Cooling of Liquids and Supercooling of Water

Jordan Walsh - 120387836

Lab Report – PY3107

University College Cork

Department of Physics

February 2023

Cooling of Liquids and Supercooling of Water

1. Introduction

This document details the third practical attended on campus for PY3107. The experiment detailed throughout is (one of five campus-based experiments) 'Cooling of Liquids and Supercooling of Water'.

1.1 Overview

This report is an investigation into the strange behaviour of water as it cools in comparison to other liquids and the phenomenon of supercooling. Supercooling is the process of chilling a liquid below its freezing point, without it becoming solid. cooling of liquids is a fundamental concept in thermodynamics and is crucial in various industries ranging from food preservation to the production of electronic devices – and more recently relevant in the cooling of quantum computers.

1.2 Theory

In liquids, the primary method of heat transfer observed is convection. When cooling takes place, the induced convection currents are a result of colder (denser) liquid sinking, while in turn warmer (less dense) liquid rises toward the surface of the liquid body. The apparatus used in the experiment uses Peltier 'devices' to cool samples. A Peltier cooler is a solid state heat pump which transfers heat from one side to the other with the consumption/input of electrical energy.

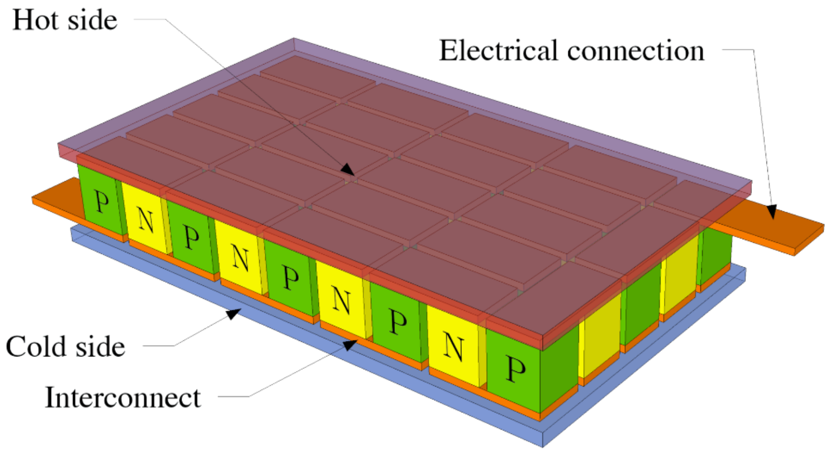

Fig 1.2.1 [2] – Peltier Element Schematic

In the experiment the particular interest is in the anomalous behaviour of the cooling of water near its maximum density temperature. From thermodynamics it can be shown that

$$\frac{dQ}{dt} = C\frac{dT}{dt}$$

where *dQ/dt* is the rate at which heat is being extracted from the system and $C = m_c c_c + m_l c_l$ *(c is the specific heat capacity of material, m = mass)*. Specific heats of materials may decrease as temperature is reduced and *dQ/dt* is not necessarily constant (because of this and the interplay of numerous factors including changes in the environment and overall system – this was investigated thoroughly in a previous practical involving heat conduction ('Heat Conduction in Sand').

2. Experimental Methods

Section 2, *Experimental Methods*, details procedure and experimental data produced from the experiment while providing brief discussion of reported data and fulfilling specified criteria of the lab brief.

2.1 Experimental Setup / Procedure

The apparatus was setup as shown in Figure 2.1.1.

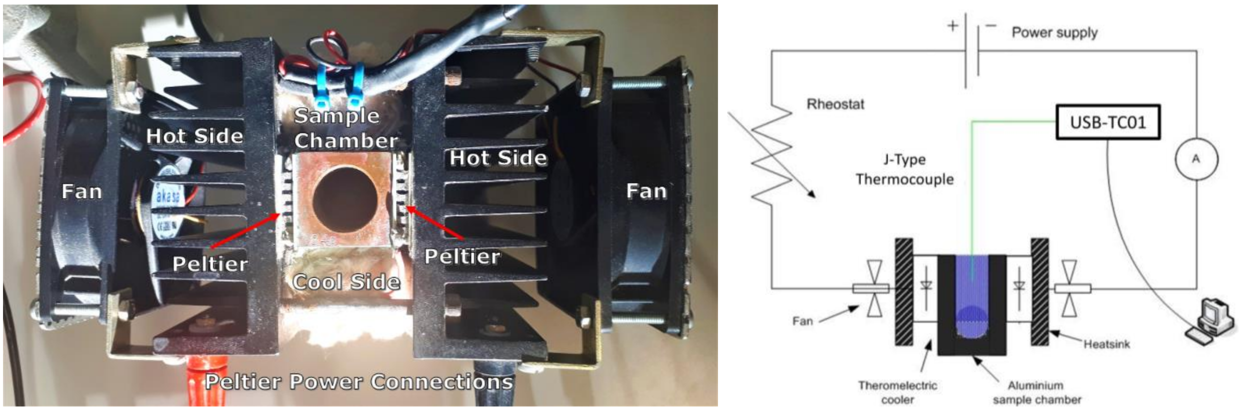

Fig 2.1.1 [1] - This apparatus has two Peltier coolers. Cooling sides of Peltier coolers are beside the sample chamber and the hot sides placed against metal heat sinks with fans.

