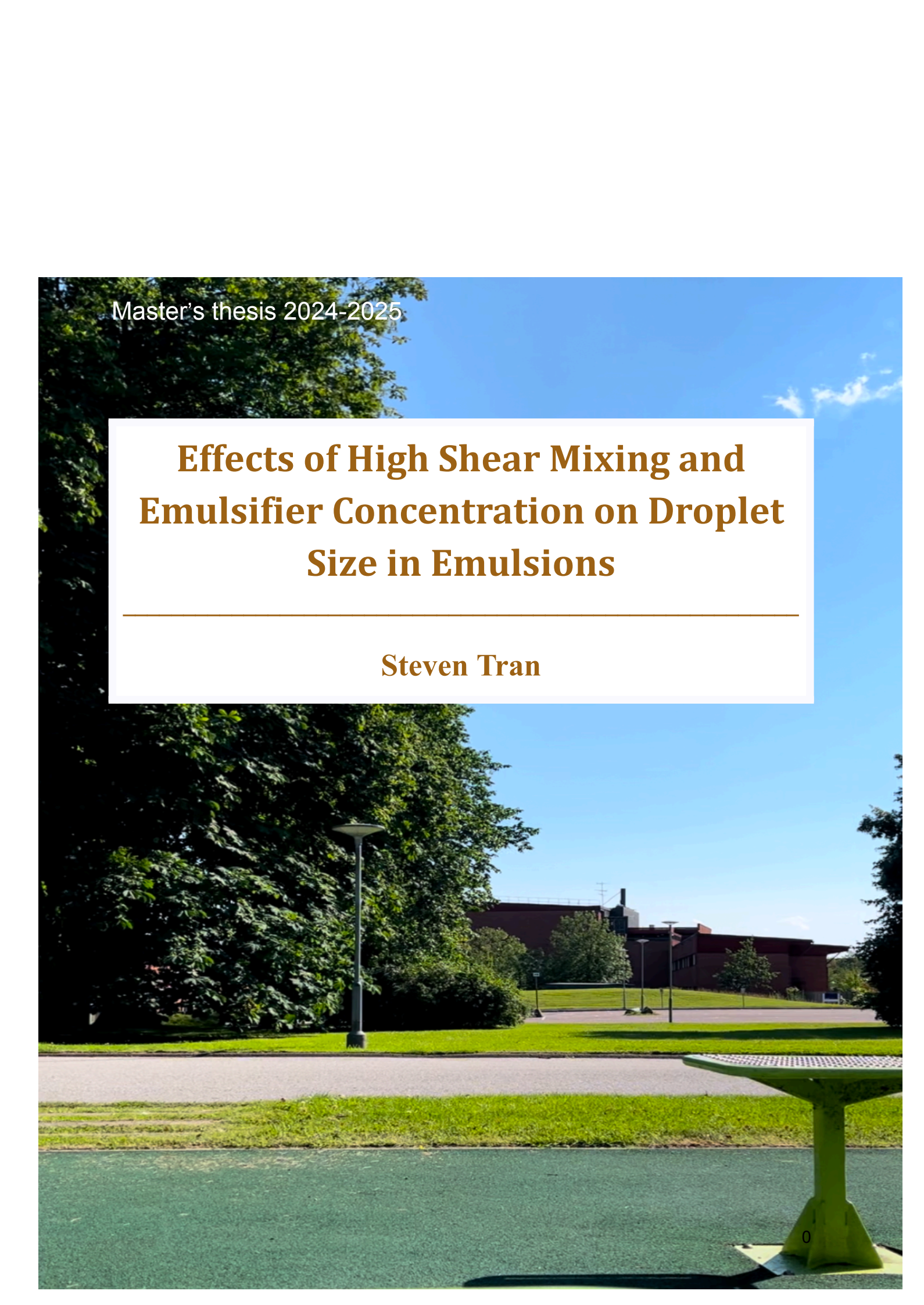


The background image shows a university campus scene. In the foreground, there is a green, textured surface, possibly a playground or sports field, with a green metal table or bench partially visible on the right. A paved path leads towards a large, modern building with a red roof in the background. The area is surrounded by lush green trees and a clear blue sky with a few wispy clouds. A tall, slender lamppost stands on the left side of the path.

Master's thesis 2024-2025

Effects of High Shear Mixing and Emulsifier Concentration on Droplet Size in Emulsions

Steven Tran

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Master's thesis work at Lund university

Supervisor: Andreas Håkansson

Examiner: Lars Nilsson

Abstract

This work investigates the relationship between three different theoretical concepts related to the experimental values from this project. The first model includes critical micelle concentration (CMC) and surface tension. The second model incorporates surface dilational modulus with the amount of emulsifier. The third concept relates the Weber number, a dimensionless number which compares inertial forces to interfacial tension forces in a fluid system. A model that predicts breakup of droplets have shown to be inversely proportional to droplet size with an exponent of -0.6.

Experiments have been done to see how well it relates to the theory. The experiments consisted of three emulsifiers - Pluronic F127, Polysorbate 20 and sodium caseinate mixed with a small amount of mygliol oil at six different rotational speeds for three minutes. The results showed that higher rotor speeds in high shear mixers generally led to smaller droplet sizes. At the lowest rotor speed there was a noticeable relationship between the amount of emulsifier and smaller droplet size, however this relationship was not consistent across all rotational speeds.

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Contents

1. Introduction	6
1.1 Background	6
1.2 Thesis Objective	7
2. Theory	8
2.1 Interfacial tension and surface tension	8
2.2 What is an emulsion?	9
2.3 Surfactants	9
2.3.1 Emulsifiers	9
2.3.2 Critical micelle concentration	10
2.4 Theoretical models to investigate correlation between emulsifier concentration and $d(0.9)$	11
2.4.1 Model 1	12
2.4.2 Surface dilational modulus	13
2.4.3 Model 2	14
2.5 Theoretical model to investigate correlation between rotor speed and $d(0.9)$	15
2.5.1 Weber number	15
2.6 Droplet size	17
2.7 High shear mixers	18
3. Material & Method	20
3.1 Emulsification experiment	20
3.1.2 Effect of waiting time on measurement accuracy	21
3.2 Cleaning of high shear mixer	22
3.3 Selection of emulsifiers	22
3.4 Selection of rotor speed	23
3.5 Drop size measurement	25
3.5.1 Working principle	25
3.5.2 Measurement procedure	26
3.5.3 Cleaning of dispersion unit between samples	27
3.5.4 Settings	27
4. Result & discussion	28
4.1 Result outline	28
4.2 Rotational speed and $d(0.9)$ for three emulsifiers	28

4.2.1 Pluronic F127	29
4.2.2 Polysorbate 20	32
4.2.3 Sodium caseinate	34
4.2.4 Weber number	37
4.3 Temperature increase during mixing	40
4.4 Concentration plotted against rotational speed	41
4.4.1 Findings from plotting concentration against $d(0.9)$	43
4.5 Sources of errors	47
4.6 Future outlook	48
5. Conclusion	49
References	50

1.Introduction

1.1 Background

In order to achieve a smooth and desirable texture for certain food products, it is essential to maintain small droplet sizes. For example in mayonnaise, large droplets can lead to grainy texture, reduced creaminess and phase separation [1]. The larger droplets can be disrupted into smaller ones by applying high amount of force by stirring. Generally the more energy that is applied, the smaller the droplets become and the more stable the emulsion becomes. One primary reason for this is due the reduced risk of the droplets merging together. However, increasing energy usage will also result in higher energy costs and negative environmental impacts. By gaining insight and understanding of the process of having smaller droplet sizes and the role of emulsifiers it could potentially lead to finding alternative ways to reduce droplet size without the use of more energy.

Homogenization methods can in broad terms be divided into two categories: high energy and low energy methods. High energy methods utilize mechanical forces to break down droplets into smaller sizes such as high shear mixing, high pressure homogenization and ultrasonic emulsification. In contrast, low energy methods for forming emulsions rely on physical and chemical properties of the system for instance phase inversion temperature [2]. High energy methods are used in the food industry for producing emulsions and will be the focus for this thesis.

1.2 Thesis Objective

The aim of this thesis is to investigate how different emulsifiers affect the value called $d(0.9)$ which represents the particle size below which 90 % of the particles fall. This study focuses on answering the following questions:

1. How do rotor speed and emulsifier concentration influence the size $d(0.9)$ value?
2. How well does a previously suggested scaling law capture the effect of rotor speed?

2. Theory

2.1 Interfacial tension and surface tension

Surface tension arises due to the imbalance of the attractive forces acting on molecules at the surface of a liquid. Inside the liquid (bulk phase), each molecule experiences equal attractive forces from surrounding molecules in all directions. However, at the surface, molecules lack attraction in the direction towards the air, which creates an asymmetry, in forces. This imbalance leads to surface energy, which manifests as surface tension - the liquid behaves as if it were surrounded by an imaginary “skin” which tends to shrink the surface and hold the fluid together [3].

The words surface tension and interfacial tension are often used synonymously. However, the latter is preferred for the boundary between two condensed phases such as oil and water, which is the interface examined in this project. In contrast the surface tension is often used for air-water interfaces.

From a thermodynamic perspective interfacial tension can be described as the amount of energy that is required to extend an interface by one unit of area. It is given by equation 1:

$$\gamma_i = \frac{E}{A} \quad (1)$$

Where γ_i is the interfacial tension. E is the energy. A is the area [4].

At equilibrium the interfacial area tends to be a minimum to minimize the energy.

Because surface tension represents additional energy, which is proportional to the area, systems naturally strive to minimize this area. This explains why liquid drops in air and bubbles take on a spherical shape [5].

A spherical shape minimizes this energy because it has the smallest surface area for a given volume. It helps keep drops or bubbles stable because any change in their shape or size increases the surface area, which takes extra energy. This extra energy acts like a barrier, making it harder to disturb the drop's shape [6].

2.2 What is an emulsion?

An emulsion is a suspension or dispersion of liquid droplets of one liquid in another [7]. An example of an emulsion is milk, where the continuous phase that surrounds the dispersed droplets is water and the dispersed phase is milk fat, this is called an oil in water (o/w) emulsion [8]. The opposite case, water in oil (w/o) emulsion occurs when water droplets are dispersed in oil, one example of that is margarine. In this case, the liquid that is mentioned second makes up the continuous phase. In this project the experiments focused on o/w emulsions.

2.3 Surfactants

Surfactants belong to a group called amphiphiles that lower the surface tension between oil-water and air-water interfaces. An amphiphile is a substance that has a segment that tends to not be water soluble (and is therefore oil soluble), a characteristic referred to as hydrophobic. In addition the amphiphilic compound contains a segment that *is* soluble in water (hydrophilic) [9]. Surfactants tend to arrange themselves at the interfaces in a way that the hydrophilic head is in the water phase and the hydrophobic tail groups are located in the non aqueous phase.

2.3.1 Emulsifiers

Emulsifiers are a group of chemicals that fall under the category of surfactants [10]. When oil is introduced to water the two liquids will naturally separate over time due to the molecular differences. In order to create a stable emulsion, there needs to be a surface

active compound that lowers the interfacial tension as well as stops the droplets from merging together. The process of when two or more droplets come in contact and merge together is called coalescence

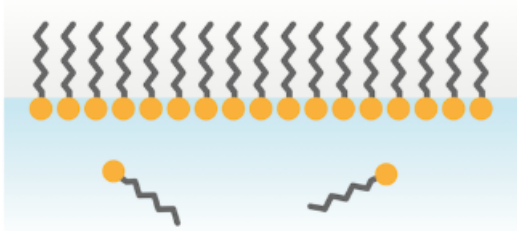
When an emulsifier is added to an oil-water mixture, it moves to the interface and adsorbs (attaches itself) there. The emulsifier's hydrophilic head is attracted to water, and the hydrophobic tail is attracted to oil. By adsorbing at the interface the emulsifier lowers the interfacial tension and reduces the driving force towards coalescence. This makes it easier to break the oil into tiny droplets and form a stable emulsion.

2.3.2 Critical micelle concentration

When the concentration of surfactant reaches the critical micelle concentration (CMC), the surfactant molecules start grouping together into structures called micelles, this can be seen in figure 1 [11]. In other words, the CMC is the surfactant concentration at when micelles start to form in an aqueous solution [12]. These micelles are tiny spheres where the hydrophilic parts face outwards and the hydrophobic parts are tucked inside.

Surface saturation ($\leq$ CMC)

Low surface tension, no micelles



High concentration ($\gg$ CMC)

Low surface tension, $\uparrow$ micelle formation

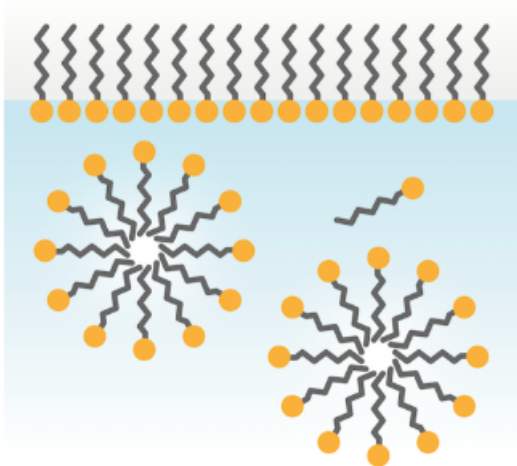


Figure 1. The picture above shows when no micelles have formed and the picture below shows when surfactant starts to form micelles. (With permission from the Dispersa.)

