



Supercooling and flash-freezing in water and ethylene glycol droplets

البرودة الفائقة والتجميد المفاجئ لقطرات الماء والايثيلين جلايكول

By:

Arwa Mustafa Azaar

Supervised by:

Dr. Khalid Eid

Birzeit, Palestine

January 2020

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Dr. Khalid Eid (Principal advisor).

Dr. Abdallah Sayyed-Ahmad (Member).

Dr. Hazem Abusara (Member).

This Thesis was submitted in partial fulfillment of the requirements for the Master Degree in Physics from the Faculty of Graduate Studies at Birzeit, Palestine.

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Dedication

To my parents and my siblings Abdul-Rahman, Noor-al-Deen, and Hedaya for their support and encouragement.

To my teacher Amal Abdul-Aziz who taught me The Holy Quran that inspires and guides me throughout my life.

Acknowledgment

I would like to thank my supervisor Dr. Khalid Eid for supporting me during the planning and development of this experimental research. Also, I would like to thank the committee members Dr. Abdallah Sayyed-Ahmad and Dr. Hazem Abusara for their valuable notes and to express my gratitude to my colleagues and friends.

Abstract

We present experimental results of the supercooling of different concentrations of ethylene glycol (E.G.) and water droplets placed on a hydrophobic copper surface that is subject to two different experimental techniques for cooling, a thermoelectric device, and liquid nitrogen. The temperature evolution with time is recorded for many droplets and different thermophysical properties such as the flash-freezing point, the freezing point, the melting point were studied. Besides, the effect of the jump in temperature -from the supercooled temperature of the droplet to its freezing point- on determining the initial solid fraction of that droplet is investigated. Notably, we found that the initial solid fraction decreases as the concentration of E.G. increases.

المخلص

نعرض في هذا البحث نتائج عملية لتراكيز مختلفة من نقاط الماء والايثيلين جلايكول الموضوعة على سطح نحاسي، والتي تم تبريدها باستخدام طريقتين، الأولى: الجهاز الكهروحراري، والثانية: النيتروجين السائل.

تم رصد التغير في درجة الحرارة مع مرور الوقت لنقاط الماء والايثيلين جلايكول على شكل رسومات بيانية ليتم تحليلها ودراسة الخصائص الفيزيائية المختلفة لهذه النقاط مثل درجة حرارة التجمد المفاجئ، درجة التجمد، درجة الانصهار.

بالإضافة إلى دراسة تأثير القفزة في درجة الحرارة من درجة البرودة الفائقة إلى درجة التجمد على نسبة التجمد الأولية في النقطة، حيث وجدنا أن النسبة الأولية المتجمدة من النقطة تقل بزيادة تركيز الماء والايثيلين جلايكول (إلى التركيز الذي تم دراسته في هذا البحث ٤٥%).

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1. Introduction:

The three common phases of matter are the solid, liquid, and gas states. Adding or removing energy to matter can cause it to change its phase among these three states, where adding energy to a solid might cause it to melt (i.e. become liquid) and adding energy to a liquid can transform it to the gaseous state. These two processes absorb energy (usually thermal energy) to compensate for the rise in entropy during phase transitions from solid to liquid or liquid to gas states. While the system absorbs energy during the phase change, the temperature typically stays constant. The opposite happens during a vapor-to-liquid phase change, where the condensing matter releases a significant amount of heat -called the latent heat of condensation- during the process. The process of solidification also releases heat energy called the latent heat of fusion. The temperature at which phase changes of a pure substance occur depends on the pressure and is usually found in phase diagrams of the given material¹. Water is a unique material that is liquid at room temperature but can be easily found in the gas (i.e. vapor) or solid (i.e. ice) phases under typical conditions on earth. So, for pure water, the solid-to-liquid phase occurs at 0C° while boiling, in which liquid changes to vapor, occurs at 100C° ².

1.1 Supercooling and flash-freezing of water:

When water is cooled below the freezing temperature (0C°) a stable solid phase (ice) will be present, while heating ice to 0C° causes it to melt². Even though the critical temperature at which the latter process happens is unique, the first is not. So, when one starts to warm ice, it will melt at 0C° every time. Contrary to that, the temperature at which a water droplet converts to ice upon

cooling is not unique. A droplet can be cooled well below 0C° while still in the liquid state. This is called supercooling³.

The supercooling process is very important in the food industry such that fresh fruits and vegetables can be stored in temperatures below their freezing point for a long time without freezing so that it will prevent the cells from damage⁴. Moreover, supercooling is necessary for cold-tolerant organisms: animals, plants, fungi, and bacteria to survive. It contains ice-binding proteins that prevent freezing and keep their body fluids liquid at a temperature below their normal equilibrium freezing/melting point⁵.

Supercooled water remains in the liquid state until an ice microcrystal precipitates in it. At that instant, the freezing process spreads through the supercooled water very rapidly in a process called flash-freezing. This behavior has been observed in different systems in nature like the supercooled water droplets in the clouds that condense into ice upon impact with airplanes⁶.

In 1938, N. Dorsey verified from the experimental data and that have been published in his epoch about the properties of water, the possibility of supercooling and freezing of water. He also did experiments on many water distilled and natural water. The results were compared with those which have been believed in that time, his study took more than ten years, many incompatibilities were found, and his final results were published in a paper in 1948^{7 8}.

In addition, there were several studies about the thermodynamics of the supercooled water. For example, the freezing temperature of supercooled water droplets has been determined as a function of pressure up to 3-kilo bars. The minimum value of the freezing temperature was determined at -92C° and 2.00-kilo bars⁹. Other experiments were done in 1987 and in 1999 to study the density and the heat capacity anomaly of supercooled water^{10 11}.

Supercooling process of water droplet splits into four stages: cooling stage of the water droplet, flash-freezing process (known as recalescence), main freezing or solidification stage, and the cooling stage of the ice¹². Despite there were a lot of researches done by physicists about this phenomenon, flash-freezing water of a droplet remains unclear. In particularly during this stage a small fraction of water droplet solidifies depending on the temperature at which the flash-freezing occurred. This solid fraction will be sufficient for the droplet to jump from its initial temperature to its equilibrium freezing point (0C°) in less than 20 ms as shown by nuclear magnetic resonance (NMR) study of the flash-freezing process of a supercooled liquid droplet¹³. Furthermore, There were several methods to measure the mass of cold-tolerant fraction created from the flash-freezing process of supercooled water droplets, one of them is based on the calorimetric measurement of the heat¹⁴ whereas we will study the thermodynamics of flash-freezing and the dependence of latent heat on the degree of supercooling temperature¹⁵.

1.2 Ethylene Glycol:

Ethylene glycol is a commonly used antifreeze in cars due to its antifreeze properties and a high boiling point so it will not get vaporized easily inside the radiator so it uses to prevent the cooling water of the radiator from converting to the ice during winter. The freezing of the radiator water can cause significant damage to the cars, so antifreeze is used to drop the freezing point in radiators to as low as -55C° . Yet, this temperature depends on the ratio of ethylene glycol to water. It's found that the concentration of 40% of E.G. is the best for a car coolant because the freezing point at that ratio is -45.97C° and the highest specific heat possible. In addition, it has been shown that the specific heat capacity and the freezing point decrease as E.G. concentration increases¹⁶. There are many experiments done to measure the freezing point data with different concentrations of E.G. to determine the solid-liquid phase diagram of ethylene glycol and water mixtures^{17 18}.

1.3 Supercooling and flash-freezing in ethylene glycol:

While the supercooling and rapid freezing processes have been well-studied, a strong interest in the field continues, which is reflected in the ever-increasing number of publications in this interesting field. Furthermore, most, if not all, papers focus on pure water behavior, while the behavior of other liquids has been poorly studied. For example, some experiments were done to investigate the effects of soluble and insoluble nuclei on the freezing temperature of water droplets, and they found that for the aqueous solutions the freezing point is reduced compared to the corresponding value for pure water^{19 20}. Other studies monitored the freezing process for pure and salty water via high-speed imaging and computer simulations, using combined visual and infrared imaging to deliver a three-dimensional and surface temperature information about their samples²¹, In this thesis, we experimentally study the supercooling and flash-freezing process for different concentrations of E.G. using temperature vs. time supercooling curves.

Over the years, there is growing attention in the chemical physics area to study the behavior of the aqueous solutions of E.G. For example, the phase behavior of E.G. as seen by dielectric spectroscopy was studied²². Moreover, the ice nucleation was investigated with different molar mass²³. E.G was also treated as cold thermal energy storage and the thermal conductivity and other properties of E.G. were determined²⁴.

In this thesis, we will study the effect of different concentrations of E.G. droplets when supercooled using different ways like thermoelectric device or liquid nitrogen, on the latent heat that released when a fraction of the droplet solidifies as a result of jumping in the temperature from its initial temperature to the equilibrium freezing point, in addition to other properties will be studied through the analysis of data.

2 Experimental Setup:

We studied the behavior of ethylene glycol: water droplets with different concentrations as they were cooled below their freezing temperatures. More specifically, the temperature of these droplets was monitored as they were ‘super-cooled’ to below their freezing temperatures and went through the liquid-to-solid phase change. We built a simple setup for these measurements of different ethylene glycol concentrations in water. This chapter shows the different components and procedures used in this research.

2.1 Sample Preparation:

We first prepared several solutions of water: ethylene glycol (E.G.) and then dispensed them as droplets on a hydrophobic copper surface for further studying. We prepared different concentrations of water and E.G. starting from 0% up to 45%. For example, to prepare 30% of E.G. in water, a volume of 6ml of E.G. was mixed with 14ml of water. This gives an E.G. concentration of $(6 / (6 + 14)) * 100\%$, which is 30%. In the same way, solutions of E.G.: water with the concentrations 0%, 15%, 22.5%, 30%, and 45% were prepared as shown in Figure 1, most vials had their droppers to avoid any mistakes regarding the concentrations.



Figure 1: Glass vials with the different concentrations of E.G. used in this thesis.

2.2 Copper surface preparation:

Smooth copper sheets were rendered hydrophobic following an HDFT-coating procedure:

Firstly, we put a small amount of heptadecafluoro-1-decanethiol (HDFT) (0.1M = 0.1 mole/Liter) in a glass container, then we immersed the copper sheet in it for 6 minutes. Secondly, we take it out and put it in 50 ml of dichloromethane CH_2Cl_2 for 20 seconds. Finally, after drying the surface, it is ready to use as a hydrophobic surface.

This procedure causes a self-assembled monolayer (SAM) to grow on the surface, as depicted in Figure 2 the heads of the HDFT molecule bond to the surface but the tails do not bond. This process allows for growing a single molecular layer on the surface^{25 26 27}. SAM is highly hydrophobic, which is beneficial in our experiment since it caused the droplets to ‘stand up’ or have a larger thickness and proper placement on the thermocouple and for imaging.

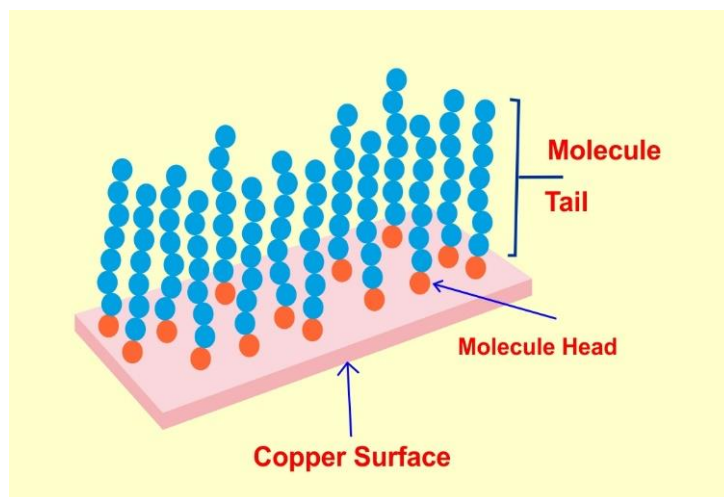


Figure 2: Cartoon of a self-assembled monolayer on the copper surface.

2.3 Cooling setup:

We cooled our systems using the thermoelectric plate and liquid nitrogen, depending on the temperature needed to cool the droplets. The thermoelectric device cooling is just up to about -30°C while the liquid nitrogen has the boiling point -196°C .

The thermoelectric device operation (TED) depends on the Peltier effect which creates a temperature difference at a junction of two different types of materials²⁸. It can be used as a cooling or heating device depending on the direction of the electric current passing through it. In our experiment we use TED as a cooling device as shown in Figure 3, we design a setup for cooling of a water droplet, by putting the TED on a piece of copper that floating on a basin of water to increase the thermal conductivity. We connect the TED with a power supply by its two terminals, followed by placing the water droplet on the top of the TED and inserting a K-type thermocouple inside the water droplet that connected to a data acquisition device (DAQ). Our DAQ has two channels used to measure the temperature connected with a computer having a LabVIEW program in order to get as much large as temperature range for every second.

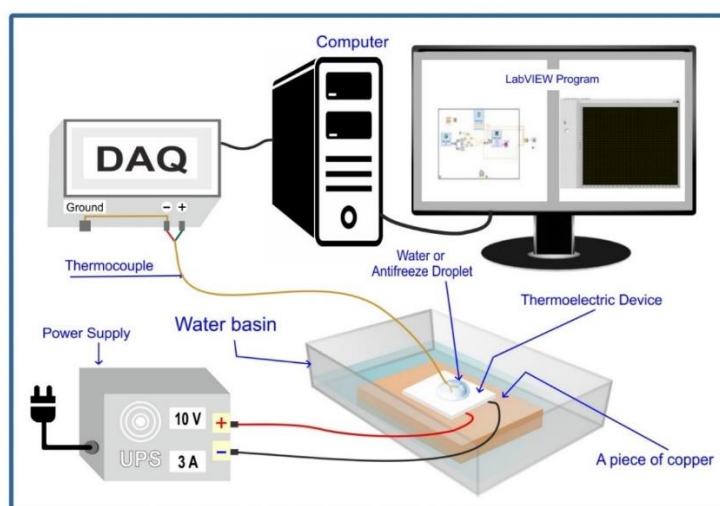


Figure 3: Setup of our experiment using the TED.

