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# **Surface freezing at the alkane water interface under acoustic levitation**

An investigation of the interface between water and hexadecane

Master's thesis in Nanotechnology

Axel Stark

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DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2025

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MASTER'S THESIS 2025

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Cover: Photo of a levitated water droplet after hexadecane was added to it causing hexadecane to start freezeing.

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## Abstract

This thesis investigates the surface freezing phenomenon between water and hexadecane that occur under acoustic levitation. The study examines the impact of impurities, potential surface-induced effects, and the role of the evaporation of the water droplet while acoustically levitated, on this phenomenon. Three purity levels of hexadecane were tested to assess impurity effects on freezing inhibition. Results suggest that impurities prevent freezing, contrary to the typical expectation where impurities often promote freezing. Surface-induced effects were evaluated through interfacial tension and spreading behavior studies, revealing minimal influence on freezing except, for the potential of creating a monolayer of organized molecules at the interface that could act as a nucleation point. Thermodynamic calculations and levitation experiments demonstrated that water evaporation contributes to freezing but may not be the sole factor. These findings highlight the need for additional investigations to fully understand the freezing mechanism, particularly regarding impurity interactions.

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# Contents

|                                                 |           |
|-------------------------------------------------|-----------|
| <b>List of Figures</b>                          | <b>IX</b> |
| <b>List of Tables</b>                           | <b>XI</b> |
| <b>1 Introduction</b>                           | <b>1</b>  |
| 1.1 Surface Freezing of alkanes . . . . .       | 1         |
| 1.2 Acoustic levitation . . . . .               | 2         |
| 1.3 Aim and objective . . . . .                 | 3         |
| <b>2 Theory</b>                                 | <b>5</b>  |
| 2.1 Acoustic levitation . . . . .               | 5         |
| 2.2 Interfacial tension and spreading . . . . . | 6         |
| 2.3 Thermodynamics . . . . .                    | 7         |
| <b>3 Materials and Method</b>                   | <b>9</b>  |
| 3.1 Chemical . . . . .                          | 9         |
| 3.2 Purification of Hexadecane . . . . .        | 9         |
| 3.3 Degassing of water . . . . .                | 9         |
| 3.4 Acoustic levitation . . . . .               | 10        |
| 3.4.1 Design . . . . .                          | 10        |
| 3.4.2 Stability . . . . .                       | 10        |
| 3.4.3 Experimental set-up . . . . .             | 10        |
| 3.4.4 Data acquisition . . . . .                | 12        |
| 3.5 Tensiometry . . . . .                       | 13        |
| 3.6 Differential Scanning Calorimetry . . . . . | 13        |
| <b>4 Results and Discussion</b>                 | <b>15</b> |
| 4.1 Impurities . . . . .                        | 15        |
| 4.2 Interfacial energy . . . . .                | 17        |



|          |                                       |             |
|----------|---------------------------------------|-------------|
| 4.3      | Effect of water evaporation . . . . . | 19          |
| <b>5</b> | <b>Conclusions</b>                    | <b>23</b>   |
| 5.1      | Future work . . . . .                 | 24          |
| <b>A</b> | <b>DSC Results</b>                    | <b>v</b>    |
| <b>B</b> | <b>Droplet evaporation</b>            | <b>xi</b>   |
| <b>C</b> | <b>Droplet Temperature</b>            | <b>xiii</b> |

# List of Figures

|     |                                                                                                                                                                                                                                                                                                                                                                                                     |    |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 3.1 | a) Photo of acoustic levitator, b) photo of acoustic levitator with two, green polystyrene beads. . . . .                                                                                                                                                                                                                                                                                           | 10 |
| 3.2 | Experimental set-up that combines the acoustic levitator, lightbox, side camera, infrared thermometer, and a separate electronic device that measures, CO <sub>2</sub> , humidity and room temperature. . . . .                                                                                                                                                                                     | 12 |
| 3.3 | a) Original picture, b) binary picture, c) original picture with superimposed contour (pink line), and rectangle (red line). . . .                                                                                                                                                                                                                                                                  | 13 |
| 4.1 | Sequence of three images captured at a time interval of 1/50 second, a) depicts hexadecane droplets suspended from a needle tip, with a neighboring water droplet, b) the hexadecane and water droplets are in close proximity, but have not made contact, yet, c) the moment when the hexadecane and water droplets came in contact. Notably, the onset of hexadecane freezing is evident. . . . . | 16 |
| 4.2 | The five times purified hexadecane when water first was added and then 20 seconds later when the hexadecane started to freeze. . . .                                                                                                                                                                                                                                                                | 17 |
| 4.3 | a) Water droplet with a 2 L volume, before hexadecane was added, b) water droplet (right side) and a 3L hexadecane droplet (left side) 30 seconds after hexadecane was added. Here it is clear that the freezing is propagating on the surface of hexadecane, c) hexadecane was completely frozen approximately 120 seconds after hexadecane was added. . . . .                                     | 19 |
| 4.4 | a) Water droplet of 1 L (up left) and hexadecane droplet of 3 L (right side) the moment after hexadecane was added. Here it is clear that the surface of hexadecane begins to freeze, b) water was almost completely evaporated and the bowl-like structure was formed, c) hexadecane melted and a low-volume water droplet still remained visible at the top of the hexadecane droplet. . . . .    | 20 |

|     |                                                                                                                                                                                                          |      |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| 4.5 | a) Instant surface freezing when a 0.5 $\mu\text{L}$ water droplet (up right) and a 3 $\mu\text{L}$ hexadecane droplet (left side) came in contact, b) maximum amount of freezing that occurred. . . . . | 20   |
| A.1 | DSC of non-purified hexadecane, with time interval 10 kelvin per minute . . . . .                                                                                                                        | v    |
| A.2 | DSC of non-purified hexadecane, with time interval 2.5 kelvin per minute . . . . .                                                                                                                       | vi   |
| A.3 | DSC of 1 time purified hexadecane, with time interval 10 kelvin per minute . . . . .                                                                                                                     | vii  |
| A.4 | DSC of 1 time purified hexadecane, with time interval 2.5 kelvin per minute . . . . .                                                                                                                    | viii |
| A.5 | DSC of 5 times purified hexadecane, with time interval 10 kelvin per minute . . . . .                                                                                                                    | ix   |
| A.6 | DSC of 5 times purified hexadecane, with time interval 2.5 kelvin per minute . . . . .                                                                                                                   | x    |
| B.1 | Volume measurement of water droplet in acoustic levitator during 20 minutes. . . . .                                                                                                                     | xi   |
| C.1 | Temperature measurements of the room and droplet temperature . . . . .                                                                                                                                   | xiii |

# List of Tables

|     |                                                  |    |
|-----|--------------------------------------------------|----|
| 4.1 | Tensiometry measurements of hexadecane . . . . . | 18 |
|-----|--------------------------------------------------|----|



# 1

## Introduction

### 1.1 Surface Freezing of alkanes

Surface melting is a phenomenon where a quasi-liquid layer can form on the surface of a solid, below its melting temperature, which has been known and well-documented since 1842 by Michael Faraday [1]. However, it was not until 90 years later when the opposite effect, known as surface freezing, referring to the formation of long-range crystalline order on a surface above the bulk freezing point, was described and reported by Müller *et al.* [2], in 1932.

In a later study, Ocko *et al.* [3] studied alkanes through X-rays and surface tension measurements, which led to the identification of different metastable phases that occur during surface freezing. They showed that alkanes with carbon chain lengths ranging from 16 to 50 atoms can form an ordered monolayer at the alkane-air interface, even up to 3°C above the bulk freezing point ( $T_f$ ) [3]. This unique monolayer persists for alkanes all the way down to  $T_f$ . It is worth noting that this ordering phenomenon is exceptionally rare, with a similar effect observed only in liquid crystals [4], and liquid metals [5]. However, in the case of liquid crystals, no true crystalline layer was observed [4].

Surface freezing is a well-known phenomenon today, but the complete understanding of its underlying mechanisms is still an active area of research. Due to the fact that surface freezing involves the formation of a monolayer at the alkane-air interface and occurs within nanoseconds [6], much of the current research is conducted through simulations. These simulations investigate the influence of various interfacial interactions on the speed of monolayer formation and the freezing behavior of different alkanes [7, 8, 9]. A recent intriguing discovery in the field was made by Hiromu Sakamoto *et al.* [10], who found that oil-in-water emulsions show higher stability when surface freezing occurs. This discovery has opened up new possibilities for the application of surface freezing in emulsion stabilization and related areas.

Since the discovery of surface freezing, numerous experiments have been conducted to investigate this phenomenon further. One early experiment utilized an electrodynamic trap in a supercooled environment, revealing that alkanes with carbon tail length from 14 to 17 undergo surface freezing before the rest of the droplet does [11]. It was also later discovered that the same is true for alkanes with a length of 8 and 9 carbons [6]. Additionally, it was later found that the surface freezing effect can also be induced at the alkane-water interface for both short and long chain alkanes by introducing a small amount of surfactant into the mixture [12, 13].

This shows that surface freezing is a sensitive surface/ interface phenomenon which makes it ideal to study in a contact free-manner. This is because a contact-free technique, such as acoustic levitation, gives the opportunity to study the interface of interest without the presence of other interfaces. That way surface induced effects are avoided.

## 1.2 Acoustic levitation

Acoustic levitation is a technique that utilizes ultrasonic sound waves to levitate objects, thus enabling the study of samples in a contact-free environment. One of the first demonstrations that showcased acoustic levitation was the so-called Kundt's Tube experiment, done in 1866 by August Kundt. This experiment was designed to measure the speed of sound, but in the process, small particles were levitated [14]. Yet acoustic levitation as we know it today started with the work of Paul Langevin and Constantin Chilowsky in 1917, who initially developed the first ultrasonic probe for submarine detection [15]. Later on, acoustic levitation was accomplished by combing the ultrasonic probe with a reflector, thus leading to a stable acoustic pressure field. Over the past century, significant advancements were made in acoustic levitation, resulting in improved stability and ability to levitate highly dense material, such as iridium [16] and large objects, compared to the wavelength of the acoustic waves [17]. Notably, researchers have even achieved the levitation of small fish [18].