Applying a current of about 2.8 A to 4 A to the Peltier devices causes the temperature of the liquid to be lowered. The thermocouple in the chamber registers the drop in temperature. Signal from the thermocouple is recorded by a PC using a National Instruments USB-TC01 interface. Using the supplied software one can then register and plot this data in the form of cooling curve. This provides the required data to plot the cooling curves *(℃ Vs. Time)* in all situations that have been specified to complete in the lab brief.

2.2 Preliminary Experiments – Cooling Curve of Ethanol

The lab brief states: *"[begin] by examining the case of a 'normal' liquid, namely ethanol. Using the apparatus, [obtain] a cooling curve for this liquid in the temperature range of about room temperature to ~ -5 0C." "By evaluating the slope at, say, 10 ℃, one may then calculate the rate dQ / dt at which heat is being extracted from the liquid at this point."*

The determined cooling curve for the ethanol sample is shown in Figure 2.2.1. From the collected data, an estimate of *dQ/dt* at the suggested temperature of 10°C was determined by finding the data point at ~10°C and determining the slope at that point by simply recognising that

$$s = \frac{rise}{run} = \frac{dT}{dt}$$

from the data, it seemed reasonable at 10°C to use data points at 2 apart from each other giving

$$\frac{\Delta T}{\Delta t} = \frac{14.2°\mathrm{C} - 14.134°\mathrm{C}}{10.179s - 10.655s} = -0.1204\, K\, s^{-1}$$

As such,

$$C = m_c c_c + m_l c_l = (0.184\, kg)(385\, J\, kg^{-1}\, K^{-1}) + (0.0061254\, kg)(2400\, J\, kg^{-1}\, K^{-1})$$
$$= 85.541\, J\, K^{-1}$$

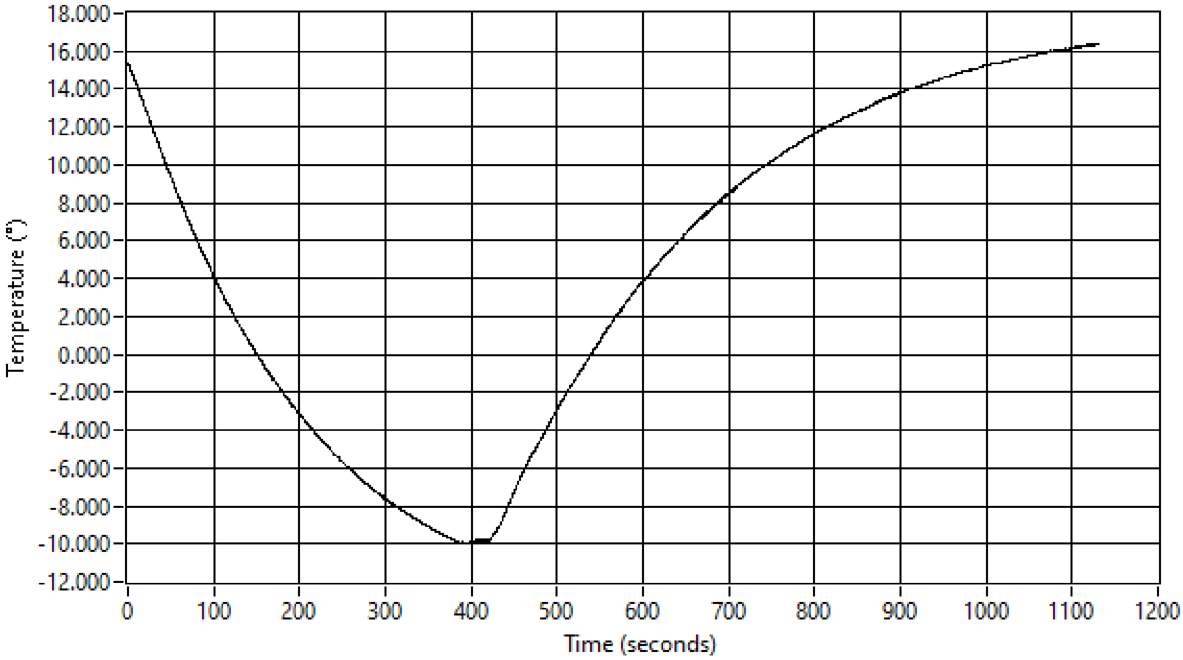

Fig 2.2.1 | °C Vs. s | determined cooling curve of ethanol.

and finally, it remains to show that

$$\frac{dQ}{dt} = C\frac{dT}{dt} = (85.541\, J\, K^{-1})(-0.1204\, K\, s^{-1}) = -10.299\, J\, s^{-1}$$

The lab brief then states: "*Compare your estimate of dQ / dt with the power at which the system is operated (current × voltage) to determine the (approximate) efficiency of the cooling process.*"

$$Voltage = (5.77 - 1.44) \pm 0.2\ [kg\ m^2 s^{-3} A^{-1}]$$

$$Current = 3.4 \pm 0.1\ [A]$$

$$P = IV \approx 14.722\ [kg\ m^2 s^{-3}]$$

$$14.722\ W\ \equiv 14.722\, J\, s^{-1}$$

As such, the efficiency is therefore:

$$\frac{Output}{Input} = \frac{10.299}{14.722} = 0.6996$$

$$Efficiency\ \approx 70\%$$

2.3 Cooling Curves of Water

The lab brief states *"Repeat this experiment [For Distilled Water] several times, taking different values of the cooling current and different positions of the thermocouple along the axis and hence obtain a mean value for T_{md}."*

Various measurements are shown in Figures 2.3.1 to 2.3.3, from which the maximum density temperature was determined using data with *clear* plateaus.