We also designed another setup that uses liquid nitrogen for cooling, as shown in Figure 4 we place the water droplet or antifreeze droplet on top of a hydrophobic copper sheet which is put on a Styrofoam box containing liquid nitrogen. We similarly insert two K-type thermocouples inside the droplet to measure its actual temperature to reduce errors, an average temperature is obtained by inserting such one of these thermocouples on the top of the droplet and the other one in its center. We put a plastic petri dish on the droplet to be not affected by the condensation of the supercooling process. Afterward, these two thermocouples were connected with a (DAQ) connected with a LabVIEW program to monitor the time evolution of temperature. The solidification of the droplet was being monitored with a microscope connected to the computer and KaPa Capture Version 6.9.7 Program.

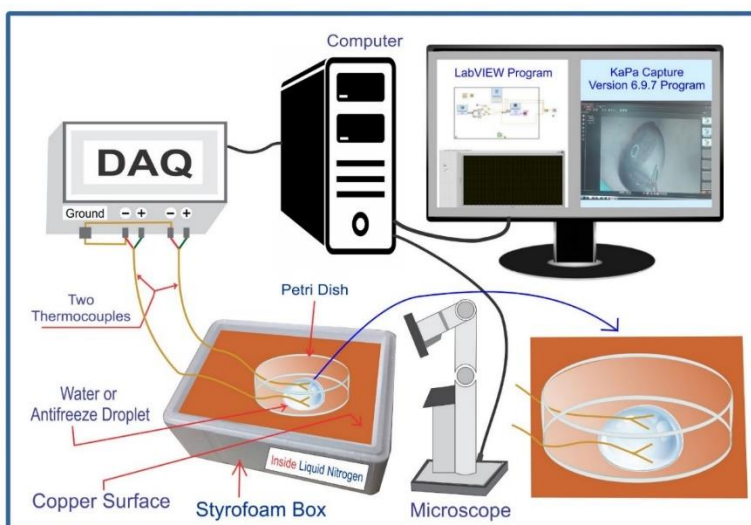


Figure 4: Setup of our experiment using liquid nitrogen.

2.4 The temperature measurement:

We measure the variation in temperature with time by two K-type thermocouples, such that the thermocouple is an electrical device made of two unlike wires created a junction when it made changes in temperature a small voltage will be created so that a wide range of temperature can be measured. There are different types of thermocouples, one of these types is type K thermocouple was developed in 1906 and was known originally as chromel versus Alumel thermocouple, which we choose in our experiment because it inexpensive and has a wide temperature range, from -270C° to $1372\text{C}^{\circ 29}$, also these thermocouples are microwires i.e. there diameter does not exceed the 100 micrometers so it was suitable to be inserted inside the droplet which has a diameter of about 4 millimeters.

Also, we make an additional experiment to make sure that the thermocouple that we use is calibrated or not as NIST listed²⁹, so we use a diode as a thermometer by connecting the circuit shown in Figure 5. We use the amplifier in the circuit to amplify the small temperature variations in the forward voltage.

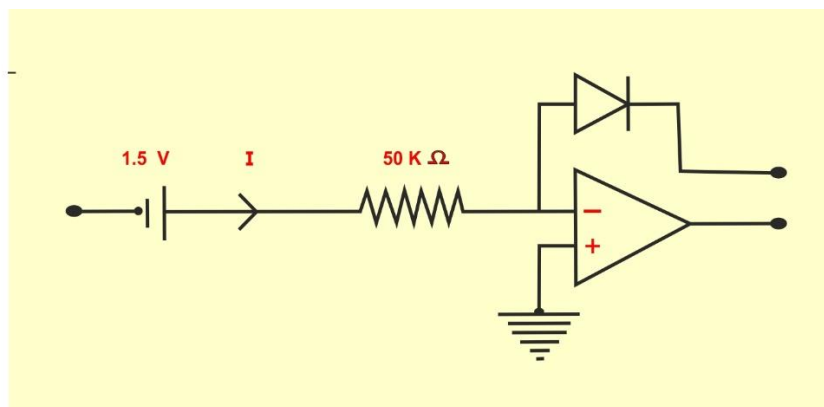


Figure 5: The circuit we connect to use a diode as a thermometer.

The current passing through the circuit is:

$$I = \frac{V}{R} = \frac{1.5}{50} = 30 \mu A. \quad 2.4.1$$

; V is the voltage difference in the circuit and R is the resistance.

While the diode connected in the circuit such that its forward current almost constant:

$$I_d = I_0(e^{(eV/K_\beta T)} + 1) \quad 2.4.2$$

; I_0 is the diode reverse saturation current at room temperature, e is the electron charge, K_β is Boltzmann constant and T is the temperature.

$$T = \frac{e}{K_\beta - \ln((I/I_0) - 1)} * V \quad 2.4.3$$

That means $T = \text{constant} * V$, so we can use the diode as a thermometer.

We connect the diode and the thermocouple with DAQ by its two channels and we built a program in LabVIEW and from the data we make a comparison between the temperature of the diode and the thermocouple and the results were very close to each other as we will see in data and analysis.

2.5 The DAQ and the LabVIEW program:

We connect the two thermocouples that we use in our experiment with the DAQ by its two channels, such that every channel has a negative and positive input, we connect the green leg of the thermocouple with the positive input and the red leg with the negative input which also connected to the ground of the DAQ to get more precise data. So we use the DAQ as shown in Figure 6 to measure the real temperatures and convert it into digital numeric values that controlled by the software program LabVIEW in the computer, this process known as ‘Analog-to-digital converters’³⁰.

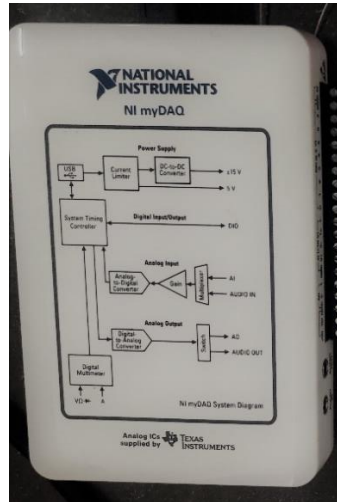


Figure 6: The DAQ

LabVIEW program is a visual graphical programming language that helps to visualize any experiment that needs to get a large number of measurement data every small interval time. This program has two windows are associated to each other, the first one is the block diagram as shown in Figure 7 (a), which uses to design the representation of the system we have, using all controls needed and tools, and the second one is the front panel that will be ready to run and take all measurement data as the system in the block diagram is wired together. These measurement data saved and the graph appear on that window as shown in Figure 7 (b)^{31 32}.

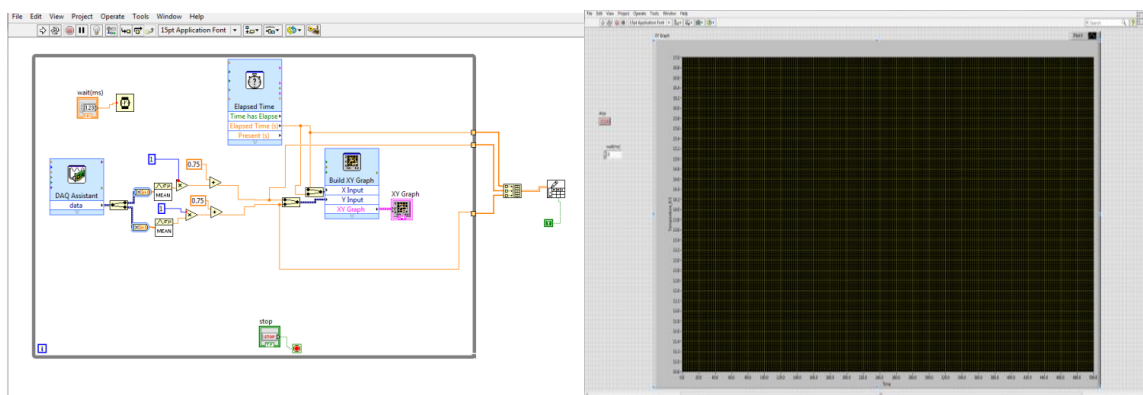


Figure 7: (a):Block diagram of LabVIEW

(b)The front panel window of LabVIEW

3 Theory:

The droplet supercooling process, as shown in Figure 8, can be described by four distinct stages:

1. The cooling stage of the liquid droplet, in which the droplet is cooled from its initial temperature to below the equilibrium freezing temperature until nucleation occurs.
2. The flash-freezing process or a recalescence stage, during which supercooling drives rapid kinetic crystal growth (initial solid fraction) from the crystal nuclei, depending on the temperature at which flash-freezing occurs, there is an abrupt jump in the temperature such that this solid fraction releases latent heat of fusion until the droplet reaches to the equilibrium freezing temperature.
3. The main freezing or solidification stage, in which the droplet is completely frozen.
4. The cooling stage of the ice, during which the solidified droplet temperature is reduced to near the ambient air temperature^{33 34}.

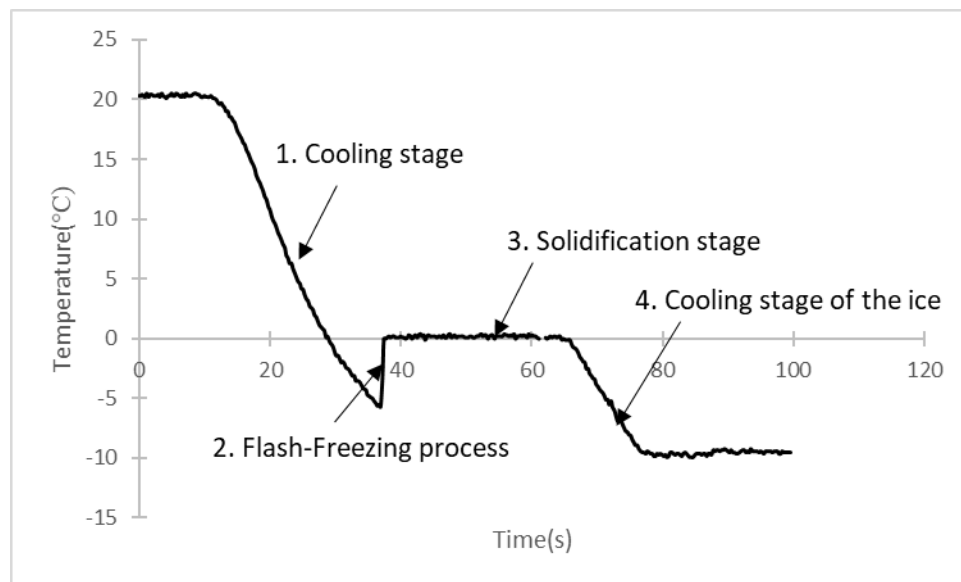


Figure 8: temperature transition of the supercooling of a water droplet with four stages.

This study is to develop an experimental method to measure the abrupt transition in temperature for different concentrations of water and E.G. droplets. Furthermore, the numerical model developed was able to predict the initial solid fraction of the droplet depending on the temperature dependence of the latent heat.

3.1 The temperature dependence of latent heat:

The objective of this study is to investigate a simple numerical model that can be applied to see the influence of the variation in temperature on the properties and the dynamics of the supercooling process. At atmospheric pressure, the flash-freezing stage in the supercooling process, that takes less than 20 ms can be regarded as a thermodynamically adiabatic system, which means that the heat transferred from the ambient are negligible.

In the supercooling process of a water droplet, the portion of the droplet that solidifies during the flash-freezing stage will be sufficient for the temperature to increase from its initial temperature to the equilibrium freezing point (0C°). This is caused suddenly due to the release of an amount of heat called latent heat.

The relationship between the latent heat and the entropy (S) is:

$$L = T \Delta S ; \Delta S = S_{water} - S_{ice} \quad 3.1.1$$

To calculate the entropy difference of supercooled water and ice at any temperature T, the heat capacity as a function of temperature (C(T)) of supercooled water and ice can be used, such that:

$$S(T) = S(T_m) - \int_T^{T_m} \frac{c(T')}{T'} dT' \quad 3.1.2$$

; T_m: the melting point

Then the latent heat can be expressed as:

$$L(T) = T \Delta S = T[S_{water}(T) - S_{ice}(T)] \quad 3.1.3$$

When a liquid is supercooled below its melting temperature, the latent heat is defined as the enthalpy difference between supercooled water and ice like³⁵:

$$L' = L_m - \int_{T_i}^{T_m} [c_w(T) - c_i(T)] dT \quad 3.1.4$$

; c_w and c_i are the specific heat capacity for supercooled water and ice respectively¹⁵.

3.2 Determination of initial ice fraction for water droplets:

We suppose that the energy released by the supercooled water with mass (m) used up by raising the temperature of both the (ice) solid fraction with mass ($f_s * m$) and the remaining water droplet with mass ($m - f_s * m$) from its initial temperature to the equilibrium freezing temperature ΔT as an adiabatic system³⁶.