2.4 Theoretical models to investigate correlation between emulsifier concentration and $d(0.9)$

In this work, two theoretical models will be presented to analyze the relationship between rotor speed, $d(0.9)$ and the surfactant/emulsifier concentration. These models, referred to as

model 1 and model 2, which will be presented below. For simplicity D_{max} , which is the largest stable droplet diameter, is assumed to have the same value as $d(0.9)$.

2.4.1 Model 1

The correlation between surfactant concentration and surface tension is well documented. As the surfactant concentration is increased, the surface tension continues to decrease until it reaches a constant level at high surfactant concentrations where the surface tension has become saturated [13]. Once the CMC is reached, any additional surfactant does not further reduce surface tension, which remains constant regardless of the added amount. This behavior is illustrated in figure 2.

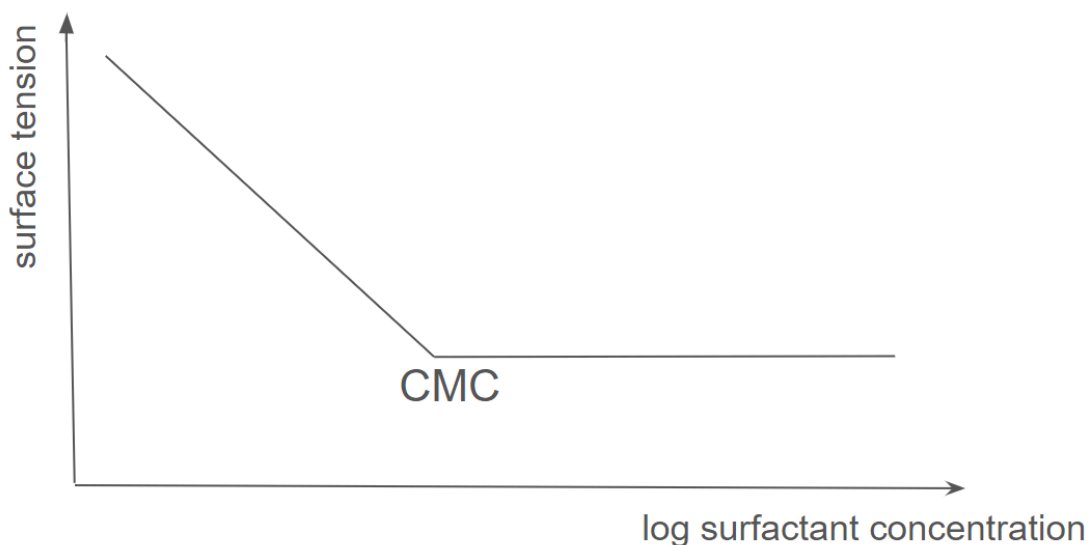


Figure 2: The interfacial tension depends on the concentration of emulsifier (The figure is inspired by Interfacial science: an introduction from figure 4.14)

Quantitative insight of the CMC can help determine the optimal concentration of the emulsifiers, preventing excess use. The reason for this is if a certain surfactant has a CMC value several times less than another variant, then a lower amount of surfactant is required to reduce surface tension. For example this is the case when comparing biosurfactant to chemical surfactants, where biosurfactants have lower CMC [14].

2.4.2 Surface dilational modulus

Another concept discussed by Padron and Calabrese in the article involves elasticity [15]. Surface dilational modulus is a measure of how elastic a surface is when it is stretched or deformed. A higher surface dilational modulus indicates a more elastic interface, which can better resist changes in shape and maintain stability during droplet deformation. (And thus not break apart). This increased elasticity makes droplet breakup more difficult compared to a system with a lower surface dilational modulus. An analogy for this would be a rubber band, the rubber bands can come in different models where some are easier to pull apart. A rubber band that is more difficult to pull apart can be seen as a droplet with high surface dilational modulus, (when moderate surfactant concentration is applied) and low and high E_{sd} value would yield lower elasticity.

To better interpret figure 3 below with surfactant concentration on x axis and surface dilational modulus on y axis, two terms need to be explained:

- Diffusion Timescale (t_D) refers to how long it takes for surfactant molecules to move from the bulk liquid (the main body of the liquid) to the interface of the droplet.
- Drop deformation Timescale (t_{dd}) is how quickly a droplet can deform under the influence of external forces, such as shear or turbulence.

In reality the model can not alone explain the droplet size, since there is another factor that affects the droplet size which is the interfacial tension. In reality at no (or very little surfactant concentration) the interfacial tension would be at the highest, but it can be seen from the figure that this is not the case.

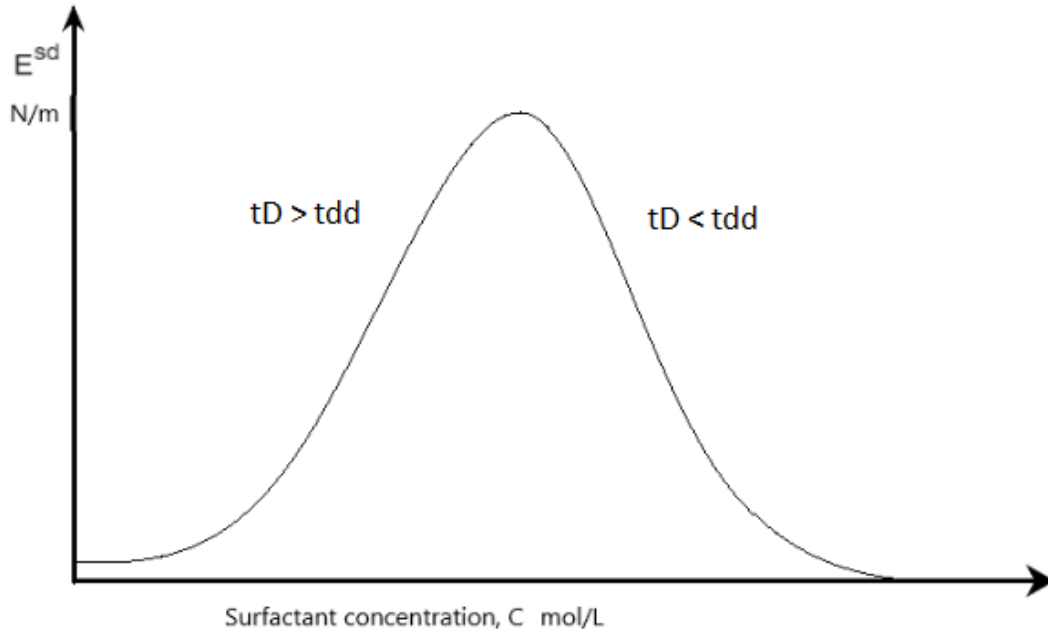


Figure 3: Representative curve of surface dilational modulus (E^{sd}) on y-axis and surfactant concentration (C) on x-axis.

In practice the model can not alone explain the droplet size, since there is another factor that affects the droplet size which is the interfacial tension. In reality, at no (or very little surfactant concentration) the interfacial tension would be at the highest, but it can be seen from the figure that this is not the case.

2.4.3 Model 2

Model 2 is therefore based on interfacial tension, surface dilational modulus and experiments done in the same article where a trend of the results looked like figure 4, with D_{max} on the y axis and surfactant concentration on the x axis. The graph has a hump like shape, where D_{max} initially increases, reaches a peak and then gradually decreases before stabilizing.

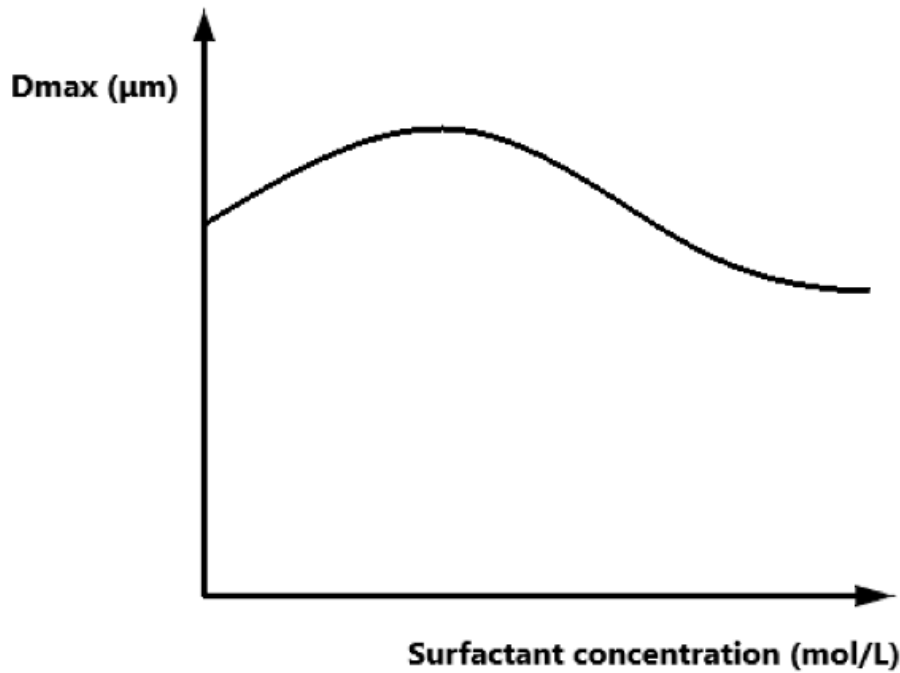


Figure 4: Model 2 with surfactant concentration on x axis and D_{max} on y axis (The figure is inspired from results from the article “Effect of surfactants and interfacial rheology on equilibrium drop size in turbulent liquid-liquid dispersions“)

2.5 Theoretical model to investigate correlation between rotor speed and $d(0.9)$

2.5.1 Weber number

The Weber number (We) describes the ratio between the inertial forces and interfacial tension forces [16]. In fluid mechanics, inertia refers to the force caused by a fluid's momentum. (mass times velocity)

$$We = \frac{\text{inertial forces}}{\text{surface tension}}$$

In the past, an experimental correlation has been observed, indicating that D_{max} is inversely proportional to the Weber number with an exponent of -0.6. In this section the validity of that value will be tested, based on the experiments. The value that changes here is the rotational speed, what is interesting is seeing if the Weber number changes depending on which emulsifier is used and if the number changes based on rotational speed. The relationship between D_{max} is mathematically expressed as the following:

$$\frac{D_{max}}{L} = A_2 \cdot We^{-3/5} \quad (2)$$

Where A_2 is a geometric constant and L represents the characteristic length scale of the equipment, such as the diameter of a rotor or pipe [15].

In order to linearize the relationship, the expression is logarithmized

$$\log(D_{max}) = \log(A_2) + \log(L) - \frac{3}{5}\log(We) \quad (3)$$

Since it is the slope that is relevant in this case, the constants $\log A_2$ and $\log L$ can be disregarded, which gives the expression:

$$\log(D_{max}) = -\frac{3}{5}\log(We) \quad (4)$$

Which can be simplified further to:

$$D_{max} = We^{-0.6} \quad (5)$$

From equation (4) it can be seen that the droplet size correlates with the Weber number by a negative factor of -0.6. The value of the Weber number obtained from the experiments during this project is plotted with help of the following formula:

$$We = (\rho_c \cdot N^2 \cdot L^3) / (\gamma_c) \quad (6)$$

ρ_c is the density of the continuous phase (water) is $\approx 1000 \text{ kg/m}^3$

N is rotator speed per second or minute and varies between 10 000 and 23 000 RPM

L is the diameter of the impeller and measured 0.007 m

The surface tension at pure triglyceride-water is ≈ 25 mN/m

2.6 Droplet size

There are many different ways to describe the size of spherical particles, including surface area, volume and sedimentation rate. For example $D[4,3]$ (volume weighted mean), $D[3,2]$ (surface area weighted mean), $d(0.1)$, $d(0.5)$ and $d(0.9)$ (indicating that 10%, 50%, and 90% of the total volume is smaller than the corresponding particle sizes). There is no standard in the industry which one of these values to choose [17]. However in this thesis the value of $d(0.9)$ is chosen since it gives an idea of the absolute vast majority of droplet size which is beneficial for applications in the food industry, in the sense that it reduces the risk of large droplets that are undesirable in for example mayonnaise and salad dressing and also causes instability. The principle of $d(0.9)$ for droplet size is illustrated in figure 5.

