Characterization of Stable Paraffin Emulsions for Use as Phase Change Slurry in Cool Thermal Energy Storage

By

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Abstract

The vast increase in demand in recent years and the predicted future growth in demand for cooling in developing and developed markets is jeopardizing the future energy supply stability. Thermal energy storage technology has the potential to help stabilize cooling demand by leveling peak load demand. Paraffin Phase Change Slurries have been studied as solutions to providing thermal energy storage for cooling demand. Phase Change Slurries are of great interest due to their ability to capitalize on the latent heat storage over a small temperature range.

It is the purpose of this thesis to develop a pragmatic strategy for the selection process of suitable emulsifiers for applications in paraffin/water emulsions for cooling application in a temperature range of 0-30°C. Paraffin in water emulsions consist of small paraffin droplets suspended in water carrier fluid. The emulsifier acts as a stabilizer for the water/oil interface. This research seeks to study the impacts of emulsifiers on droplet size /dispersion and thermal properties.

This research recommends the use of and emulsifier mixture that has an HLB value of 12, prepared at a temperature of 80°C, using a mixing speed of 11,000 rpm for 3 min., with a 1.5 wt. % emulsifier concentration and 30 wt. % paraffin concentration in order to form a kinetically stable emulsion. This emulsion exhibits monodispersed droplet distributions and droplets sizes ranging from 1-10 μm, while also having limited degrees of subcooling, as defined by less than 5K. This emulsion also exhibited a steady viscosity of less than 10 mPas during 20 cooling/heating cycles and a semi-steady viscosity of less than 36 mPas during 60 cooling/heating cycles.

<p style="text-align:center">Biographical Sketch</p>

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Nomenclature

Symbols

ΔA	interfacial area, nm^2
Ca	capillary number
Cp	specific heat. Kg/kg
d	diameter, nm
ΔG	Gibs free energy, J
m	mass, kg
M^+	organic or inorganic cation
P	pressure, N/m^2
Q	heat, kJ
r	radius, nm
R-	hydrophobic group
ΔS	entropy, J/K
T	temperature, K
X^-	anion

Greek Symbols

α	power law constant (varies)
σ	surface or interfacial tension, N/m
τ	stress, N/m^2
η	viscosity, $N{\cdot}s/m^2$
ρ	density, kg/m^3
ϕ	volume fraction

Subscripts

c	continuous phase
conf	configerational
cr	critical
d	dispersed phase
def	deformation
f	final
form	formation

Subscripts (continued)

h	hydrophile
hom	homogenizer
i	initial
L	Laplace
max	maximum
sh	shear

Abbreviation

BRA	Brazil
CPA	Centrally-Planned Asia
CTES	Cool Thermal Energy Storage
ES	Energy Storage
EO	Ethylene Oxide
IEA	International Energy Agency
IND	India
INDO	Indonesia
LAM	Latin America
MEA	Middle East
MEX	Mexico
NAF	North Africa
o/w	oil-in-water
PCM	Phase Change Material
PCS	Phase Change Slurry
RT	Rubitherm Technologies
SAS-PAS	Other Asia
SSA	Sub-Sahara Africa
TES	Thermal Energy Storage
UV	ultraviolet
w/o	water-in-oil

Units

C	Celsius
K	Kelvin

hrs	hours
nm	nanometer, 10^{-9}
μm	micrometer, 10^{-6}
s	seconds

1. Introduction

Scientist and economists have linked growth in world energy demand and global and personal economical growth. Despite the recession that began in 2008, energy demand has continued to grow, especially in developing countries. However, the economic growth distribution and energy growth distribution have been disproportionately in favor of developing countries. Throughout the recession developing countries' economies and energy demand has been more robust, whereas developed countries have seen slower economic recovery and energy demand growth [IEO11].

In 2010, global energy consumption was estimated to be 12,800 Mtoe[1] or 148 billion[2] kWh[3], a 5.5% increase from 2009 [Ener11]. The United States Energy Information Administration predicts that energy demand could increase to 181 billion kWh by 2020 and 211 billion kWh by 2030 [IEO11]. Of this global energy demand the International Energy Agency (IEA) estimates that one-third is from building energy demand. Space heating and cooling and water heating are estimated to account for roughly half of the energy demand from buildings [IEA11]. This translates into more than 2,000 Mtoe or 23 billion kWh per year being used for space heating and cooling. Cooling demand is an especially important topic in connection with grid staiblity due to the high energy demand of current cooling systems and the disproportionate effects cooling units have on peak energy demand [McNe07]. Energy demand from cooling units contribute to daily and seasonal energy peaks. Energy demand for cooling has increased in recent years due to several factors, which include, global warming, use of light building materials, and a global rise in indoor comfort expectations.

1.1. Developed World

In the developed world the cooling industry can be divided into two major markets, the American and the European market. The American market has seen only slight growth in the last two decades from 68%-87% of households owning a cooling unit [RCES11]. Since the market is nearing saturation, growth in the American market is expected to be slow in the future. However, regional usage varies greatly from almost 67% of household using units daily during warm

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[1] Mtoe stands for million metric tons of oil equivalent.
[2] billion refers to the long scale used in Europe and is equivalent to 10^{12}, in the American short scale version this would be called trillion
[3] kWh stands for kilowatt-hour, 1kWh= 3600 kilojoules=3412.3 Btu

months in the south to only 35% in the northeast [RCES11]. However, as climate change effects increases and warm periods intensify, there is a potential for drastic increases in energy consumption from the cooling sector due to increased usage in more temperate climates like the northeast and higher energy consmuption from southern regions due to increased degrees of cooling. The European market, unlike its American counterpart has recently seen significant growth. Even in the more moderate temperature areas like Central and Northern Europe, cooling demand has seen significant growth. Much of this demand is due to lightweight building materials and increased indoor comfort level expectations [Artm06]. In a study on increased air conditioning usage in Europe in 2005, Henderson concluded that even with an increase in households owning cooling units, overall electrical consumption would only modestly increase. However, Henderson also concluded that peak electrical demand, especially in mediterranean countries would be a great cause for concern. This study also concluded that there is a correlation between cooling degree days and electricity consumption from air conditioning. This means that energy demand will rise as climate change impacts increase and days where cooling is needed increase [Hend05]. Energy demand by the cooling sector in temperate European coutnries like Switzerland, Germany, France, ect., could potentially increase by 13%, with 7.5% of this due to climate change temperature increases [Aebi07]. In Southern European countries, with warmer climates, the increase in summer peak cooling demand is so great that new electricity generation plants are being considered just to cover this peak demand [Papa03].

1.2. Developing World

In the developing world, an increase in air conditioning usage could have an even larger impact on global energy demand and peak demand load. There are three main reasons that developing nations are of such high interest to future energy stability. First, the developing world consists of countries that are located in warmer climates where these is a large cooling degree days demand (e.g. India, Brazil, Indonesia, Mexico) [McNe07 & Siva09]. Secondly, many of these countries have in recent years shown a tendency for resiliance to economic recessions. Unlike their developed nation counterparts many of these countries have seen improvements in their populations average personal incomes. This has lead to a tendency for more electrical appliance consumption and usage. A previous study conducted by McNeil and Letschert suggests that as incomes rise in developing countries, there is a direct increase in rate of appliances owned, including cooling units, and electricity consumption. Developing countries with a high

electrification rate and a high urban population tend to show the strongest correlation between rising incomes and increased appliance ownership and energy demand [McNe05]. In India air conditioning purchases are growing at a average rate of 20% per year. McNeil and Letschert's
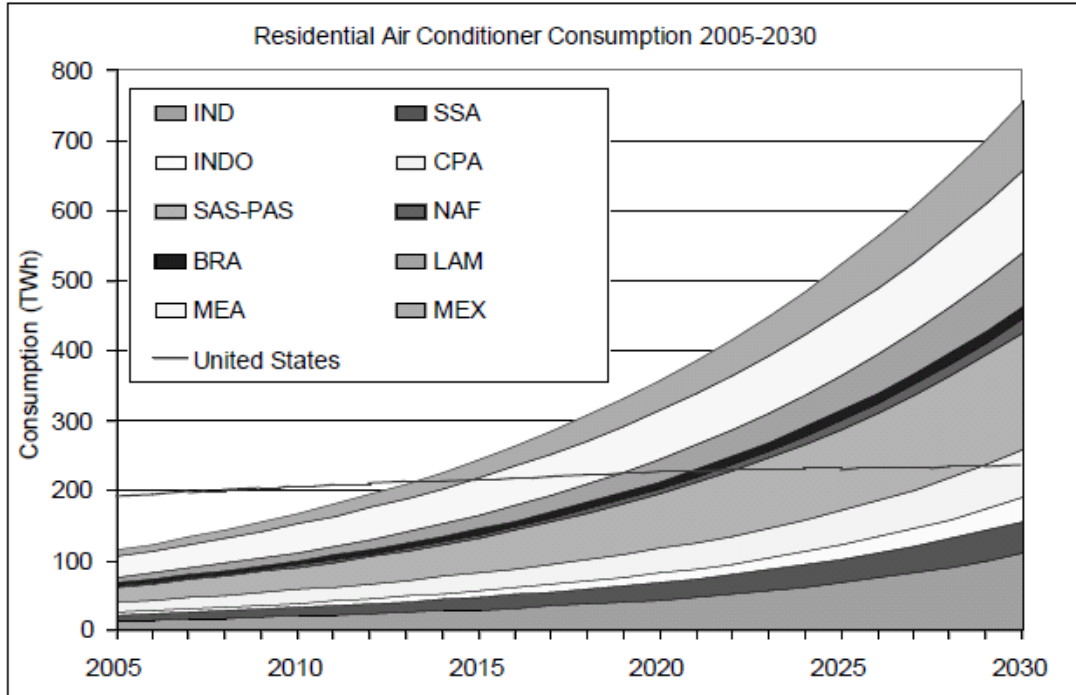
Figure 1: Future Energy demand from cooling in developing countries (IND-India, SSA-Sub-Sahara Africa, INDO-Indonesia, CPA-Centrally-Planned Asia, SAS-PAS-Other Asia, NAF-North Africa, BRA-Brazil, LAM-Latin America, MEA-Middle East, MEX-Mexico) [McNe07]