Then the energy balance is given by:

$$L * f_s * m = c_i * f_s * m * \Delta T + c_w * (m - f_s * m) * \Delta T \quad 3.2.1$$

And the initial solid fraction is:

$$f_s = \frac{c_w \Delta T}{L - (c_i - c_w) * \Delta T} * 100\% \quad 3.2.2$$

3.3 The initial solid fraction for different concentrations of E.G. droplets:

To find the initial solid fraction for the different concentrations, if we follow the same steps as for a water droplet, we will get the following equation:

$$f_{s \text{ E.G.}\%} = \frac{c_{l \text{ E.G.}\%} \Delta T}{L_{\text{E.G.}\%} - (c_{s \text{ E.G.}\%} - c_{l \text{ E.G.}\%}) * \Delta T} * 100\% \quad 3.3.1$$

; $c_{l\ E.G.\%}$ and $c_{s\ E.G.\%}$ are the liquid specific heat and the frozen specific heat respectively for the different concentrations of E.G.

In general, we can find the specific heat capacity for a mixture from the pure components³⁷, which are E.G. and water in our case, by using the following equation:

$$c_{E.G.\%} = x_1 * c_{pure\ E.G.} + x_2 * c_{water}. \quad 3.3.2$$

where x_1 and x_2 are the concentrations of E.G. and water respectively.

4 Data and Calculations

In this chapter we present the data we got from our experiment for the water droplets and for the different concentrations of E.G. droplets, and study how the physical properties vary with the variation of the E.G. %.

4.1 Thermoelectric cooling device with and without water droplets:

According to Newton's law of cooling, the rate of loss of heat of a body is directly proportional to the temperature difference between the body and its surrounding³⁸ i.e.

$$\frac{dT}{dt} \propto (T - T_f) \quad 4.1.1$$

; where T is the temperature of the body at any given time, t is the time and T_f is the final temperature of the body (which is typically the temperature of the surroundings, but need not be so here, since it might be the target cooling temperature in the cooling device). Rearranging and integrating both sides of the equation we get:

$$\int_{T_0}^T \frac{dT'}{T' - T_f} = \int_0^t -K dt' \quad 4.1.2$$

In this equation T_0 is the initial temperature of the body and K is a positive proportionality constant that represents the rate at which the body heats or cools.

Solving Equation 4.1.1 gives the following equation:

$$T = T_f + (T_0 - T_f)e^{-Kt} \quad 4.1.3$$

Similarly, Newton's law of heating describes the change in temperature in a body which is colder than its surroundings. In this case too, the rate of change of the body's temperature is directly

proportional to the temperature difference between the surroundings and the body. The solution of the heating case in Newton's law is³⁹:

$$T = T_f - (T_f - T_0)e^{-Kt} \quad 4.1.4$$

We first examine experimentally the cooling and heating behavior of the thermoelectric device without water droplet and compare it to Newton's law for both cooling and heating. We use a very thin K-type thermocouple to measure the variation of the temperature with time as shown in Figure 9. No cooling is started initially, then when we turn on the device (at time around 18 seconds on the x-axis) the temperature decreases from its initial value ($T_0 = 15^\circ\text{C}$) down to the final temperature of cooling ($T_f = -2^\circ\text{C}$). We then turn off the cooling device and the system warms up starting from ($T_0 = -2^\circ\text{C}$) to the final temperature ($T_f = 15^\circ\text{C}$). Inspecting Figures 9 and 10 shows that the device agrees with the Newton's law of cooling and heating quite closely.

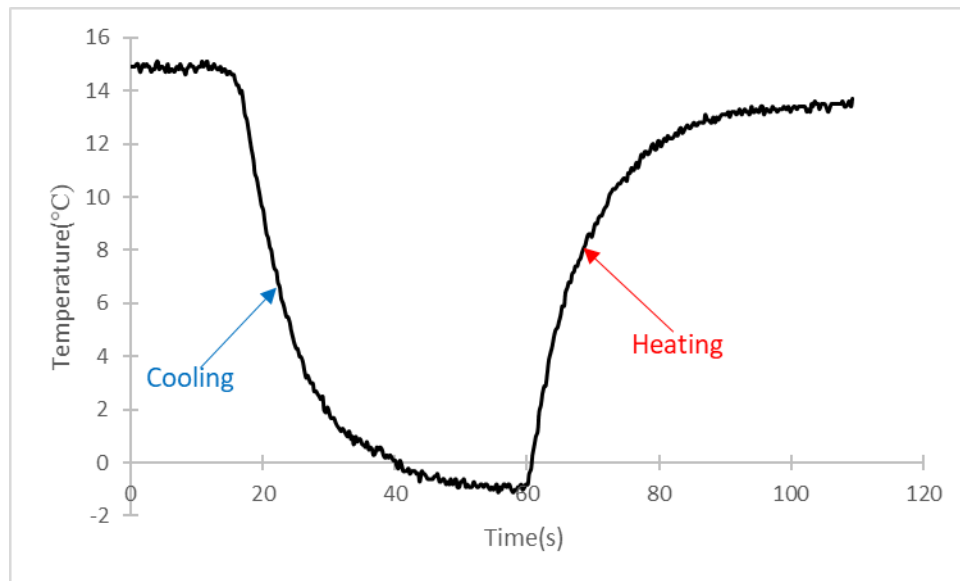


Figure 9: The temperature evolution with time for the thermoelectric device without a water droplet.

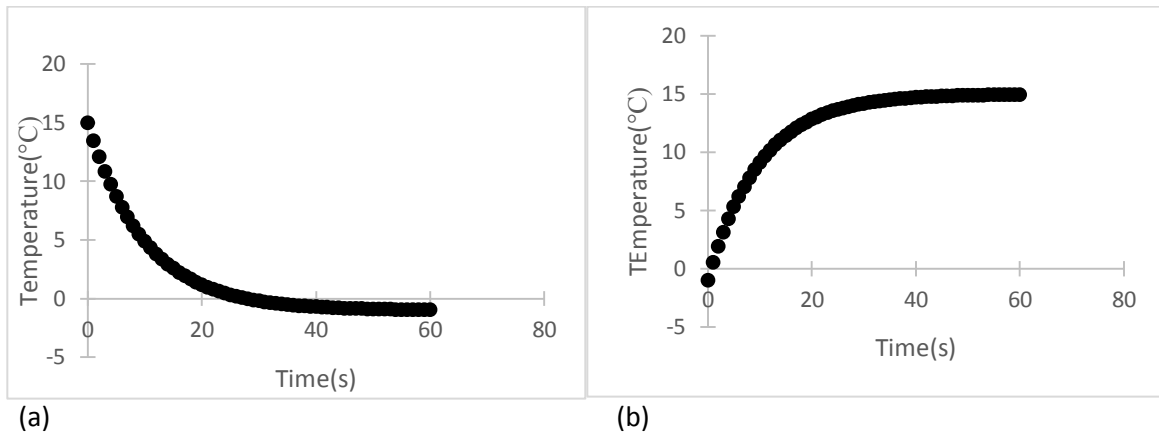
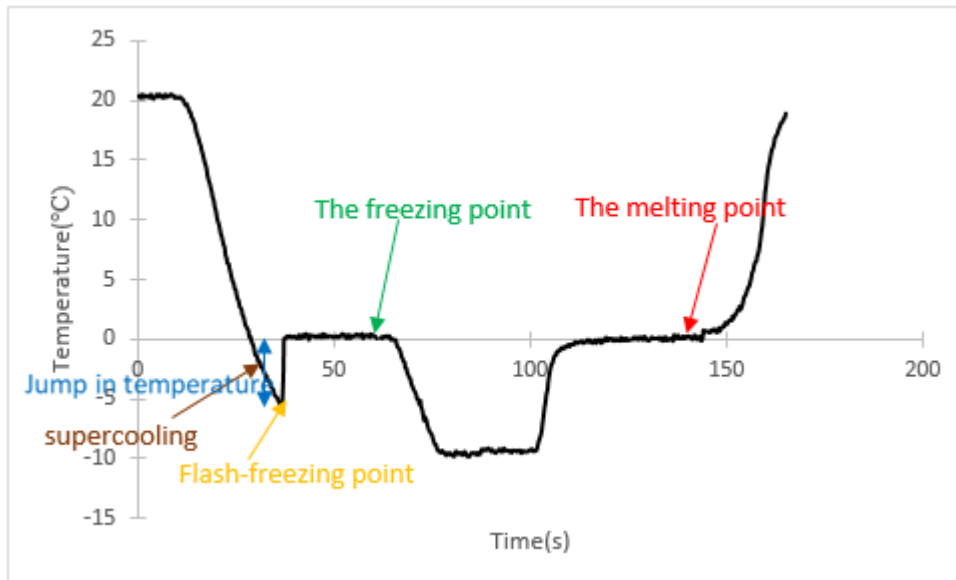


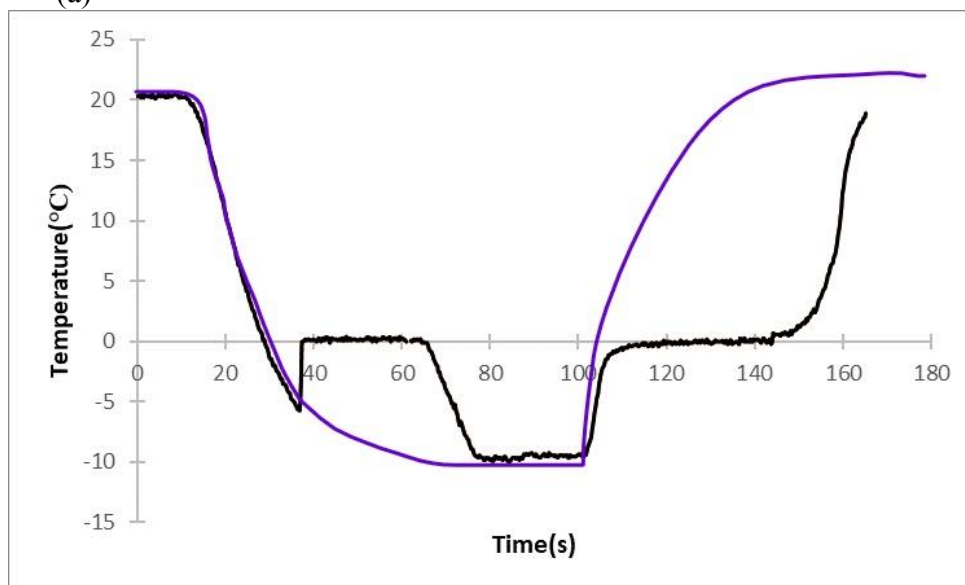
Figure 10: The temperature evolution with time for Newton's law of (a) cooling and (b) heating.

When placing a water droplet over the tip of the Type-K thermocouple on the thermoelectric device (TED) such that the thermocouple tip is completely submerged in the water droplet, the cooling - as well as the heating- curve changes completely, as we see in Figure 11 (a). When we cool the water droplet, it reaches to a temperature of -5.7°C , which is well below its equilibrium freezing point (0°C), while still in its liquid state. This is called supercooled water. A sudden rise (or jump) in temperature to 0°C then takes place within a few milliseconds and is referred to as flash-freezing. During flash-freezing a small fraction of the droplet solidifies and this freezing process is sufficient to raise the temperature up to the freezing point of water. The phase change of the rest of the droplet then proceeds much slower, and it takes around one minute for the droplet to completely solidify. The frozen droplet then cools down to the final cooling temperature for the given settings of the TED. After the temperature stabilizes at its lowest value, we turn off the current through the TED and let it warm up naturally. Instead of observing the typical asymptotic (i.e. exponential) change in the temperature in accordance with the Newton's law of cooling and heating, the temperature has a clear plateau at 0°C (which is the melting point of water) for more

than half a minute. The temperature finally rises to the ambient value after that. Figure 11 (b), displays what we expect from Newton's law for cooling and heating and the actual behavior of the temperature of the water droplet. The supercooling, the flash-freezing and the melting processes are quite apparent when comparing the two curves.



(a)



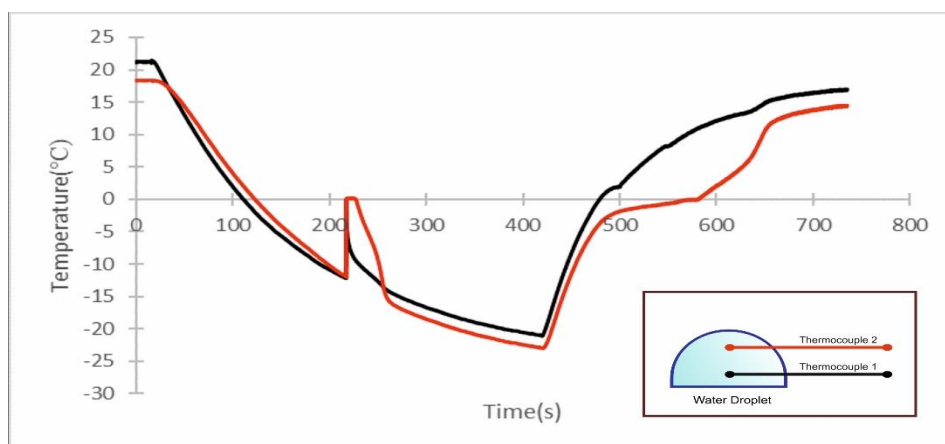
(b)

Figure 11: (a)The temperature evolution with time for the thermoelectric device with a water droplet,(b) the comparison between the result of the temperature evolution with time for the thermoelectric device without and with a water droplet.

