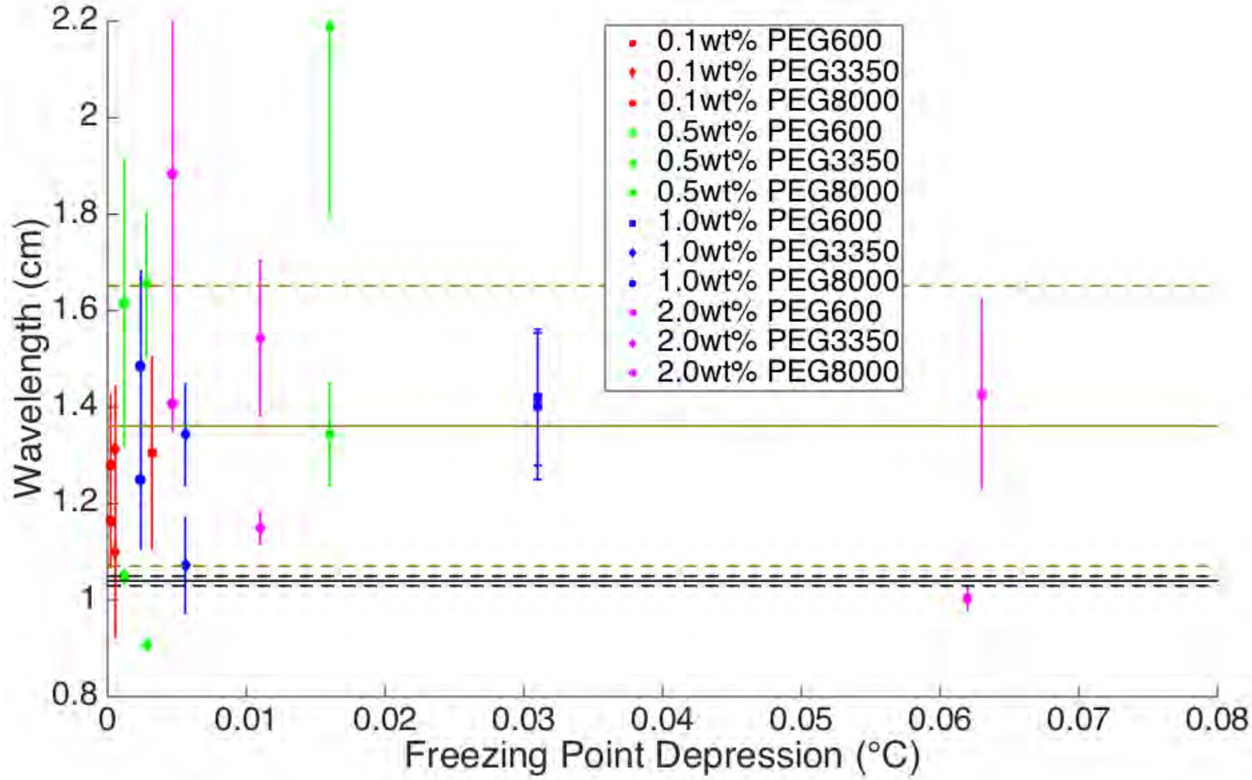

Figure 3.4: Plots of average ripple wavelength over a single run for various solutions of PEG600, PEG3350 and PEG8000 plotted as a function of freezing point depression. The average wavelength of icicles previously grown is shown as a black solid line, with one standard deviation represented as a black dashed line. Likewise, the mean and standard deviation for the present analysis is represented by gold solid and dashed lines respectively

solution was dilute [11]. Therefore as the concentration (in wt%) gets larger, the accuracy of this assumption decreases. Furthermore as we can see from our values of freezing point depression, the depression is linearly related to the concentration. However this is not always the case, as can be seen in the work by Steuter [12]. In fact, Steuters work shows that PEG solutions specifically deviate from this linear behavior. In his work, the water potential changes in a nonlinear way with concentration, and in fact the molecular weight of the PEG being used also affects this relationship. The water potential is affected by the osmotic potential, which is the potential of the water as a result of an added solute [13]. The reduction in water potential with increasing concentration in the work by Steuter can be thought of as a change in the osmotic potential of the water as more solute is added. This osmotic potential is linearly related to the freezing point of water [14]. Thus the idealized scenario presented in equation 3.1, which was used to generate the data for the freezing point depression in this study, may in fact not show the true values of the freezing point depression. For reference the freezing point depression for salt based on equation 3.1 is shown in figure 3.5 alongside the freezing point depressions calculated for the three different PEG's used. It is clear that solutions of PEG have drastically lower freezing point depressions than salt. Despite the deviation from linearity expected from the work of Steuter, our experiments only investigate the lower end of the concentration regime, where the relationship between freezing point depression and concentration can be taken to be linear.