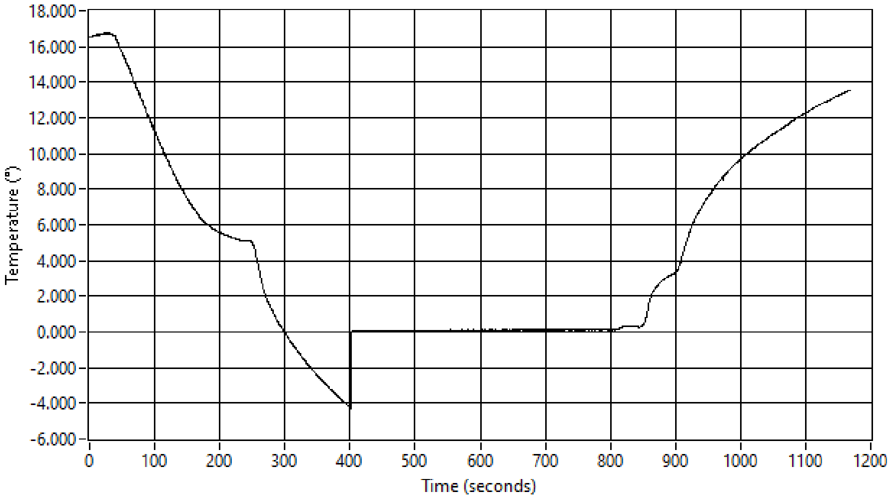

Fig 2.3.1 | °C Vs. s | determined cooling curve of water | 4.33V, 3.4A | Thermocouple deep in container

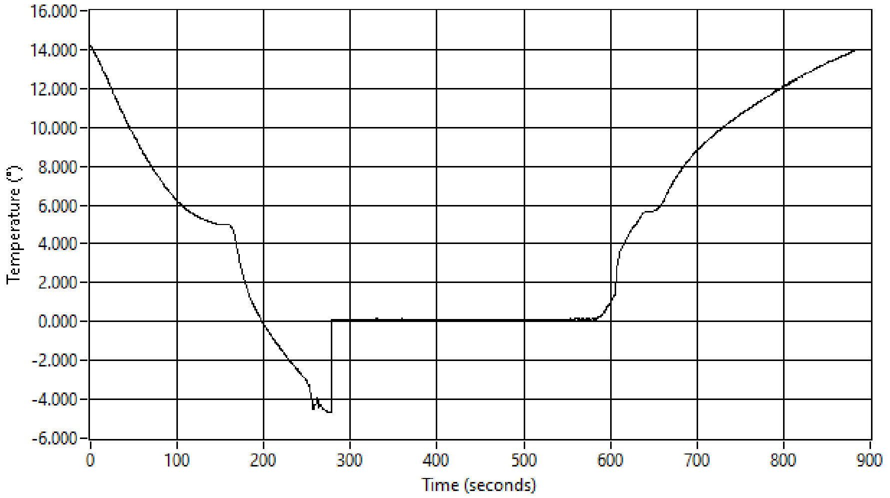

Fig 2.3.2 | °C Vs. s | determined cooling curve of water | 5.3V, 4.2A | Thermocouple deep in container

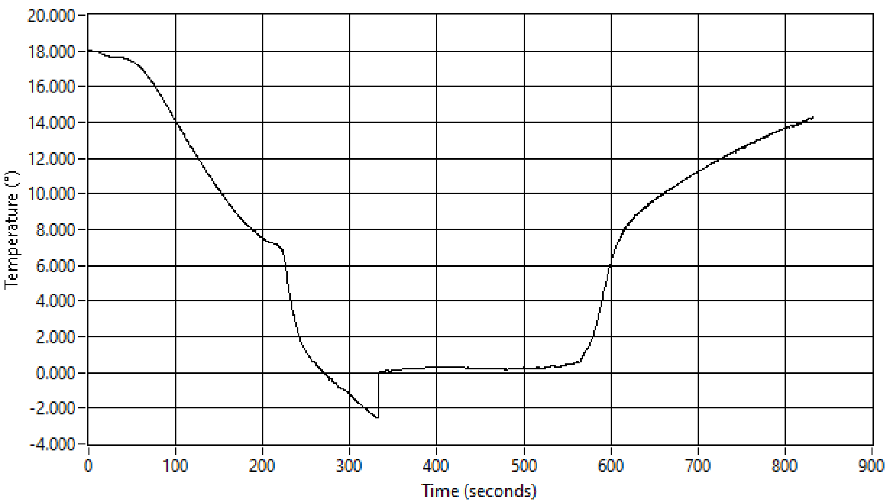

Fig 2.3.3 | °C Vs. s | determined cooling curve of water | 5.3V, 4.2A | Thermocouple closer to surface of water