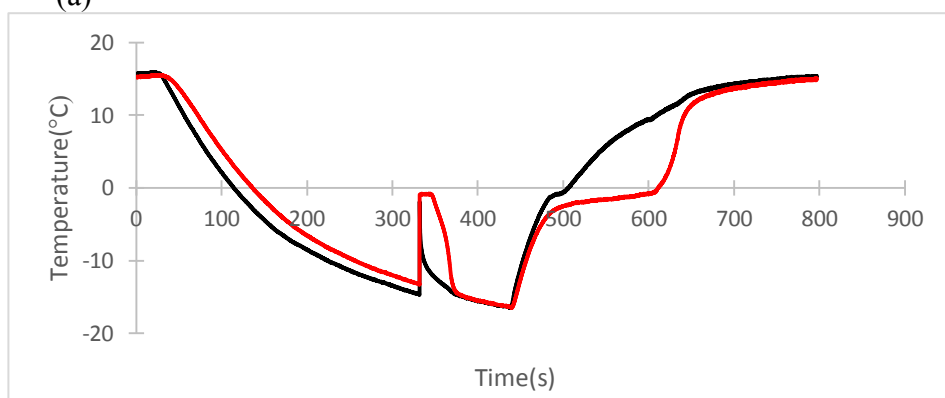
4.2 Further studies of water droplets:

We start our experiments with water droplets (i.e. ethylene glycol solutions with 0% concentration), in order to analyze some of their properties like the flash-freezing point, the freezing point, and the melting point, in addition to other properties that we will discuss later.

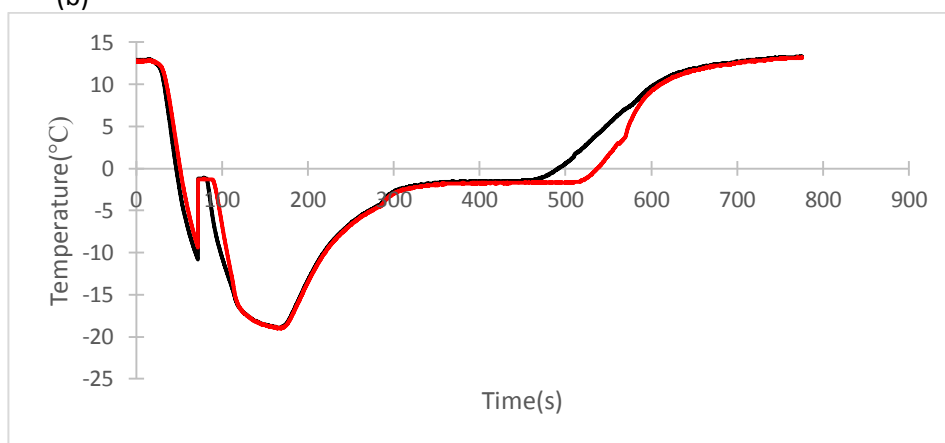
Figure 12 shows the results of multiple trials of supercooling and flash-freezing with a water droplet. We insert the two K-type thermocouples in the water droplet as shown in the inset in Figure 12 (a), in that figure for the first thermocouple the flash-freezing point (FFP1) is -12.2°C and for the second thermocouple (FFP2) is -11.9°C , also the freezing point for the two thermocouples (FP1), (FP2) respectively are -0.2°C , 0.1°C , so the jump in the temperature from the initial temperature to the equilibrium freezing temperature for the first and second thermocouple (ΔFF1), (ΔFF2) is 12°C . Notice that the first thermocouple is closer to the cooling surface than the second one, which causes the second thermocouple to stay at zero temperature for a longer time than the first one. This is because the droplet freezes from the bottom-up after the initial flash-freezing. So, the temperature of any part of the liquid stays at zero until that part freezes, where the temperature of the ice starts dropping gradually. Points in the droplet which are above the ice will stay at zero until that liquid freezes so that its temperature starts dipping below zero. As a result, the thermocouple placed lower in the droplet will be surrounded by ice sooner than the higher thermocouple and will only stay at 0°C for a shorter time immediately after flash-freezing. It is also seen from the figure that the melting point for the first thermocouple (MP1) is 1.7°C and for the second thermocouple (MP2) is -1.3°C .



(a)



(b)



(c)

Figure 12: The evolution of temperature with time for the water droplet (0% E.G.). (a): The first trial. (b): The second trial. (c): The third trial.

Table 1 summarizes the different properties for the several trials of the water droplet freezing and melting.

Table 1: The results of the different properties for the water droplet from Figures 12 (a), (b), and (c).

Figure12	FFP1(°C)	FFP2(°C)	FP1(°C)	FP2(°C)	MP1(°C)	MP2(°C)	ΔFF1(°C)	ΔFF2(°C)
(a)	-12.2	-11.9	-0.2	0.1	1.7	-1.3	12	12
(b)	-14.7	-13.3	-1.9	-1	-0.6	-1.9	12.8	12.3
(c)	-10.8	-9.4	-1.2	-1.3	-1.6	-1.9	9.6	8.1

Based on this temperature behavior, we can find the initial solid fraction for the water droplet as it flash-freezes and its temperature suddenly jumps to the equilibrium freezing point. Let us first look at the previous trials and take the average value for the previous properties we have studied in Table 1 for the two K-type thermocouples:

The average value for the flash-freezing point is -12.05°C , while the average value for the freezing point is -0.9°C and the average value for the melting point: -0.9°C . Thus, the average value for the jump in temperature upon the flash-freezing event is 11.13°C .

Equation 3.2.2 gave the solid fraction for the water droplet as:

$$f_s = \frac{c_w \Delta T}{L - (c_i - c_w) \Delta T} * 100\%$$

The specific heat capacity is $4.200 \frac{\text{KJ}}{\text{Kg.K}}$ ⁴⁰ and $2.093 \frac{\text{KJ}}{\text{Kg.K}}$ ⁴¹ for water and ice respectively, and the latent heat for the water is $334 \frac{\text{KJ}}{\text{Kg}}$ ⁴². Based on these numbers, the initial solid fraction for the water droplet is 15.1%.

Inspecting table 1, we see that the results of our experiment for the water droplet are very close to each other.

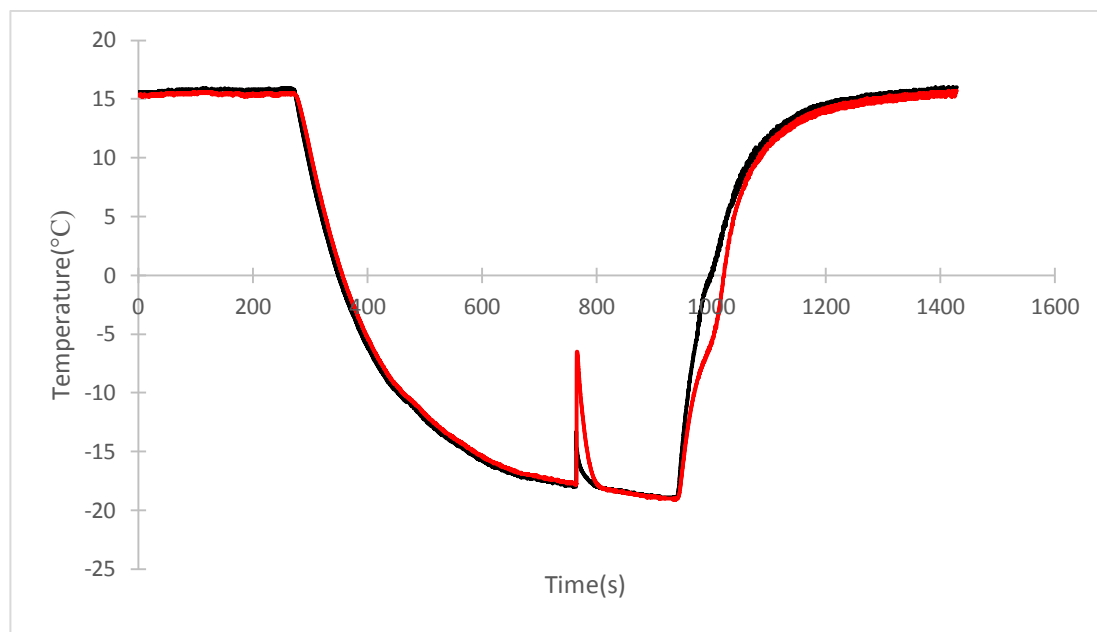
Now we use droplets with different concentrations of ethylene glycol and water in order to study the same properties above (i.e. supercooling, flash-freezing, melting, ...etc.). We do our experiments with E.G. concentrations of 0%, 15%, 22.5%, 30%, and 45%.

4.3 Ethylene glycol droplets:

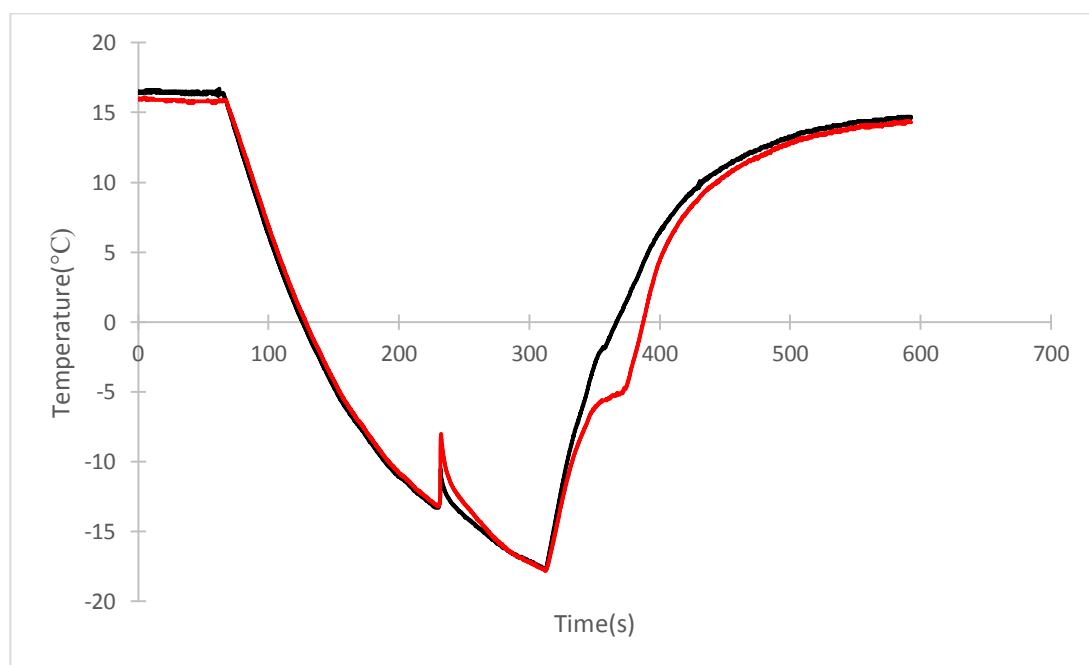
Even though there were several studies that studied the thermophysical properties of the different concentrations of E.G. and water, like the thermal conductivity, the viscosity, the vapor pressure, the specific heat, and the freezing point⁴⁰, a detailed study of the supercooling and flash-freezing of ethylene glycol is lacking. we will find experimentally the flash-freezing point, the melting point, in addition to other properties depending on the different concentrations of E.G.

A) 15% E.G. droplets:

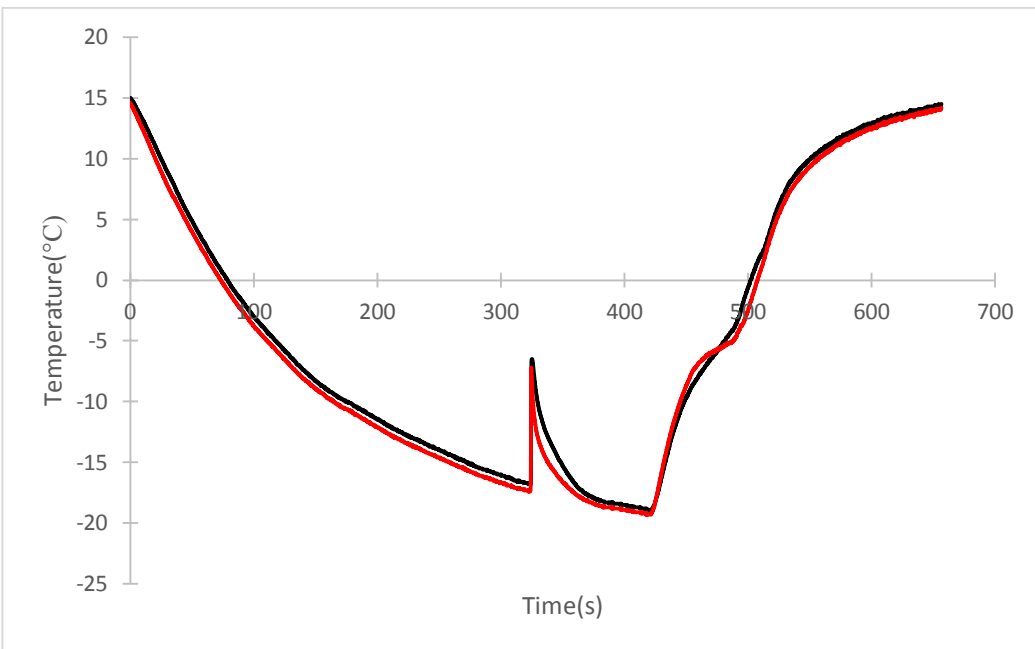
When we put two K-type thermocouples in the antifreeze droplet, we notice that the general behavior will be the same as water, but the temperature of the different properties will decrease as the concentration of E.G. increases. For example, when we use a 15% E.G. droplet we deduce from the results illustrated in Figure 13 (a) that the flash-freezing point for the first thermocouple is -17.6°C while for the second thermocouple is -17.8°C . We repeat our experiment with this concentration three times as shown in Figure 13 (b), (c), and (d) in order to confirm the reproducibility of the results.