A possible next step in this approach would be to obtain data on how the freezing point depression of water is affected by these PEG solutes, in order to better map the wavelengths to appropriate values of the freezing point depression. As stated by Steuter [12] there are many other factors that come into play into how the water potential changes as more solute is added. In other words, to get a clear picture of

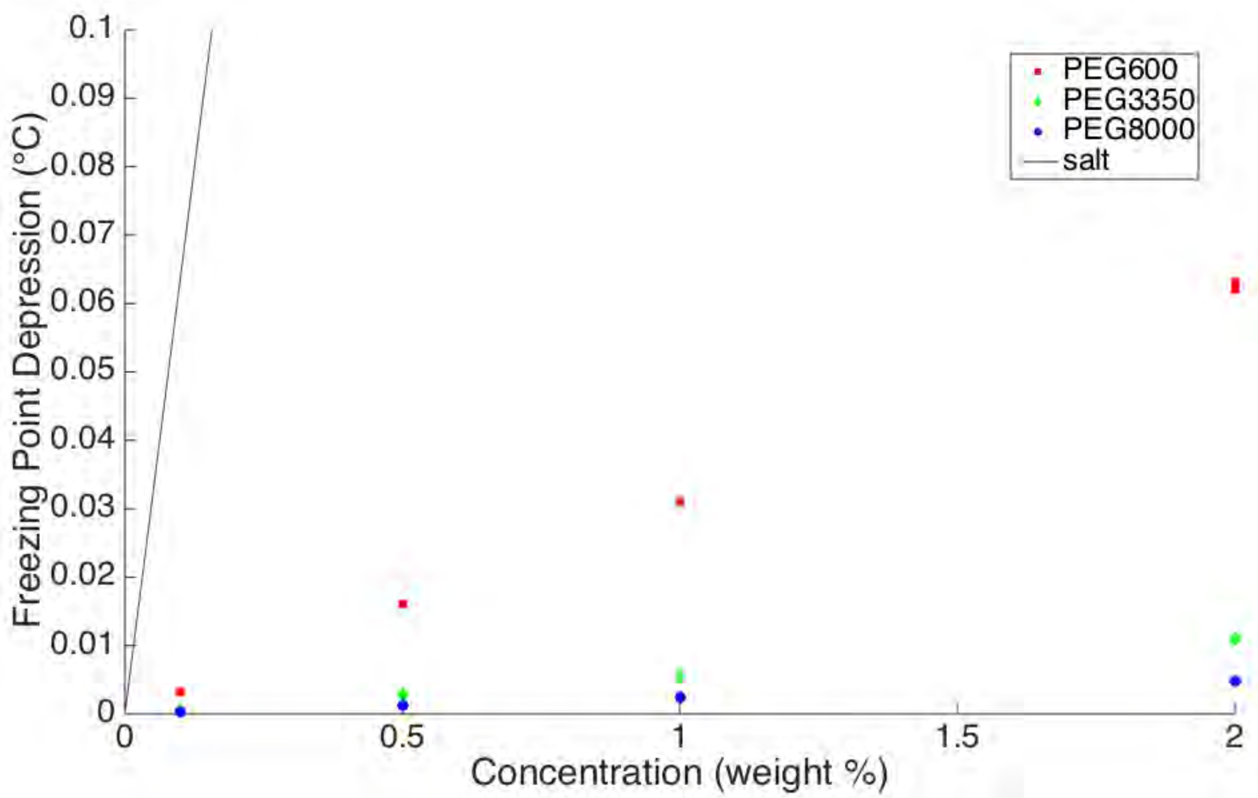

Figure 3.5: Plots of average ripple wavelength over a single run for various solutions of PEG600, PEG3350 and PEG8000 plotted as a function of freezing point depression. The average wavelength of icicles previously grown is shown as a black solid line, with one standard deviation represented as a black dashed line. Likewise, the mean and standard deviation for the present analysis is represented by gold solid and dashed lines respectively