model of air conditioning growth in developing countries and increase energy demand can be found in figure 1[McNe07]. The market for cooling is rapidly expanding in developing countries and with large portions of the world's population residing in these countries this could put extreme pressure on energy demand. Of the fifty largest metropolitans in the world, thirty-eight of them are located in developing countries [Siva09]. Third, the developing world's electricity markets are already unstable and experienceing chronic power shortages. If there are massive increases in peak demand due to cooling this can only worsen. An increase in chronic power shortages has the potential to cause significant economic and social impacts within developing nations.

Cooling demand, whether in the developed or developing world, is a growing concerns in respect to future energy systems. Thermal energy storage (TES) technology has the potential to help create stablility for energy systems. TES shifts peak load demand by providing off-peak cooling production/storage for use during daytime peak-demand. A variety of different storage materials

have previously been investigated. Convential TES systems use water as a storage medium because of its relatively high sensible heat capacity over a small temperature range. Research indicates that storage capacity can be increased by capitalizing on the latent heat storage of Phase Change Materials (PCMs). In a PCM storage system, the energy is stored during a phase change e.g. solid-liquid transition. PCM systems, and like water offer a high storage capacity over a relatively small temperature range. However, there are two main disadvantages of PCM systems. First, for the heat transfer between the PCM and the heat/cold source, PCM systems require an additional transfer fluid due to their phase change. Secondly, most PCMs have low thermal conductivity. Due to these disadvantages, Phase Change Slurries (PCSs) have been investigated. PCSs consist of two major components, a PCM as the dispered phase and a carrier fluid, usually water, as the continuous phase. PCS systems can be continually pumped in a charging and discharging cycle without needing an additional fluid. PCSs also have a high thermal conductivity because of the large surface area to volume ratio of the dispersed phase. Not only are PCS systems able to avoid the disadvantage presented by PCM systems, but they also increase storage capacity by using the sensible heat capacity of the carrier fluid and the latent heat capacity of the disperesed phase. PCS systems are an excellent choice for cool thermal energy storage (CTES) because of their increase storage capacity and ability to avoid the disadvantages of PCMs.

A variety of materials have been studied for the dispersed phase of a PCS, including ice slurries, hydrate slurries (organic or non-organic solutoins), PCM microcapsule slurries, PCM emulsion slurries, diphasic slurries of carbonic anhydride, and shape-stabilized laten heat material [Inab03]. This research focuses on PCM emulsions, with the objective of developing and characterizing kinetically and mechanical-thermally stable paraffin/water emulsions that exhibit small subcooling effects within a temperature range of 0-30 ℃. The goal of this research is to characterize the effects of temperature, concentration, preparation method, and emulsifier chemical properties on the kinetic and mechanical-thermal stability of emulsions.

2. State of the Art

2.1. Energy Storage

Due to recent developments in technology and the field of material science, energy storage has been developed to a point where it could significantly impact the future of the energy supply chain. Energy storage (ES) is especially important in energy systems that rely on intermittent supplies like solar and other renewable energy sources. ES systems are also important because of
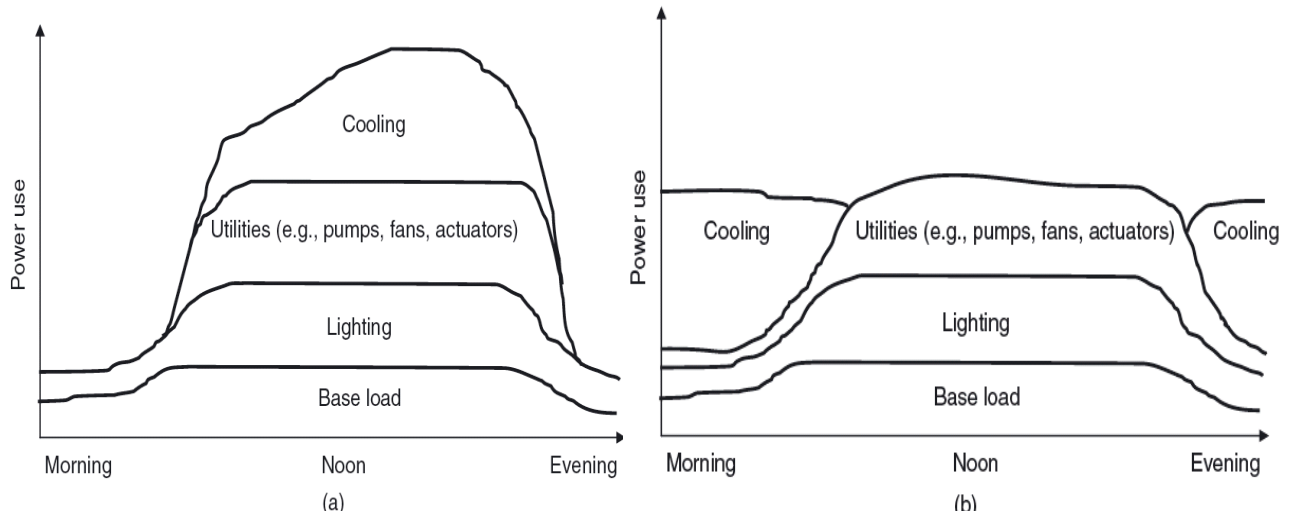
Figure 3: Peak load energy demand (a) without CTES (b) with CTES [Dinc11, pg. 484]

their potential to decrease initial investments costs and increase efficiency for energy supply
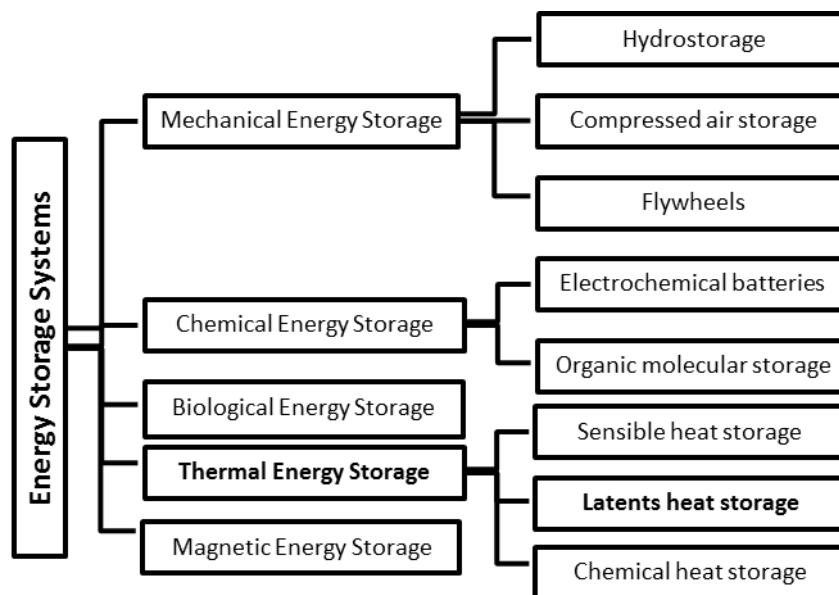
Figure 2: Classification of energy storage [Gil10]

plants. As shown in figure 3 power demand is not steady, but fluctuating with time of day [Dinc11, pg. 484]. This same peak demand fluctuation occurs seasonally, with demand being greater during warm months due to cooling. Power generation systems must be built to meet the peak demand, and at non-peak daily and seasonal times these systems operate inefficinelty and below their full capacity. With a ES system a smaller generation capacity can be built and at non-peak times, the energy can be stored for use during peak intervals. There are four main types of ES systems as shown in figure 2 [Gil10]. Even with energy efficiency losses due to conversion, load management techniques like ES systems can sometimes reduce the intial investment costs of power generation by allowing smaller capacity generation plants to be built. ES systems can also be introduced at the source of consumption in residential or commercial buildings. ES systems can be used as a load management technique to reduce the space-heating or cooling demand of a building [Dinc11].