The progress made in acoustic levitation has led to its application in various fields, including chemistry and biology, [19, 20]. This technique offers new possibilities for surface-induced effects. By utilizing acoustic levitation, the only interface in contact with the levitated object is the surrounding air, which allows performing dynamic studies and observing the evolution of chemical systems during evaporation.

The water-alkane surface freezing interface is a phenomenon that requires a controlled environment for accurate investigation. In this regard, acoustic levitation proves to be a perfect tool for studying this phenomenon, as it allows full control over the interacting surfaces. By levitating the water-alkane system, we can control the influence of external factors, thus allowing a detailed analysis of the surface freezing process.

### 1.3 Aim and objective

During the experimental work for this thesis it was observed that when a droplet of water was acoustically levitated and hexadecane was added onto it, the droplet of hexadecane underwent freezing. However, when the process was reversed, meaning that while hexadecane was levitated and water was added, the droplet of hexadecane did not freeze. This intriguing initial observation posed a significant question that was investigated in this master thesis. The primary objective was to explore the underlying factors responsible for the two distinct freezing behaviors in the water-hexadecane interface.

To achieve this objective, several key aspects were examined. Firstly, the surface and interfacial tension of water and hexadecane were determined through the pendant drop method. Following, thermodynamic calculations were made to determine the theoretical contributions in the process. Additionally, the purity of hexadecane and its potential impact on the freezing behavior was assessed. Furthermore, the role of temperature in the observed phenomena was explored. Experimental investigations were conducted using an acoustic levitator, showcasing its suitability as a reliable tool for studying complex phenomena such as this.

By addressing these research objectives, this thesis aims to provide insights into the selective freezing behavior observed in the water-hexadecane system, contributing to our understanding of interfacial phenomena and phase transitions.





# 2

## Theory

### 2.1 Acoustic levitation

Acoustic levitation is a technique that allows objects to be suspended and manipulated in mid-air using ultrasonic sound waves. It relies on the phenomenon of standing waves that results from the interactions between at least two opposing acoustic waves. A standing wave presents nodes, which are regions of low pressure, and antinodes, which are regions of high pressure.

Objects placed at the low-pressure nodes are subjected to minimal acoustic pressure and become trapped in mid-air, seemingly defying gravity. This is because the acoustic radiation pressure pushing the object upwards is balanced by the gravitational force pulling it downwards. By adjusting the designing parameters (*i.e.*, distance of opposing arrays, cavity aperture, number and arrangement of transducers, *etc.*) of the acoustic levitator and the properties of the sound waves, such as phase and intensity, the position and stability of the levitated object can be controlled. The acoustic pressure field generated by the transducers can be simulated through the summation of the individual pressures,  $p_j$  each source generates from the equation:

$$p_j = \frac{e^{ikr_j}}{r} J_0(kr_j \sin \theta_j) \quad (2.1)$$

where,  $r$  is the effective radius of the transducer,  $r_j$  is the distance between the transducer  $j$  and the levitation point,  $k$  is the wavenumber,  $J_0$  is the Bessel function of the first kind of order 0, and  $\theta_j$  is the angle between the transducer and the z-axis.

Herein, a more general description of acoustic levitation was presented. For a more detailed description of the basic principles, you can refer to the licentiate thesis by Argyri [21].

## 2.2 Interfacial tension and spreading

Surface energy is defined as the energy required to increase the surface area of an interface per unit area. It arises from an imbalance of cohesive forces between molecules at the interface and in the bulk of the liquid. In the bulk, molecules experience equal cohesive forces in all directions, resulting from the surrounding molecules. However, at the interface, the molecules experience a net inward force, primarily caused by the absence of molecules at the interface. This inward force leads to the formation of a curved surface, as this minimizes the surface area between the liquid and the surrounding medium, such as air or another immiscible liquid.

The quantitative empirical studies conducted by Thomas Young [22] and the mathematical analysis performed by Pierre-Simon Laplace [23] laid the foundation for the development of the Young-Laplace equation. This equation calculates the capillary pressure, which leads to the determination of the surface tension of liquids. A modified version of the Young-Laplace equation can be applied specifically to pendant drops [24]. The equation is given by:

$$\gamma = \frac{\Delta\rho g R_0}{\beta} \quad (2.2)$$

Here,  $\gamma$  represents the surface tension,  $\Delta\rho$  is the density difference between the two fluids,  $g$  is the gravitational constant,  $R_0$  denotes the radius of curvature at the apex of the droplet, and  $\beta$  represents the shape factor associated with the pendant drop's geometry. Typically, the shape factor ( $\beta$ ) is determined by fitting a profile of the pendant drop's curvature, but numerical solutions are also available in the literature.[24]

The spreading of oil over water is governed by the balance between the interfacial tensions of the oil-water  $\gamma_{ow}$ , water-air  $\gamma_w$  and oil-air  $\gamma_o$  interfaces. The extent of spreading can be predicted using the spreading coefficient equation:

$$S = \gamma_w - (\gamma_o + \gamma_{ow}) \quad (2.3)$$

The sign of the spreading coefficient,  $S$ , determines the behavior of oil spreading. If  $S > 0$ , complete spreading occurs, resulting in the formation of a thin, monomolecular film of oil across the water surface. Conversely, if  $S < 0$ , partial spreading occurs, characterized by the formation of a spatial liquid lens. It is worth noting that the magnitude of the spreading coefficient ( $S$ ) relates to the degree of oil spreading, where lower values indicate reduced spreading. The surface energy of a

substance can be calculated as.

$$E_{\text{surf}} = \gamma A \quad (2.4)$$

Where  $E_{\text{surf}}$  is the surface energy,  $\gamma$  is the surface tension and  $A$  is the surface area. When a new interface is formed energy can be generated, which is calculated by.

$$E = E_{\text{new}} - E_{\text{old}} \quad (2.5)$$

## 2.3 Thermodynamics

During evaporation, molecules close to the surface of a liquid absorb energy in the form of heat which breaks the bonds with the surrounding molecules and make them transit into the gas phase. This occurs for volatile liquids at any temperature above the freezing point, not only when boiling. In addition to the absorbed energy from the environment, the molecules near the surface of the liquid have higher kinetic energy compared to those in the bulk, and they can utilize this energy to evaporate. While volatile liquids can evaporate at any temperature above the freezing point, the temperature still makes a difference in the evaporation rate. Increasing the temperature raises the average kinetic energy of the molecules, making it easier for the molecules on the surface to evaporate. Therefore, higher temperatures generally result in faster evaporation.

When a molecule at the surface evaporates, it takes away heat energy from the remaining molecules in the bulk, resulting in a cooling effect. This phenomenon is known as evaporative cooling effect [25]. To counteract this cooling effect, the liquid (*e.g.*, water) absorbs energy from the surroundings. This is why we often feel cooled after a shower, as the water on our skin draws heat from our bodies and evaporates. The energy required for evaporation is commonly referred to as heat of vaporization ( $\Delta H_{\text{vap}}$ ) and is typically measured in joules per mole (J/mol). To calculate the energy needed for a certain amount of water to evaporate is calculated as:

$$E_{\text{vap}} = n\Delta H_{\text{vap}} \quad (2.6)$$

When a substance undergoes freezing or solidification, the opposite of evaporative cooling occurs. As the kinetic energy of the molecules decreases during freezing, the intermolecular forces bind the molecules together more strongly, leading to the formation of a solid. The decrease in kinetic energy during freezing releases heat, which is absorbed by the surroundings. This heat is known as the heat of fusion ( $\Delta H_{\text{sub}}$ ) and is also expressed in joules per mole (J/mol). To calculate the energy needed for a volume to freeze a modified version of Equation (2.6) is used where instead of  $\Delta H_{\text{vap}}$  one uses  $\Delta H_{\text{sub}}$ .



# 3

## Materials and Method

### 3.1 Chemical

Hexadecane (99% pure) was purchased from Sigma-Aldrich, Sweden AB, and stored at room temperature.

### 3.2 Purification of Hexadecane

Hexadecane was purified by passing the solvent through a small glass funnel that contained cotton filled with aluminum oxide and collected in a glass beaker. While this method can effectively remove impurities, it may need to be repeated up to five times to ensure complete purification [26]. To examine the effects of impurities on the experiment, three different stages of purification were tested: unpurified, 1 time purified, and 5 times purified. For the 5 times purified sample, the funnel was cleaned, filled with fresh cotton, and filled with new aluminum oxide before each purification cycle.