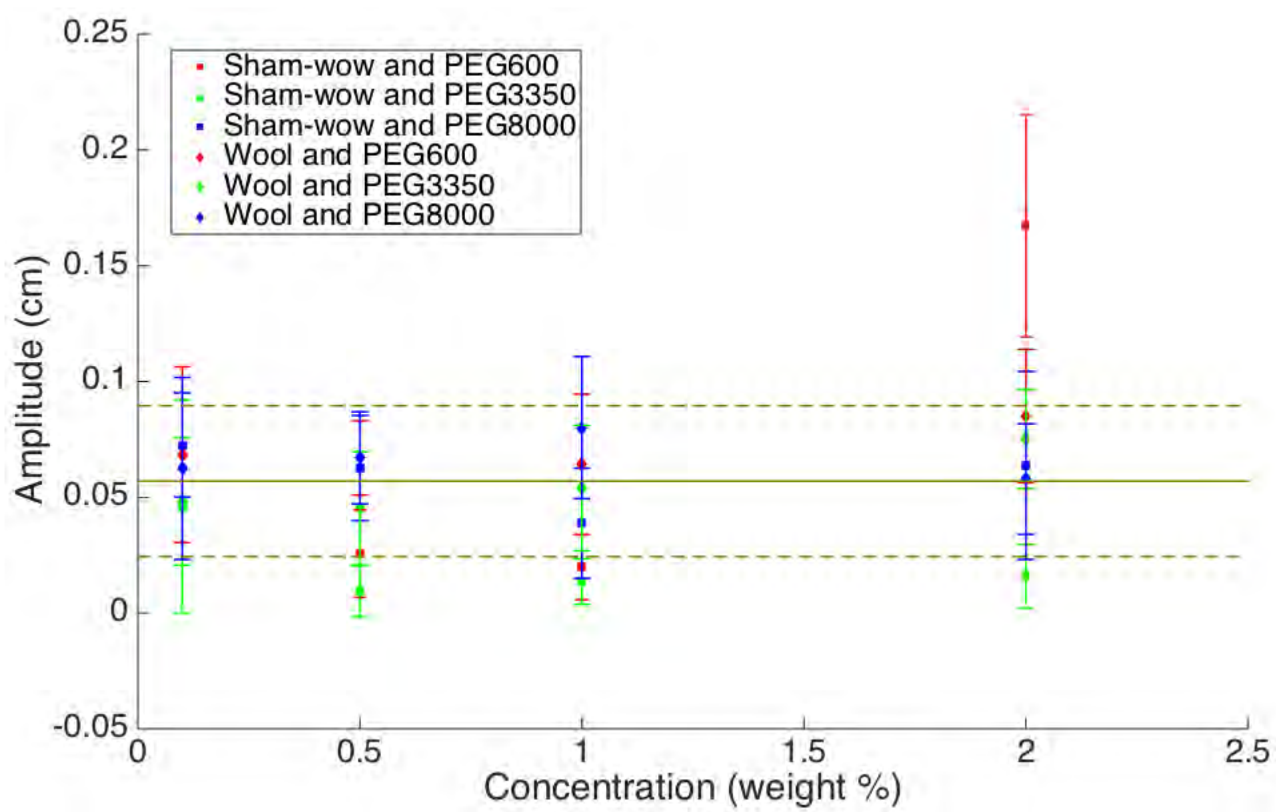

Figure 3.6: Plots of average ripple amplitude over a single run for various solutions of PEG600, PEG3350 and PEG8000, plotted as a function of concentration. The mean and standard deviation of the amplitudes is represented by gold solid and dashed lines respectively.

the true behavior of the freezing point depression resulting from various chain lengths of PEG's an experimental evaluation of the freezing point depression for each solution would give a clearer picture of how the freezing point changes.

The amplitude of the icicle ripples was also obtained for each icicle studied in a similar way to the above wavelength analysis. A plot of the amplitude of the ripples with respect to the concentration can be seen in figure 3.6.