2.2 Thermal Energy Storage

Thermal energy storage is an important component of ES technology because the majority of global energy produced and transferred is from heat [Dinc11]. TES functions by reversibly changing the physical properties (temperature or phase) of a material. These reversible processes
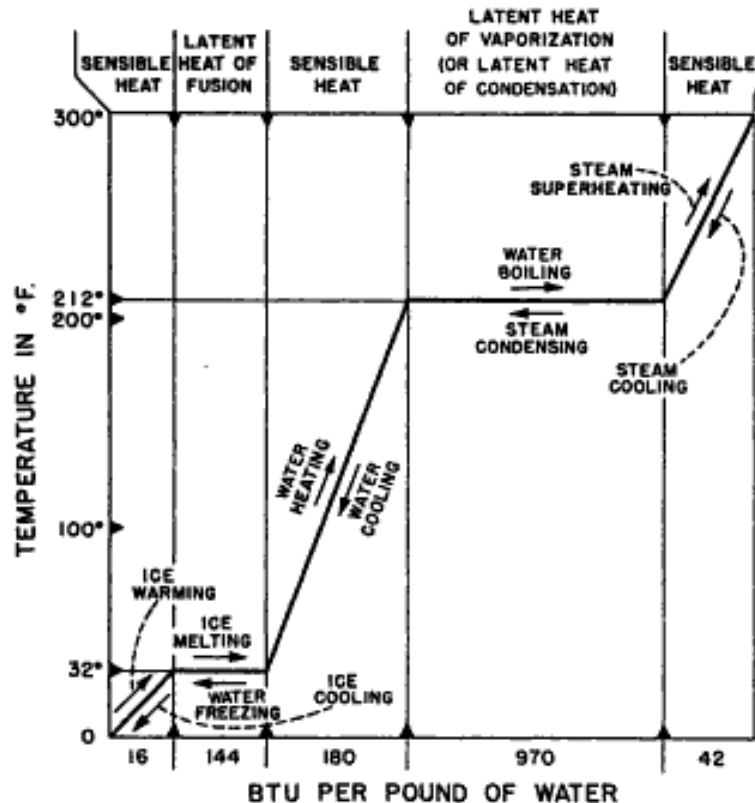
Figure 4: Latent and sensible heat energy storage potential of water [Blan85]

include heating, cooling, solidifying, melting, and vaporizing [Dinc11].

As previously shown in figure 2 there are three types of TES sensible heat, latent heat and chemical energy. Sensible heat storage functions by raising or lowering the temperature of a material; the effectiveness depends on the specific heat of the storage material. Storage/release by phase change is known as latent heat storage [Dinc11]. As can be observed in Figure 4, higher amounts of energy can be stored or released over a shorter temperature range with latent heat transitions rather than during senesible heat transitions [Shar04 & Blan85].

Cooling thermal energy storage (CTES) is the application of TES technology for cooling purposes. An example of CTES is the storage of ice created during evening (off-peak hours), then melted during the daytime peak demand to be used for cooling [Hasn98]. This nighttime generation of cooling is more efficient due to lower ambient temperatures [Zhan11]. This higher efficiency combined with cheaper off-peak electricity production makes CTES systems economically attractive. By using CTES systems energy peak load cooling demand is shifted from daytime to nighttime. As pictured in figure 5, there are three main strategies for accomplishing this, full-storage, partial storage load-leveling and partial storage load limiting [Dinc11, pg. 143]. Full-storage is designed to fully decouple the generation and the peak load. In partial-storage, the CTES system is designed to level the load and meet part of the peak-period cooling demand, while the other part is met from a normal chiller. In load leveling, the chiller is
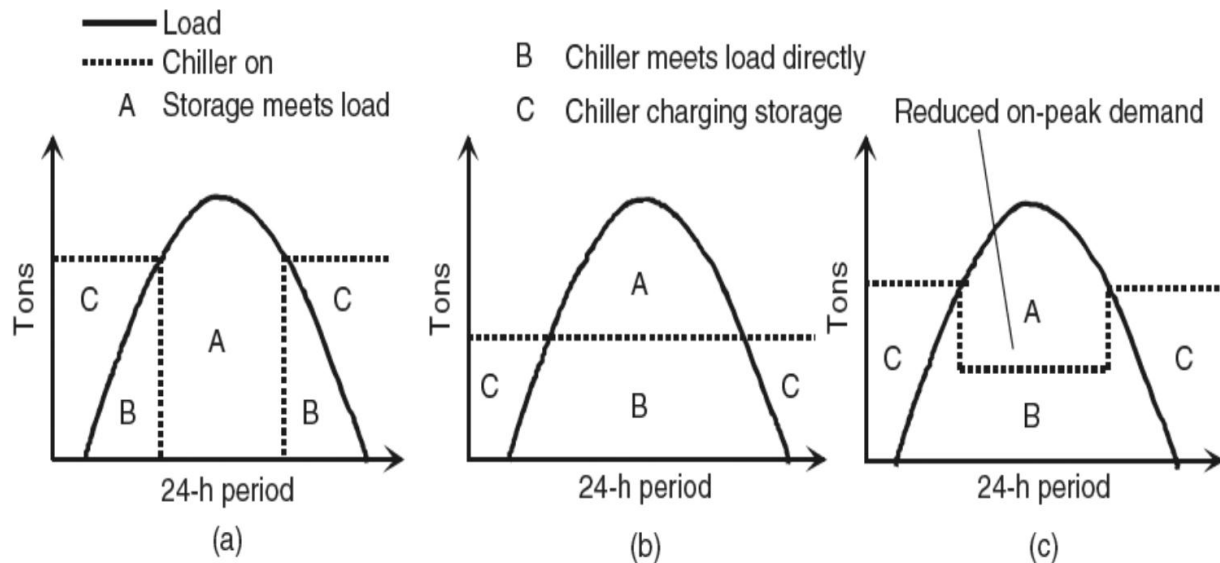
Figure 5: CTES system types (a) full-storage (b) partial storage load leveling (c) partial storage demand-limiting [Dinc11, pg. 143]

sized to meet full capacity for 24 hrs on the hottest days. In the demand-limiting system, the chiller is designed to run at a reduced capacity during peak hours to reduce a facilities peak demand energy costs. Demand-limiting systems have a higher equipment cost than for load-leveling systems, but lower than for a full-storage system [Dinc11, pg. 1143]. When using water as a CTES medium, only the sensible heat can be used for storage. Therefore, phase change materials (PCMs) have been investigated in order to take advanatage of the greater storage capapcity of latent heat storage.

2.3 Thermal Energy Storage Media
Sensible Energy Storage Materials

Traditional sensible energy storage materials include fluids like water, inorganic molten salts, and oils, and solids such as rocks, pebbles and refractory [Atae06]. Materials are selected based on the temperature level of the application. Water is usually used for temperatures below 100°C, while refractory bricks are used for temperatures around 1,000°C. Sensible heat storage systems have the disadvantage of being larger in size than latent heat storage systems; however, they do have the advantage of being simpler systems and being capable of storing energy over a larger range [Atae06]. The size of a sensible heat system depends on the temperature range. Sensible heat storage capacity is directly linked to the heat capacity of the fluid/solid being used and the volume, as shown in equation 1[Shar09].

$$Q = \int_{T_i}^{T_f} mC_P \Delta T = mC_P(T_f - T_i)$$

Equation 1: Sensible heat storage capacity [Shar09]

Water is the most common type of media for cold storage/transfer because of its low cost, environmentally friendliness, and high specific heat capacity.