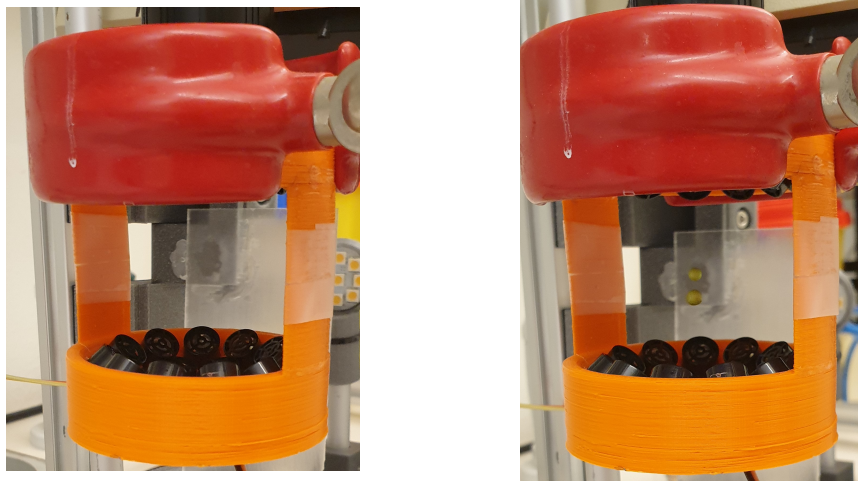
### 3.3 Degassing of water

Degassing of the water samples was conducted using a syringe-based method. The water was placed inside the barrel of a syringe, and the hub of the syringe was tightly closed to create a sealed environment. The plunger of the syringe was then pulled back, creating a decrease in pressure within the syringe barrel. This decrease in pressure allowed any dissolved gases in the water to escape. After degassing, the hub of the syringe was opened again, allowing the pressure inside the barrel to equalize with the surroundings. The degassing process was repeated three times for each water sample to ensure effective removal of dissolved gases.

## 3.4 Acoustic levitation

### 3.4.1 Design

The acoustic levitator Mk1 [21] was utilized in this study. It is a multiple-transducers acoustic levitator that has 34 ultrasonic transducers (Manorshi, MSO-P1040H07T) placed in a concentric, circular configuration that operated at 40 kHz. The transducers were glued to the 3D-printed scaffold made of polylactic acid (PLA). The Mk1 levitator has a distance of opposing arrays of 52 mm, a radius of curvature of 28 mm, and a cavity aperture of 38 mm. A photograph of the Mk1 levitator is shown in Figure 3.1.



**Figure 3.1:** a) Photo of acoustic levitator, b) photo of acoustic levitator with two, green polystyrene beads.

### 3.4.2 Stability

The stability of the Mk1 levitator was investigated at three different voltages: 7 V, 8 V, and 9 V. This was accomplished by recording a droplet of Milli-Q water using a digital camera (acA1440-220um, Basler, Germany) operating at 1 frame per second (fps) for a duration of 10 minutes. The volume over time, as well as the horizontal and vertical movement of the droplet, were extracted from the recorded photographs. This measurement was repeated three times for each voltage.

### 3.4.3 Experimental set-up

The Mk1 levitator was placed inside a lightbox (PULUZ Mini Photo Studio Light Box with 2 x 20 LED Lights Beads, 24cm x 23cm), while a digital color

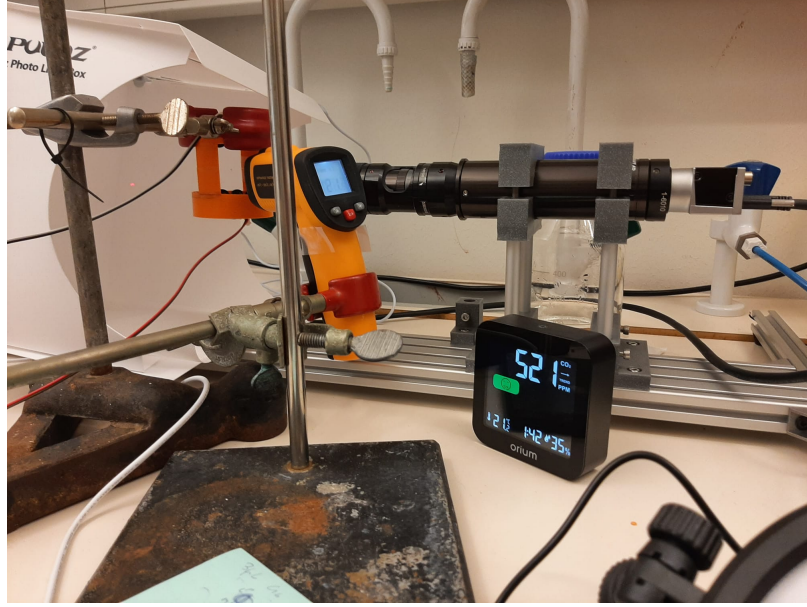
camera (acA1440-220uc, Basler, Germany) was positioned above it and a monochromatic camera was placed to the side perpendicularly to the first one, enabling the capturing of photographs from two different angles. The cameras were equipped with a Navitar lens (1-60135) connected to the cameras *via* a Navitar 1X adapter (1-6245), and Navitar coupler (1-6010). A Python script was used to control the cameras. Where stated an additional light source was added to reach an acceptable frame rate.

A single-use plastic syringe (2 ml, B. BRAUN) with a disposable needle tip (Sterican, B. BRAUN) was used to dispense water into the levitator. In contrast, a glass syringe was used for hexadecane to prevent impurities. To regulate the amount of liquid dispensed into the levitator, a syringe pump (NE-1000, New Era Pump Systems Inc, USA) was employed.

When investigating the effect of temperature on the experiment, a heating element was utilized to raise the temperature of the laboratory. The temperature of the laboratory was monitored and controlled using a reference thermometer (KM20REF, Comark Ltd, United Kingdom).

To measure the temperature of an evaporating water droplet, a non-contact digital laser temperature gun (H Helect) was employed. The temperature gun was securely fixed in place to ensure its stability throughout the entire evaporation process of the water droplet. This setup allowed accurate and continuous temperature measurements to be recorded. The set-up is shown in Figure 3.2



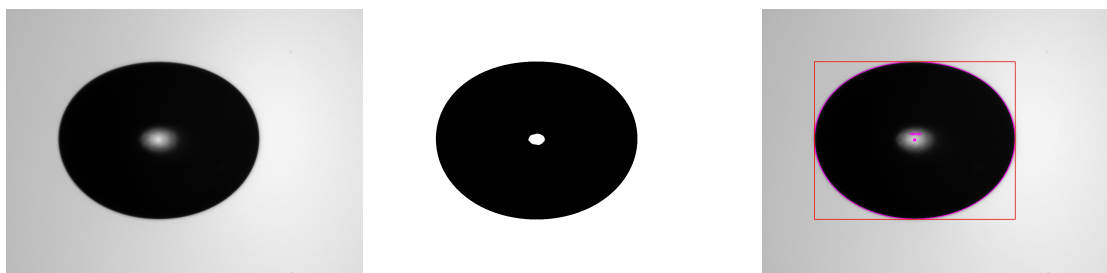


**Figure 3.2:** Experimental set-up that combines the acoustic levitator, lightbox, side camera, infrared thermometer, and a separate electronic device that measures, CO<sub>2</sub>, humidity and room temperature.

#### 3.4.4 Data acquisition

The data acquisition involved connecting the cameras to the computer and controlling them through the Python OpenCV package [27]. The image processing began with converting the captured images (Figure 3.3a) to grayscale, followed by applying a binary thresholding technique. Binary thresholding involves assigning a pixel value of 255 (maximum value) to pixels with intensities above a specified threshold value, thereby turning them white. Conversely, pixels with intensities below the threshold value were assigned a value of 0, turning them black. This conversion resulted in a black-and-white image (Figure 3.3b), which facilitated the straightforward detection of contours. These contours were then superimposed on the original image, thus allowing visual representation (Figure 3.3c). The center of the droplet was marked based on the detected contours, and a rectangle was fitted to the contour. This rectangle was subsequently used to calculate the aspect ratio of the droplet, while the volume,  $v$  was calculate based on the Disk Method, integrated along the axis of symmetry,  $z$ :

$$v = \pi \int z^2 dz \quad (3.1)$$



**Figure 3.3:** a) Original picture, b) binary picture, c) original picture with superimposed contour (pink line), and rectangle (red line).

### 3.5 Tensiometry

The pendant drop method was used for determining the surface tension of water and hexadecane. For that purpose a stainless steel needle of 0.718 mm, external diameter and an Attension Theta optical tensiometer, by Biolin Scientific, Finland were used. A minimum of 10 droplets were formed and recorded using a monochromatic digital camera. The software detected the contour of the droplet and fitted the Young-Laplace equation to determine the surface tension. The measurements were conducted at room temperature, and the surface tension was determined by averaging the values from at least 10 droplets.

The interfacial tension between water and hexadecane was determined by immersing the metallic needle inside a 1x1 cm<sup>2</sup> cuvette and forming droplets inside of the other liquid, and then fitting the Young-Laplace equation to the contour. In the case of hexadecane, a hook metallic needle was used to form the droplets in water, due to its lower density compared to water. The measurements were conducted at room temperature, and the interfacial tension was calculated in the same way by averaging the values from a minimum of 10 droplets.

### 3.6 Differential Scanning Calorimetry

To determine the freezing and melting temperatures of hexadecane, Differential Scanning Calorimetry (DSC) was used. DSC measures the difference in heat flow between a sample and a reference material as the temperature of the sample is changed. This was done for the non-purified, 1 times purified, and 5 times purified samples at two different rates, 10 K/min and 2.5 K/min. The sample mass of the hexadecane used was 7.1-7.9 mg and sealed in the metallic holders, without the presence of holes.



# 4

## Results and Discussion

The Results and Discussion section is divided into distinct sections, each investigating potential factors that could contribute to the freezing of hexadecane. Each section explores a specific cause to provide a comprehensive understanding of the freezing phenomenon.

The first section focuses on investigating the role of impurities in the freezing process. This analysis aims to determine whether impurities have an impact on hexadecane's freezing behavior, and if so, how this influence manifests.

Subsequently, the following section delves into the investigation of surface effects, particularly interfacial tension and spreading behavior. This examination seeks to elucidate the relationship between surface properties and the freezing of hexadecane.

In the final section, the focus shifts toward exploring the effects of water evaporation and laboratory temperature on the freezing of hexadecane. This investigation aims to assess the influence of water evaporation dynamics and environmental temperature on the observed freezing phenomenon.