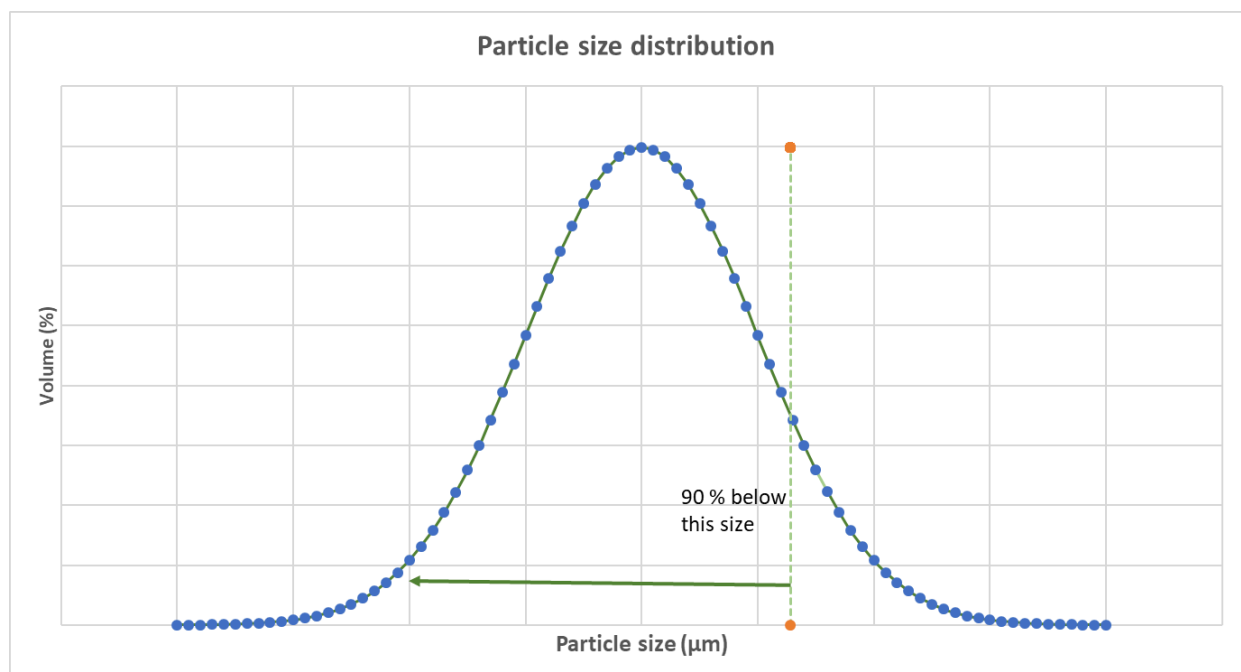


Figure 5, example of how a particle size distribution curve looks like with volume % on y axis and particle size on x axis.

2.7 High shear mixers

High shear mixers consist of a moving rotor part and a stationary stator part. This can be seen in figure 6 [18]. The stator consists of holes or openings that the fluid passes through. The rotor draws the fluid towards the center in an axial direction, where it is milled between the rotor blades and the stator and then the liquid is pushed out and pushes it through the stator holes.

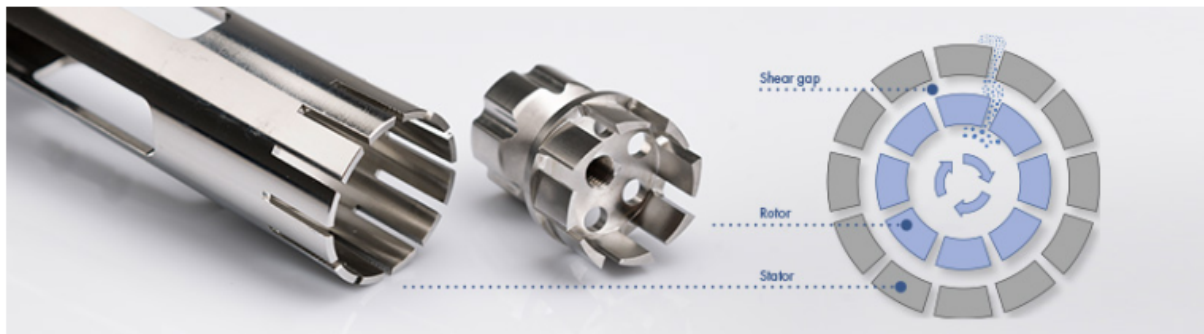


Figure 6: Illustrates the rotor and stator in a high shear mixer. (With permission from Dispermat)

The high shear mixer is a frequently used instrument to directly homogenize oil and aqueous phases, which helps to form emulsions. The high-speed rotation of the mixing head induces a combination of radial, longitudinal, and rotational velocity gradients in the fluids which results in the larger droplets breaking into smaller ones [19] , which can be seen in figure 7 [20].

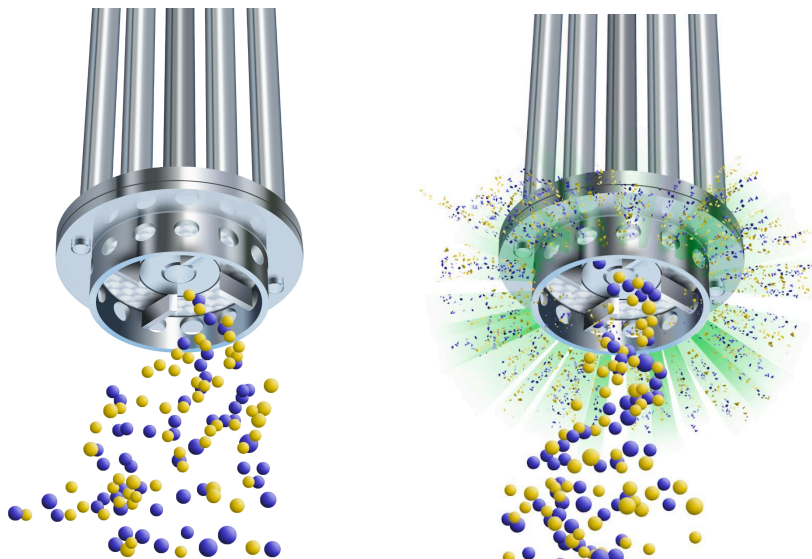


Figure 7: The rotor blades of the high shear mixer cleave the particles into smaller ones.
(Image from Silverson, 2023 with permission from the publisher)

3. Material & Method

3.1 Emulsification experiment

The dispersion was emulsified using a high shear mixer which can be seen in figure 8, (Silentcrusher M, Heidolph Instruments, Schwabach, Germany). Emulsifiers and distilled water were combined with 1 ml of miglyol oil in an erlenmeyer flask. The amount of emulsifier and distilled water depended on the CMC of each emulsifier (explained more in section 3.3.1) and the concentration of it.



Figure 8. Shows the high shear mixer silentcrusher together with an erlenmeyer flask that is filled with distilled water, Pluronic F127, and miglyol oil.

The mixture was homogenized to RPM of between 10 000-23 000 RPM for 3 min to emulsify the oil. The emulsion in the container was transferred with a pasteur pipette to a centrifugal tube (that was prefilled with two ml of emulsifier) to the 10 ml mark.

3.1.2 Effect of waiting time on measurement accuracy

In order to have experiments that are reproducible and not influenced by random errors it is important to not have unnecessary long delays between the emulsification experiment and the drop size measurements. To test whether waiting time had an impact, an experiment was conducted to compare measurements taken after different intervals with Pluronic F127 at 13000 RPM which can be seen in figure 9. The values seem to decrease but at the same time reach the second highest value after 5 hours, therefore it seems as though the waiting time did not influence the values to a large extent, confirming that the particle size distribution remained stable. Consequently, based on the results it seems that using six or twelve samples for measurements did not introduce notable variability.

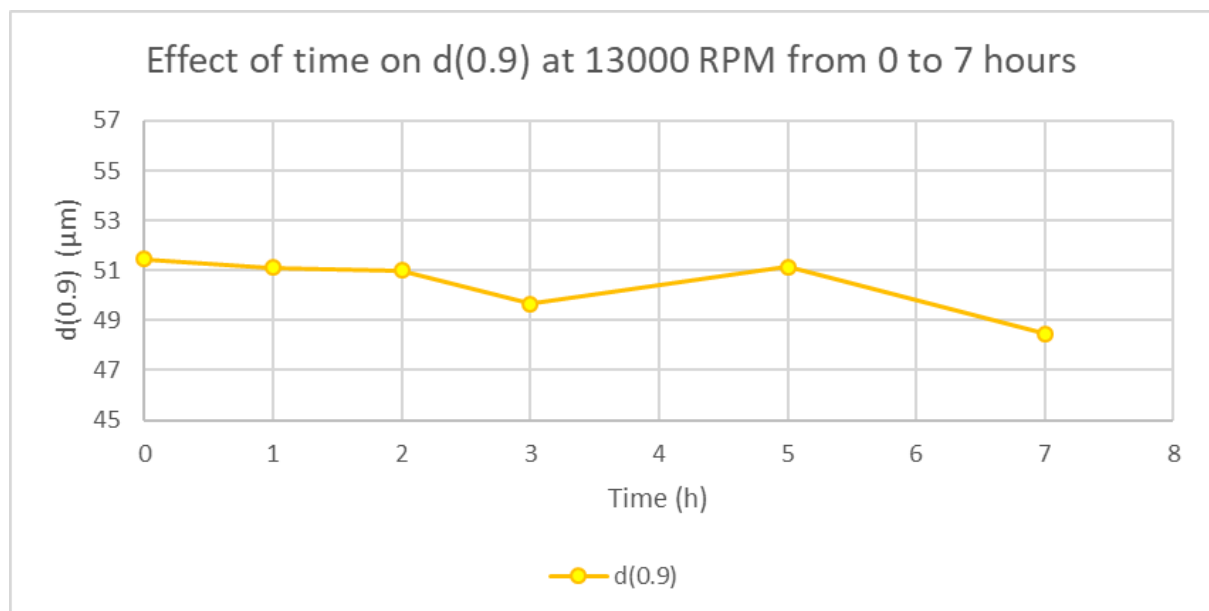


Figure 9: The x axis is time in hours measured at intervals from 0 to 7 hours. The y-axis shows particle size based on d(0.9)

3.2 Cleaning of high shear mixer

A container with hot water was filled and the mixer was started at a medium/lower speed for a short time and repeated this process two times. Thereafter a bottle with a nozzle that released a stream of distilled water was used to clean the stirrer spindle and stirrer head. The final step in the cleaning process involved filling the container with distilled water and starting the mixer.

3.3 Selection of emulsifiers

During the experimental phase, three emulsifiers were selected. The selection was from emulsifiers that were available in the food department and relatively non toxic. The selected emulsifiers were as follows:

- Pluronic F127
- Polysorbate 20
- Sodium caseinate

Pluronic F127 is a surface active polymer. It is a molecule that is made up of three parts, the middle part of repeating units of polypopylene oxide (PPO) and the outer parts are of polyethylene oxide (PEO) blocks. Pluronic F127 is relatively large with an average molecular weight of 12 600 g/mol [21].

Polysorbate 20 is a nonionic surfactant used in household, pharmaceutical, and industrial products. It contains 20 polyethylene glycol units. It acts as a washing agent, a stabilizer and solubilizer in lab and industrial processes [22]. Polysorbate has a molar weight of 1228 g/mol [23].

Sodium caseinate is derived from casein, the main protein in milk. Sodium caseinate is a substance that appears as white or pale yellow granules or powder and is practically odorless. Its primary functional uses include acting as an emulsifier and stabilizer, making it a versatile ingredient in various food and industrial applications [24]. The molar weight can be found in the range around 30–575 kg/mol [25].

3.3.1 CMC determination of emulsifiers

The CMC values for Pluronic F127 and Polysorbate 20 in the experiments were determined by finding the values in the literature. The value at room temperature was not available for Pluronic F127, however the CMC value for 10 °C and 30 °C was available [26] from these values an interpolation at 25 °C was done giving a value of 443 mg/L.

For Polysorbate 20 the CMC value was 600 mg/L [27].

The sodium caseinate does not have a CMC value, the 5x concentration was determined by dissolving a relatively large amount in one liter of water, this amount was 20 g and used both as 5x concentration and a stock solution. The lower concentrations were prepared as dilutions of this stock, 2x was 40 % of 5x (8 g/L), 1x was 20 % of 5x (4 g/L), 0.5x was 10 % of 5x (2 g/L) and 0.2x was 4 % of 5x.

3.4 Selection of rotor speed

Based on experiments it was clear that from around 6000 and 9000 RPM the values for $d(0.9)$ had a broad interval from the lowest to the highest when performing the particle size measurement. This is shown in figure 10, where it can be seen that the error bars are higher on the two first rotational speeds, 6000 and 9000, and that the standard deviation after that becomes so small that the error bars are not visible. All experiments were done in duplicates therefore the error bars were calculated by comparing two values obtained by calculating the standard deviation in Excel. The mentioned here showed that for speeds around 13 000 and above, the average values from the equipment were very similar but 9000 and below the values differed more. Based on these findings, the new range of rotational speeds was set between 10 000 and 23 000 RPM, the exact values can be seen in table 1.

It is worth noting that for this experiment, the liquid from the erlenmeyer flask was poured directly into the centrifugal tube, rather than using a pasteur pipette from the middle of the flask as in subsequent experiments. However similar trend as this experiment were noted in later experiments, which is that the rotational speed of 10 000 RPM generally had more absolute standard deviation than the sample values at 23 000 RPM. Additionally, the ratio between emulsifier and distilled water was not identical to that used in later experiments, as this trial was conducted during the preliminary phase to optimize the procedure.