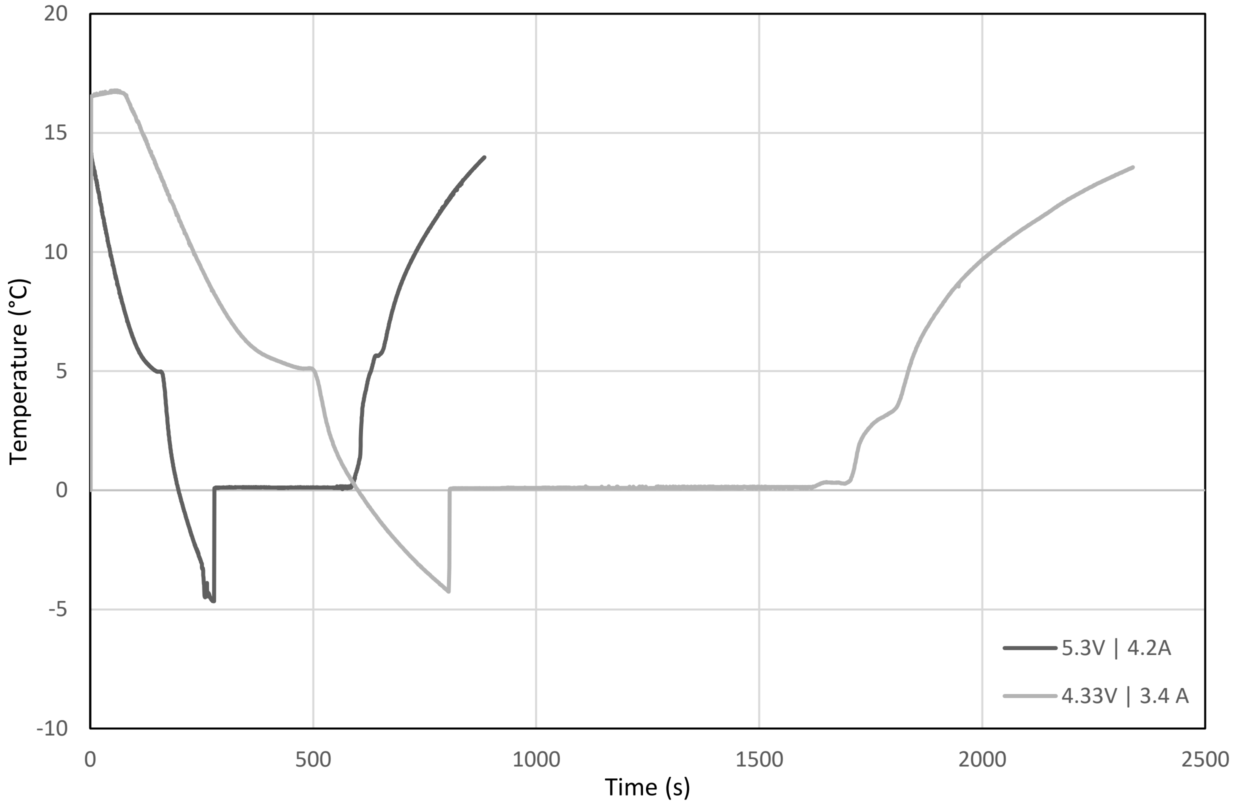

Fig 2.3.4 | °C Vs. s | Superimposed graph (evident plateaus) | Combination of Fig 2.3.1 and Fig 2.3.2

Only 2 of 3 measurements were useful here. Unfortunately, due to time limitations, it was not possible to take any more measurements. From Figure 2.3.4 we can make an estimate of T_{md}.

$$T_{md}\ (5.3V, 4.2A) = \frac{4.989℃ + 5.721℃}{2} = 5.355℃$$

$$T_{md}\ (4.33V, 3.4A) = \frac{5.117℃ + 3.372℃}{2} = 4.2445℃$$

$$\rightarrow \bar{T}_{md} = \frac{5.355℃ + 4.2445℃}{2} = 4.79975℃$$

A brief analysis of error will show

$$\Delta\bar{T}_{md} = \sqrt{\frac{\sum_{x=1}^{2}(T_{md\,x} - \bar{T}_{md})^2}{2}} = \sqrt{\frac{(5.355℃ - 4.79975℃)^2 + (4.2445℃ - 4.79975℃)^2}{2}}$$
$$= 0.55525\ ℃$$

$$\therefore T_{md} \approx 4.8 \pm 0.6\ ℃$$

2.4 Cooling Curves of Aqueous Solutions

The lab brief states "*investigate how the maximum density temperature will vary if you add salt, for example, or an alcohol such as ethanol, to water. Carry out these experiments and plot graphs of Tmd vs. concentration for the solute used.*"

2.4.1 Water-Ethanol Solution

Determined curves for various water-ethanol mixes are shown in Figures 2.4.1 – 2.4.3.