Through the comprehensive analysis of these distinct sections, we aim to provide a comprehensive understanding of the factors contributing to the freezing of hexadecane. By unraveling the underlying mechanisms and exploring the interplay between impurities, surface effects, water evaporation, and temperature, we can gain valuable insights into this intriguing phenomenon.

### 4.1 Impurities

To investigate the influence of impurities on the freezing process, three distinct batches of hexadecane were prepared: the first batch used hexadecane directly from the bottle, the second batch underwent one purification cycle, and the third batch underwent five purification cycles. The system was initially examined by

levitating a microliter water droplet and subsequently adding on it a microliter hexadecane droplet. In all cases, irrespectively of the purification level, immediate freezing of hexadecane occurred upon contact with water. To ensure that the surface freezing was not attributed to dissolved gas in the water phase, degassing of the water was performed, but no difference in the results was observed. The highest frame rate achieved by the cameras recording the freezing process was 50 frames per second (fps), and the freezing of hexadecane was initiated within the span of a single frame. Figure 4.1 visually captures this rapid freezing process



**Figure 4.1:** Sequence of three images captured at a time interval of  $1/50$  second, a) depicts hexadecane droplets suspended from a needle tip, with a neighboring water droplet, b) the hexadecane and water droplets are in close proximity, but have not made contact, yet, c) the moment when the hexadecane and water droplets came in contact. Notably, the onset of hexadecane freezing is evident.

Despite variations in the purification levels of hexadecane and the degassing of water, the hexadecane froze immediately upon contact with the water droplet. Hence, it appears that the presence of impurities in hexadecane or dissolved gas in water have minimal or negligible effects on the freezing behavior, when the hexadecane droplet is added to the water droplet.

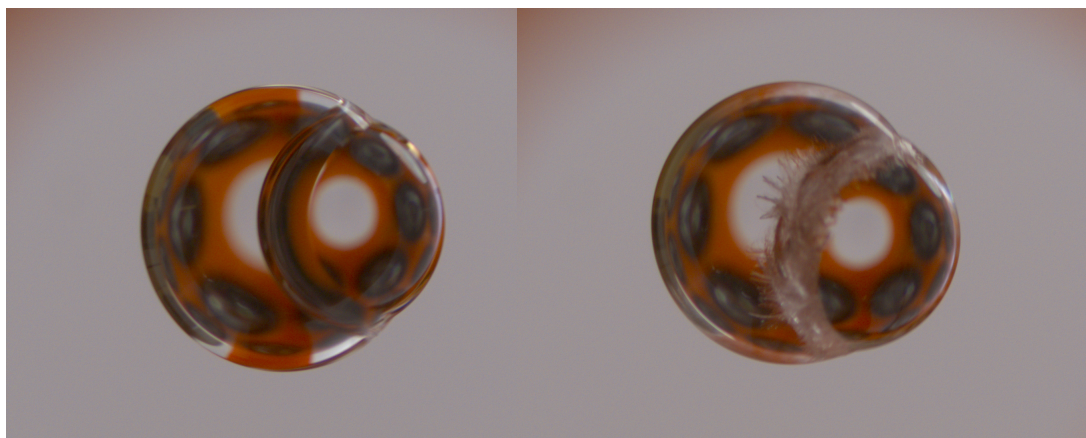
The system was further investigated by levitating a microliter droplet of hexadecane and subsequently adding a microliter water droplet to it. When water was added to the non-purified and one-time purified hexadecane, no freezing occurred throughout the evaporation process of the water droplet. However, when water was added to the five-times purified hexadecane, no immediate freezing was observed upon contact either. Instead, after a delay of approximately 20-30 seconds, the hexadecane started to freeze in a manner similar to when water droplet was levitated. This delayed freezing phenomenon is illustrated in Figure 4.2.

To ensure the accuracy of the hexadecane purification process, two additional

batches of hexadecane were prepared at each purification level. The results obtained from these new batches were consistent with the previous findings. This suggests that the freezing behavior of hexadecane may indeed be sensitive to impurities. When hexadecane is levitated in the acoustic levitator, impurities have sufficient time to accumulate at the surface, potentially preventing freezing when water is later introduced.

To investigate this further, water was levitated in the acoustic levitator, and before hexadecane was added, it was allowed to rest on the needle tip for one minute to provide ample time for impurities to reach the surface. However, this additional step did not alter the previous results. The hexadecane still froze immediately upon contact with the levitated water, regardless of the purification level. This indicates that impurities in the hexadecane do influence the freezing phenomenon, but the extent of their impact remains uncertain.

Further investigations and characterization of the impurities present in the hexadecane are necessary to gain a deeper understanding of their role in the freezing process. It is essential to identify the specific impurities and determine their concentration and chemical nature to understand their effect on the freezing behavior.



**Figure 4.2:** The five times purified hexadecane when water first was added and then 20 seconds later when the hexadecane started to freeze.

## 4.2 Interfacial energy

The interfacial tensions between water and hexadecane were measured to investigate the possibility of a surface-induced effect contributing to the observed

freezing. The measured surface and interfacial tensions for water and hexadecane are presented in Table 4.1.

**Table 4.1:** Surface and interfacial tensions for both the non-purified and 5 times purified hexadecane.

| Chemical  | Surface/Interfacial tension [mN/m <sup>2</sup> ] |                 |
|-----------|--------------------------------------------------|-----------------|
|           | x0 Purified C16                                  | x5 Purified C16 |
| Water-Air | 72.5                                             | 72.5            |
| C16-Air   | 27.4                                             | 27.5            |
| Water-C16 | 55.0                                             | 55.6            |
| C16-Water | 45.5                                             | 56.4            |

It is clear from Table 4.1 that the impurities in the hexadecane affect the interfacial tension with water as expected. However, small differences are found in the surface tension values.

The calculation of the spreading coefficients were done through Equation (2.3) and the values from Table 4.1, this gave a negative value for both the purified and the non-purified hexadecane measurements indicating that hexadecane does not spread extensively on water. For the non-purified hexadecane the spreading coefficient was  $-0.4$  and  $-10.4$  for the purified hexadecane. The non-purified hexadecane is close to zero meaning that spreading almost occurs but since it still is negative, the water droplet does not get completely covered by the hexadecane. The purified hexadecane is very clearly negative which aligns with the visual evidence in Figure 4.2, where it is apparent that a significant portion of the water surface remains uncovered by the purified hexadecane droplet.

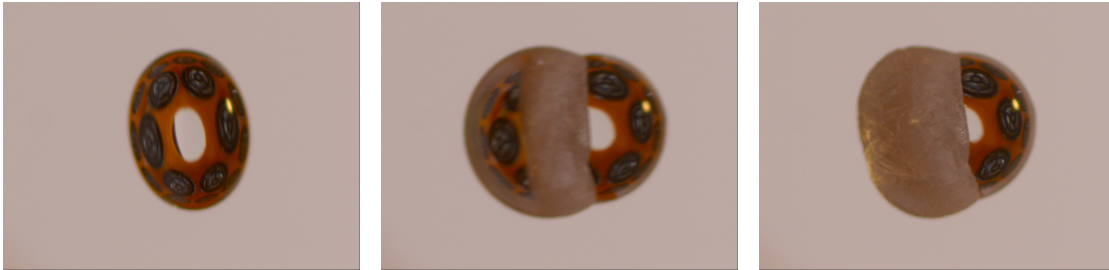
Using Equation (2.4) and Equation (2.5), and the data provided in Table 4.1, the energy gain from creating a new interface between water and hexadecane was calculated by approximating the surface area between the water and hexadecane and assuming that the water droplet was spherical. The generated energy for the interface was found to be very small for both the non-purified and purified hexadecane. This energy was enough to freeze about 0.02% of the molecules in a 3 $\mu$ L hexadecane droplet. While this energy alone is not sufficient to freeze a large portion of the molecules in a 3  $\mu$ L droplet, it may be significant enough to form a small monolayer of surface freezing. This monolayer could serve as a nucleation point for the propagation of freezing throughout the droplet.



### 4.3 Effect of water evaporation

To investigate the effect of water evaporation on the freezing process, the system was examined with water levitated first in the levitator, and hexadecane was subsequently added to the suspended water droplet. Different volumes of water were levitated, namely, 3  $\mu\text{L}$ , 2  $\mu\text{L}$ , 1  $\mu\text{L}$ , and 0.5  $\mu\text{L}$ . Approximately the same amount of hexadecane (around  $3 \pm 0.3 \mu\text{L}$ ) was added to each of these different volumes, with the variation in volume arising from the inherent difficulty in achieving precise measurements with a syringe.

The results obtained for 3  $\mu\text{L}$  and 2  $\mu\text{L}$  volumes were identical. Upon adding hexadecane, instant freezing of the droplet occurred, and within 40 seconds, the entire added hexadecane droplet was frozen. This freezing behavior was observed for all purification levels of hexadecane. Figure 4.3 provides a visual representation of the hexadecane freezing process. The hexadecane stayed frozen until only a minimal amount of water remained creating a bowl-like structure of the hexadecane. Then, it melted and a tiny volume of water could be seen on the surface of the hexadecane. An example of the bowl-like structure and the small water droplet on the surface of hexadecane can be seen in Figure 4.4 but for a smaller volume of water.



**Figure 4.3:** a) Water droplet with a 2 L volume, before hexadecane was added, b) water droplet (right side) and a 3L hexadecane droplet (left side) 30 seconds after hexadecane was added. Here it is clear that the freezing is propagating on the surface of hexadecane, c) hexadecane was completely frozen approximately 120 seconds after hexadecane was added.

For the 1  $\mu\text{L}$  water droplet, the instant freezing phenomenon still occurred upon adding hexadecane. However, in this case, only approximately half of the hexadecane droplet froze as the water started to evaporate. As the water evaporated, the bowl-like structure of the droplet formed again until the hexadecane began to melt. Eventually, only a small droplet of water remained.