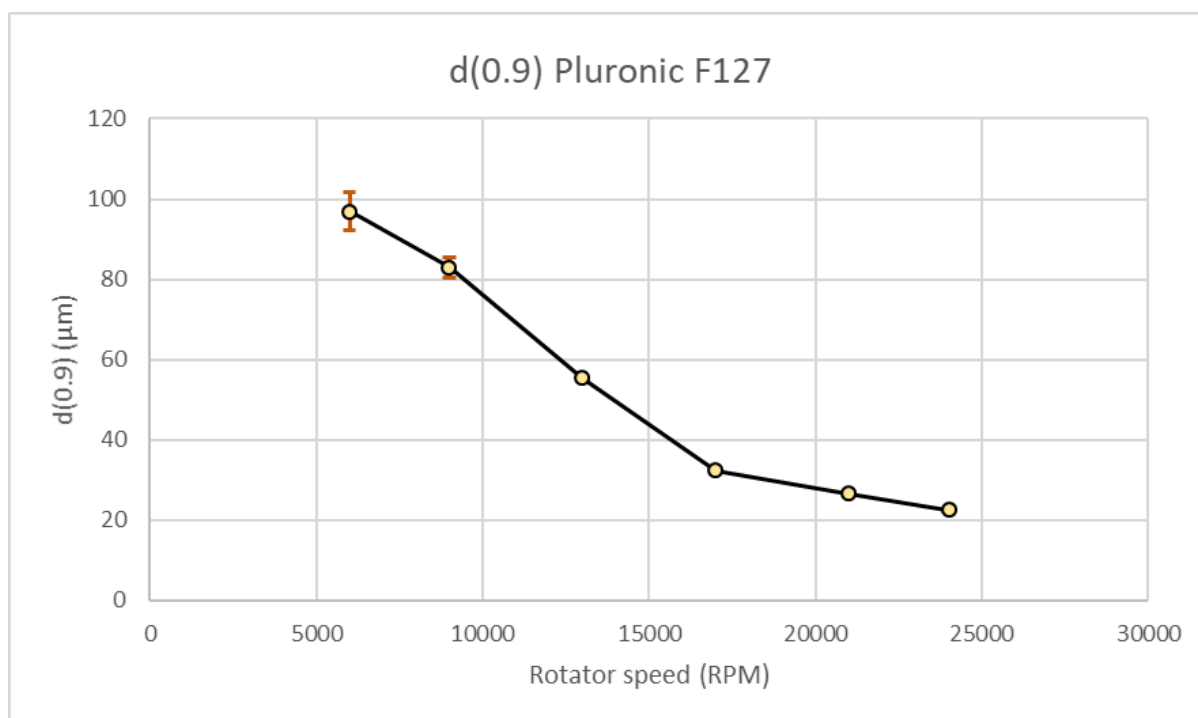


Figure 10: The figure shows that the standard deviation is highest at 6000 RPM and 9000 RPM. For rotational speeds of 13 000 RPM and above, the error bars are so minimal that they are not visible in the figure.

Table 1: Rotational speed used for mixer Silentcrusher in the experiments.

Sample number	Rotational speed - Rotations per minute used with mixer Silentcrusher
1	10000
2	13000
3	16000
4	19000
5	21000
6	23000

3.5 Drop size measurement

3.5.1 Working principle

Most modern particle size equipment use a laser beam that measures the angular scattering from dispersed particles. The scattering angle is inversely related to particle size: smaller particles scatter light at wider angles, while larger particles scatter light at narrower angles, this can be seen in figure 11. The scattering pattern is analyzed using mathematical models to calculate the distribution of the particles.

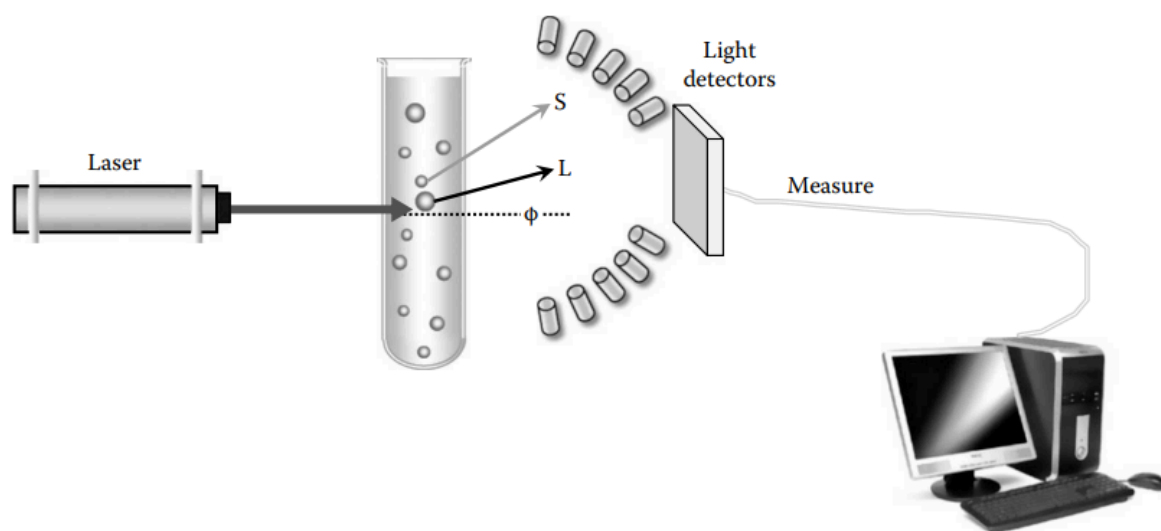


Figure 11: With the principle of light scattering the droplet sizes can be measured using static light scattering. Permission from the author.

The droplets of miglyol oil scatters the laser light in a measurable manner, allowing the system to determine the particle size distribution. The dispersant is deionized water since that is the medium used to suspend the particles for measurement.

Part of the mixed emulsion was added dropwise until the instrument gave an optimal laser obscuration of around 10 %. A proper obscuration level has a balance between having too few particles, which reduces the statistical accuracy of the measurement, and having too many particles, which can lead to multiple scattering. This happens because multiple scattering confuses the instrument, making it difficult to correctly identify the true size of the

particles. The laser intensity was around 75 % when performing the experiments.

The stirrer speed of the controller unit was set to 1000 RPM. Using a pasteur pipette, liquid from the middle of the centrifuge tube was drawn and introduced drop by drop into the dispersion units opening. This continued until the laser obscuration reached approximately 10 %. After that the program was started and the equipment proceeded to analyze the sample.

3.5.2 Measurement procedure

The drop size measurement was measured with a laser diffraction technique. (Mastersizer 2000, Malvern Instruments, Worcestershire, UK), The equipment consists of the dispersion unit, the controller unit and the flow cell. The main housing of the setup contains both the pump and stirrer and that is the dispersion unit. The controller is responsible for adjusting and displaying the speed of the pump and stirrer. The flow cell holds the sample as it passes through the analyzer beam for particle size measurement. These three components can be seen in the figure 12. The Mastersizer software operates on a computer, controlling both the optical and dispersion units while also processing the raw data collected by the system.

Liquid from the middle of the centrifuge tube was drawn and introduced drop by drop into the dispersion units opening. This continued until the laser obscuration reached approximately 10 %. After that the program was started and the equipment proceeded to analyze the sample.



Figure 12, shows the controller unit and the dispersion unit and flow cell apparatus

3.5.3 Cleaning of dispersion unit between samples

The cleaning procedure involves first rinsing the inlet with deionized water. The distilled water is poured into the inlet until it is full, then drained. This step is repeated three times. Finally the inlet is filled with milli-Q water, an ultrapure water produced by a specialized filtration system.

3.5.4 Settings

The refractive index values used in the mastersizer system for the particle size analysis were set to 1.444 for the particles and 1.330 for the dispersant. The particles are represented by miglyol oil and the dispersant is milli-Q water. The settings for the particles were set as spherical. Obscuration level was between 8-12 %, and laser intensity around 75 %.

4. Result & discussion

4.1 Result outline

As outlined in the introduction the objective is to evaluate the effect of rotor speed and emulsifier concentration on the $d(0.9)$ value. Different sections will be categorized in result & discussion those are:

- Rotational speed plotted against $d(0.9)$ for three emulsifiers
- Rotational speed in connection with the Weber number
- Effect of high shear mixer temperature on experimental results
- Concentration plotted against rotational speed

4.2 Rotational speed and $d(0.9)$ for three emulsifiers

The most consistent finding was with experiments using the same concentration, increasing rotor speed led to smaller $d(0.9)$ values. This relationship with higher rotor speed resulting in smaller droplet size is well documented. [15]

However there was one exception. For Pluronic F127 at rotor speeds 21 000 and 23 000 RPM, the value of $d(0.9)$ increased instead. With the values 27.37 μm at 21 000 RPM and 27.44 μm 23 000 RPM, this is marked in red in table 2 which shows the $d(0.9)$ value at different rotational speed and emulsifier concentrations. Three significant digits have been used for the $d(0.9)$ values and therefore the increase is not evident from the table.

4.2.1 Pluronic F127

For Pluronic, at the lowest rotor speed 10 000-13000 RPM the droplet size followed the expected theoretical behaviour - where a higher emulsifier concentration reduces interfacial tension, leading to smaller droplets. The error bars were larger at 10 000 RPM compared to higher speeds, it was similar for all three emulsifiers with a higher absolute error in the 10 000 RPM range.

Pluronic also showed a noticeable increase in droplet size from 2x CMC to 5x CMC at the two highest rotor speeds (highlighted in red and also mentioned in section above in 4.2). For all emulsifiers, the highest shear led to an increase in droplet size at the highest concentration, contrary to what could be expected. This suggests that when both emulsifier concentration and rotor speed are high, their combined effect results in droplet growth. A study by Jinhe Liu (2024) showed that the highest emulsifier concentration did not yield the highest emulsifying rate constant [28]. However, no scientific source was found indicating that increased rotor speed alone causes larger droplets, though the experimental results suggest an interaction effect when excessive emulsifiers are present. The reason for this effect is not known.

Table 2: experimentally measured drop size $d(0.9)$ for five different concentrations for Pluronic F127.

Pluronic F127					
RPM	0.2x CMC	0.5x CMC	1x CMC	2x CMC	5x CMC
10 000	86.5	70.8	71.20	70.7	62.6
13 000	52.5	52.0	51.8	49.6	47.3
16 000	35.8	37.6	35.6	38.3	37.4
19 000	31.9	30.1	29.9	29.5	29.9
21 000	23.5	27.5	21.3	23.0	27.4
23 000	20.4	23.7	17.8	17.8	27.4

To provide greater clarity for the reader, all values from the table are presented in corresponding plots, either as pairs or individually, as combining all plots into a single graph would make it more difficult to distinguish the data. Figure 13 displays 0.2x CMC & 0.5x CMC. Figure 14 is displaying 1x CMC and 5x CMC and figure 15 displays 2x CMC.

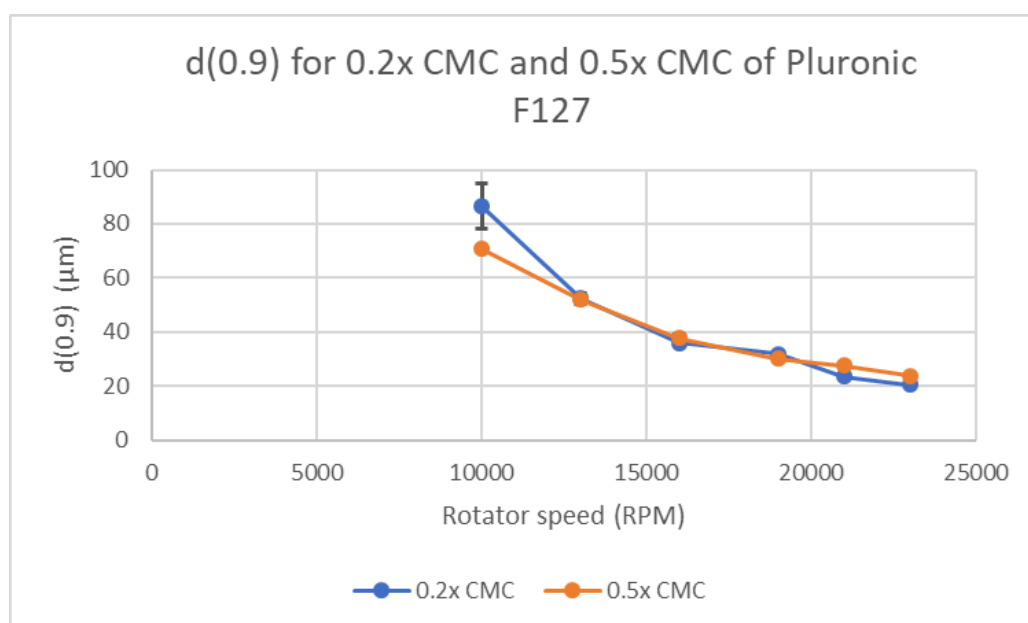


Figure 13 - Variation of $d(0.9)$ with rotor speed for 0.2x CMC and 0.5x CMC. rotor speed on x axis and $d(0.9)$ on y axis.