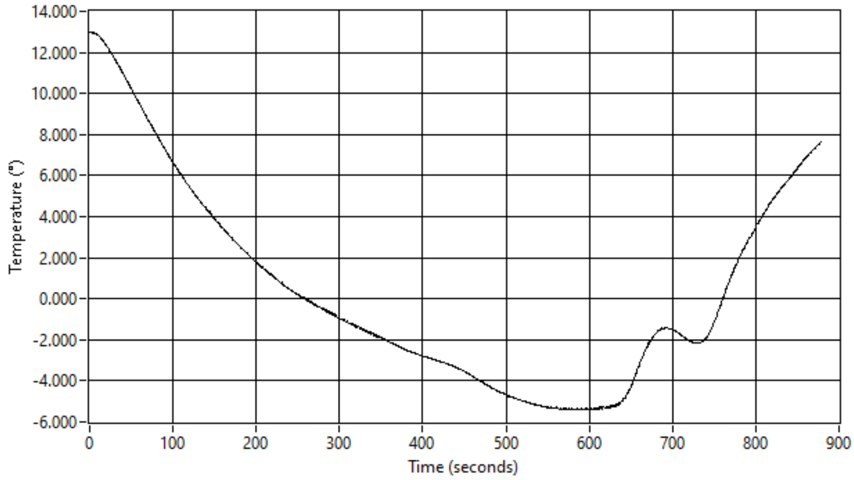

Fig 2.4.1 | °C Vs. s | Water-Ethanol solution at a ratio ~ 1:10 | Mix 1

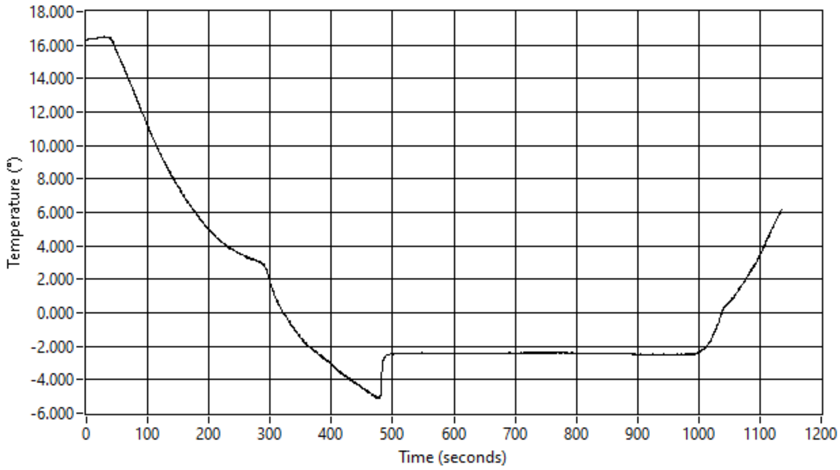

Fig 2.4.2 | °C Vs. s | Water-Ethanol solution at a ratio ~ 1:15 | Mix 2

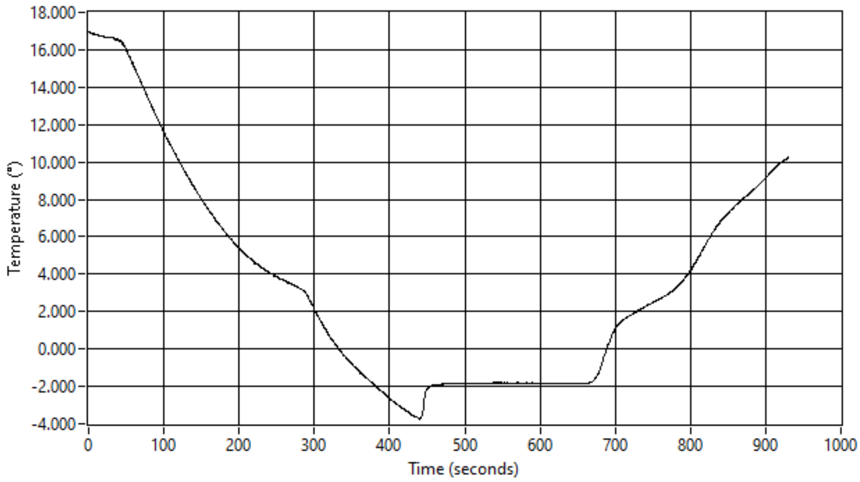

Fig 2.4.3 | °C Vs. s | Water-Ethanol solution at a ratio ~ 1:20 | Mix 3

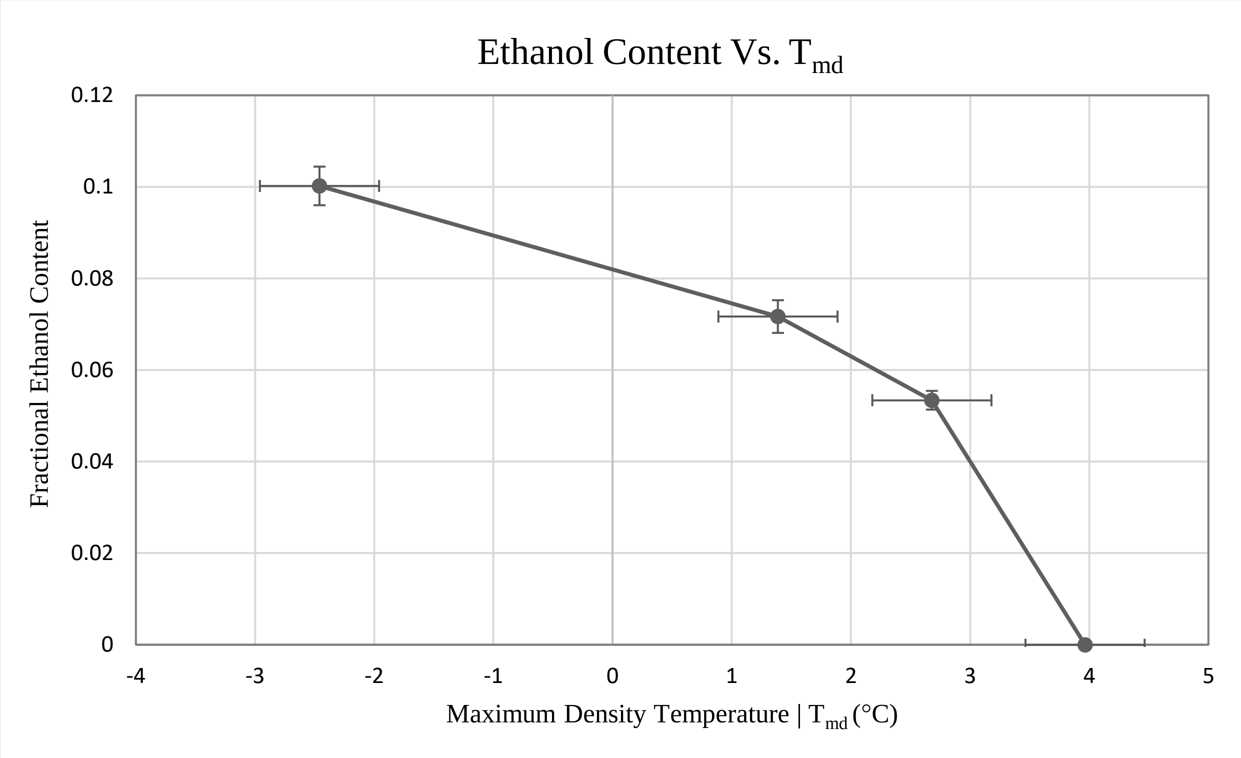

Fig 2.4.4 | Based on the data of Table 2.4.1 and Table 2.4.2

Ethanol	Plateau $_{(left)}$ °C	Plateau $_{(right\ max)}$ °C	Plateau $_{(right\ max)}$ °C	Plateau $_{(right\ mean)}$ °C	Mean °C	
Mix 1	-3.105	-1.457	-2.17	-1.8135	-2.4592	
Mix 3	2.677	0.198	0	0.099	1.388	
Mix 2	3.07	1.257	3.321	2.289	2.6795	
Water 1					3.965	±0.5

Tab 2.4.1 | Experimental Data determined from Fig 2.4.1 – 2.4.3

Ethanol	Ethanol g	D_Water g	Water / Ethanol	Ethanol / Water
Mix 1	0.523	5.22	9.980879541	0.100191571
Mix 3	0.43	6	13.95348837	0.071666667
Mix 2	0.55	10.3	18.72727273	0.053398058
Water 1	0	N/A		0
	±0.02	±0.02		

Tab 2.4.2 | Experimental Data from Chemical Scales

2.4.2 Water-Salt Solution

Determined curves for various water-salt mixes are shown in Figures 2.4.5 – 2.4.7.