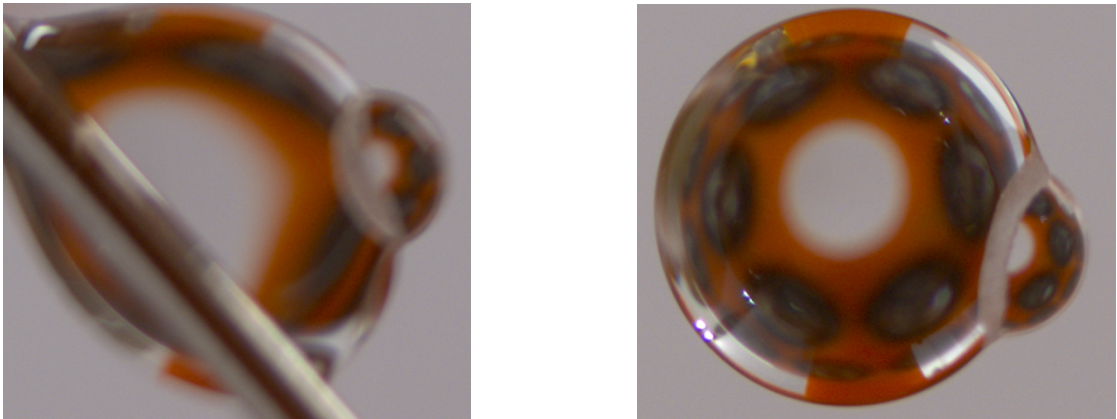


Figure 4.4 visually illustrates this process for the 1  $\mu\text{L}$  case.



**Figure 4.4:** a) Water droplet of 1  $\mu\text{L}$  (up left) and hexadecane droplet of 3  $\mu\text{L}$  (right side) the moment after hexadecane was added. Here it is clear that the surface of hexadecane begins to freeze, b) water was almost completely evaporated and the bowl-like structure was formed, c) hexadecane melted and a low-volume water droplet still remained visible at the top of the hexadecane droplet.

For the 0.5  $\mu\text{L}$  water droplet, the phenomenon of instant freezing still occurred upon contact between hexadecane and water. However, in this case, the freezing did not spread significantly beyond the initial contact point. As a result, only a small portion of the hexadecane droplet froze, while the rest remained in a liquid state. Figure 4.5 illustrates the freezing that occurred for the 0.5  $\mu\text{L}$  case.



**Figure 4.5:** a) Instant surface freezing when a 0.5  $\mu\text{L}$  water droplet (up right) and a 3  $\mu\text{L}$  hexadecane droplet (left side) came in contact, b) maximum amount of freezing that occurred.

By comparing the different cases illustrated in Figure 4.3 to Figure 4.5, it is evident that the initial volume of levitated water has a significant effect on the

observed freezing behavior. By calculating the volume of the droplets with the method mentioned subsection 3.4.4 and using Equation (2.6) shows that if the water absorbs all the heat from the hexadecane and assuming a room temperature of 20°C, only 0.07  $\mu\text{L}$  of water would need to evaporate to cool down and freeze 1  $\mu\text{L}$  of hexadecane, which was determined to freeze at 16°C using differential scanning calorimetry (DSC) Figure A.1. This suggests that approximately 0.21  $\mu\text{L}$  of water would need to evaporate to cool down and freeze 3  $\mu\text{L}$  of hexadecane. Measurements done in the Mk1 showed that within the first 2 minute 0.4  $\mu\text{L}$  of water evaporated, can be seen in the appendix in Figure B.1. Further analysis of the experimental results supports the notion that the volume of water, and evaporation play a crucial role in the propagation of surface freezing of hexadecane. This is evident from the observation that the droplet of hexadecane melts when the water droplet becomes too small to provide sufficient cooling for the hexadecane to remain frozen. Considering the previously mentioned evaporation rate of water with 0.4  $\mu\text{L}$  evaporation within the first 2 minute and assuming that water does not absorb all the heat from the hexadecane, the time scale of 120 seconds required to freeze 3  $\mu\text{L}$  of hexadecane, as shown in Figure 4.3, is reasonable.

To investigate whether the temperature decrease during the evaporation of levitated water droplets contributes to the freezing of hexadecane, the temperature of a water droplet was measured every 1 minute over a 40-minute period. This was done to ensure that the temperature drop observed in previous studies, where levitated water droplets reached temperatures as low as 13°C in a room with a temperature of 25°C [28], was not a significant factor in the hexadecane freezing process. During the investigation, the humidity in the room was recorded to be 35%, while the room temperature was  $21.55 \pm 0.5^\circ\text{C}$ , with fluctuations occurring within the specified range. When water was added to the acoustic levitator, its temperature was measured to be 21.15°C. The temperature deviation of  $\pm 0.5^\circ\text{C}$  coincided with the fluctuations in the room temperature Figure C.1.

The results of the temperature measurement revealed that the difference between the room temperature and the surface temperature of the water droplet during evaporation were within the error range of the temperature probes ( $\pm 1^\circ\text{C}$ ). During evaporation of a single droplet the heat entering the droplet from its surroundings equals the energy lost due to the heat of vaporization. That is why there is no temperature drop. But when we have two droplets it is possible that there is a transfer of energy leading to a temperature drop.

Following, the temperature of the laboratory was increased from 20°C to 27-30°C

to examine how the increase in temperature will affect the surface freezing. The results indicated that increasing the temperature indeed halted the freezing of hexadecane. These findings suggest that although the evaporation rate of water increased, the room temperature was too high to reach the freezing temperature of hexadecane.

# 5

## Conclusions

In this work, the freezing of hexadecane that occurs when it comes in contact with water under acoustic levitation was studied. Three main aspects of the freezing have been investigated; impurities in the hexadecane, interfacial interaction between water and hexadecane, and water evaporation, with respect to the order of addition.

The presence of impurities in hexadecane has been observed to have an impact on its freezing behavior, although the exact mechanism remains unclear. Typically, impurities promote freezing and can serve as nucleation points. However, in the system where water is added to a hexadecane droplet, it was observed that impurities in hexadecane seem to prevent freezing instead. This was evident from the delayed freezing observed in the case of five-times purified hexadecane, which was not observed in less purified samples. The underlying reasons and mechanisms behind this phenomenon are not yet fully understood and require further investigation.

The energy generated from the change in interfacial area may be small, but it could be sufficient to create a surface freezing monolayer, which then serves as a nucleation point for the propagation of hexadecane freezing. This process is primarily driven by the evaporation of water. As the water volume decreases and its evaporation rate decreases, the hexadecane eventually melts. Showing that water evaporation is a leading factor to the surface freezing of hexadecane. But water evaporation by itself is not sufficient to freeze the hexadecane droplet based on the lack of freezing for the non-purified and one-time purified hexadecane when it was levitated first and water was added to it. Furthermore, it was observed that water evaporation alone did not result in a significant cooling of the levitated water droplet at room temperature. This suggests that the temperature of the water droplet itself is not the sole factor driving the freezing of hexadecane.

### 5.1 Future work

Further studies can explore the freezing of hexadecane by combining X-ray analysis with acoustic levitation to examine the phase transitions in more detail. The introduction of a surfactant to the system could be a valuable avenue for further investigation. By studying the impact of a surfactant on the interfacial tension between water and hexadecane, valuable insights could be gained into the role of interfacial energy in the freezing process. This could shed light on the mechanisms underlying the observed freezing phenomena and contribute to a more comprehensive understanding of the system.

Additionally, investigating the interaction between water and hexadecane under higher acoustic pressure conditions which alters the spherical shape and interfacial area, could yield valuable information related to the effect of surface curvature on the interfacial behavior and its impact on freezing dynamics.

Finally, conducting a study on the impurities present in hexadecane would be beneficial. This investigation would aim to determine the surface activity of these impurities and understand why they have a preventive effect on freezing, contrary to the more common scenario where impurities promote freezing. By examining the properties and behavior of these impurities at the interface, valuable insights could be obtained, shedding light on the mechanisms underlying the observed phenomenon.