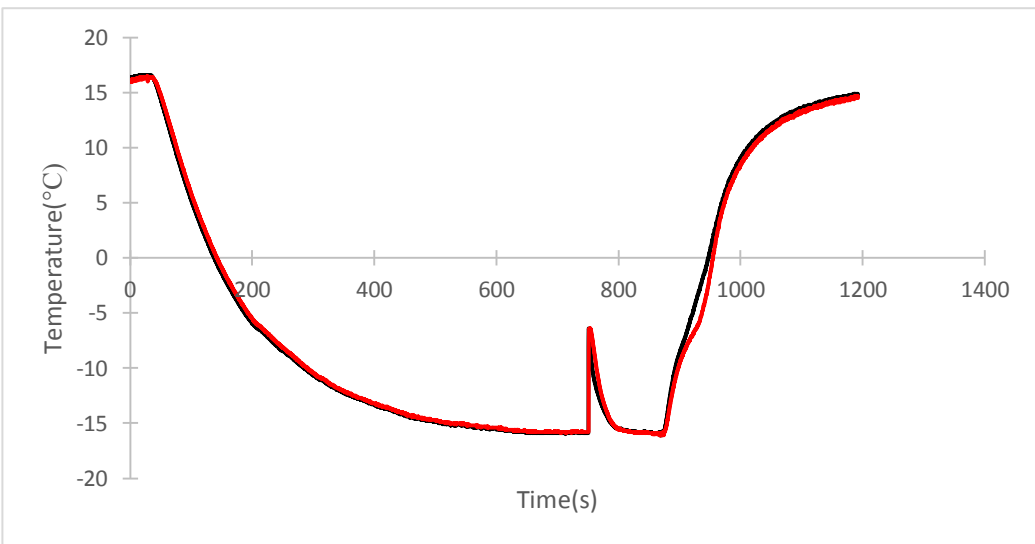
(a)



(b)



(c)



(d)

Figure 13: The evolution of temperature with time for the antifreeze droplet (15% E.G.). (a): The first trial. (b): The second trial. (c): The third trial. (d): the fourth trial.

In the same way that we have found the initial solid fraction for the water droplet, we can find the initial solid fraction for different trials of 15%E.G. As shown Equation 3.3.1:

$$f_{S\ E.G.\%} = \frac{c_{l\ E.G.\%} \Delta T}{L_{E.G.\%} - ((c_{s\ E.G.\%} - c_{l\ E.G.\%}) * \Delta T)} * 100\%$$

To find the specific heat for 15% E.G.⁴⁰, we have the following:

$$c_{15\% \ E.G.} = \frac{15}{100} * 3.820 + \frac{85}{100} * 4.225 = 4.1642 \frac{KJ}{Kg.K}$$

We also assume that the frozen specific heat for the different concentrations of E.G. is one half the liquid specific heat. So the frozen specific heat for 15% E.G. is $2.0821 \frac{KJ}{Kg.K}$. Finally, the latent heat for this concentration is $320 \frac{KJ}{Kg}$.⁴²

This gives an initial solid fraction of 10.17% for the 15% E.G. $f_{15\%E.G.}$, which is less than the initial solid fraction for the water droplets.

Table 2 below summarizes the different properties of the several trials of 15% E.G. droplet.

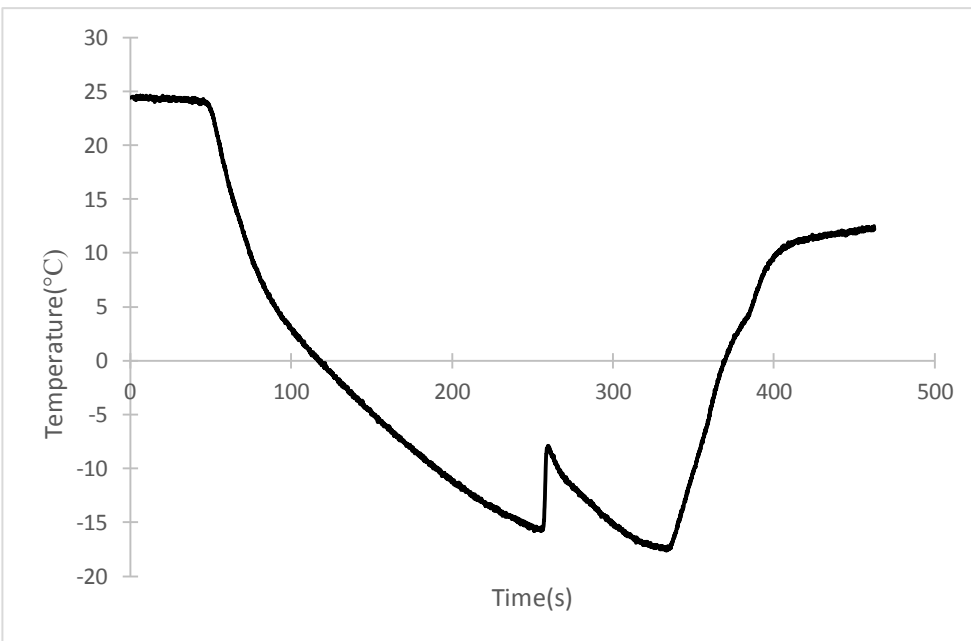
Table 2: The results of the different properties for 15% E.G. droplet from Figure 13 (a), (b), (c), and (d).

Figure13	FFP1(°C)	FFP2(°C)	FP1(°C)	FP2(°C)	MP1(°C)	MP2(°C)	ΔFF1(°C)	ΔFF2(°C)
(a)	-17.6	-17.8	-14.1	-7	-0.2	-6	3.5	10.8
(b)	-12.8	-13.1	-10.5	-8.5	-1.9	-5.4	2.3	4.6
(c)	-16.8	-17.4	-6.9	-7.5	-4.7	-6	9.9	9.9
(d)	-15.9	-15.8	-6.7	-6.5	-4.8	-6.3	9.2	9.3

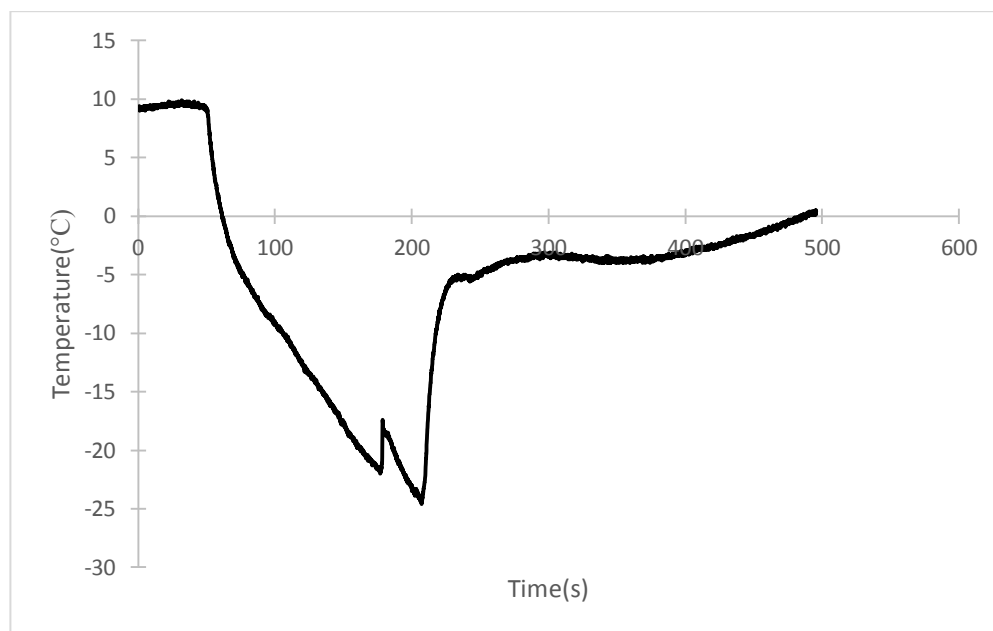
B) 22.5% E.G. droplets:

We will use one K-type thermocouple from now on, since the results of the two thermocouples are basically the same. Figure 14 shows the cooling behavior of several 22.5% E.G. droplets. Notice in Figure 14 (a), (b), (c), and (d) that the freezing point is about -15°C , the melting point is about -8°C , and the jump in temperature from the flash-freezing point up to the freezing point is about 5°C , which are all less than the corresponding values for 15% E.G.

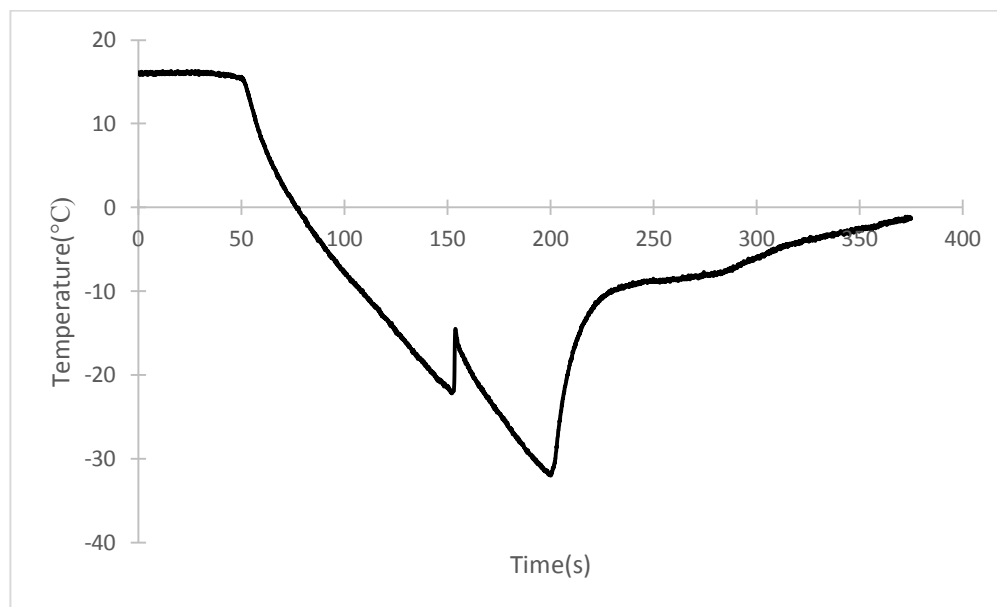
Also notice that the droplet takes more time to melt in the second, third, and fourth trials, while it melts suddenly in the first trial. This behavior is indicative of the large fluctuations in the experiment conditions like the rate of cooling or heating in each trial as well as the statistical nature of flash-freezing.



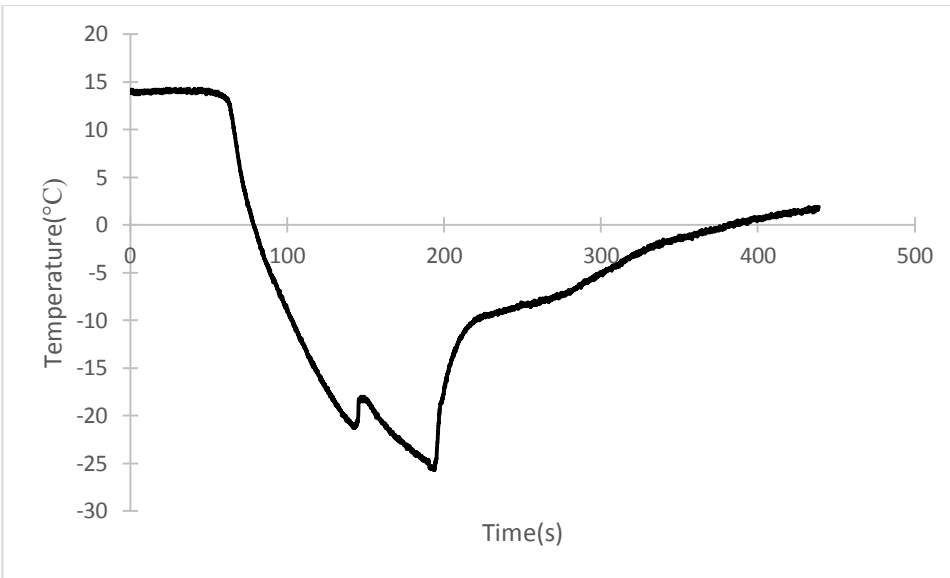
(a)



(b)



(c)



(d)

Figure 14: The evolution of temperature with time for the antifreeze droplet (22.5% E.G.). (a): The first trial. (b): The second trial. (c): The third trial. (d): the fourth trial.

Table 3 below shows the different properties we deduce from Figure 14 (a), (b), (c), and (d) for 22.5% E.G. droplet.

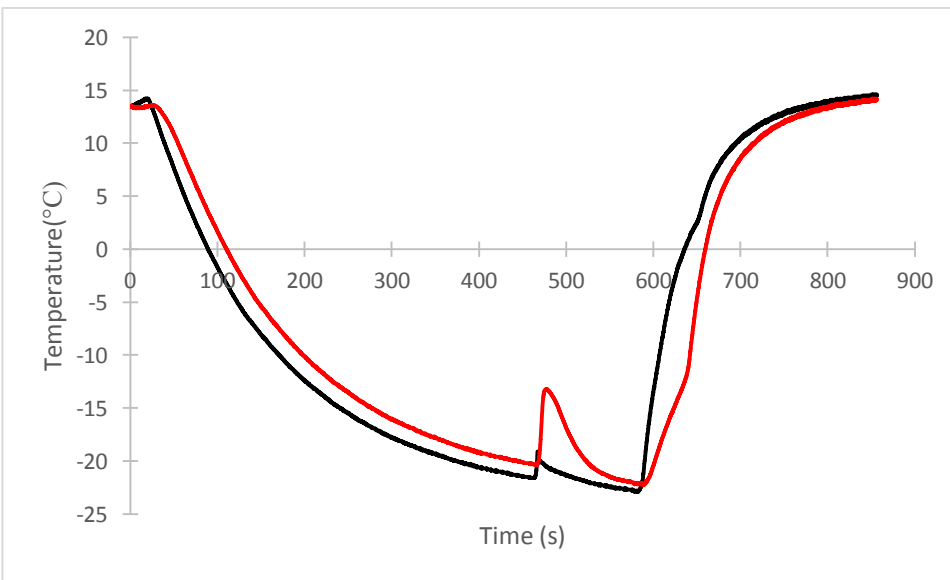
Table 3: The results of the different properties for 22.5% E.G. droplet from Figure 14 (a), (b), (c), and (d).