Phase Change Materials

Classification

Latent heat storage is used because of its high energy storage density with a small temperature swing. PCMs can be categorized as organic, inorganic, or eutectic materials that store energy mainly during a phase change process, usually a solid-liquid transition. Figure 6 details the different material categories of solid-liquid transition PCMs [Zalb03 & Zhou12]. All PCMs are selected based on thermodynamic, kinetic, chemical and economical properties. PCMs should
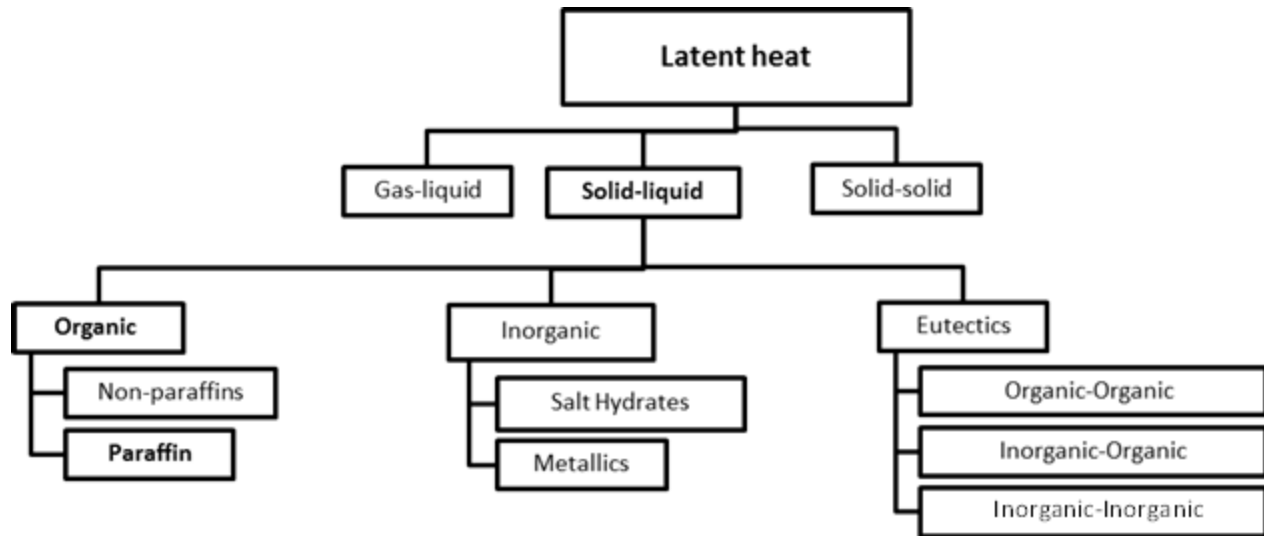
Figure 6: Thermal energy storage material classification [Zalb03 & Zhou 12]

exhibit the following thermodynamic properties: melting temperature within set range, high thermal conductivity, high heat of fusion per unit volume, high specific heat, high density, small volume changes during phase transitions, and congruent melting. PCMs are expected to have the following kinetic properties: high nucleation rate and high rate of crystal growth. When selecting a PCM, materials should be non-corrosive, non-toxic, non-flammable, chemically stable, have a reversible freezing/melting cycle, and not degrade after repeated cooling/heating cycles. They should also be low cost and readily available materials [Abha83]. Initially inorganic PCMs were studied in great detail due to their low cost, availability, high heat of fusion and high thermal conductivity. However, inorganic PCMs (e.g. salt hydrates) tend to melt incongruently so that repeated cooling and heating cycle result in segregation and a drift in the transition zone. In order to avoid these problems associated with inorganic PCMs, organic PCMs have been investigated [Khud04].

Inorganics

Inorganic PCMs can be further classified into salt hydrates and metals, as seen in figure 6. Salt hydrates are alloys of inorganic salts and water. They are typically used for their high heat of fusion and high thermal conductivity. They also have small volume changes when transitioning from solid to liquid form and are typically inexpensive enough to be usable in thermal energy storage applications. However, they tend to have poor nucleating properties and thus exhibit subcooling, or cooling below the melting temperature without crystallization and many inorganics are corrosive. They also tend to melt incongruently or semi-congruently, which eventually leads to separation and an irreversible cooling/heating of the salt. Table 1 lists the full

advantages and disadvantages of using inorganic PCMs. There are very few salt hydrates that

	Advantages	Disadvantages
Inorganic PCMs	1. High latent heat values 2. Non-flammable 3. Low-cost and readily available	1. Corrosiveness 2. Instability 3. Improper re-solidification 4. Supercooling

Table 1: Advantages and Disadvantages of Inorganic PCMS [Zalb 03]

melt within the range of 0-30ºC, which is required for CTES. Salt hydrides are better suited for heating thermal energy storage [Shar09]. Metals on the other hand have not been seriously studied due to their low heat of fusion per unit weight. Although metals have a high heat of fusion they are extremely heavy and thus present some unusual engineering problems. There are also very few metals suited for CTES due to their tendency to have higher melting temperatures [Shar09].

Eutectics

Eutectics are composed of two or more PCMs that melt and freeze congruently [Shar09]. Eutectics can be classified into three categories: organic-organic, inorganic-organic, or inorganic-inorganic. There is little to no problem with segregation in concern with eutectics. Eutectics are also considered good PCMs because of their narrow melting temperature ranges and high volumetric thermal storage density [Abha83]. There is limited information on eutectic PCMs in literature due to lack of research focuses. Most research conducted on eutectic PCMs focuses on the thermo physical properties of eutectics [Bara03]. For application in CTES systems eutectic salts have been commercially used. Eutectic salts used in CTES are usually a combination of inorganic salts, water and other elements combined to form a mixture that freezes at a desired temperature [Dinc11].

Organics

There are two main branches of organic PCMs, non-paraffins and paraffins (alkane mixtures) [Zalb03]. The main advantages and disadvantages of using organic PCMs as storage media can be found in table 2 [Abha83]. Non-paraffins include fatty acids and other chemicals. Unlike the paraffin sub-group, non-paraffin materials have distinct individual properties. Non-paraffins are considered the largest category of materials for phase change storage and include alcohols, fatty acids, and glycols. One of the major drawbacks of non-paraffins is that many are considered flammable materials and cannot be exposed to excessively high heat, flames or oxidizing agents.

Fatty acids are chemically considered to be better suited than paraffins for energy storage due to

Table 2: Advantages and Disadvantages of Organic PCMs [Abha83]

	Advanatages	Disadvantages
Organic PCMs	1. Availability over large temperature range 2. High heat of fusion 3. Chemically stable 4. Recyclable 5. Compatability with other materials 6. Little to no supercooling	1. Low thermal conductivity 2. Relatively large volume change 3. Flammable

their lack of subcooling and generally higher heat of fusion values. However, they tend to be around 2-2.5 times more expensive than paraffins and mildly corrosive, thus limiting their commerciality [Shar09].

Paraffin PCMs are mostly alkanes or mixtures of alkanes. The melting point and heat of fusion increase with respect to increasing chain length, thus most paraffins used as PCMs range from 14-34 carbons in chain length [Shar09]. Due to cost considerations polymer blends are preferred. Paraffins with even numbered chain lengths are also preferred due to their higher heat of fusion and better suitability as PCMs. PCMs tend to have poor thermal conductivity and thus require a carrier fluid. Therefore, phase change slurries (PCSs) have been investigated.

Phase Change Slurries

PCSs consist of two main components, a dispersed phase consisting of a PCM and a carrier fluid [Huan10c]. PCSs are desirable for commercial applications because they are able to combine the latent heat storage of a PCM and the sensible heat storage of the carrier fluid (usually water) to produce a larger overall heat storage, while still remaining pump-able during phase transitions [Huan09b & Huan10a]. The introduction of a carrier fluid helps improve the poor thermal conductivity of pure PCMs. A PCS has a much larger surface area between the PCM and the carrier fluid and is thus able to increase the heat transfer. Desirable characteristics of PSCs can be categorized in the following way: thermophysical properties, rheological properties, manageability, ecological properties and economical properties. The following characteristics shown in table 3 are desirable PCS characteristics [Noer03 and Shar04 as cited in Huan09a].

Table 3: Desirable characteristics of PCS [Noer03 & Shar04 as cited in Huan09a]

Thermophysical properties
High heat capacity (>2 times that of water)
Melting temperature within operating range
Small temperature swing during phase transition, little subcooling
High heat transfer
Stable during storage
Stable during freezing/melting cycles (in pump system)
Rheology
Low pressure drop (pumpable)
Manageability
Non-corrosive to system
Applicable in current systems, compatible with current technology
Ecological properties
Non-toxic, inflammable or low flammability and non-explosive
Biodegradable, no or low hazard to water
Economic properties
Low cost
Available for large scale production

PCSs can be organized into the categories: ice slurries, hydrate slurries (organic or non-organic solutions), PCM microcapsule slurries, PCM microemulsion slurries, shape-stabilized latent heat material, and diphasic slurries of carbonic anhydride [Inab03]. Three of these categories are PCSs based on paraffin: PCM microcapsulated paraffin-in-water suspension, paraffin-in-water emulsions, and paraffin-in-water shape-stabilized suspensions [Huan09b]. This research focuses only on paraffin-in-water emulsion.