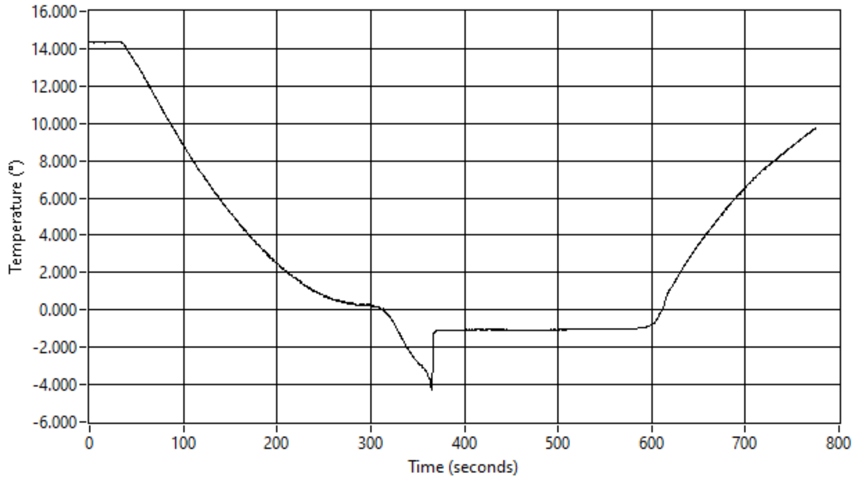

Fig 2.4.5 | °C Vs. s | Water-Salt solution at a ratio ~ 1:50

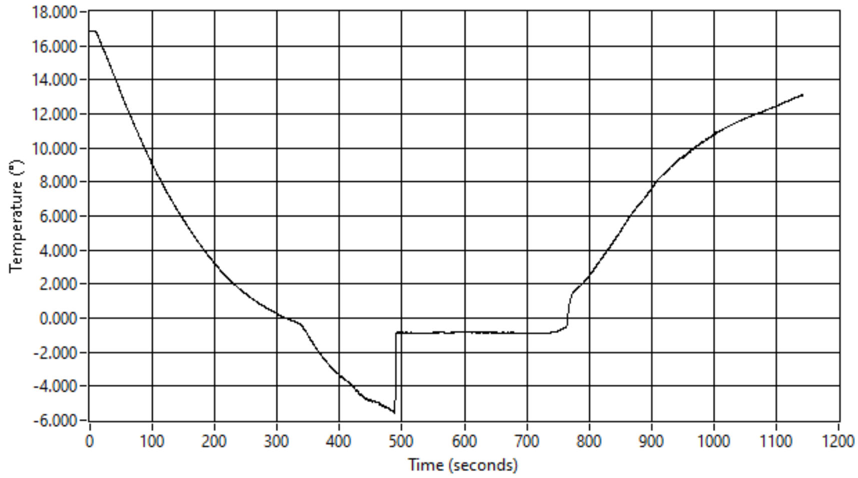

Fig 2.4.6 | °C Vs. s | Water-Salt solution at a ratio ~ 1:60

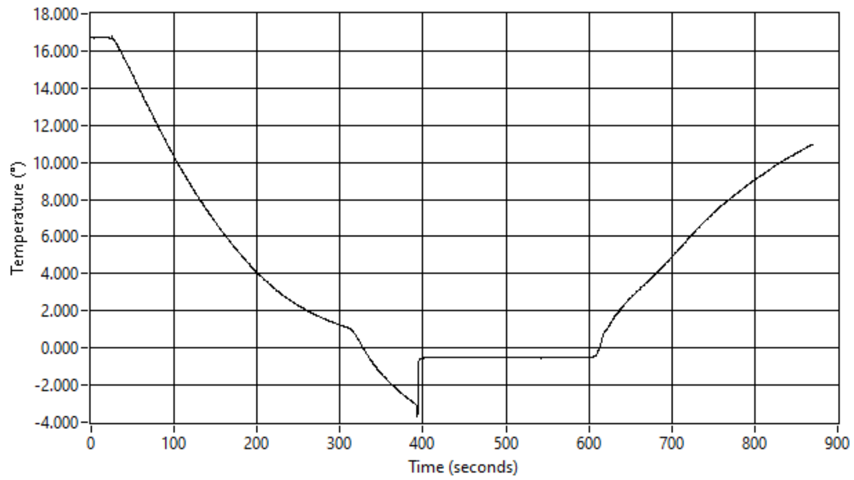

Fig 2.4.7 | °C Vs. s | Water-Salt solution at a ratio ~ 1:70

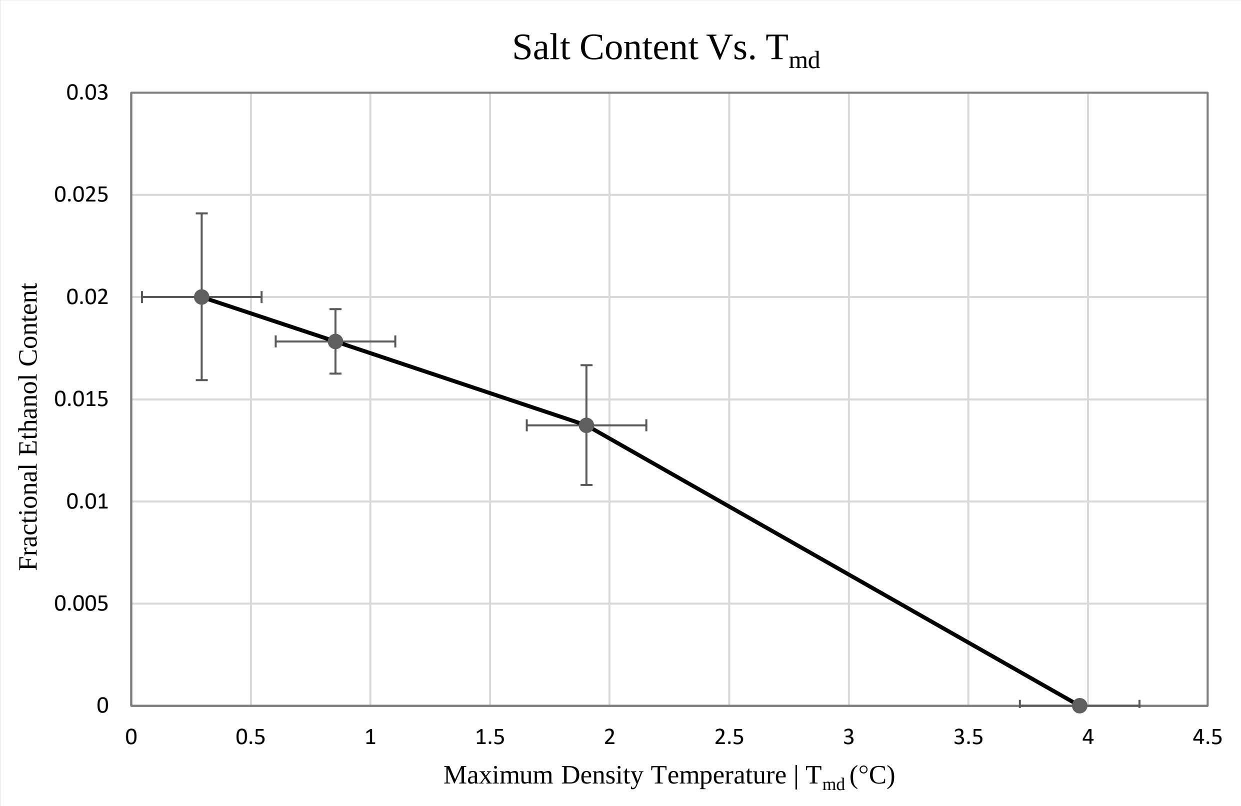

Fig 2.4.7 | Based on the data of Table 2.4.3

Salt	Plateau (left min) °C	Plateau (right max) °C	Mean °C	Salt g	Water g	Water Salt	Salt Water
Mix 1	0.132	0.458	0.295	0.1	5	50	0.02
Mix 2	-0.62	2.328	0.854	0.23	12.9	56.08696	0.017829
Mix 3	0.976	2.831	1.9035	0.095	6.92	72.84211	0.013728
Water 1			3.965	0	N/A		0
			±0.3	±0.02	±0.02		

Tab 2.4.3 | Experimental Data from Chemical Scales and Fig 2.4.5 – 2.4.7

4 Discussion

Supercooling is not a topic that I was particularly familiar with before completing this experiment. I've found the idea of cooling liquids below its typical freezing point to be very interesting throughout this experiment.

A point that I would like to bring attention to is the intense time-constraint experienced whilst completing this experiment. If time had permit, there would have been many more measurements taken, particularly for Section 2.3 (The Cooling Curves of Water), where I am not satisfied with the result produced. The measurements simply take too long (~10 to 15 minutes each) to produce a palpable and experimentally grounded result.