Figure14	FFP(°C)	FP(°C)	MP(°C)	ΔFF(°C)
(a)	-15.6	-8	-10	7.6
(b)	-22	-18.5	-4	3.5
(c)	-22	-15	-9	7
(d)	-21	-18.2	-9	2.8

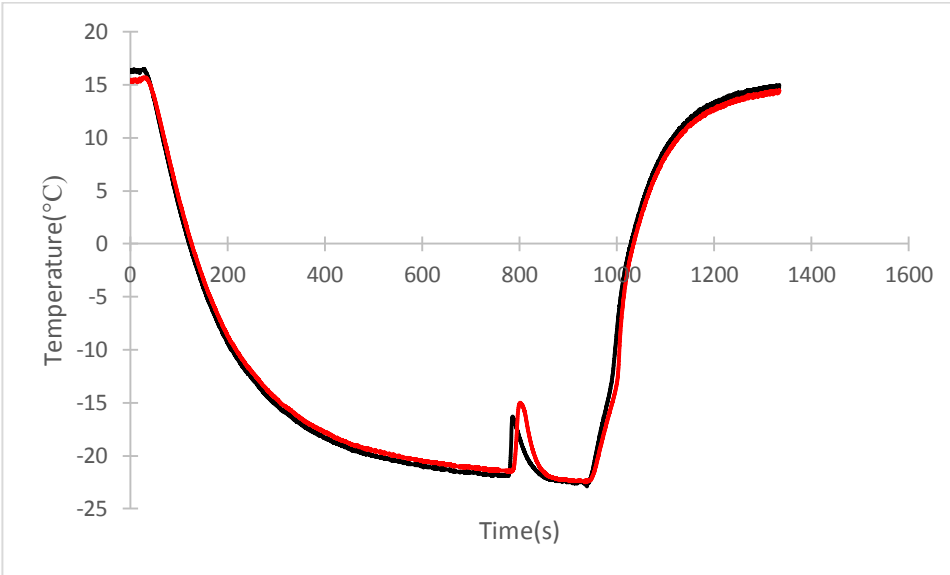
Now the initial solid fraction for 22.5% E.G. $f_{22.5\%E.G.}$ is 7.21%. The liquid specific heat for this concentration is $4.1294 \frac{KJ}{Kg.K}$ ⁴⁰ the frozen specific heat is $2.0647 \frac{KJ}{Kg.K}$ and the latent heat is $310 \frac{KJ}{Kg}$.⁴²

C) 30% E.G. droplet:

For a 30% droplet sample, we have only two successful trials as shown in Figure 15 (a) and (b). As we see from the results of these two trials, the flash-freezing point decreases as the concentration of E.G. increases and the jump in temperature decreases. We like to notice here that we can only determine a lower limit of the jump in temperature upon flash-freezing, since it is not possible to determine the melting temperature with confidence from these curves. Table 3 summarizes the different properties of this concentration.



(a)



(b)

Figure 15: The evolution of temperature with time for the antifreeze droplet (30% E.G.). (a): The first trial. (b): The second trial.

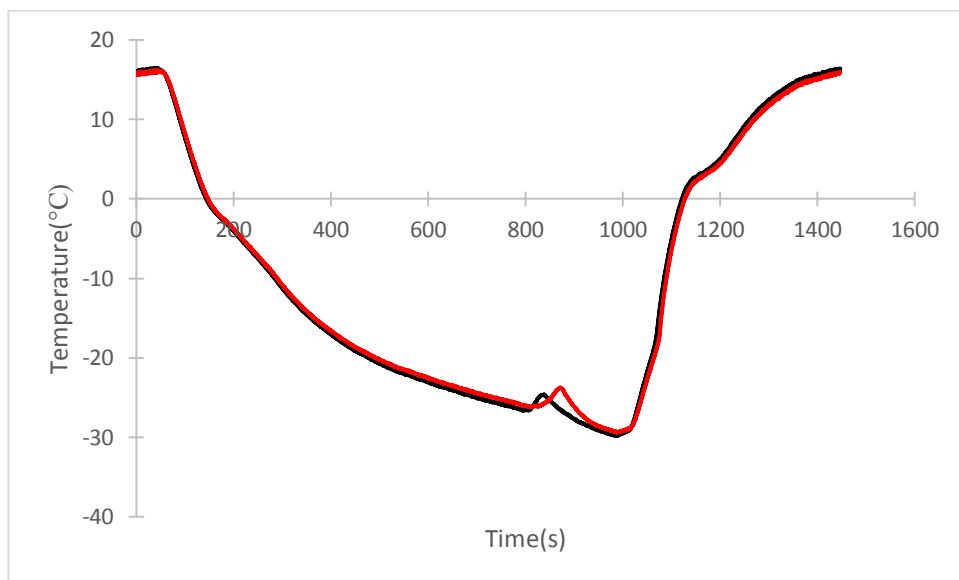
Table 4: The results of the different properties for 30% E.G. droplet from Figure 15 (a), and (b).

Figure15	FFP1(°C)	FFP2(°C)	FP1(°C)	FP2(°C)	MP1(°C)	MP2(°C)	ΔFF1(°C)	ΔFF2(°C)
(a)	-20.5	-20.3	-20	-13.4	-13	-12.1	0.5	6.9
(b)	-21.9	-21.3	-16.6	-15.4	-13.3	-14.1	5.3	5.9

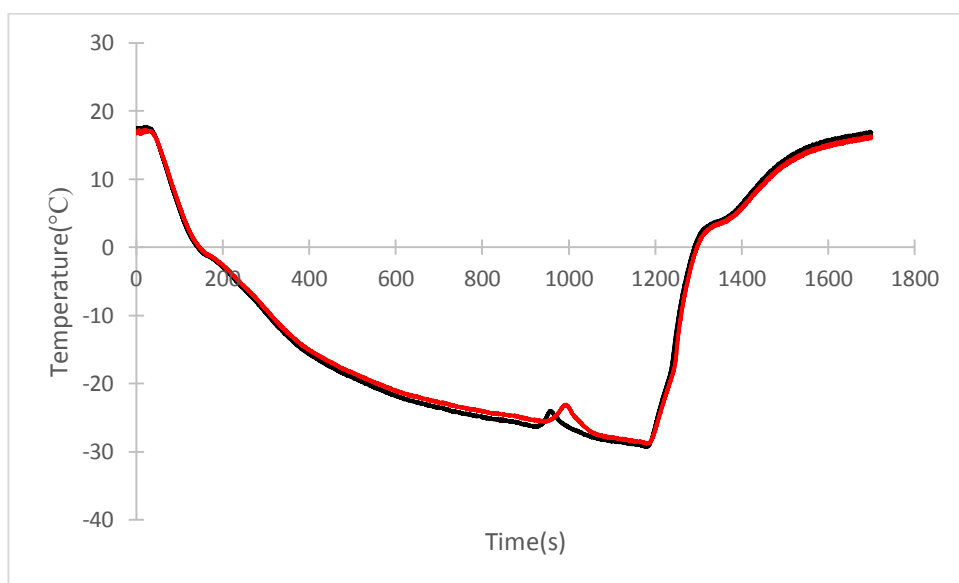
To find the initial solid fraction for 30% E.G. droplet, we have to find the approximate liquid specific heat for this concentration which is $4.0810 \frac{KJ}{Kg.K}$,⁴⁰ the frozen specific heat, which is $2.0405 \frac{KJ}{Kg.K}$, and the latent heat, which is $292 \frac{KJ}{Kg}$.⁴² These give an initial solid fraction $f_{30\%E.G.}$ of 6.72%.

D) 45% E.G. droplet:

Finally, we do our experiment with a 45% E.G. droplet two times. The temperature evolution with time is presented in Figure 16 (a), and (b), and the results are summarized in Table 5.



(a)



(b)

Figure 16: The evolution of temperature with time for the antifreeze droplet (45% E.G.). (a): The first one. (b) the second trial.

Table 5: The results of the different properties for 45% E.G. droplet from Figure 16 (a), and (b).

Figure16	FFP1(°C)	FFP2(°C)	FPI(°C)	FP2(°C)	MP1(°C)	MP2(°C)	ΔFF1(°C)	ΔFF2(°C)
(a)	-26.4	-25.9	-25	-24	-20.2	-18.8	1.4	1.9
(b)	-25.5	-25.4	-24.5	-23.2	-19.1	-19.4	1	2.2

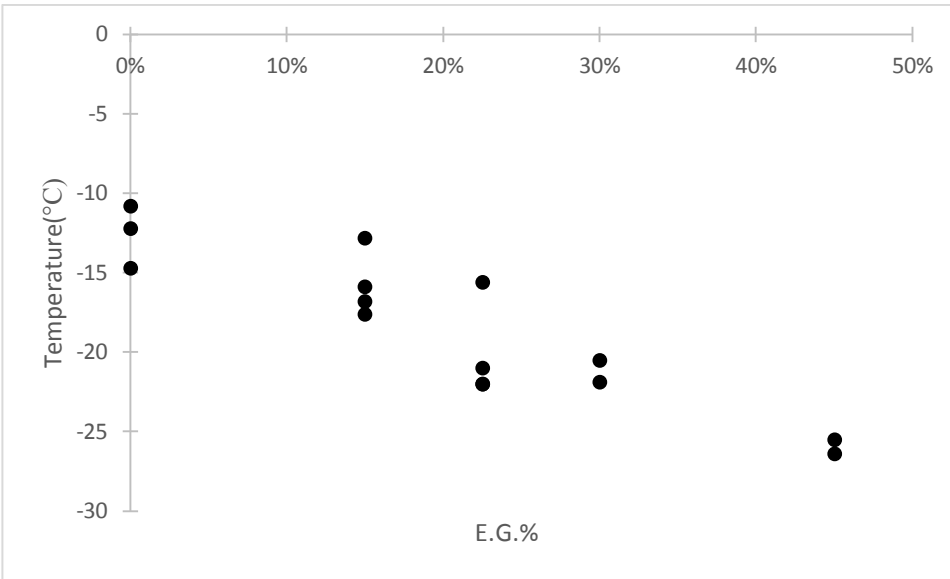
The initial solid fraction of 45% E.G. droplet is 2.03%. In this concentration the liquid specific heat is $3.2135 \frac{KJ}{Kg.K}$ ⁴³, the frozen specific heat is $1.6075 \frac{KJ}{Kg.K}$ and the latent heat is $260 \frac{KJ}{Kg}$.⁴²

4.4 Further analysis:

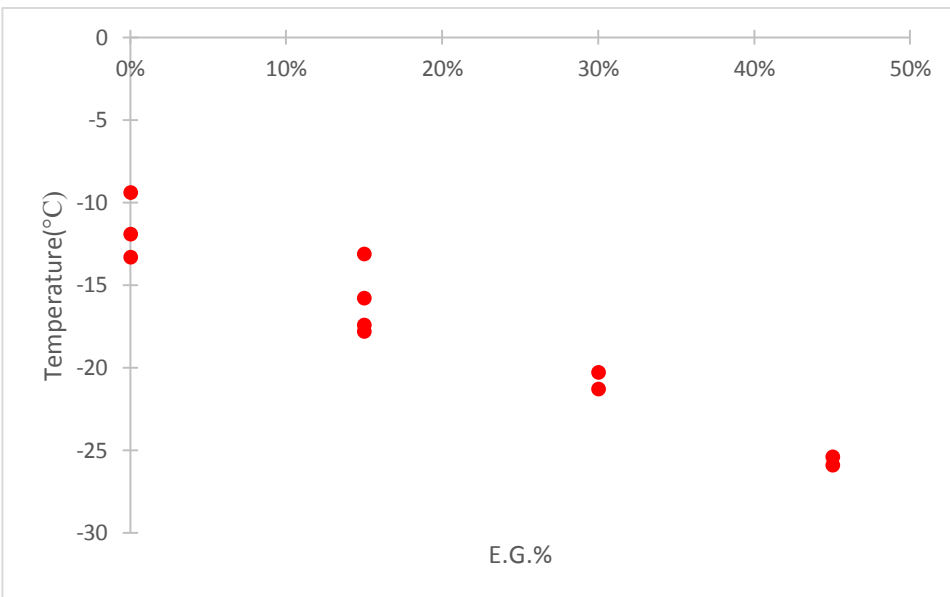
In this section, we will analyze the different properties of different concentrations of E.G. by graphing the variation of every property with the different concentrations of E.G.

4.4.1 The flash-freezing temperature:

The first property we will study is the flash-freezing point for the antifreeze droplets with two K-type thermocouples. As shown in Figure 17 (a), and (b) the flash-freezing point decreases as the concentration of E.G. increases.