2.4. Emulsions
2.4.1. Classifications

Colloid dispersions are systems that consist of small particles between the ranges of 1-1000 nm [Moll01, pg. 1]. Simple colloid dispersions are two-phase systems consisting of a dispersed phase and a continuous phase. Figure 7 shows the different classifications of simple colloidal dispersions [Moll01, pg. 5]. Emulsions are liquid-liquid dispersions comprised of two "insoluble" liquids that are thermodynamically unstable [Moll01, pg. 62]. In emulsions, the two liquids are present in two different forms. One forms the continuous phase in which the other dispersed phase forms spherical droplets. There are two main types of emulsions that can be

Figure 7: Simple colloid dispersion classifications [Moll01, pg. 5]

formed: oil-in-water (o/w) or water-in-oil (w/o). In PCS paraffin emulsions for application in CTES o/w emulsions are ideal. Determining the type of emulsion produced is difficult to do with the naked eye. Therefore, to determine the type of emulsion created there are five simple tests: dilution, dye-solubility, filter paper ($CoCl_2$), fluorescence and conductivity. The dilution technique is based on the solubility of the continuous phase. O/w emulsions can be diluted with water and w/o emulsions can be diluted with oil. The dye-solubility test uses either a water-soluble or oil-soluble dye and then observes the emulsion. If a water-soluble dye is used then an o/w emulsion will have a dyed continuous phase and a w/o will have a dyed dispersed phase. The filter paper tests involve impregnating filter paper with $CoCl_2$. After the paper is dried it should be a blue tint, if dipped in an o/w emulsion the filter paper will change from blue to pink. The fluorescence test operates on the idea that under UV light some oils are fluorescent. When using this test o/w emulsions show spotty patterns, while w/o emulsions are fluorescent. The conductivity test requires a light bulb attached with wires to two electrodes. When the electrodes are dipped in the emulsion a o/w emulsion will cause the bulb to glow due to waters ability to be a good conductor, while a w/o emulsion will not glow due to oils low conductivity [Taue06].

2.4.2. Formulation

How Emulsions Are Formed

To form a stable emulsion, in addition to oil and water an emulsifier must be present. Due to the immiscibility of oil and water the emulsion is naturally unstable. However, if an emulsifier is added the emulsion can become kinetically stabilized. Emulsifiers improve stability by lowering the interfacial tension. The lower the interfacial tension is the less energy required to form the emulsion [Ever88, pg. 182]. Emulsifiers are structured to have a hydrophilic head that is attracted to the water phase and a hydrophobic or lipophilic tail attracted to the oil phase,
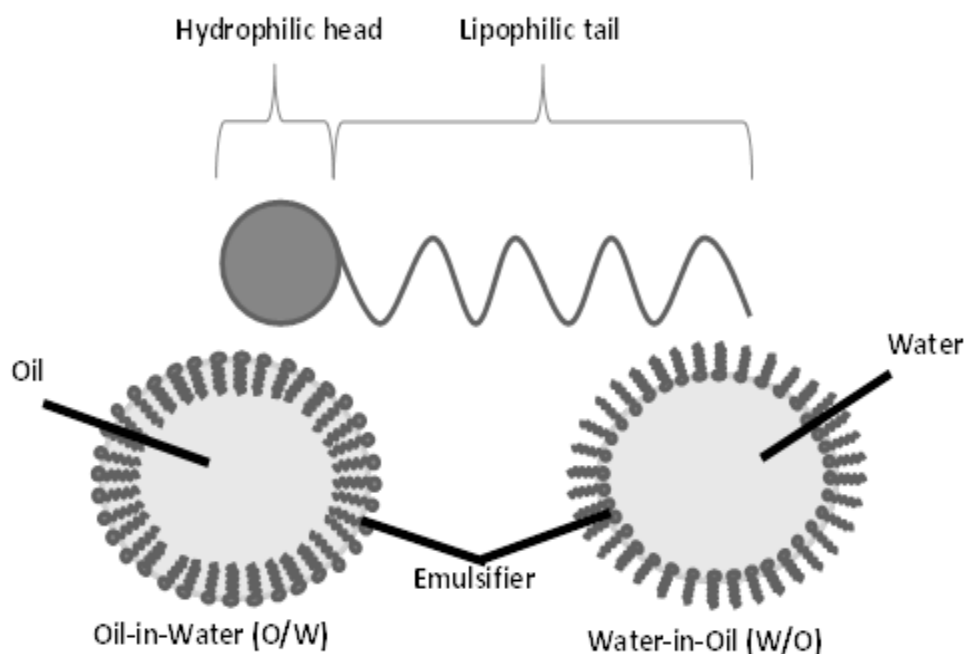
Figure 8: Structure of o/w and w/o emulsions

pictured at the top of figure 8. Emulsifiers act as a protective layer between the droplet phase and the continuous phase that prevents the droplet from being broken [Moll01, pg. 62]. The composition, type of emulsifier, and formulation process all help determine the type of emulsion produced. If the ratio of the two phase volumes is low, the phase that has the lowest volume is typically the dispersed phase, while the phase with the larger volume is the continuous phase. However, if the phases are roughly equal in volume, than other factors can influence which phase is the continuous and which phase is the dispersed phase [Ever88, pg. 182]. For CTES applications oil-in-water emulsions are desired.

The process of emulsification, or droplet break-up is governed by surface forces. The energy required to form droplets from a bulk liquid can be described by the free energy formation, illustrated in figure 9 and given by equation 2Equation 2, where ΔA is the increase in interfacial area, σ is the interfacial tension and ΔS_{conf} is the entropy increase when large numbers of droplets are formed [Isaa92, pg. 51-52].

$$\Delta G_{form} = \Delta A\sigma - T\Delta S_{conf}$$

Equation 2: Free energy of formation [Isaa92, pg. 51]

Normally $\Delta A\sigma \gg T\Delta S_{conf}$, and thus emulsification is non-spontaneous. However, the actual energy required for emulsification is much larger than $\Delta A\sigma$. This is because there is an additional energy requirement for creating a curved interface with a smaller radius. This additional energy
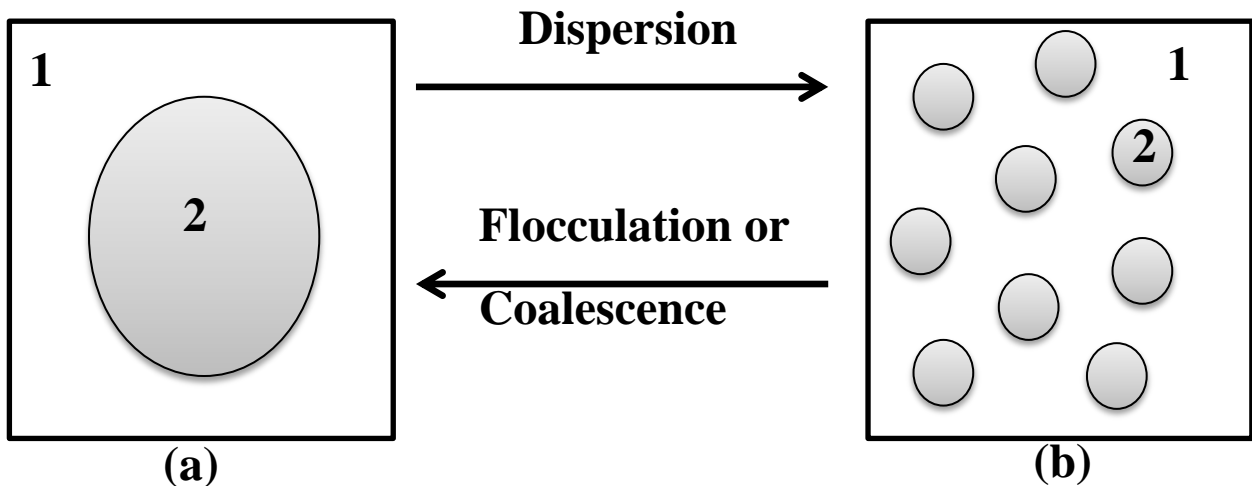
Figure 9: Emulsion formation through breakdown in (b) 1 is the continuous phase and 2 is the dispersed phase [Isaa92, pg. 52]

can be described by the Young-Laplace equation given in equation 3,

$$\Delta P = \sigma \left[\frac{1}{R}\right]$$

Equation 3: Young-Laplace equation [Isaa92, pg. 52]

where ΔP is the Laplace pressure difference and R is the principle radius of the curvature. However, in the presence of an emulsifier the emulsification energy can be significantly lowered. In emulsion preparation the phenomenon of droplet breakup plays a very important role. The energy provided for emulsion formation highly influences the droplet size. As shown in figure
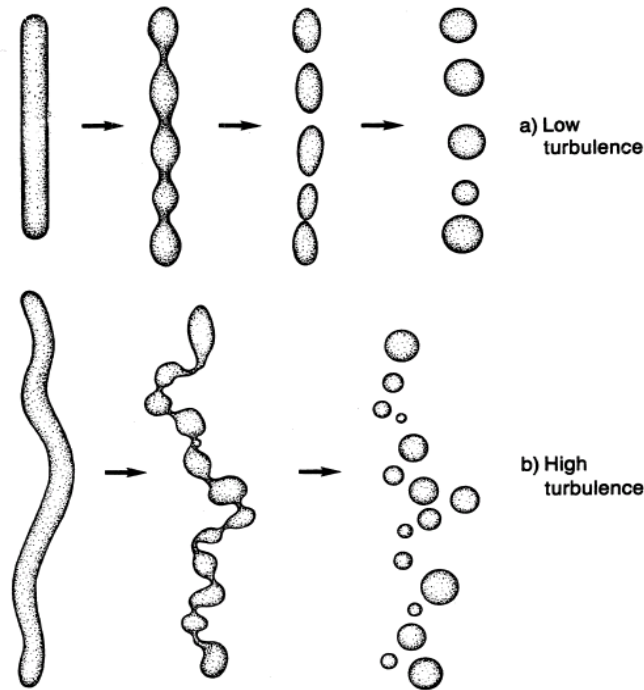
Figure 10: Droplet formation, influence of turbulence [Isaa92, pg. 53]