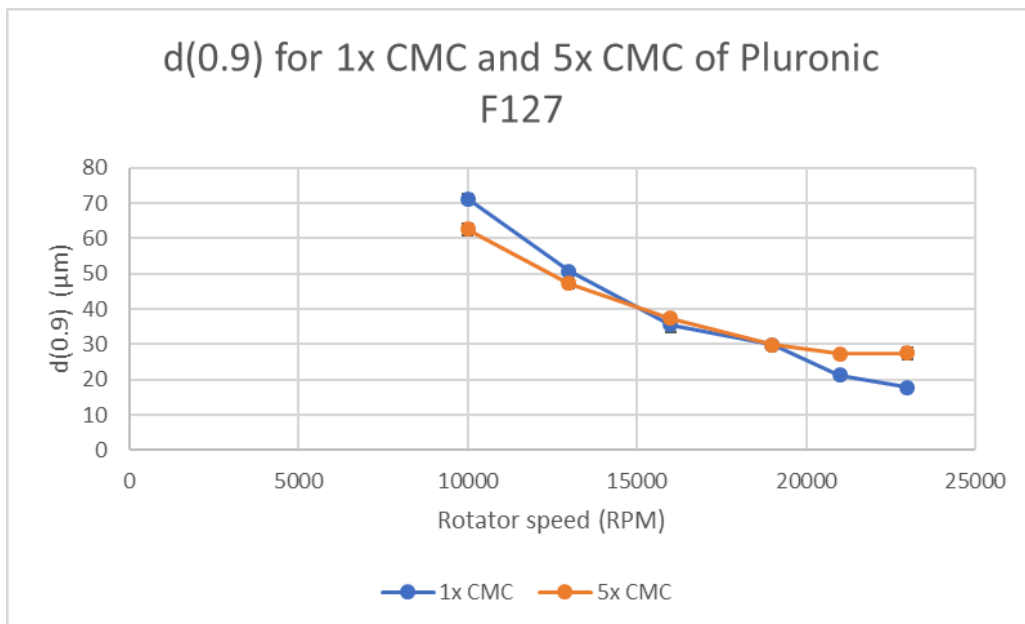


Figure 14 - Variation of $d(0.9)$ with rotor speed for 1x CMC and 5x CMC. rotor speed on x axis and $d(0.9)$ on y axis.

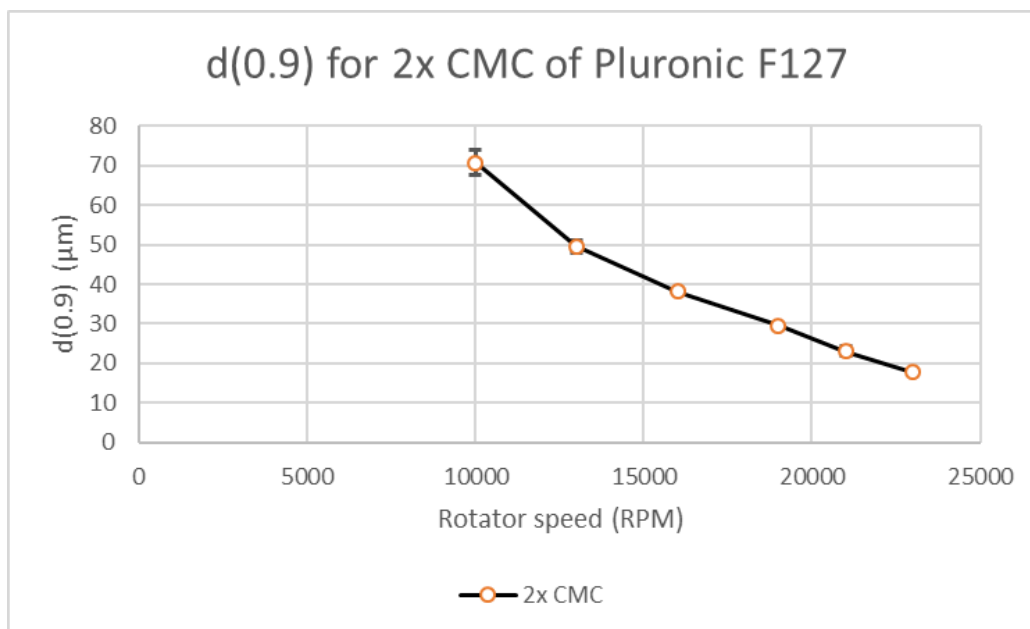


Figure 15 - Variation of $d(0.9)$ with rotor speed for 2x CMC rotor speed on x axis and $d(0.9)$ on y axis.

4.2.2 Polysorbate 20

For Polysorbate 20, it was noted that the $d(0.9)$ value increased on some occasions at the “low to middle” rotor speed range, despite the addition of more emulsifier. This is highlighted in orange in table 3 below. (For Pluronic F127 this only occurred at the highest rotor speeds).

Polysorbate 20 had the smallest particles of the three emulsifiers, the reason for this is not clear. A study was done with similar emulsifiers Pluronic F127, Polysorbate **80** and sodium caseinate and found that Polysorbate **80** resulted in the smallest particle sizes [29].

Table 3: experimentally measured drop size $d(0.9)$ for five different concentrations for Polysorbate 20.

Polysorbate 20					
RPM	0.2x CMC	0.5x CMC	1x CMC	2x CMC	5x CMC
10 000	66.1	70.1	60.7	66.6	62.0
13 000	47.6	46.6	45.8	43.8	45.6
16 000	41.7	35.5	32.8	32.5	34.7
19 000	30.9	30.1	29.6	28.7	28.6
21 000	24.7	24.2	25.1	27.6	26.6
23 000	22.0	20.3	21.7	23.2	23.8

Just as with Pluronic F127, more zoomed in plots are displayed below, figure 16 displaying 0.2x CMC & 0.5x CMC. Figure 17 displaying 1x CMC & 5x CMC. Figure 18 displaying 2x CMC.

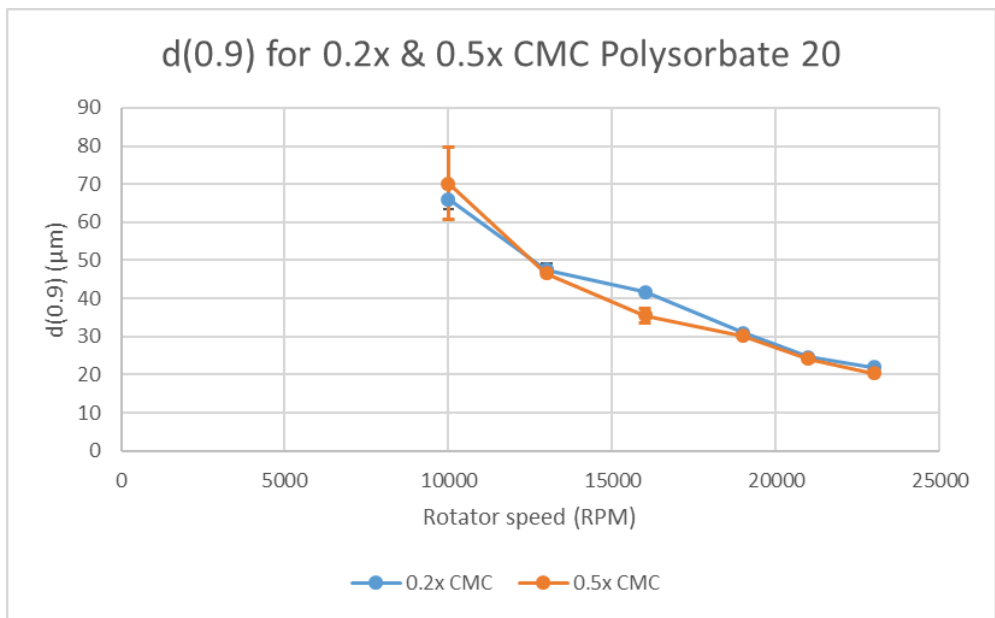


Figure 16 - Variation of $d(0.9)$ with rotor speed for 0.2x CMC & 0.5x CMC. Rotor speed on x axis and $d(0.9)$ on y axis.

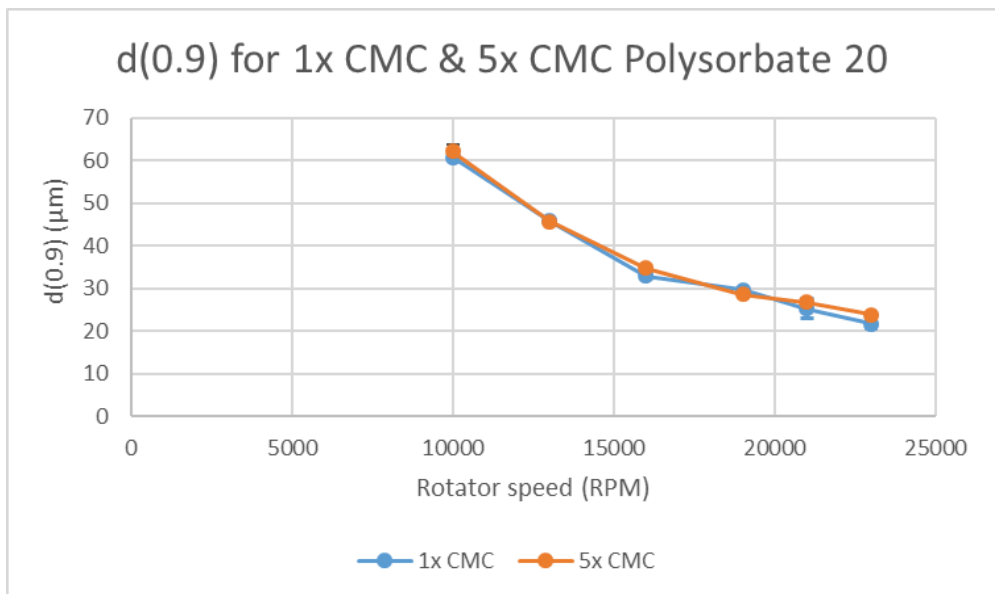


Figure 17 - Variation of $d(0.9)$ with rotor speed for 1x CMC & 5x CMC. Rotor speed on x axis and $d(0.9)$ on y axis.

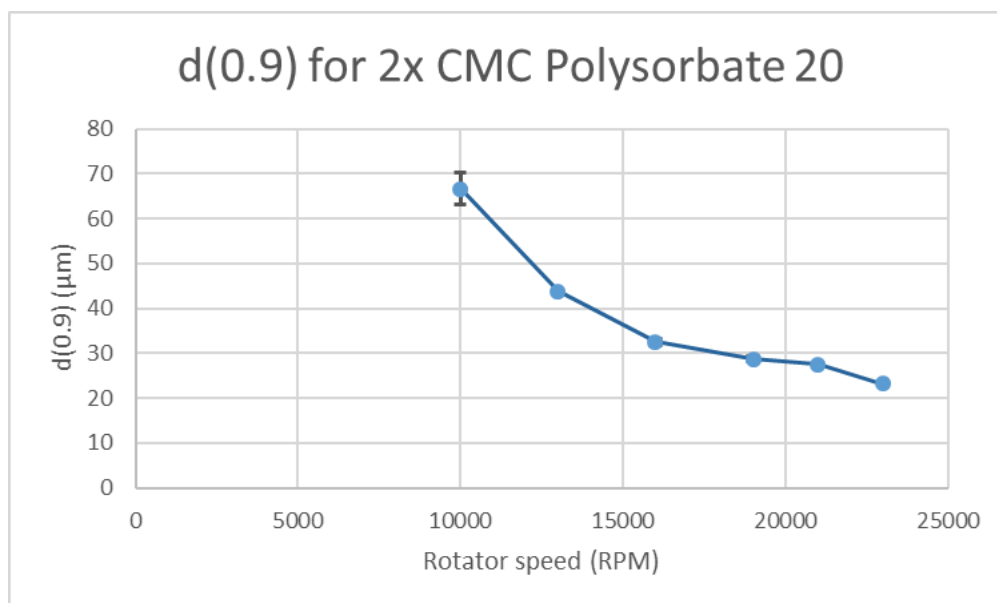


Figure 18 - Variation of $d(0.9)$ with rotor speed for 2x CMC. Rotor speed on x axis and $d(0.9)$ on y axis.

4.2.3 Sodium caseinate

As the RPM increases, $d(0.9)$ decreases across all concentrations, which can be seen in table 4. Sodium caseinate showed the most inconsistent results of all the emulsifiers, although the reason for this is unclear. Though it could be noticeable both visually and through smell that the stock solution of sodium caseinate changed more than the other emulsifiers after a couple of days, this could indicate that when there were some days between the experiments it had more impact on sodium caseinate than the other emulsifiers.

Figure 19 displays 0.2x CMC & 0.5x CMC. Figure 20 displays 1x CMC & 5x CMC. Figure 21 displaying 2x CMC.

Table 4: experimentally measured drop size $d(0.9)$ for five different concentrations for sodium caseinate.