(a)

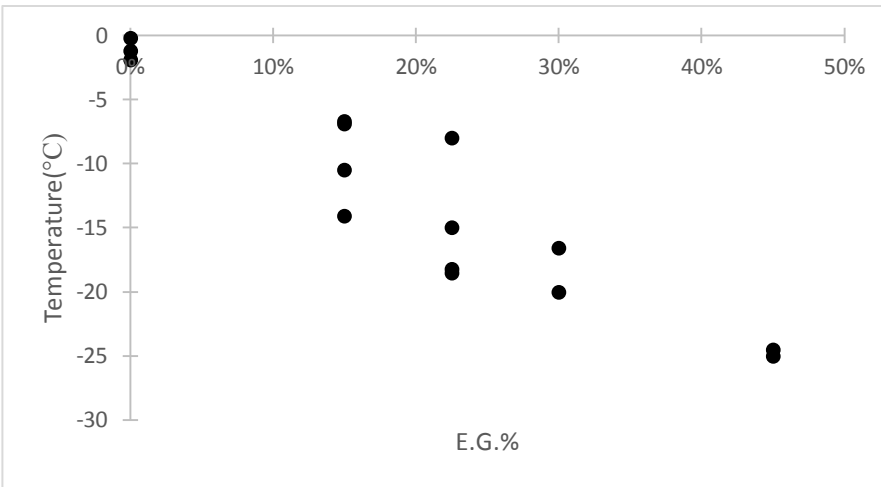


(b)

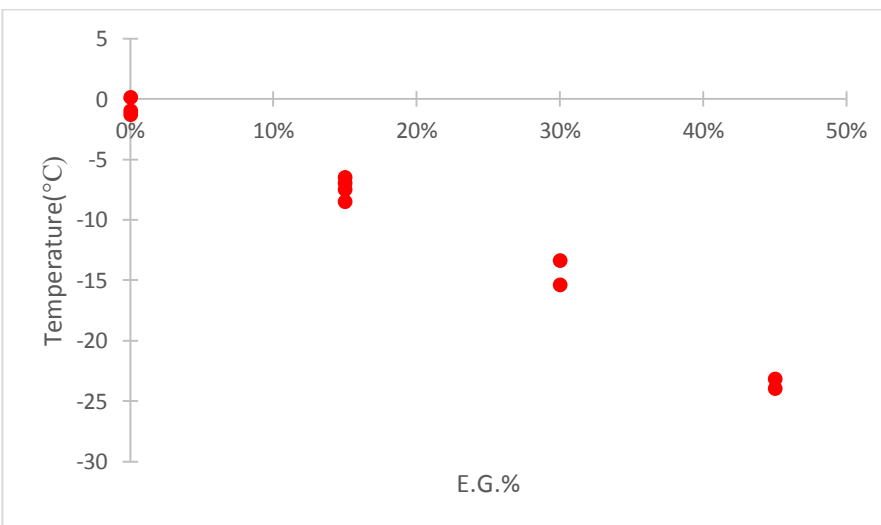
Figure 17: The variation of the flash-freezing point with different E.G.%. (a): For the first thermocouple. (b): For the second thermocouple.

4.4.2 The freezing temperature:

The freezing point also decreases as we increase the concentration of E.G., as shown in Figure 18 (a), and (b). The spread of the data points gives an idea about the uncertainty in these measurements.



(a)



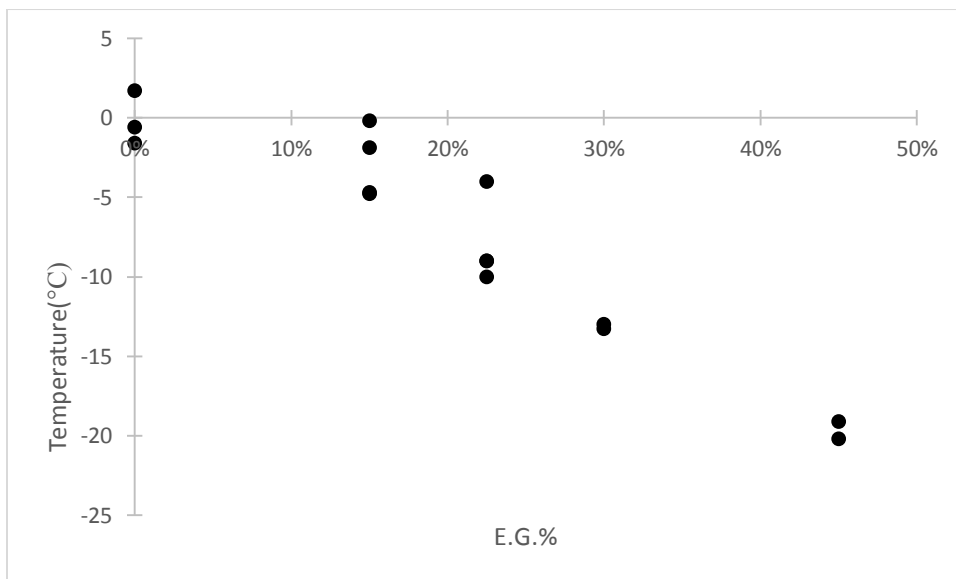
(b)

Figure 18: The variation of the freezing point with different E.G.%. (a): For the first thermocouple.

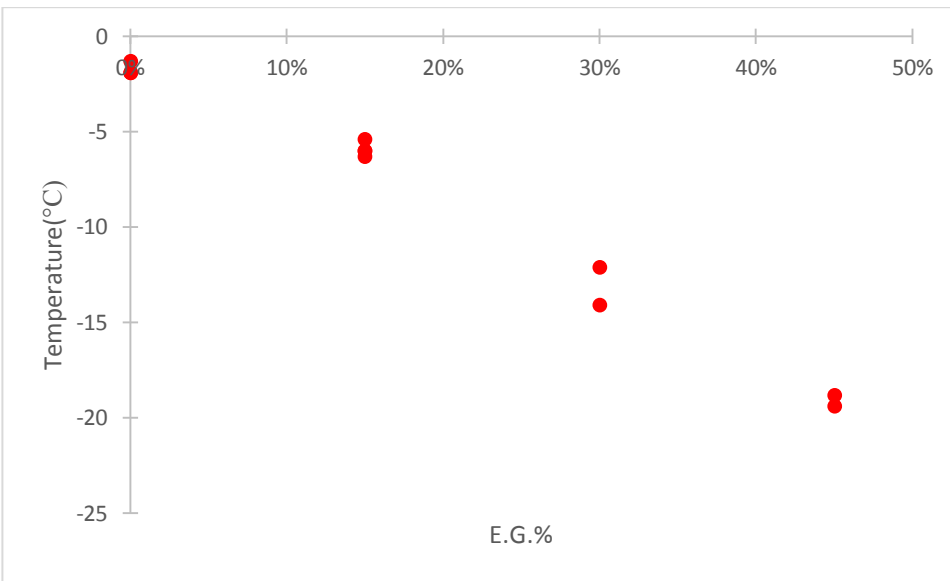
(b): For the second thermocouple.

4.4.3 The melting temperature:

The melting point, shown in Figure 19 (a), and (b), also varies with the concentrations of E.G. Such that as we increase the concentration of E.G. the melting point decreases. Of course, the melting temperature is expected to be the same as the freezing temperature for any given concentration of the antifreeze-water mixture. Yet, we see a noticeable difference here, which is likely due to the difficulty in determining these two temperatures from the data: The temperature does not rise to a stable value upon flash-freezing; instead it goes through a sharp cusp and then quickly dips back to lower values. Similarly, the temperature does not stabilize at the melting point long enough for us to be able to define the melting temperature. This is likely because the melting/freezing temperature is much lower than the room temperature, making the energy flow rate and the change in temperature quite fast at these points.



(a)



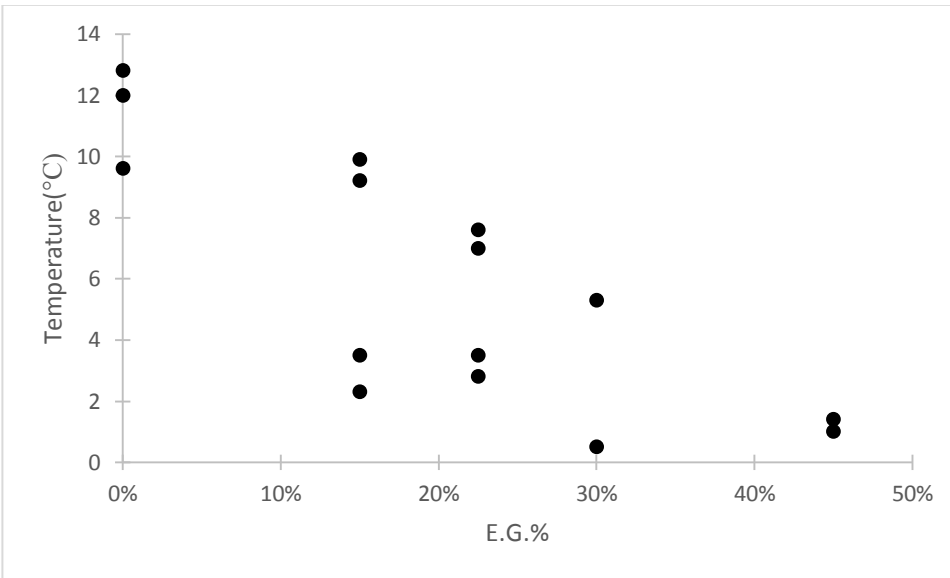
(b)

Figure 19: The variation of the melting point with different E.G.%. (a): For the first thermocouple.

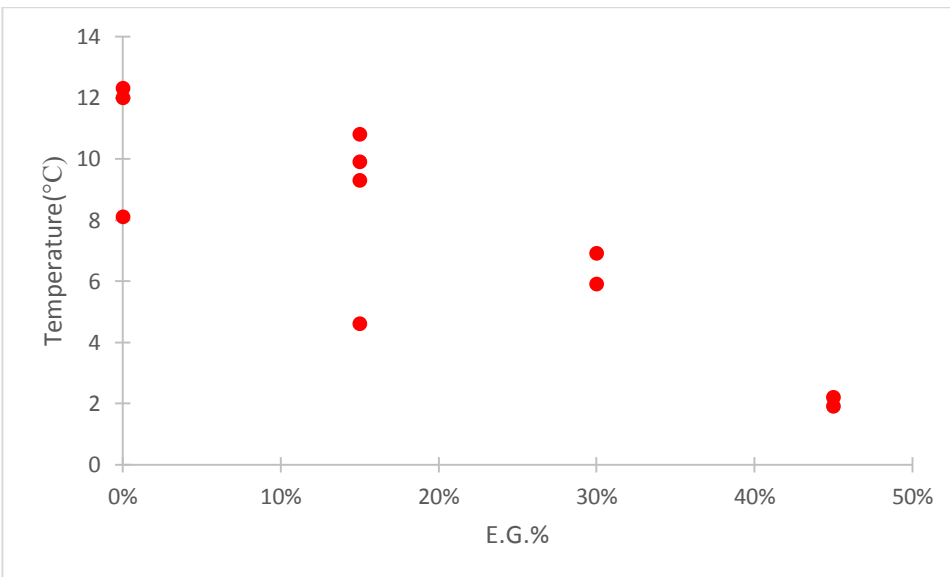
(b): For the second thermocouple.

4.4.4 The temperature jump at flash-freezing:

The fourth property we studied is the jump in temperature between the initial temperature of the antifreeze droplet when flash-freezing occurred and the equilibrium freezing point, as shown in Figures 20 (a), and (b). We see that as we increase the concentration of E.G. the jump in the temperature from the flash-freezing point up to the freezing point decreases (i.e. becomes closer to zero).



(a)



(b)

Figure 20: The variation of the jump in temperature with different E.G.% (a): For the first thermocouple. (b): For the second thermocouple.

4.4.5 Initial solid fraction at flash-freezing:

Finally, we can study the relationship between the initial solid fraction of the antifreeze droplets with the different concentrations as illustrated in the Table 6 below:

Table 6: The relation between the initial solid fraction for the antifreeze droplets and the E.G.%.

E.G.%	f_s
0%	15.07%
15%	10.17%
22.50%	7.21%
30%	6.72%
45%	2.03%

If we plot the previous Table, we get Figure 21. Obviously, the behavior of the initial solid fraction with concentration is reminiscent of the dependence of the temperature jump at flash-freezing on the concentration. This is because the temperature jump is used to calculate the initial solid fraction according to Equation 3.2.2.