10, if a liquid is introduced into another liquid in which it is immiscible, it may form an unstable cylinder that breaks up into droplets. If the introduction rate is high enough to produce turbulence or if the liquid impinges against a surface, then smaller droplets are produced. The dispersion process is also influenced by the shear in the system, viscosity of the phases, interfacial energy, the pressure of solid particles, and dissolved substances [Isaa92, pg. 53]. Droplet breakup can be determined by the critical Weber number. The critical Weber number for turbulent flow is also dependent on the density and viscosity of the dispersed phase, as well as, the droplet diameter and interfacial tension. The Weber dimension is defined by equation 4, where τ_{def} is the deformation stress, r is the radius of the droplet, and σ

$$\mathbf{We} = \frac{\boldsymbol{\tau}_{def}\mathbf{r}}{\boldsymbol{\sigma}}$$

Equation 4: Weber number [Isaa92, pg. 53]

is the interfacial tension. When the following two conditions are met droplet break up takes place [Isaa92, pg.53]. Frist, when the Weber number is greater than the critical Weber number. The second condition is that the deformation time must be longer than the critical deformation time. The critical deformation time is shown in equation 5, where η_d is the viscosity of the dispersed phase and ΔP is the Laplace pressure difference [Isaa92, pg. 54].

$$\mathbf{t}_{def,cr} = \frac{\boldsymbol{\eta}_d}{\boldsymbol{\tau}_{def} - \Delta\mathbf{P}}$$

Equation 5: Critical deformation time [Isaa92, pg. 54]

Emulsions formulation and droplet size are heavily dependent on the method used, the emulsifier concentration, dispersed phase concentration, energy input, and temperature. The influence of these factors will be discussed in more detail in the following section.

Emulsion Preparation Methods

High-Pressure Homogenization
High-pressure homogenization is a method typically used in the food and dairy industries to produce emulsions. It consists of forcing two fluids into a mixing chamber through an inlet valve under high pressure. The average droplet size produced is between 50 nm and 5 µm [Leal07, pg. 6]. There are two types of regimes that can exist when producing an emulsion with high-pressure homogenization, emulsifier rich and emulsifier poor regimes. An emulsifier poor regime is defined by the emulsifier concentration being less than ten percent of the critical micelle concentration. In an emulsifier poor regime the average droplet size is weakly dependent on the pressure of the system. Instead this regime has a high level of coalescence of droplets, which leads to average droplet diameters of $.3 - 2$ µm. Emulsifier rich regimes are defined as having emulsifier concentrations greater than ten times the critical micelle concentration and have a much smaller droplet diameter, typically varying from 50-250 nm [Leal07, pg. 6]. Although, coalescence still

$$d \propto P_{hom}^{-\alpha}$$

Equation 6: Emulsifier rich regime droplet diameter [Leal07, pg. 6]

occurs, recombination is at a low level and the droplet diameter being defined by equation 6, where d is the droplet diameter, P_{hom} is the homiginizer pressure and α is a power law constant.

Membrane Emulsification

A membrane emulsification preparation method consists of using pressure to force the dispersed phase to permeate through a membrane with a uniform pore size into the continuous phase. Figure 11**Figure 11** is a schematic of membrane emulsification [Leal07, pg. 7]. Membrane
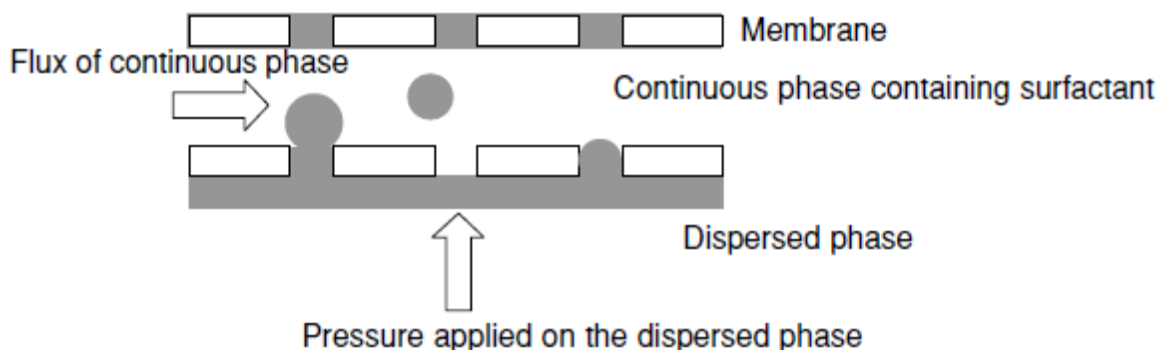
Figure 11: Membrane emulsification schematic [Leal07, pg. 7]

emulsification is much more complex due to the droplet size dependency on many parameters, such as membrane properties, fluxes, and formulation. Usually the drop size formed is proportional to the pore size, but if the pore density is too large, coalescence of newly formed drops occurs. However, if pore density is too low, then the speed of production is insufficient. For an oil-in-water emulsion to be formed a hydrophilic membrane should be used. Low interfacial tension and high velocity of the continuous phase help promote small droplet sizes. Membrane emulsification requires finding a balance between high pressure, which promotes large droplets, or a dispersed phase jet and low pressure, which decreases the production rate [Leal07, pg. 7].

Microchannel Emulsification

Microchannel emulsification technology is similar to membrane emulsification in that the dispersed phase is forced through small openings into the continuous phase. Microchannel emulsification requires the dispersed phase to flow through a microchannel. Once it reaches the opening into the continuous phase there is a terrace where the dispersed phase inflates into a disk-like shape. At the end of the terrace, the disk-like shape falls onto the well and a drop detaches. A schematic of microchannel emulsification is shown in figure 12 [Leal07, pg8]. The spherical shape and detachment of the dispersed phase from the well depend on the interfacial tension. A key advantage of using microchannel emulsification is the ability to control the geometry of the emulsification.
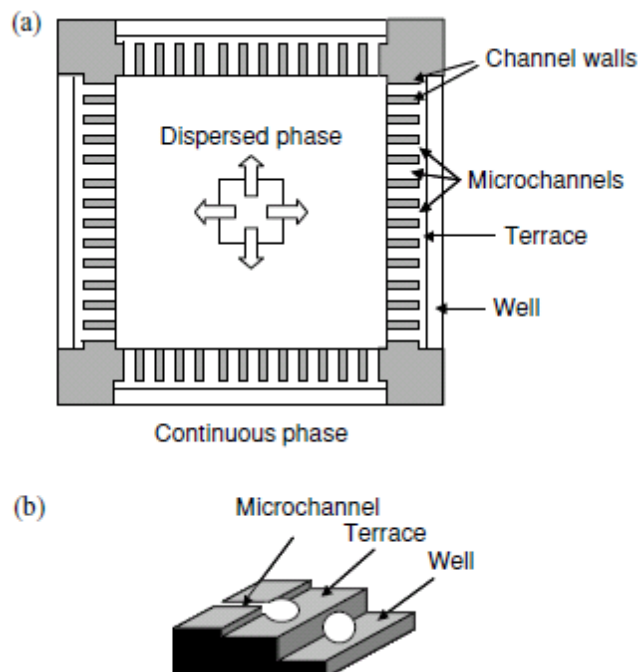
Figure 12: Microchannel schematic (a) top view (b) side view [Leal07, pg. 8]

Spontaneous Emulsification

Spontaneous emulsification is the process of emulsification without any external energy supply. In this process, two immiscible fluids are emulsified due to very low interfacial tension. Spontaneous emulsification was first reported in 1878 by Johannes Gad. Despite its historic discovery, spontaneous emulsification is still not fully understood. Currently there are three main theories on the mechanisms for spontaneous emulsification, interfacial turbulence, negative interfacial tension, and diffusion and stranding. Interfacial turbulence attributes spontaneous emulsification to a non-uniform distribution of emulsifier molecules on the shared surface. This instability of the interface produces small droplets. Negative interfacial tension credits the ability to adsorb emulsifier molecules at the interfacial surface in order to create ultra-low interfacial tension and eventually a negative interfacial tension. Therefore, the interfacial tension is able to increase and the fluctuation causes a break-up of the dispersed phase. Both of these mechanisms attribute emulsification to mechanical instability. Diffusion and stranding is based on chemical stability and can take place for high or low interfacial tensions. An example of diffusion and stranding is when alcohol and oil are combined and then added to water. The alcohol diffuses from the oil phase into the water. However, as it diffuses it carries small amounts of oil with it that then form droplets. Diffusion and stranding occurs when a solvent is used that is soluble in

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both phases. Spontaneous emulsification applies to volume fractions of less than 10% [Leal07, pg. 10-11].