Sodium caseinate					
RPM	0.2x	0.5x	1x	2x	5x
10 000	88.3	77.8	83.9	92.9	81.4
13 000	58.5	57.9	63.8	64.8	56.9
16 000	46.2	43.0	49.8	51.8	45.9
19 000	37.4	34.5	37.0	38.1	36.9
21 000	34.6	31.5	33.6	36.6	34.9
23 000	28.5	30.0	33.5	29.1	31.3

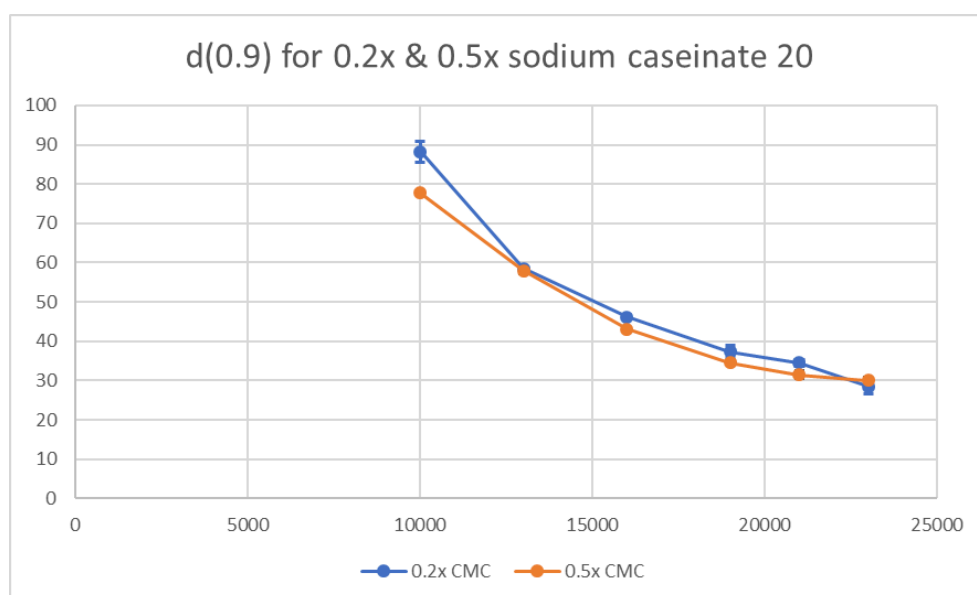


Figure 19: experimentally measured drop size $d(0.9)$ for two different concentrations for sodium caseinate. The y-axis represents $d(0.9)$ in μm , and the x-axis represents rotor speed in RPM.

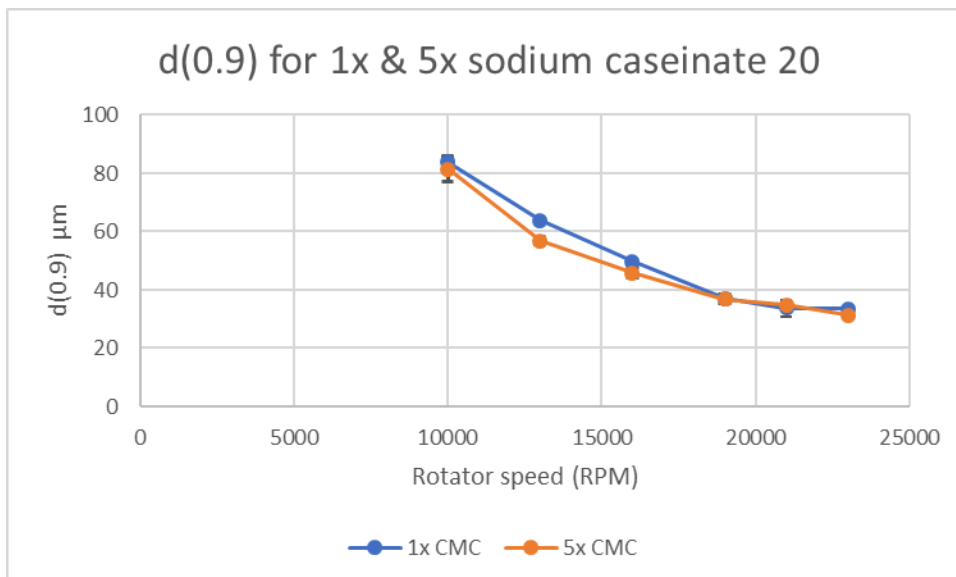


Figure 20: experimentally measured drop size $d(0.9)$ for two different concentrations for sodium caseinate. The y-axis represents $d(0.9)$ in μm , and the x-axis represents rotor speed in RPM.

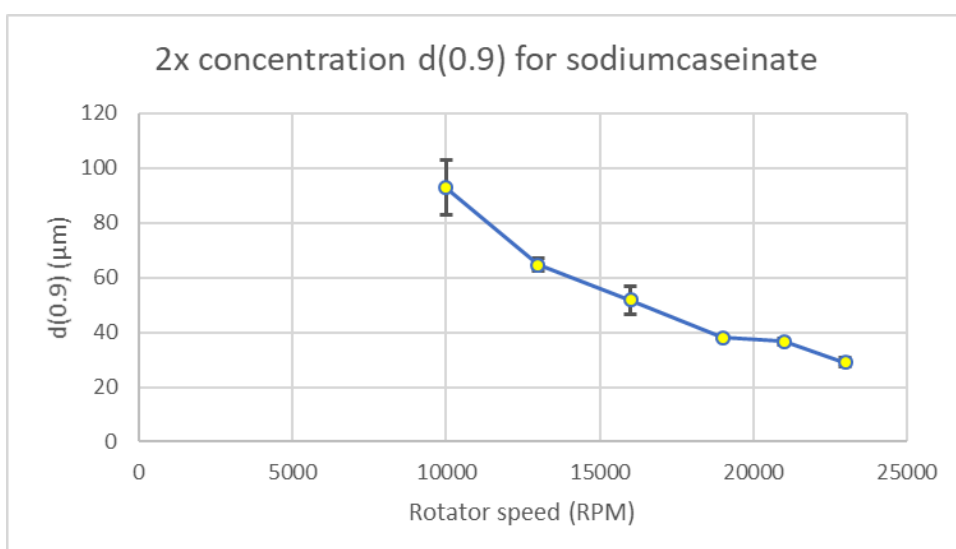


Figure 21: experimentally measured drop size $d(0.9)$ 2x concentrations for sodium caseinate. The y-axis represents $d(0.9)$ in μm , and the x-axis represents rotor speed in RPM.

4.2.4 Weber number

Since rotational speed plays an important role in influencing droplet size, its effect can be further analyzed using the Weber number. By considering the Weber number it is possible to see if the theory of droplet size relates to what was done experimentally in this project, a logarithmic relationship between the Weber number and D_{max} was presented in the theory section from equation (4).

$$\log(D_{max}) = -\frac{3}{5}\log(We) \quad (4)$$

To illustrate the linear regression more clearly, a graph of Pluronic F127 at 0.2x CMC is presented below in Figure 22 as an example. The graph shows the relationship between the Weber number and droplet size, together with the regression line.

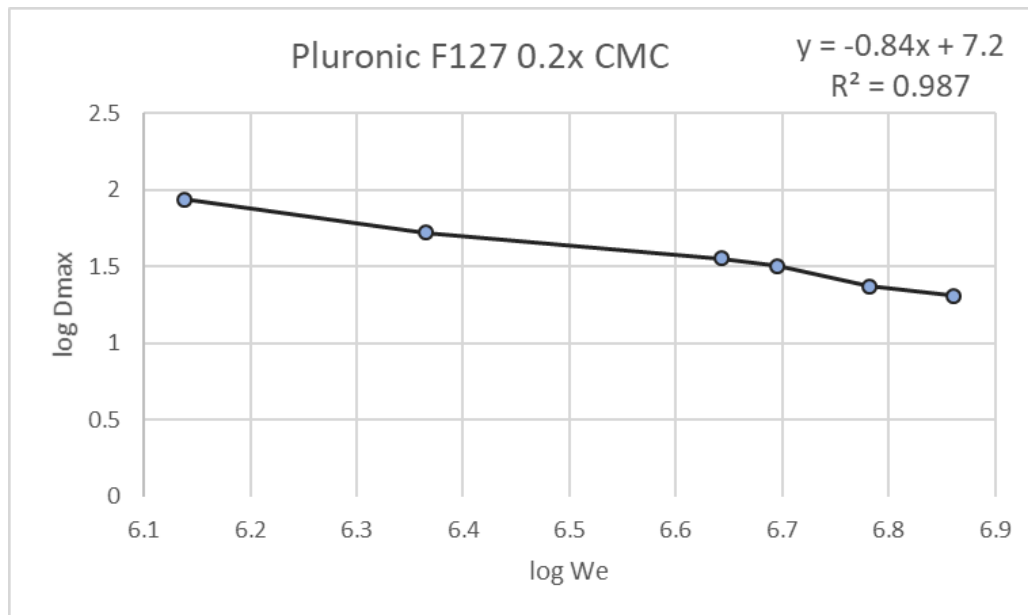


Figure 22: Logarithmic relationship between $\log(D_{max})$ on y axis and $\log(We)$ on x axis for 0.2x CMC Pluronic F127.

A summary of all the linear regression values for the three emulsifiers can be seen below in table 5-7. The R^2 value indicates the strength of the correlation between the Weber number. While k is the slope of the regression model for the data points, the theoretical value of k is

-0.6 for the model investigated. From the experiments the following values were obtained:

- **Pluronic F127** showed a steeper slope at **-0.73**.
- **Polysorbate 20** had a slope that followed the theoretical value at **-0.63**.
- **Sodium caseinate** had a similar value of **-0.62**.

Three confidence intervals of 95 % for respective emulsifier were calculated:

-Pluronic F127: Confidence interval = [-0.83; -0.63]

-Polysorbate 20: Confidence interval = [-0.67; -0.59]

-Sodium caseinate: Confidence interval = [-0.65; -0.59]

From the confidence intervals it can be seen that Pluronic F127 is below the theoretical value, while Polysorbate 20 and sodium caseinate fall within the theoretical range with a 95 % confidence level.

Table 5: regression parameters R^2 and k at five different concentrations of Pluronic F127. The mean and standard deviation for each column is also calculated.

Pluronic F127		
Concentration	R^2	k
0.2x CMC	0.987	-0.84
0.5x CMC	0.997	-0.66
1x CMC	0.979	-0.82
2x CMC	0.977	-0.79
5x CMC	0.986	-0.53
Mean	0.985	-0.73
Standard deviation	0.00644	0.12

Table 6: regression parameters R^2 and k at five different concentrations of Polysorbate 20. The mean and standard deviation for each column is also calculated.

Polysorbate 20		
Concentration	R^2	k
0.2x CMC	0.975	-0.66
0.5x CMC	0.991	-0.71
1x CMC	0.99	-0.61
2x CMC	0.974	-0.60
5x CMC	0.997	-0.58
Mean	0.985	-0.63
Standard deviation	0.00724	0.049

Table 7: regression parameters R^2 and k at five different concentrations of sodium caseinate at varying concentrations.

Sodium caseinate		
Concentration	R^2	k
0.2x	0.993	-0.65
0.5x	0.993	-0.60
1x	0.984	-0.60
2x	0.990	-0.67
5x	0.994	-0.57
Mean	0.991	-0.62
Standard deviation	0.0037	0.037

4.3 Temperature increase during mixing

Possible theories for the increased droplet size between 21 000 and 23 000 RPM could be that after using the high shear mixer for many replicates it becomes warmer. According to McClements when an emulsion with non ionic surfactant is heated the head groups of the surfactant could become dehydrated, which reduces the steric repulsion between droplets and can make them come closer, leading to coalescence. [30]

The effect of temperature increase on the emulsion from the high shear mixer was tested for sodium caseinate at 1x concentration, though it is not a non-ionic surfactant it was used to quantify the temperature increase at higher rotor speeds. The results showed that the temperature did not increase more than 2.4 °C which can be seen in table 8. An increase that small likely does not affect the droplet size.

Table 8: shows the temperature for sodium caseinate at 1x concentration before and after mixing.

RPM	T (°C) before mixing	T (°C) after mixing	ΔT (°C) Temperature Change
16000	19.3	20.7	1.4
19000	19.8	21.9	2.1
21000	20.0	21.8	1.8
23000	19.9	22.3	2.4

4.4 Concentration plotted against rotational speed

Five different concentrations at six different rotational speeds for all three emulsifiers were plotted as can be seen in figure 23-25.

The figures below showed what was already mentioned in section 4.2, instead of displaying rotor speed on the x axis the concentration is plotted. The findings were that at the highest concentration and rotor speed the droplet size value increased. Furthermore it could be seen that at the two lowest rotor speed (10 000 and 13 000 RPM) the droplet size for all three emulsifiers was smaller in the highest concentration in comparison to the lowest concentration. This finding correlates with literature that more surfactant would decrease interfacial tension and make the droplets easier to break up (until it plateaus). Additionally the highest rotor speed and surfactant concentration led to larger droplets. In section 4.4.1 it will be investigated if the emulsifier concentration followed model 1, model 2 or neither.