From this plot it seems then that the amplitudes remain relatively consistent between runs, without much if any variation with concentration. In the previous study the amplitudes appeared to vary from just above 0.01 for the very low concentrations, up to just above 0.06 for icicles whose concentrations approached the lower end of the scale used in this study (about $0.1wt\%$). The average amplitude values obtained in this study are of similar magnitude to those obtained by Chen [3](and indeed the previous results lie within one or two standard deviation from the mean result in this study). It was seen in the work on icicles containing salt as the impurity that the amplitude of the ripples was larger for higher concentrations, a result that doesn't appear in our analysis on PEG grown icicles. That being said, the previous study was carried out on icicles grown over a range of concentrations that spanned three orders of magnitude, while the icicles studied here only span a range of two orders of magnitude. Furthermore, the range of concentrations studied in this work are generally greater than those of the previous work (between 0.1 and 2.0 as opposed to between 10^{-3} and 0.1). Despite this difference the amplitudes vary considerably between runs however there is no clear dependance on the concentration in this case as opposed to the previous work, where it tended to increase with concentration.

Exploring the behavior of the amplitude further, we can look at how it behaves as a function of the molecular weight as in figure 3.7.

We see again that there is no significant trend in the amplitude with molecular weight. While it appears that the PEG 8000 icicles have generally larger amplitudes (there are no instances of PEG 8000 icicles with an amplitude below one standard deviation, unlike the other two PEG's) however this apparent increase is subtle at best and would require more observations to be identified as relevant.

Finally, we can observe the behavior of the amplitude with the freezing point depression calculated previously. The results of this analysis can be found in figure 3.8.

As was said previously, the freezing point depression changes much more rapidly as a function of the concentration for salt than it does for PEG. As such all of the icicles grown in this study had freezing point depression which lie on the lower end of