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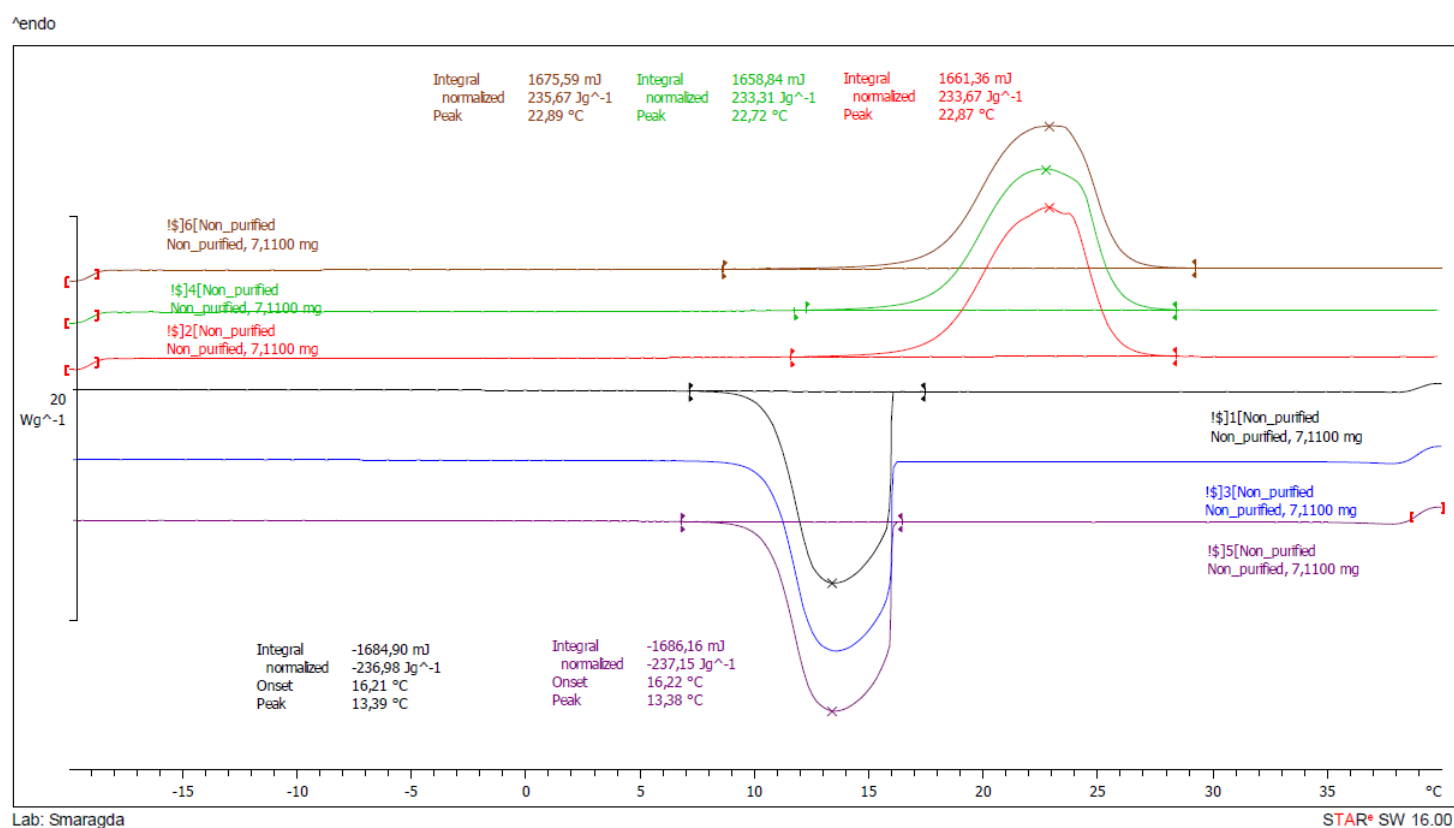




# A

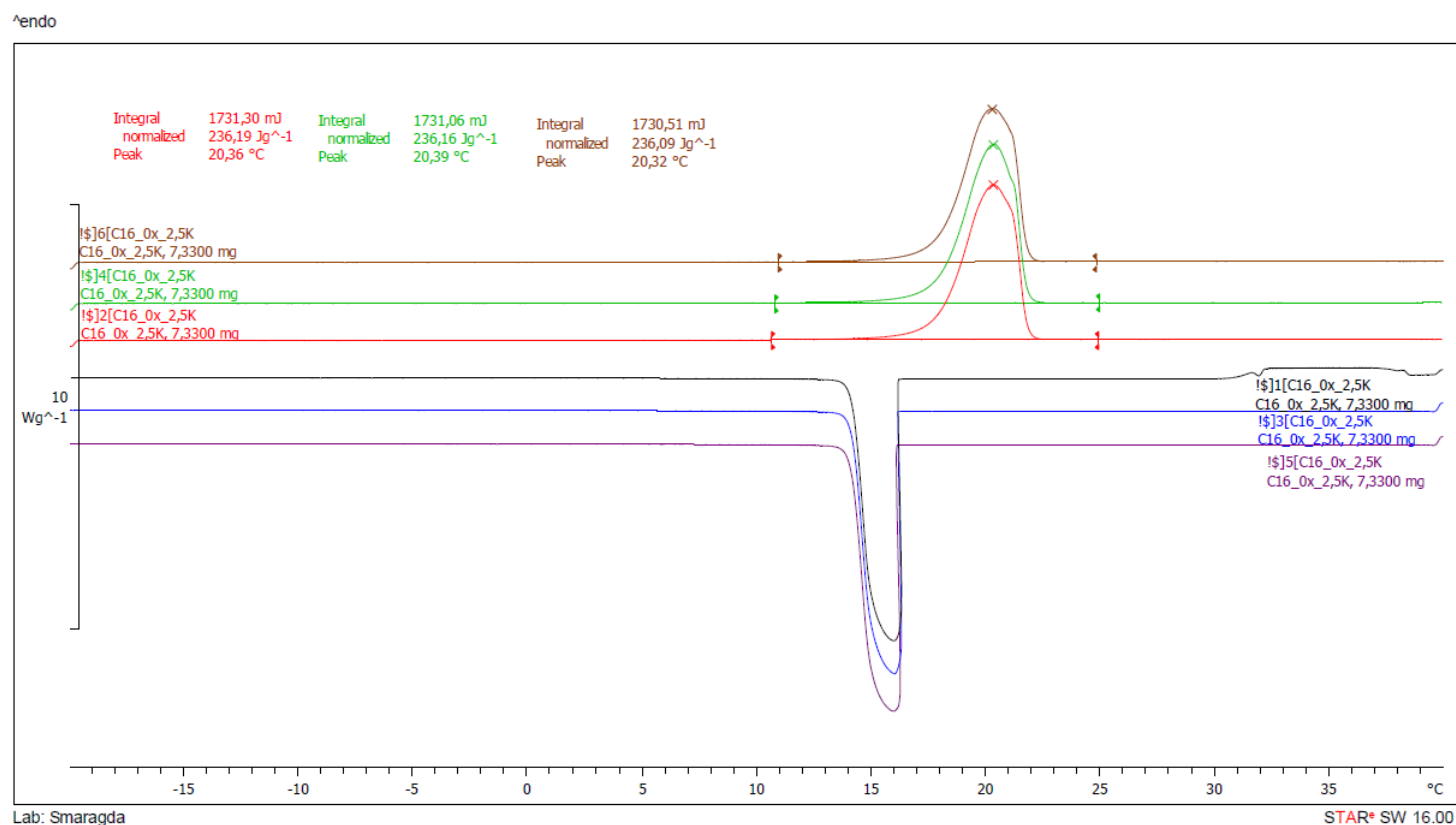
## DSC Results

Here are the graphs from the DSC measurements that was used to investigate if impurities changed the freezing of hexadecane.



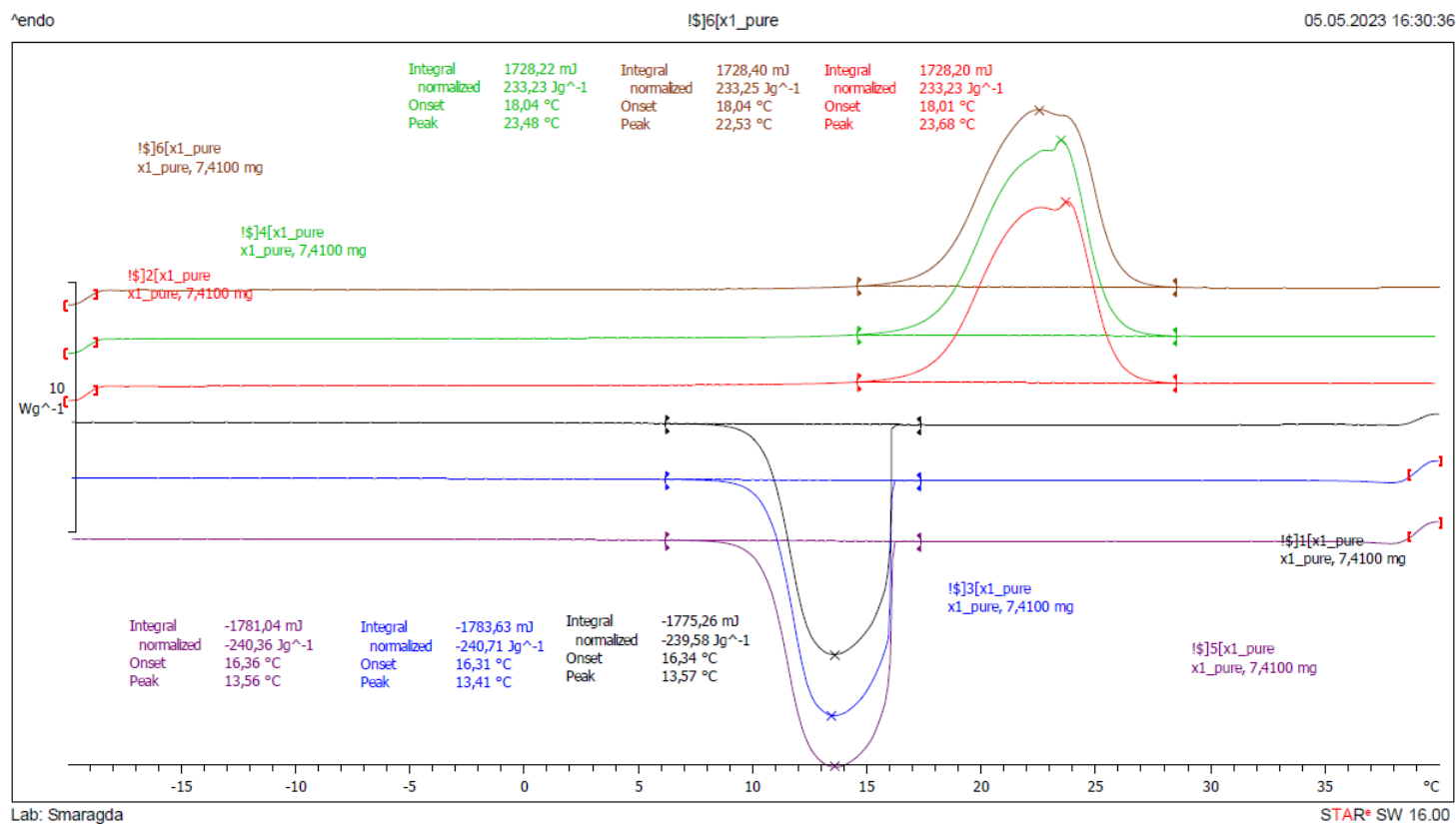
**Figure A.1:** DSC of non-purified hexadecane, with time interval 10 kelvin per minute