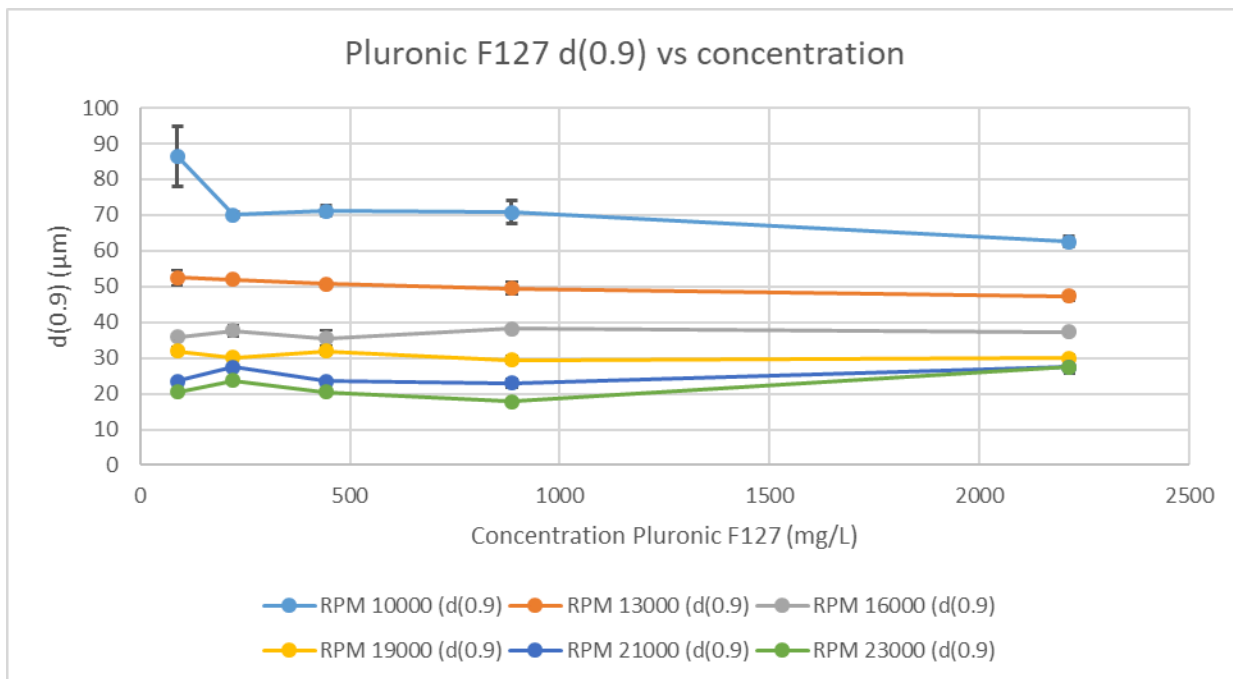


Figure 23: Shows how $d(0.9)$ varies with concentration for Pluronic F127 at six different rotational speed. Concentration on x axis and $d(0.9)$ on y axis.

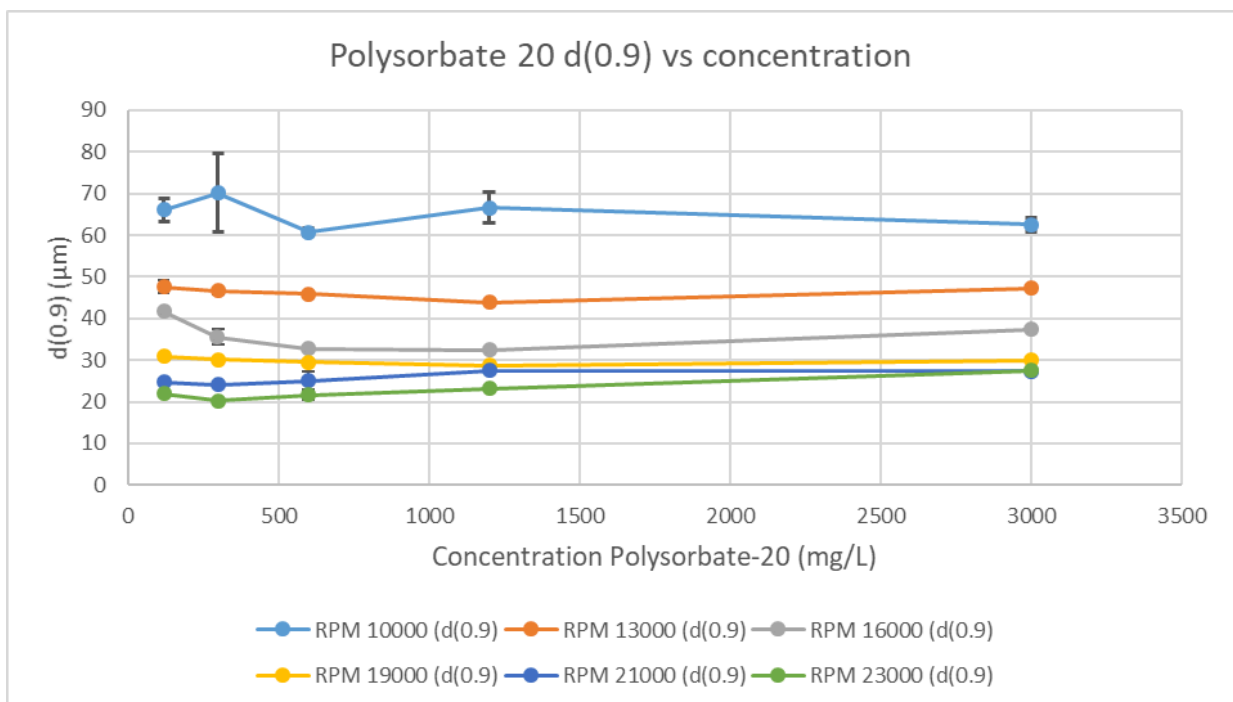


Figure 24: Shows how $d(0.9)$ varies with concentration for Polysorbate 20 at six different rotational speed. Concentration (mg/L) on x axis and $d(0.9)$ on y axis.

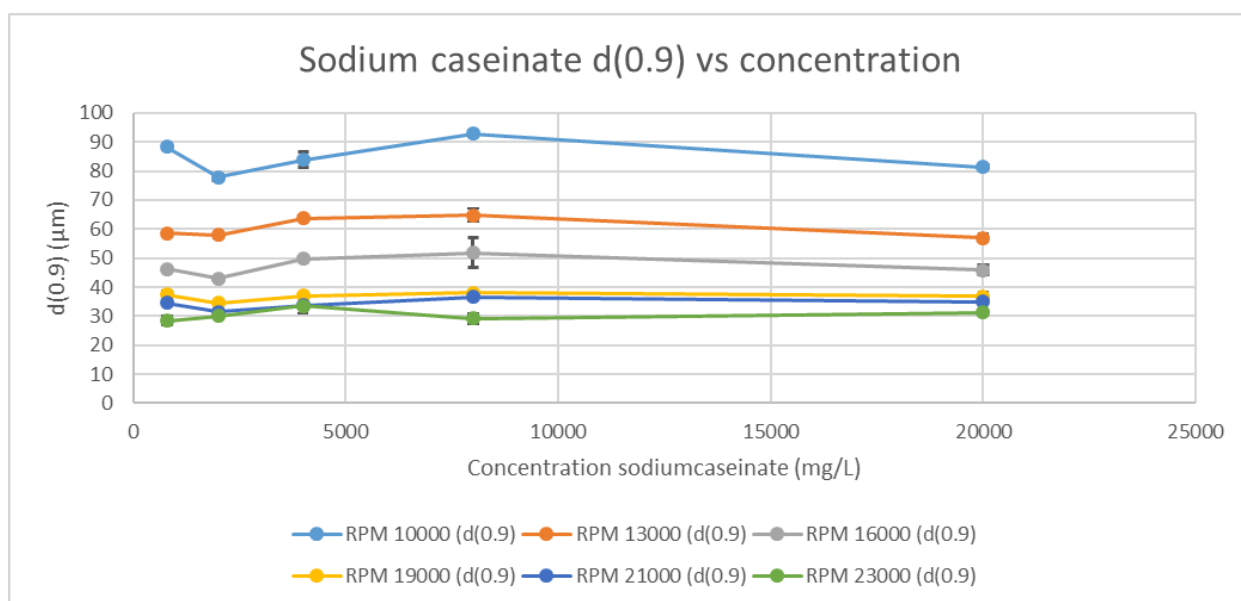


Figure 25: Shows how $d(0.9)$ varies with concentration for Sodium caseinate at six different rotational speed. Concentration (mg/L) on x axis and $d(0.9)$ on y axis.

4.4.1 Findings from plotting concentration against $d(0.9)$

How the concentration of the emulsifier correlates to $d(0.9)$ can be seen in table 9. The table takes into consideration the rotational speed for 5 different concentrations to see if it relates more to Model 1, (can be seen in figure 2) or Model 2, (can be seen in figure 4), or neither of them. From the experiments it was clear that for almost all of the trials there were no clear resemblance with the two models described in the report. However for sodium caseinate at rotor speeds at 13 000 RPM there were similarities with model 2. The following numbering was used to provide an overview:

- 1 = Theory 1
- 2 = Theory 2
- 3 = Neither of theory 1 or 2

Table 9: Overview of how three emulsifiers relate to theoretical model 1 and 2 or neither one.

Rotor speed	Pluronic F127	Polysorbate 20	Sodium caseinate
10 000	3	3	3
13 000	3	3	3
16 000	3	1	3
19 000	1	3	3
21 000	3	3	3
23 000	3	3	3

To provide a clearer illustration, examples from model 1 and model 2 are shown below.

Starting with model 1

Two different experimental configurations correlated with model 1. At 19 000 RPM the droplet size for Pluronic F127 shows the highest value in the beginning and then a sharp decline, between point 2-5 it varies slightly but remains relatively at a similar level. This behaviour can be seen in figure 26 with $d(0.9)$ on y axis and surfactant concentration on x axis. The first dot in the graph represents 0.2x CMC, number 2 represents 0.5x CMC and so on. The third dot at 443 mg/L is the estimated CMC value (1x CMC). This trend is similar to model 1, where the surface tension decreases and then reaches a level where it stays the same.

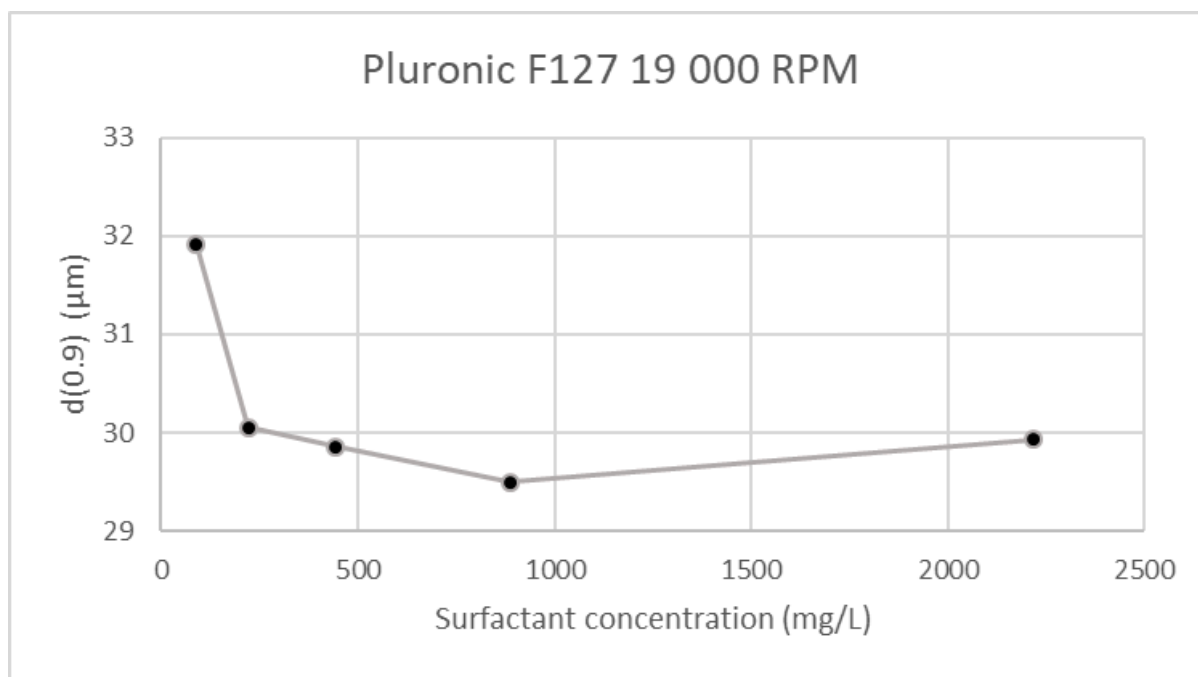


Figure 26, effect of Pluronic F127 on particle size $d(0.9)$ at 19 000 RPM, gives a steep decline and then holds nearly constant, similar to model 1.

The other condition that correlated with model 1 was Polysorbate at 16 000 RPM which can be seen in figure 27 with $d(0.9)$ on y axis and surfactant concentration on x axis. It exhibited a similar look as the one described above with the initial decline followed by a fairly constant value. The approximated CMC value is indicated by the third data point in this graph as well.