I am however satisfied with the observed relationships throughout the rest of the report. The trends seen in Fig 2.4.7 and 2.4.4 are in line with what would be expected from a more general *density* measurement with respect to concentration as shown in Figure 4.1. While Figure 4.1 related directly to ethanol, it is reasonable to assume the same trends apply to salt-water mixtures.°

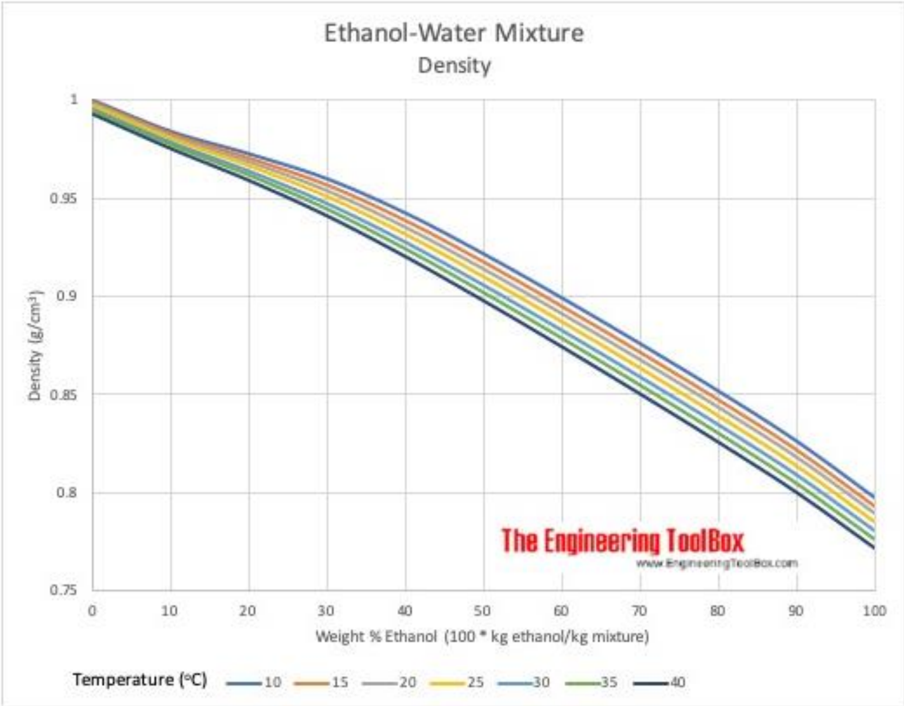

Fig 4.1 | Experiment Results sourced online, see reference for source

Speaking more generally, investigation of the composure of the curves shown throughout the report, the curves for water have irregular plateaus not seen in those of pure ethanol. These were expected to be at approximately 4°C according to literature, which is in fact in line with what we observe (See Section 2.3). These curves also show a discontinuous jump at various sub-zero temperatures (generally around -4°C), which signify freezing of the super cooled liquid, bringing the temperature readings back to 0°C (note: *contradictory to the lab manual*, the thermocouple did have a significant 0 point error while in use for our experiment – when we expected a reading of 0°C, we observed a reading of 0.01°C through our LabVIEW interface. As such we did not take drastic measures to recalibrate the graphs shown throughout as the difference was effectively negligible and no thorough error analysis was required).

The plateaus mentioned previously did in fact drop in temperature in the presence of ethanol. This would have been expected considering the freezing point of pure ethanol is more than 100°C less than water. This posed significant challenges in the lab, as the mixtures had to be very meticulously composed so that the aforementioned plateaus could be recorded at all. This, in truth, wasted a lot of time. It would be advantageous to potentially provide approximate mixture ratios to start from. Much of the data collected during the allotted time was effectively useless and was discarded as no conclusions could be drawn to them (The liquid would freeze solid before plateaus could be observed in the data).

This experiment, though not heavy in intense calculation (most of the results throughout are in raw graphical form), personally provided good insight into the nature of cooling for liquids and introduced me to the concepts of supercooling and thermoelectrical cooling. Overall, I am satisfied with produced results (especially in comparison to my peers) and the conclusions they have allowed me to draw from the experiment as a whole.

References

[1] : Figure from UCC Department of Physics, Source: https://www.ucc.ie/en/physics/study/undergraduate/thelabratories/thirdyearphysicslab/investigationofcoolingcurvesandsupercooling/

[2] : Wikipedia, Source: https://en.wikipedia.org/wiki/Thermoelectric_cooling#/media/File:Peltierelement.png

[3] : Source: https://www.engineeringtoolbox.com/ethanol-water-mixture-density-d_2162.html

Density of Ethanol-Water Mixure							
Ethanol Weight (%)	Temperature (°C)						
	10	15	20	25	30	35	40
0	1.000	0.999	0.998	0.997	0.996	0.994	0.992
10	0.984	0.983	0.982	0.980	0.979	0.977	0.975
20	0.972	0.971	0.969	0.966	0.964	0.961	0.959
30	0.960	0.957	0.954	0.951	0.947	0.944	0.941
40	0.942	0.939	0.935	0.931	0.928	0.924	0.920
50	0.922	0.918	0.914	0.910	0.906	0.902	0.897
60	0.899	0.895	0.891	0.887	0.883	0.878	0.874
70	0.876	0.872	0.868	0.863	0.859	0.855	0.850
80	0.852	0.848	0.843	0.839	0.835	0.830	0.826
90	0.827	0.822	0.818	0.814	0.809	0.805	0.800
100	0.798	0.794	0.789	0.785	0.781	0.776	0.772