## A. DSC Results



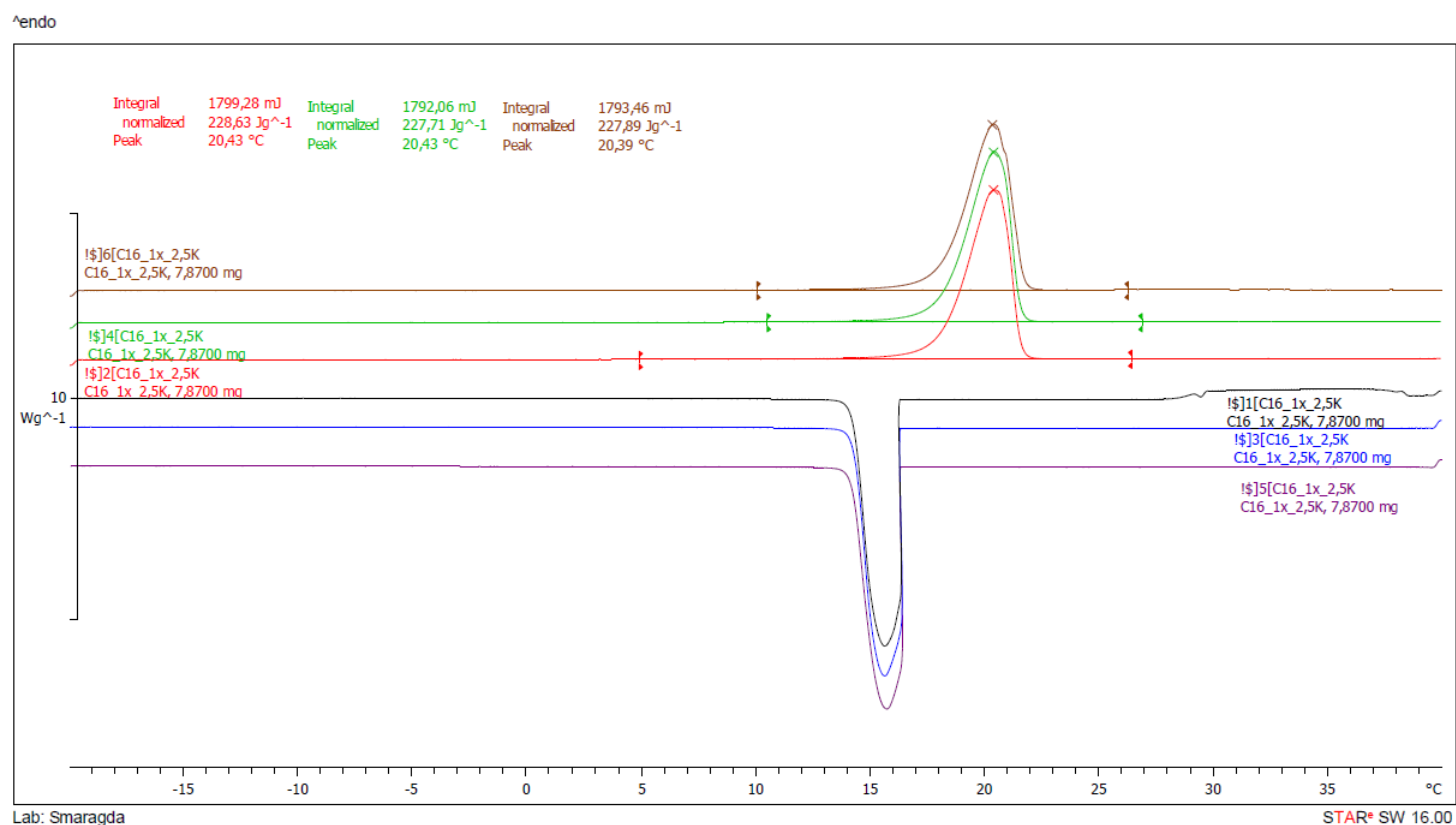
**Figure A.2:** DSC of non-purified hexadecane, with time interval 2.5 kelvin per minute

## A. DSC Results



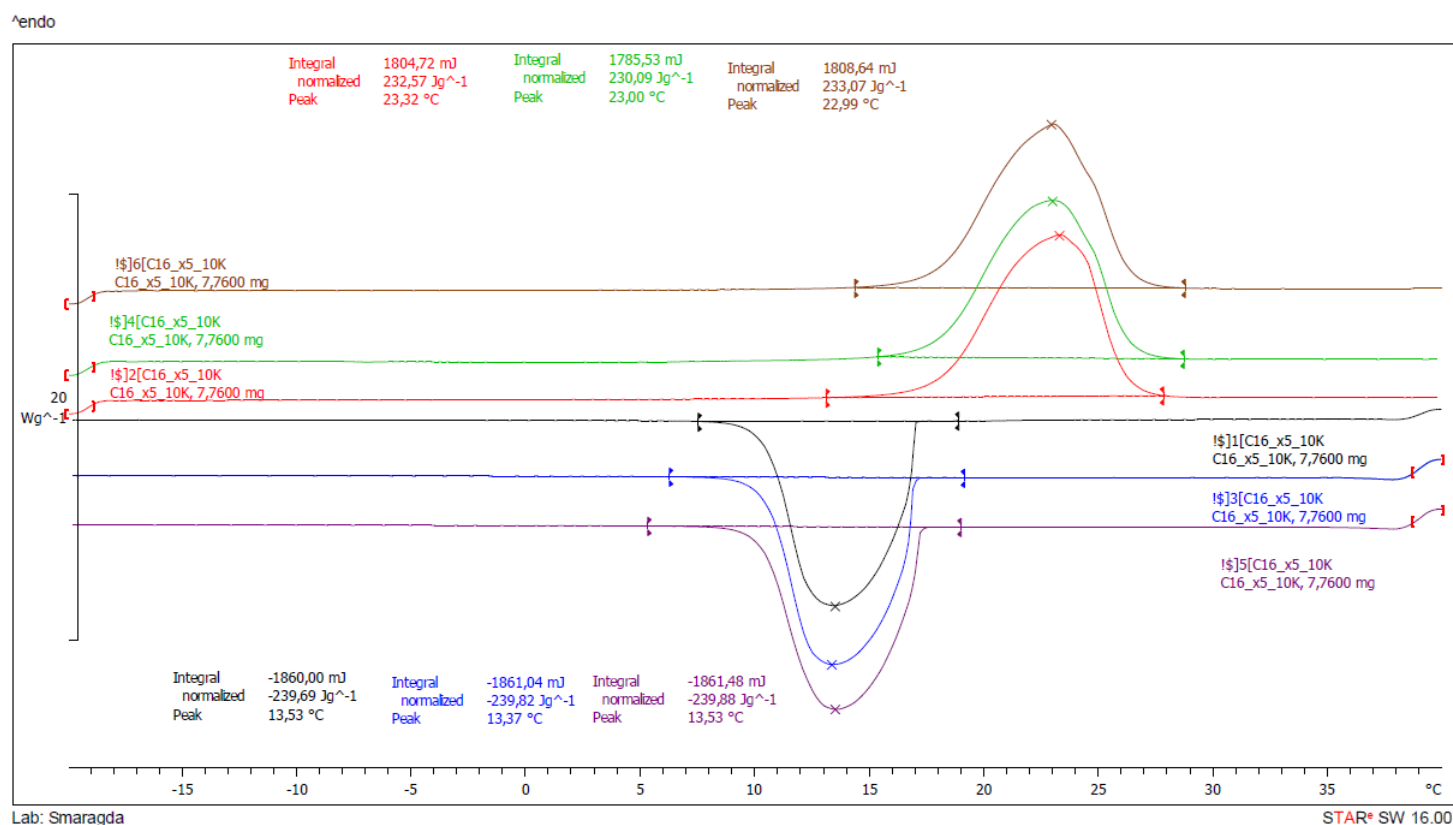
**Figure A.3:** DSC of 1 time purified hexadecane, with time interval 10 kelvin per minute