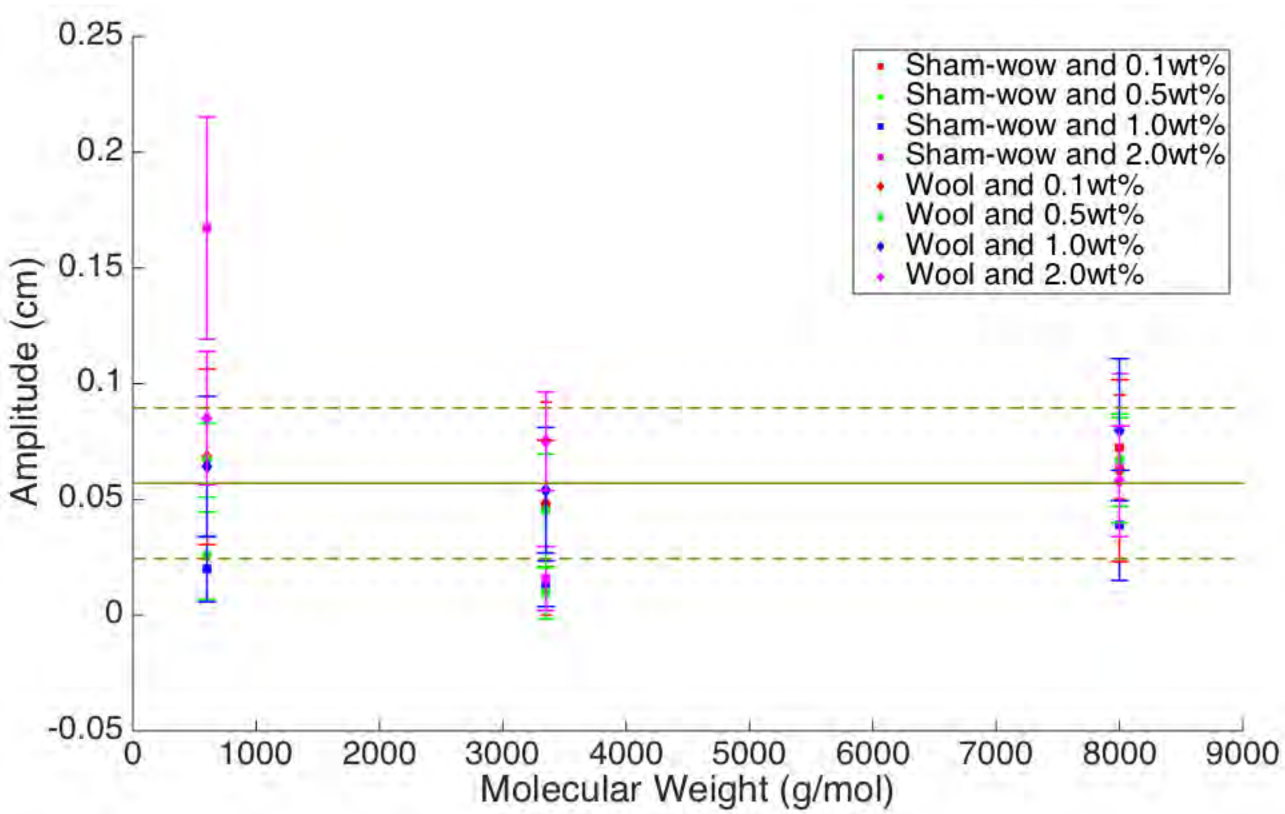

Figure 3.7: Plots of average ripple amplitude over a single run for various solutions of PEG600, PEG3350 and PEG8000 plotted as a function of molecular weight. The mean and standard deviation of the amplitudes is represented by gold solid and dashed lines respectively.