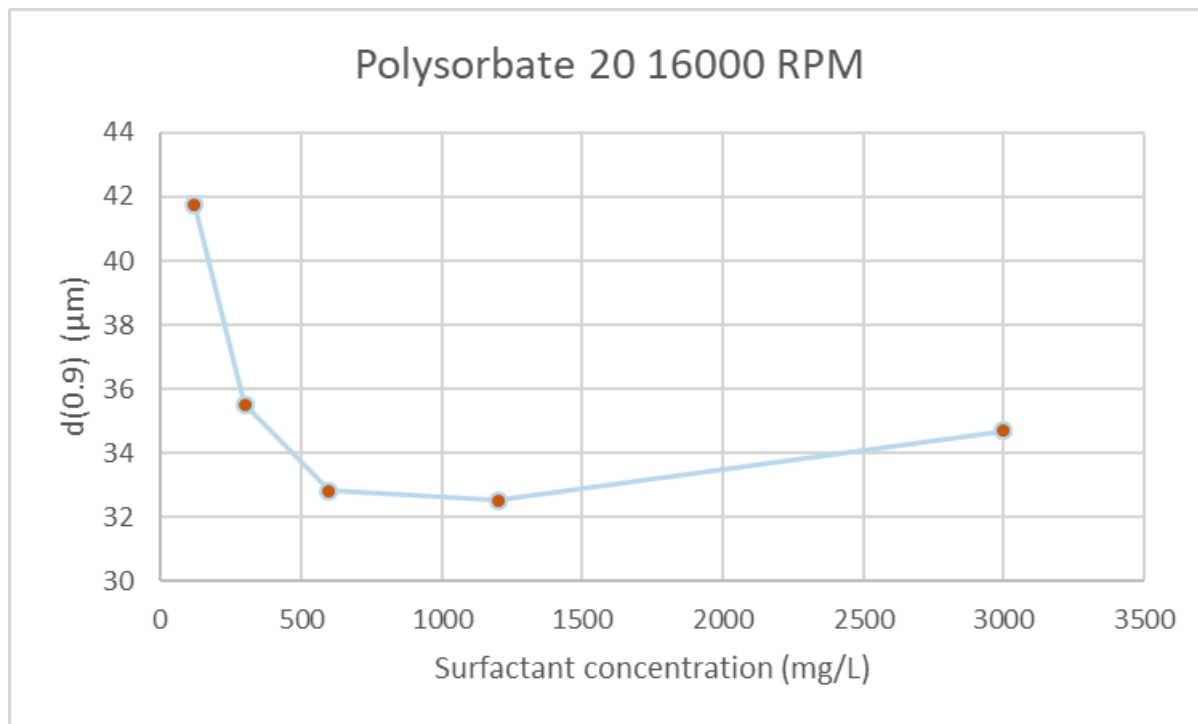


Figure 27, effect of Polysorbate 20 on particle size $d(0.9)$ at 16 000 RPM, showing a steep decline and then holds nearly constant, similar to model 1.

Continuing with model 2

For model 2, no correlating plots were observed for any of the emulsifiers at any of the rotational speeds.

Neither model 1 or 2

From table 9 it is evident that the vast majority of the plotted values for $d(0.9)$ did not align closely to either model 1 or model 2. The overall pattern showed a big variation and most experimental results can not be fully explained by either model and therefore is not representative for all values, but one example is shown below in figure 28.

The reason for no corresponding plot for model 2 could be that the model was based on experiments in the article from Padron done at 3000 and 7000 RPM. Meanwhile the experiments performed in this report were at higher rotor speeds, with the lowest speed at 10 000 RPM, surpassing the highest rotor speed mentioned in the study by Padron above. Furthermore the experiment in this report used a different type of oil.

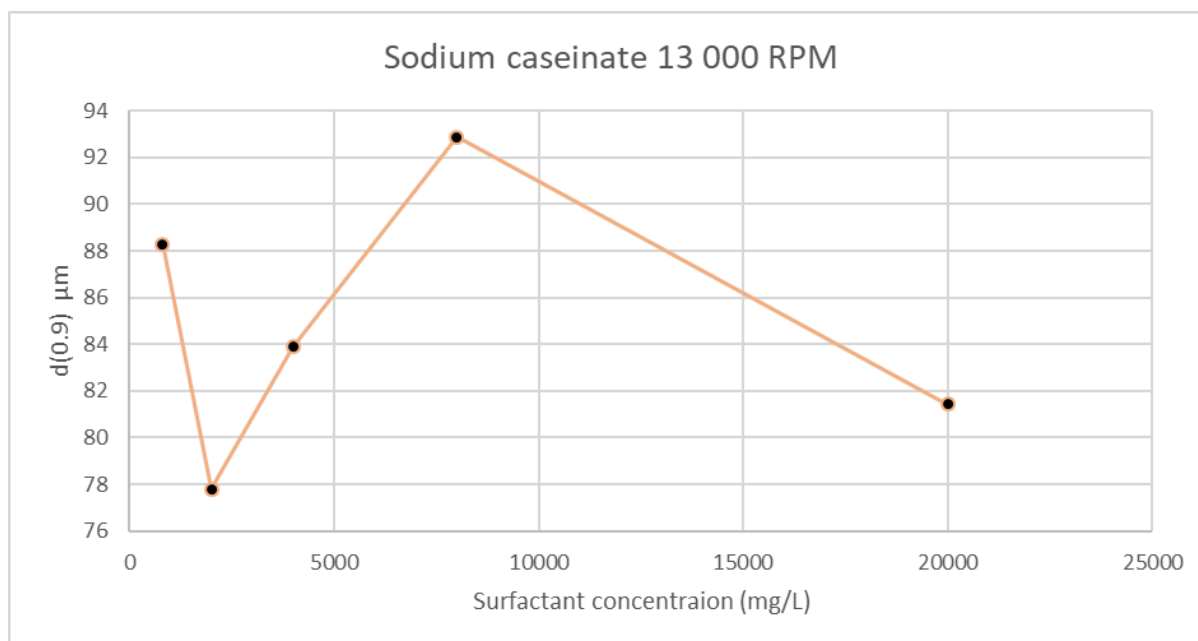


Figure 28, effect of sodium caseinate on particle size $d(0.9)$ at 13 000 RPM. The illustration is not similar to model 1 or model 2.

4.5 Sources of errors

The Silentcrusher mixer has an adjustable handle with increments of 1000 RPM between each adjustment, it was sometimes necessary to readjust the speed to find the right rotational speed, however this lasted for a shorter amount of time when it occurred.

The instrument Mastersizer 2000, have optimal ranges of laser intensity and when the instrument has been used, the laser intensity often decreases, which in turn could lead to inaccurate measurements. However a test experiment with 70 % and just above 75 % laser intensity was tested for a sample of sodium caseinate and resulted in $d(0.9)$ values of 32.0 and 32.3 μm , a difference that is minimal.

The CMC values for Pluronic F127 and Polysorbate 20 were estimated based on sources found on the internet, which showed some variation. These values may be higher or lower than reported.

The emulsifiers were from the Department of Process and Life Science Engineering at Lund university, the expiration date was not visible on all products.

4.6 Future outlook

The literature review indicates that previous experiments on droplet size and different emulsifiers were mainly conducted at significantly lower rotor speeds than those used in this project. This is despite the fact that the available equipment is capable of operating at higher rotor speeds. This discrepancy suggests an opportunity for further research to explore the effects of high rotor speeds on droplet formation and emulsification efficiency and also test with more emulsifiers to see if any conclusions can be drawn from it.

5. Conclusion

The study showed that higher rotor speeds in the same concentration resulted in smaller $d(0.9)$ values, with an exception, which is Pluronic F127 at higher speeds.

Pluronic F127 falls below the theoretical value of $k = -0.6$ derived from the logarithmic relationship between D_{max} and the Weber number. In contrast Polysorbate 20 and sodium caseinate align with the theoretical value.

The exceptions noted in the experiment suggest that the relationship between emulsifier concentration, high shear mixing and droplet size is more complex than theory alone predicts. Further research is needed to better understand the values that didn't align with theory to investigate if there are limitations to the theoretical models or that the results that could not be explained were from experimental factors.

References

- [1] Mishra P., van Dijk M., Wintermeyer C., Sabater C., Bot A., Verkleij T., et al. At-line and inline prediction of droplet size in mayonnaise with near-infrared spectroscopy. *Infrared Physics & Technology*. Volume 123: (2022) <https://doi.org/10.1016/j.infrared.2022.104155> (Accessed 19 January 2025)
- [2] McClements, D.J. Emulsion Formation. Food Emulsions: Principles, Practice, and Techniques. Third edition. CRC Press, Taylor & Francis group, London. p.3
- [3] Dickinson, E. An introduction to Food Colloids. Oxford university press. 1992. p.31
- [4] Gonçalves dos Santos, R. Fundamentals of Surface Thermodynamics: Phase Behavior and Its Related Properties. *Springer International Publishing AG*. (2024). DOI: 10.1007/978-3-031-52466-0.
- [5] Barnes, G. Gentle, I. Interfacial science an introduction. Second edition. Oxford university press. 2011. p.5
- [6] Binyaminov, H., Abdullah, F., Zargargazadeh, L., & Elliott, J.A.W. Thermodynamic investigation of droplet–droplet and bubble–droplet equilibrium in an immiscible medium. *The Journal of Physical Chemistry B*, 125(30). (2021) <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c02877> (Accessed 27 december 2024).
- [7] Dickinson, E. An introduction to Food Colloids. Oxford university press. 1992. p.1
- [8] Bylund, G., *Dairy processing handbook*. 2015. Tetra Pak Processing Systems AB. Chapter 2.
- [9] Barnes, G. Gentle, I. Interfacial science an introduction. Second edition. Oxford university press. 2011. p.70
- [10] Hörner, D. Emulsifiers. Chapter 14. *Encyclopedia of Lubricants and Lubrication*. (Springer, 2014). p.482-486 https://doi.org/10.1007/978-3-642-22647-2_234
- [11] Ahmed, Eisha. 2020. “Breaking Down” Surfactants: What They Are, How They Work, and Their Role in the Pandemic.’ *Dispersa*, September 25, 2020. <https://www.dispersa.ca/blog/what-are-surfactants-and-how-do-they-work/>. (With permission from Dispersa)

- [12] Dickinson, E. An introduction to Food Colloids. Oxford university press. 1992. p.44
- [13] Barnes, G. Gentle, I. Interfacial science an introduction. Second edition. Oxford university press. 2011. p.76-77
- [14] Esmaeili, H., Mousavi, S. M., Hashemi, S. A., Lai, C. W., Chiang, W. H., & Bahrani, S. (2021). Application of biosurfactants in the removal of oil from emulsion. *In Green Sustainable Process for Chemical and Environmental Engineering and Science: Biosurfactants for the Bioremediation of Polluted Environments* pages 107-127. <https://doi.org/10.1016/B978-0-12-822696-4.00008-5>
- [15] Padron, Gustavo A., Calabrese, Richard V. Effects of surfactants and interfacial rheology on equilibrium drop size in turbulent liquid-liquid dispersions. *Chemical Engineering Research and Design*. Volume 195. (2023). Pages 447-465. <https://doi.org/10.1016/j.cherd.2023.05.046>.
- [16] Rapp, B. E. *Microfluidics: Modeling, Mechanics, and Mathematics*. Elsevier. Chapter 9. (Episode 9.9.12) (2017).
- [17] Ransmark, E., Svensson, B., Svedberg, I., Göransson, A., & Skoglund, T. Measurement of homogenisation efficiency of milk by laser diffraction and centrifugation. (2015). *International Dairy Journal*, 96, p.93–97.
- [18] Dispermat. DISPERMAT® mixers
High shear mixers / Rotor-Stator dispersers. <https://www.dispermat.com/mixers.html>
(Accessed 6 feb 2025)
- [19] Vikash, V., & Kumar, V. Design and development of high shear mixers: Fundamentals, applications and recent progress. *Chemical Engineering Science*, 232. (2021). <https://doi.org/10.1016/j.ces.2020.116296>
- [20] Silverson Machines. How the Silverson Batch Mixer works [Video]. YouTube. Retrieved February 14, 2025, from <https://www.youtube.com>
- [21] Khaliq, N. U., Lee, J., Kim, S., Sung, D., & Kim, H. Pluronic F-68 and F-127 based nanomedicines for advancing combination cancer therapy. *Pharmaceutics*, 15(8), 2102. (2023): p.4 <https://doi.org/10.3390/pharmaceutics15082102>
- [22] National Center for Biotechnology Information (NCBI). Polysorbate 20. PubChem Compound Summary. From <https://pubchem.ncbi.nlm.nih.gov/compound/Polysorbate-20>
(Accessed 9 December 2024)

- [23] Sigma-Aldrich. Product 137172: Polysorbate 20. (Accessed 8 February 8 2025), from <https://www.sigmaaldrich.com/SE/en/product/mm/137172>
- [24] Food and Agriculture Organization (FAO). Sodium Caseinate. https://www.fao.org/fileadmin/user_upload/jecfa_additives/docs/Monograph1/Additive-398.pdf (Accessed: 27 December 2024).
- [25] Lucey, J. A., Srinivasan, M., Singh, H., & Munro, P. A. *Characterization of commercial and experimental sodium caseinates by multiangle laser light scattering and size-exclusion chromatography*. ACS Publications. (2000). 10.1021/jf990769z
- [26] Bohorquez, M., Koch, C., Trygstad, T., & Pandit, N. A study of the temperature-dependent micellization of Pluronic F127. *Journal of Colloid and Interface Science*, volume 216 number 1, 34–40. (1999). <https://doi.org/10.1006/jcis.1999.6273>
- [27] Sigma-Aldrich. Product 137172: Polysorbate 20. (Accessed February 13, 2025) <https://www.sigmaaldrich.com/SE/en/product/mm/137172>
- [28] Liu, J., Sun, C., Lun, Z., Li, Y., Tang, X., Zhang, Q., & Yang, P. Study on the kinetics of formation process of emulsion of heavy oil and its functional group components. *Scientific Reports*, 14, Article 8916. (2024). <https://doi.org/10.1038/s41598-024-59637-9>
- [29] Serieye, S., Moitzi, C., Salentinig, S., Sagalowicz, L., Leser, M.E., and Glatter, O. Direct and indirect thermal transitions from hexosomes to emulsified micro-emulsions in oil-loaded monoglyceride-based particles. *Journal of Colloid and Interface Science*, (2017), 496, pages 26-34. <https://doi.org/10.1016/j.jcis.2017.01.059>
- [30] McClements, D.J. *Emulsion Formation. Food Emulsions: Principles, Practice, and Techniques*. Third edition. CRC Press, Taylor & Francis group, London. p.281