## A. DSC Results



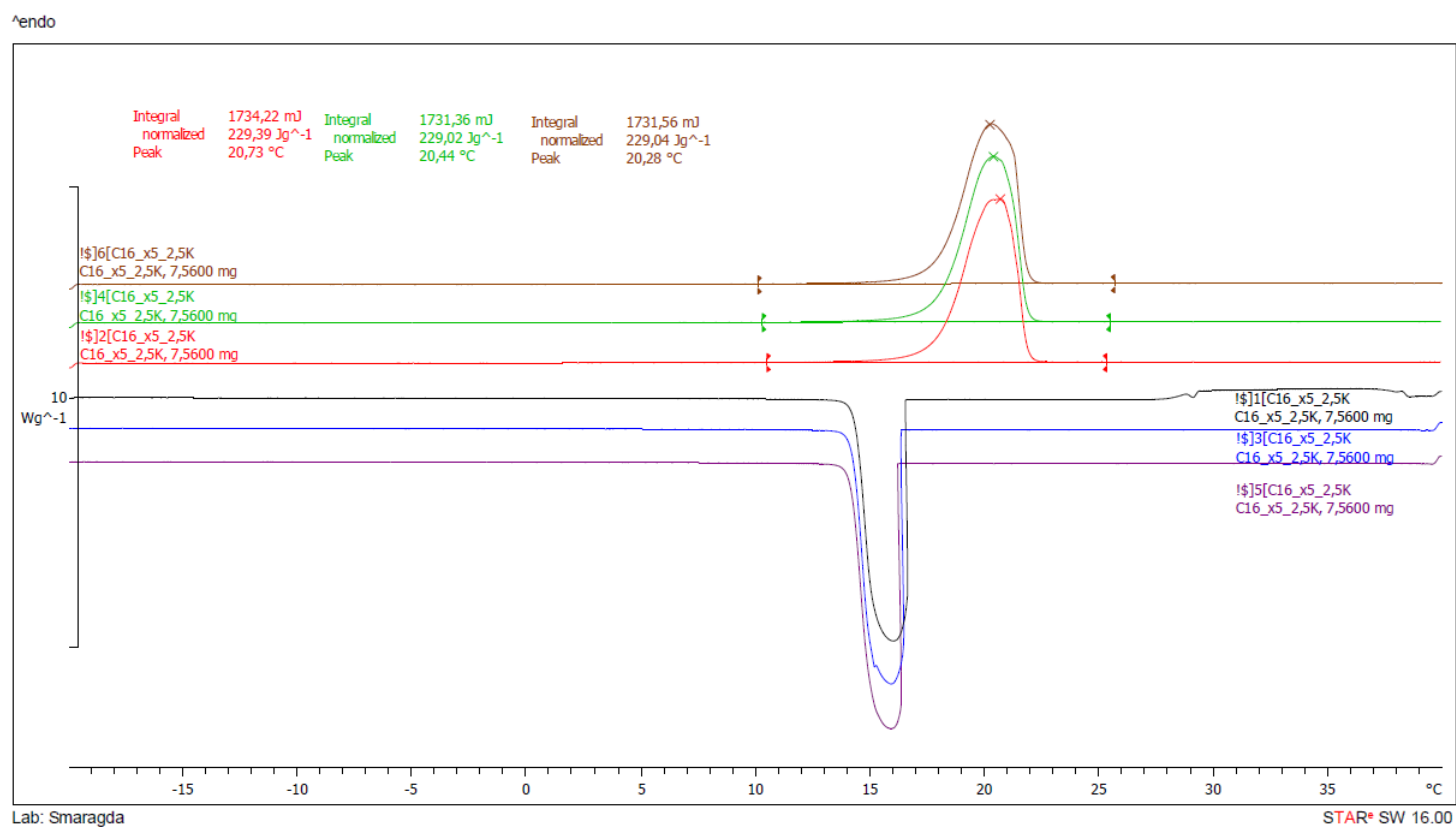
**Figure A.4:** DSC of 1 time purified hexadecane, with time interval 2.5 kelvin per minute

## A. DSC Results



**Figure A.5:** DSC of 5 times purified hexadecane, with time interval 10 kelvin per minute

## A. DSC Results

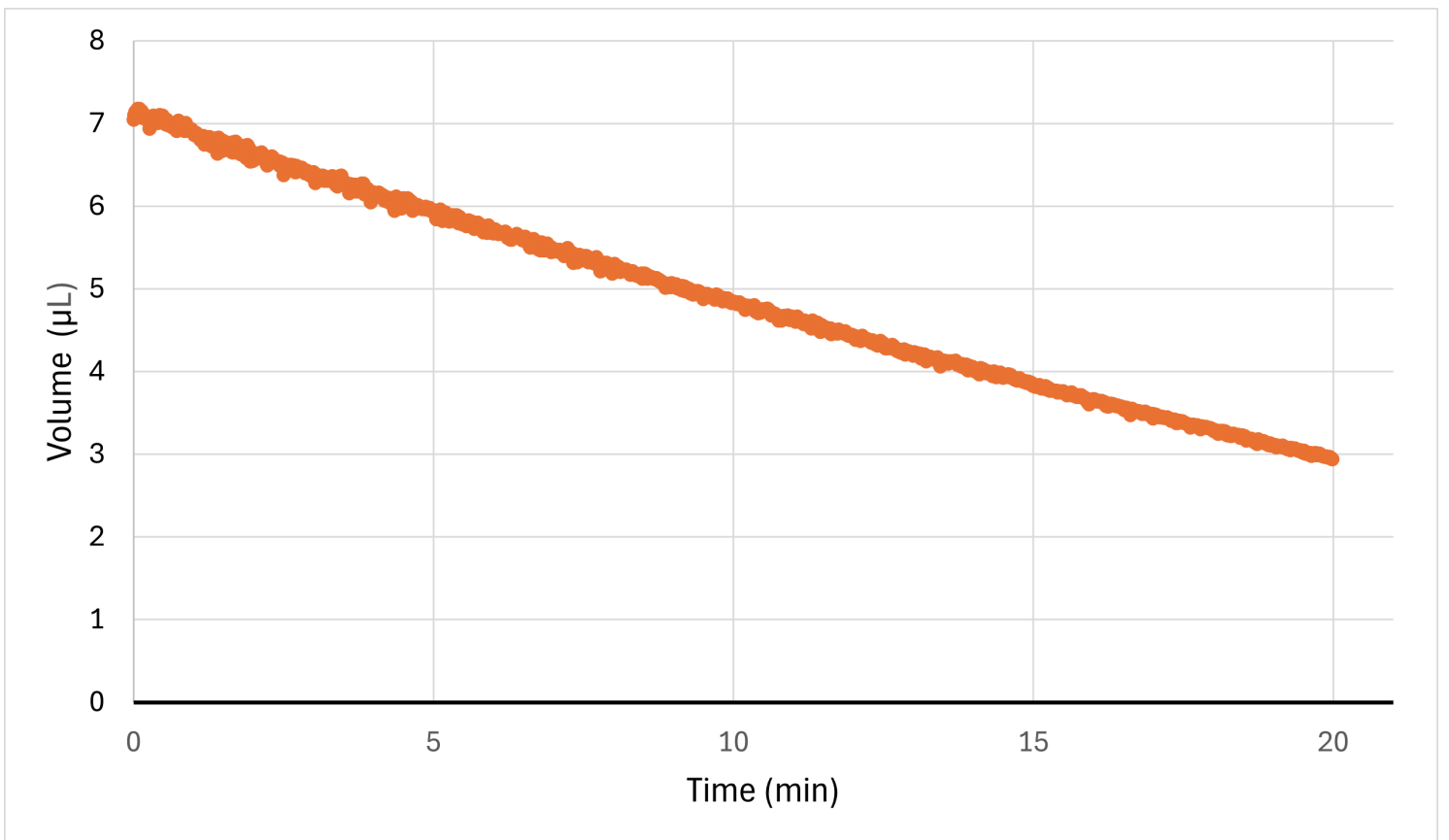


**Figure A.6:** DSC of 5 times purified hexadecane, with time interval 2.5 kelvin per minute

# B

## Droplet evaporation

Figure B.1 shows how water evaporate with time while present in the acoustic levitator.



**Figure B.1:** Volume measurement of water droplet in acoustic levitator during 20 minutes.

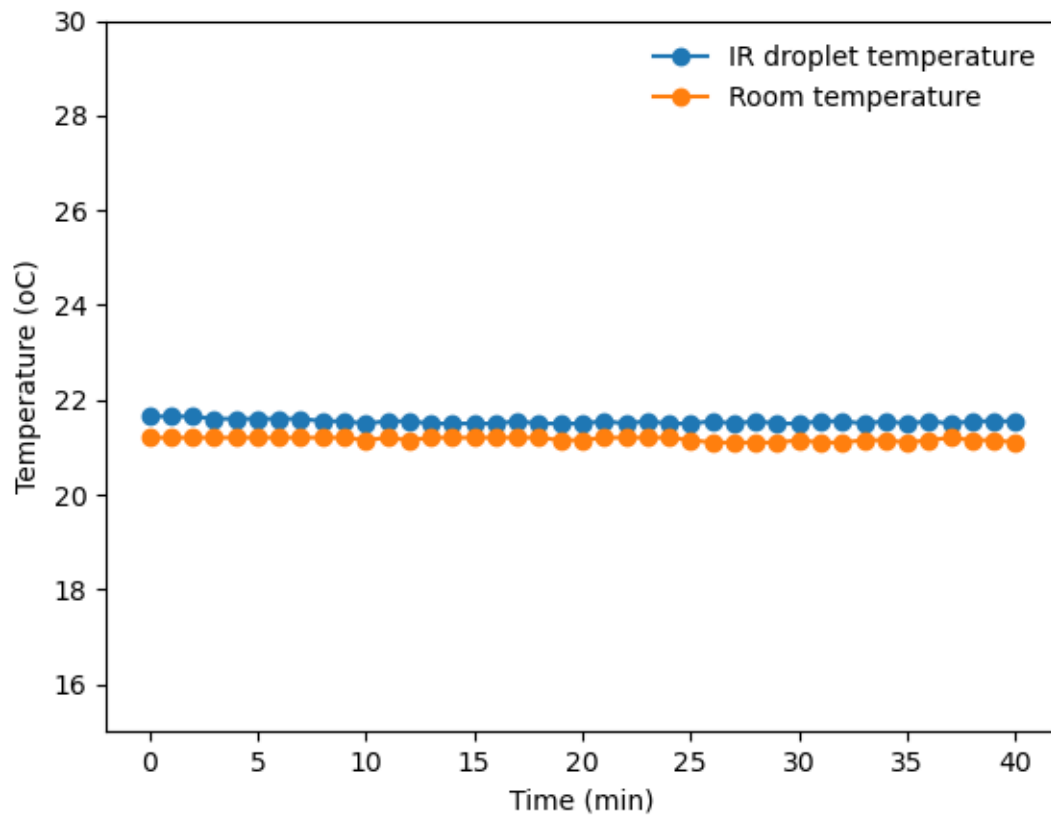




# C

## Droplet Temperature

Figure C.1 shows the measurements from the room and droplet temperature.



**Figure C.1:** Temperature measurements of the room and droplet temperature

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