Phase Inversion

Phase inversion is most often considered a type of spontaneous emulsification because of its low input energy. However, unlike the previously mentioned spontaneous emulsification mechanisms phase inversion has the advantage of producing concentrated emulsions. Emulsions from phase inversion tend to be fine and monodispersed. Phase inversion occurs when the structure of the emulsion inverts and the continuous phase becomes the dispersed phase or vice versa. Phase inversion can occur when changing the temperature, pressure, salinity, by introducing a co-emulsifier, or increasing the volume of the dispersed phase. Figure 13, shows a molecular representation of the change that occurs during phase inversion from an oil-in-water emulsion to a water-in-oil emulsion [Leal07, pg 12]. The most common method of phase inversion is the phase inversion temperature method (PIT). In nonionic emulsifiers as the temperature increases, the emulsifier head group becomes less soluble in water due to decreased hydration. Phase inversion is controlled by changing the spontaneous curvature. This can be achieved by changing
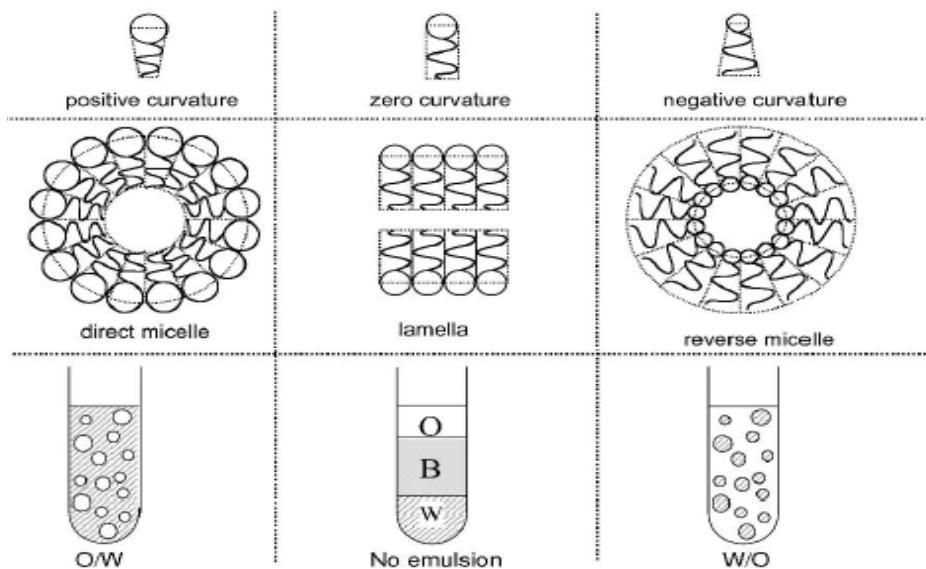
Figure 13: Phase inversion (a) emulsifier morphology, (b) type of assembly, (c) emulsion type [Leal07, pg. 12]

the properties of the emulsion, such as temperature, salinity, pressure, etc. Shinoda and Saito found that when creating an emulsion the preparation temperature has a significant effect on the average droplet diameter of the emulsion.

Controlled Shear

Emulsion creation through controlled shear stress involves adding energy to two immiscible fluids by stirring. Ideally, a monodispersed system will be created through control of the parameters controlling droplet formation. In 1934, Taylor published an experimental work on droplet deformation. This experimentation proved that droplets submitted to quasi-static flow deform and burst under well-defined parameters. The droplet will burst if the Ca, capillary number, exceeds some critical value Ca_{cr} critical. The Ca_{cr} is defined by the shear stress over half of the Laplace pressure as shown in equation 7, where P_L is the Laplace pressure and σ is the surface tension [Leal07, pg. 19].

$$C_a = \frac{2\sigma}{P_L}$$

Equation 7: Capillary number [Leal07, pg. 19]

Ca_{cr} is dependent on the ratio of the viscosities of the dispersed and continuous phases as shown in equation 8 [Leal07, pg. 19].

$$\rho = \frac{\eta_d}{\eta_c}$$

Equation 8: Viscosity ratio [Leal07, pg. 19]

Ca_{cr} as a function of the density under conditions of simple shear flow and extensional flow is shown in figure 14. Rupturing of a droplet has been contributed to the following mechanisms [Leal07, pg. 19]. First, development of a Rayleigh instability, in which an undulation at the surface of the droplet is developed and continues to grow until it deforms the droplet into a cylinder shape and then breaks the droplet. Secondly, tip streaming, where a droplet is deformed and comes to a pointed end. This pointed end then produces very small droplets. The third mechanism is end pinching, which is where the ends of the original droplet that has been deformed into a cylinder are progressively pinched into smaller droplets [Leal07, pg. 19]. However, under normal controlled shear emulsion formation, the conditions would be described as non-quasi-static conditions [Leal07, pg. 20].
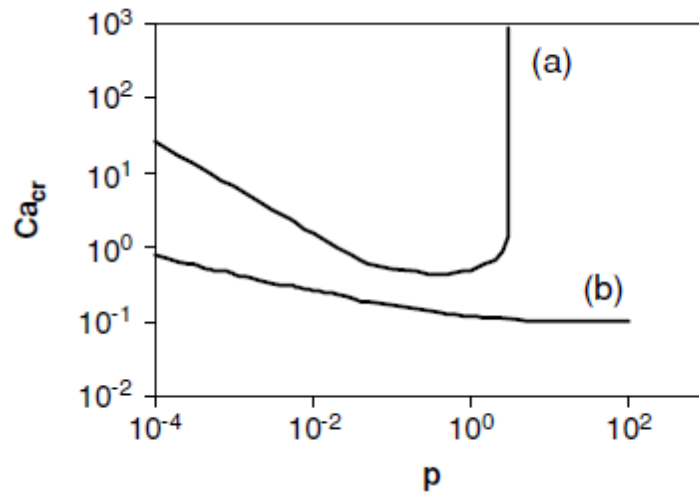
Figure 14: Critical capillary number under quasi-static deformation (a) as a function of simple shear flow (b) as a function of extensional flow [Leal07, pg. 19]

It has been shown that the droplet diameter is a function of the shearing time and rate. Different shear rates influence the droplet size. Mabille showed that by submitting a heterodispersed emulsion to a shear rate of $500s^{-1}$ for a duration ranging from 1 to 1500s monodispersed emulsions could be formed. Mabille also showed that the droplet size decreases over time until at a characteristic time, the droplet will reach an asymptotic diameter [Leal07, pg. 21]. Thus different shearing rates can create droplets with different diameter ranges, as long as the droplet is submitted to shear flow for a time period equal to or greater than the characteristic time for that specific shear rate.

During droplet breakup there are two main regimes, the fast regime which occurs due to Rayleigh instability under shear flow and the slow regime, which has little effect on the droplet in comparison to the fast regime [Leal07, pg. 21 &25]. During the first regime which is controlled by the Rayleigh instability, certain parameters control the mean droplet diameter, the applied stress σ, the viscosity ratio p, the way the shear is applied, and the rheological behavior. Through experimentation the influence of σ on the droplet size and distribution was studied [Leal07, pg. 26]. An empirical law, equation 9 was determined to be useful in predicting the droplet size resulting from monodispersed fragmentation [Schm03, pg. 201].

$$d = \alpha \frac{4\sigma}{\gamma}$$

Equation 9: Mean droplet diameter, influence of the applied stress [Schm03, pg. 201]

α is a dimensionless constant that essentially is dependent on ρ (the density), σ is the surface tension and γ shear rate. When shear stress is applied suddenly, the Laplace pressure is proportional to the stress and the Ca_{cr} ($Ca_{cr} \approx 2\alpha$) is similar to the Ca_{cr} ($Ca_{cr} \approx 2\alpha$) determined for quasi-static conditions. The influence of the viscosity ratio was also experimentally studied. It was discovered that the mean droplet diameter is only weakly dependent on the viscosity ratio. However, the monodispersity is heavily dependent on the viscosity ratio of the emulsion [Schm03, pg. 195-201]. For quasi-static conditions, the Ca_{cr} diverges for a viscosity ratio greater than three, meaning that when the dispersed phase is at least three times as viscous as the continuous phase fragmentation no longer occurs. However, if shear is applied even solutions with high viscosity ratios can be broken into droplets.