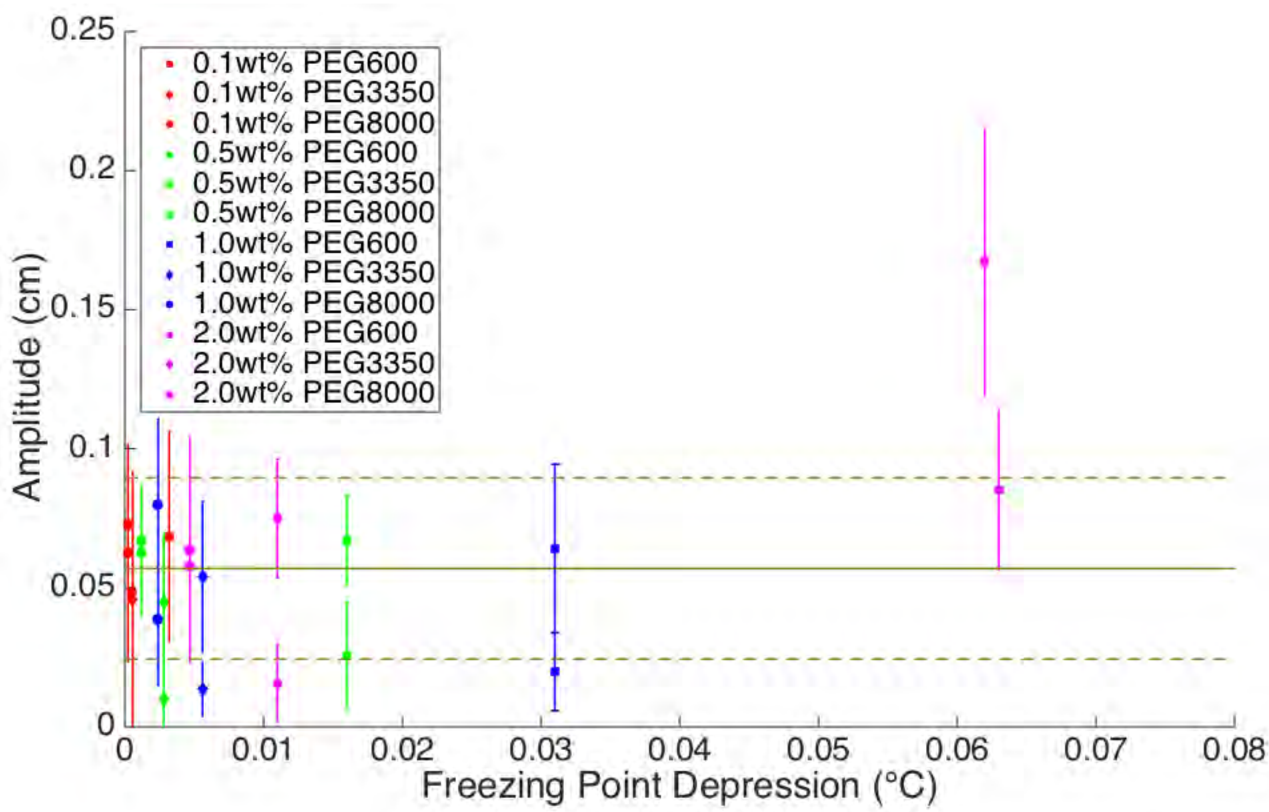

Figure 3.8: Plots of average ripple amplitude over a single run for various solutions of PEG600, PEG3350 and PEG8000 plotted as a function of freezing point depression. The mean and standard deviation of the amplitudes is represented by gold solid and dashed lines respectively.

the scale for that of salt icicles. It is perhaps not surprising then, that the icicles in this study have very little fluctuation in amplitude with respect to the various parameters varied throughout this study. If indeed the freezing point depression plays a role in the variation of ripple amplitudes, the effects of that depression would be much more subtle for PEG, whose freezing point depression varies relatively slowly, compared to the salt icicles of Chen's work. As such, while it appeared that the amplitudes of the icicles grown in the previous work varied with concentration, the reason we do not see such a trend in this study may be a result of the fact that while the concentrations are the same, the effect of those concentrations on the freezing point's of the solutions is much weaker for PEG.

In order to gain more definitive answers to the question of the behavior of icicle ripples as the concentration, molecular weight and freezing point depression vary it may be necessary to explore even higher concentration solutions, in order to further increase the freezing point depression towards values observed in previous studies. Furthermore it would be useful to explore different molecular weights of PEG, or an entirely different set of polymer compounds whose molecular weight can be varied. PEG was chosen because it is available in a variety of molecular weights, which allowed for the exploration of how the molecular weight affected the ripples. Despite this, the discrepancy between the freezing point depressions of all the PEG's compared to salt is quite significant, and the use of a material with different properties than PEG may help to further explore the variation in ripple properties with molecular weight. Studying such properties as the ripple travel speed and growth rates may help further elucidate variations in the ripple properties as the concentrations and molecular weights vary. Finally, and perhaps most important, further studies into the effects of PEG on the growth of icicle ripples requires more data over a wider range of values for the concentrations and molecular weights as well as a greater quantity of data within the ranges studied in this work. Obtaining a greater quantity of data would not only provide a greater range of values to explore but also potentially help reduce the standard deviations of the values and allow any patterns in the behavior of the ripples become more apparent and quantifiable.

Chapter 4

Conclusion

In this study we have grown icicles from a variety of solutions and observed the resultant properties of those icicles. In general, two parameters were varied for the various icicles grown, the concentration of the solution and the molecular weight of the solute being used. From these experiments we observed the effects of the molecular weight and concentration on icicle ripple growth, including both the wavelength of these ripples and their amplitude. Furthermore we calculated the freezing point depression, using the basic model which assumes the solutions are dilute, in order to observe the behavior of these icicles as their freezing point depression varies.

It was found that the icicles grown using PEG's of varying molecular weights in general have an overall longer wavelength than those grown from salt solutions. This difference however was only seen within one standard deviation, and indeed beyond that the average wavelengths for these two sets of experiments appeared to overlap. A slight upwards trend was also noticed in the wavelength with increasing concentration, however more data would be required to determine whether this trend is significant. Further study of icicles grown from solutions of PEG, both within the parameters used in this study and beyond, would help further identify if this is indeed a property of these icicles. On the other hand, the behavior of wavelength with molecular weight appears to be more clearly uniform that that of the wavelength, although further data acquisition would help solidify this claim. The icicle ripple amplitude also appeared to remain relatively constant as a function of these parameters, despite previous observations to the contrary.

Future studies into this topic are necessary to further evaluate trends in ripple properties with growth conditions. Two possible avenues of study include growing icicles using PEG of different molecular weights than were used here as wells as doing a more in depth analysis of changes in freezing point depression as the concentration of these PEG solutions increase. Simply trying a different material, whose molecular weight can also vary, to see it's effects and the effects that any changes in it's molecular weight may have on the ripple properties would also help our understanding of how the molecular weight in general affects the ripples. Such a study would not only be interesting independently, but may also allow us to gain more insight into the behavior of icicle ripples grown with PEG.

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