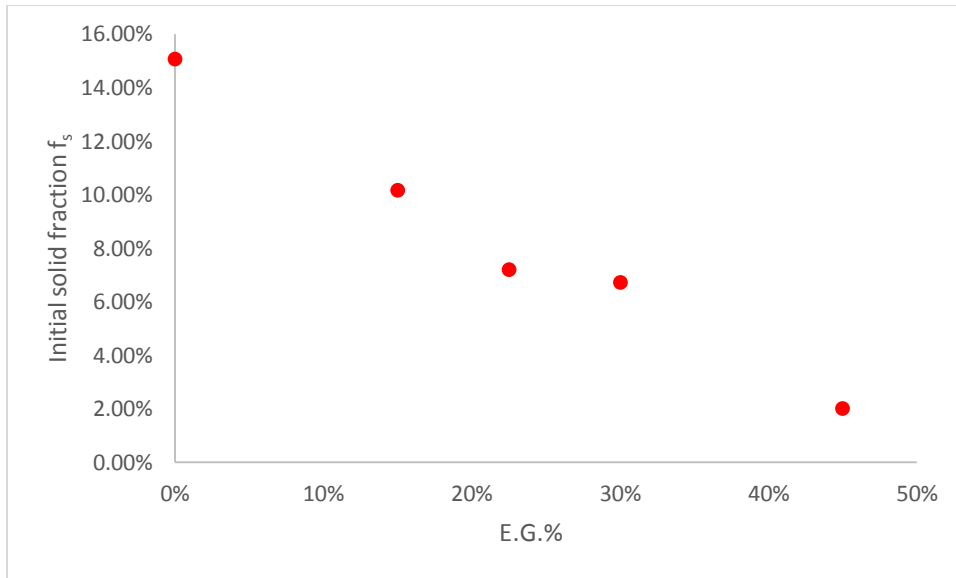


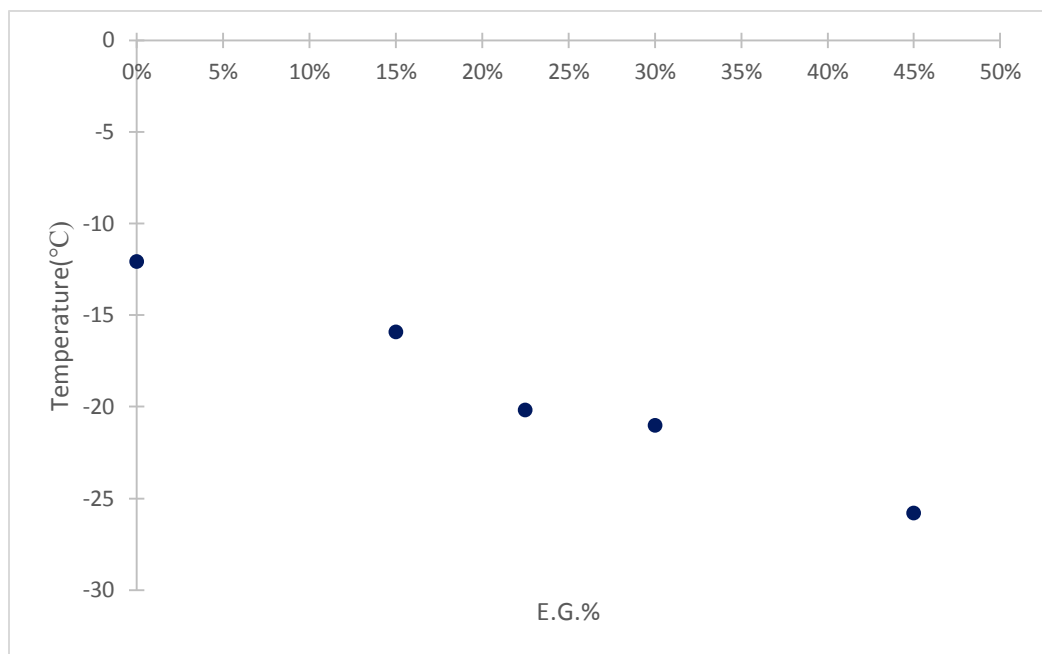
Figure 21: The variation of the initial solid fraction of the antifreeze droplets with different E.G.%.

Notice that as we increase the concentration of E.G. the initial solid fraction of the droplet decreases.

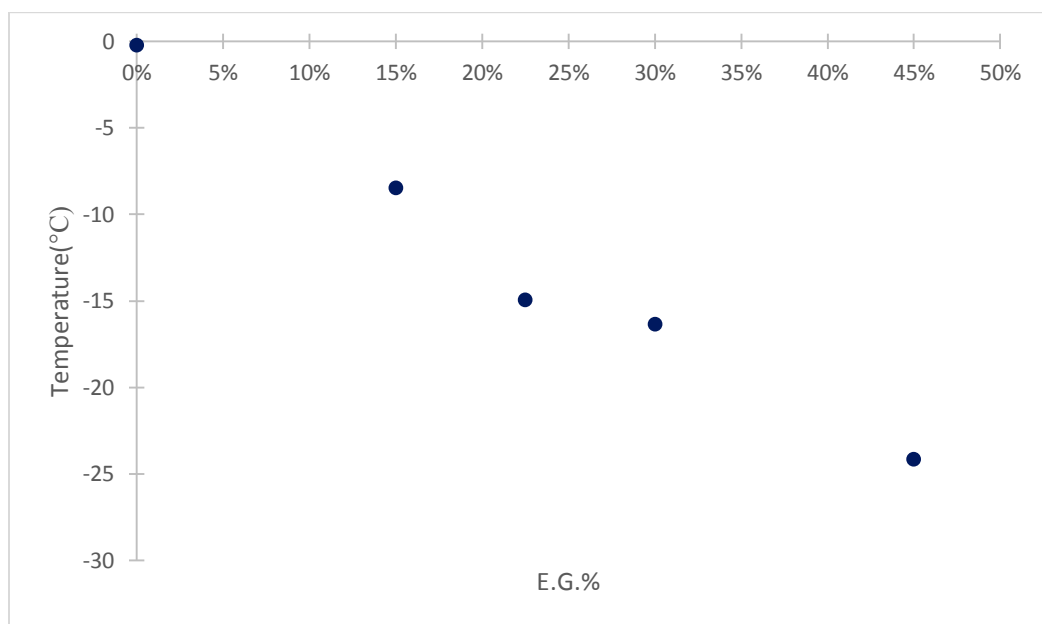
For more precise data for the different concentrations of E.G., we take the average value of the several trials in every concentration for each property as we see in Table 7. Also, we plot the variation for every property with different E.G.% in Figure 22 (a), (b), (c), and (d).

Table 7: The average value of each property for different concentrations of E.G.

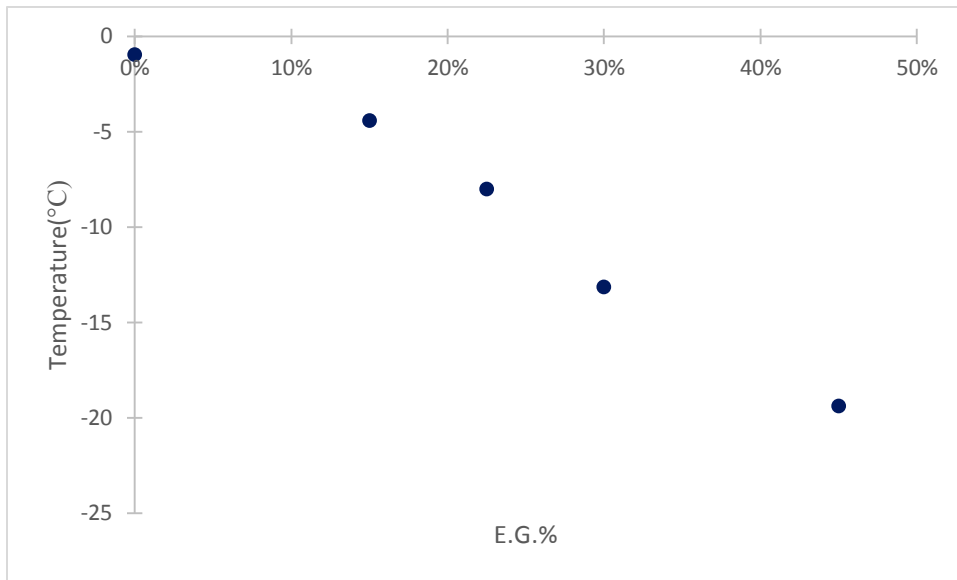
E.G.%	FF_avg(°C)	FP_avg(°C)	MP_avg(°C)	ΔFF_avg(°C)
0%	-12.0	-0.2	-0.9	11.1
15%	-15.9	-8.5	-4.4	7.4
22.5%	-20.2	-14.9	-8.0	5.2
30%	-21.0	-16.4	-13.1	4.6
45%	-25.8	-24.2	-19.4	1.6



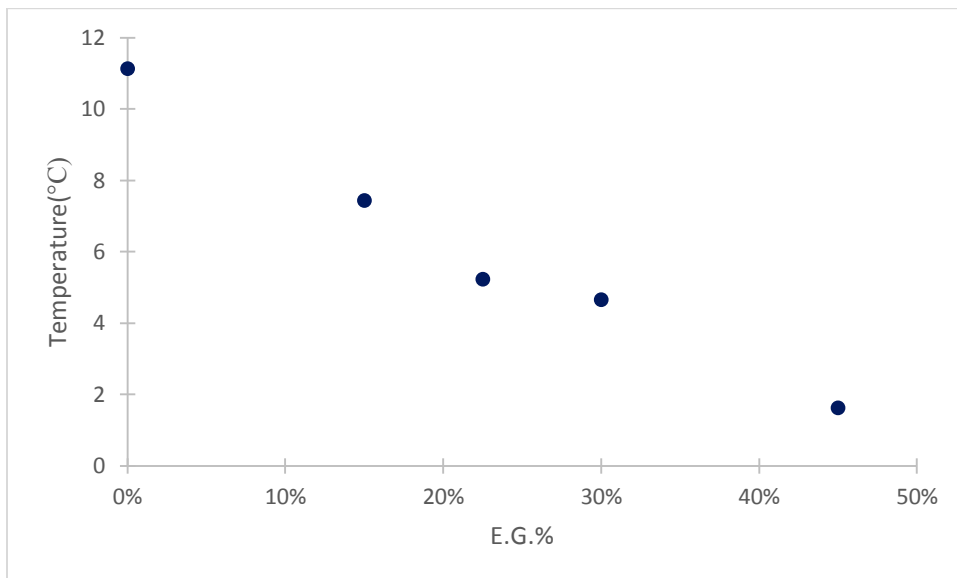
(a)



(b)



(c)



(d)

Figure 22: The variation for each property with different E.G.%. (a): For The flash-freezing point. (b): For the freezing point. (c): For the melting point. (d): For the jump in temperature.

Figure 23 below shows the plot of all properties with different E.G.%.

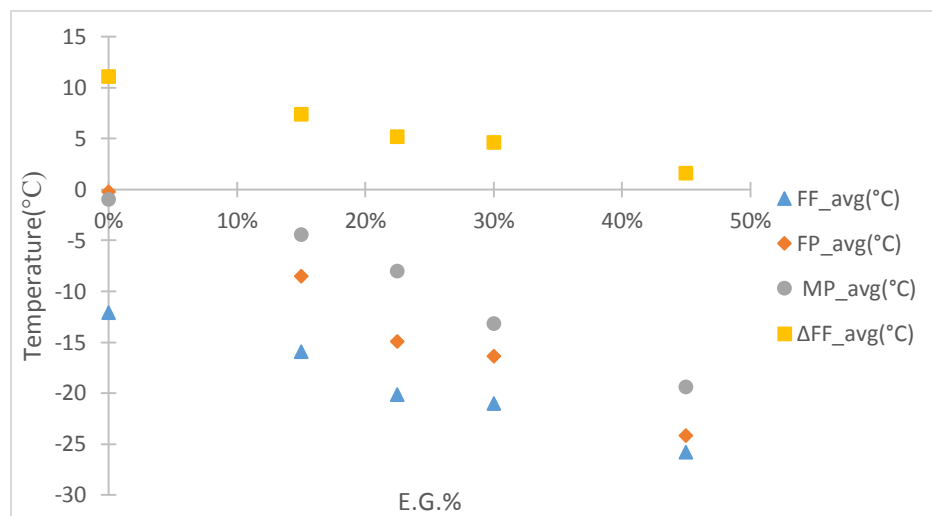


Figure 23: The average value of the different properties with different E.G.%.

Finally, figure 24 below compares the values of the freezing point we get from our experiment to the values from previous workers⁴⁴. Our data generally agrees well with the published literature.

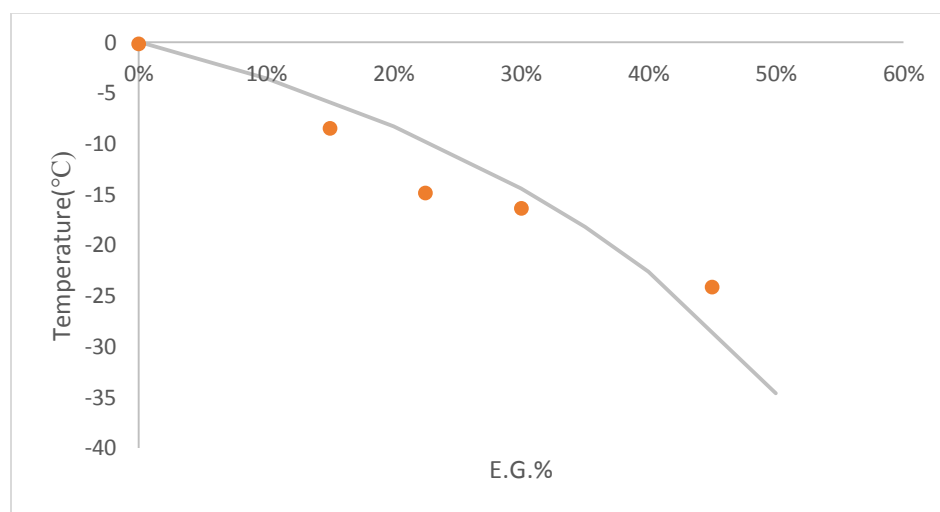


Figure 24: The comparison between the freezing point from our experiment with different E.G.% (points) and the data of previous workers (solid line).

5 Conclusion:

We carried a systematic set of experimental measurements to study the supercooling and flash-freezing behavior of droplets of ethylene glycol mixed with water at different concentrations. We found from our experiments the relationship between the different concentrations of E.G. and the different properties like the flash-freezing point, the freezing point, the melting point, and the initial solid fraction of the droplet.

We found that when we were increased the concentration of E.G. both the freezing point and the melting point decreased. Also we found mathematically the initial solid fraction for the different concentrations of E.G., which depends on the latent heat temperature dependence and the liquid and solid specific heat. When we increased the E.G. concentration, the initial solid fraction decreased such that the jump in temperature from the initial temperature of the droplet to its freezing point also decreased.

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