2.4.3. Emulsion Components

Emulsions are created when two immiscible fluids are mixed using an input of energy to create droplets. Stable emulsions are formed when a third component, an emulsifier is used to stabilize the droplets created by forming a thin film around the interfacial surface between the droplet and the continuous phase. In these studies the two immiscible fluids are paraffin and water.

Paraffin

When a PCM is selected for use in CTES applications it should melt within the temperature range of 0 and 30 ℃ [Huan09b]. There are five pure paraffin forms that have melting points within this range, tetradecane, pentadecane, hexadecane, heptadecane and octadecane. However, due to their higher latent heat of fusions, paraffins with even number chain lengths are considered better for use in CTES technology [Shar09]. Due to costs polymers blends are preferred. This research will focus on octadecane and commercially available blends from different suppliers.

Paraffin Concentration

Concentration of the dispersed phase influences droplet size, with large fractions favoring collisions and coalescence. The volume fraction, ϕ has a reduced influence on the average droplet size for concentrations where ϕ < 30% [Leal07, pg.].

Emulsifier

In an emulsion the emulsifier plays a very important role. The type and properties of the emulsifier greatly impact the stability, both mechanical and kinetic. There are currently different methods for selecting emulsifiers. However, even with previous research there are gaps of knowledge on the exact role the emulsifier plays in creating a stable emulsion with the desired PCS properties listed in figure 8. Therefore, more research needs to be conducted relating physical and chemical properties that are used in selection methods to desired PCS properties.

Classification

Commercially, emulsifiers are usually classified according to their use. However, this causes confusion due to multiple uses for the same emulsifier. From a scientific standpoint, most emulsifiers are classified based on their dissociation in water. There are four main groups of emulsifiers: nonionic, anionic, cationic and amphoteric (zwitterionic) [Moll01, pg. 68].

Nonionic Emulsifiers

Nonionic emulsifiers do not ionize in aqueous solution due to the hydrophilic group being non-dissociable. Nonionic emulsifiers are the second most used emulsifiers, making up roughly forty percent of the world's emulsifier production. The hydrophilic portion usually has a polyethylene chain formed from a polycondensed ethylene oxide. The presence of the chain makes the head group hydrophilic. The lipophilic group is usually an alkyl or alkylbenzene created from a polycondensed propylene oxide [Sala02]. Some nonionic emulsifiers exhibit very low toxicity levels. There are four main types of nonionic emulsifiers, ethoxylated linear alcohols, ethoxylated alkyl phenols, fatty acid esters and amine and amide derivatives. Many nonionic emulsifiers including the polyoxyethylene family exhibit an inverse temperature-solubility relationship. This means that as the temperature of the emulsion increases the solubility will decrease due to decreased solubility in water. The temperature where the emulsifier will begin to precipitate out of the solution is called the cloud point temperature.

Anionic Emulsifiers

Anionic emulsifiers dissociate into an anion[4] and a cation[5] in water. The cation is usually either an alkaline metal or a quaternary ammonium. Anionic emulsifiers are the most commonly used

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[4] Anion: negatively (-) charged ion, moves toward an anode during electrolysis
[5] Cation: positively (+) charged ion, moves toward a cathode during electrolysis

emulsifiers, accounting for about fifty percent of the world's production of emulsifiers [Sala02].

Cationic Emulsifiers

Cationic emulsifiers dissociate into a cation and an anion in water. They generally correspond to nitrogen compounds like fatty amine salts and quaternary ammoniums. Cationic emulsifiers tend to be more expensive than anionic emulsifiers because during their synthesis a high pressure hydrogenation reaction must be carried out [Sala02].

Amphoteric (Zwitterionic)

Amphoteric emulsifiers exhibit both cationic and anionic dissociation. Some amphoteric

Table 4: Commonly used hydrophilic groups for commercially available emulsifiers [Myer06]

General Class Name	General Solubilizing Structure
Sulfonate	$R - SO_3^- M^+$
Sulfate	$R - OSO_3^- M^+$
Carboxylate	$R - COO^- M^+$
Phosphate	$R - OPO_3^- M^+$
Ammonium	$R - N^+ R'_x H_y X - (x = 1 - 3, y = 3 - 1)$
Quaternary ammonium	$R - N^+ R'_3 X$
Betaines	$R - N^+ (CH_3)_2 CH_2 COO^-$
Sulfobetaines	$R - N^+ (CH_3)_2 CH_2 CH_2 SO_3^-$
Polyoxyethylene (POE)	$R - OCH_2 CH_2 (OCH_2 CH_2)_n OH$
Polyoxyethylene sulfates	$R - OCH_2 CH_2 (OCH_2 CH_2)_n OSO_3^- M^+$
Polyols	$R - OCH_2 - CH(OH) - CH_2 OH$
Sucrose esters	$R - O - C_6 H_7 O(OH)_3 - O - C_6 H_7 (OH)_4$
Polyglycidyl esters	$R - (OCH_2 CH[CH_2 OH] CH_2)_n CH(OH) - - OCH_2 CH[CH_2 OH] CH_2 OH$

emulsifiers are insensitive to pH, while others change between cationic dissociation at low pH and anionic dissociation at high pH. Amphoteric emulsifiers are generally very expensive and thus only used in specialized cosmetics [Sala02].

In general the hydrophobic group of an emulsifier can be more varied than the hydrophile group. Typical hydrophile groups can include structures such as those shown in table 4, where R stands for a suitable hydrophobic group, M^+ is an organic or inorganic cation, and X^- is an anion. The most common hydrophobic groups are hydrocarbon radicals having between 8-22 carbon atoms [Myer06, pg. 38-39].

Selection Process

Choosing a suitable emulsifier is a difficult due to a wide variety of choices and the many factors that help determine what makes a potential emulsifier a good candidate. Factors include the

chemical structure, economics, regulations, ecological impacts, input energy. It is important to evaluate the relative role of the emulsifier in the emulsion and the emulsifier's physicochemical characteristics. Things to consider when selecting an emulsifier are

1. The surface and interfacial properties that must be controlled in the specific application
2. Relationships between structural properties of the emulsifiers and their effects on the interfacial surface properties
3. The chemical and physical properties of available emulsifiers
4. Specific biological or chemical compatibility requirements
5. Regulations that might prohibit the use of certain materials due to toxicity, ecological impacts, or allergenic reactions) [Myer06, pg. 33]

Hydrophilic-Lipophilic Balance

Hydrophilic-lipophilic balance (HLB) is a quantitative characterization of the hydrophilic versus the lipophilic sections of a nonionic emulsifier. In 1948, the first ever quantitative characterization of the HLB was introduced by William C. Griffin [Krug00, pg. 146]. This characterization used arbitrary numbers to describe the ratio between the hydrophile and lipophile of various classes of emulsifiers. Each emulsifier is designated a dimensionless number ranging from 0 to 20, where zero represents emulsifiers that are oil-soluble and hydrophobic and 20 are water-soluble and hydrophilic [Moll01, pg. 69]. Nonionic emulsifiers can me combined when two emulsifiers with the same chemical type are used [Moll01, pg. 73]. HLB values help enable one to make certain predictions of the behavior of the emulsifier. HLB numbering was introduced to help classify emulsifiers in a way to improve choice selection of emulsifying agents [Krug00, pg. 146-147]. Literature suggests that to form oil-in-water paraffin emulsions an emulsifier with a HLB value ranging from 10-15 should be used [Moll01, pg. 75]. Further research by Orafidiya and Oladimeji suggests that liquid paraffin emulsions are most stable when mixed with nonionic emulsifiers with an HLB from 11.8-12 [Oraf02]. According to Griffin's scale, HLB values are calculated using equation 10 [Moll01, pg. 70].

$$HLB\ value = \frac{molar\ mass\ of\ the\ hydrophilic\ part}{molar\ mass\ of\ the\ emulsifier} * 20 = \frac{m_h}{m} * 20$$

Equation 10: Griffin's HLB value equation for nonionic emulsifiers [Moll01, pg. 70]

Griffin's equation is suitable for nonionic emulsifiers. Many correctional factors have been proposed for ionic emulsifiers [Moll01, pg. 70-71]. However, since this research deals with nonionic emulsifiers, these correctional factors will not be discussed. There are also scientific debates on the validity of the HLB scale the Griffin's assigned HLB values of emulsifiers. However, in this research HLB values from the Griffin scale were used for all calculations. Previous research by Shinoda and Saito indicates that the HLB value greatly influences the stability of an emulsion; therefore it is important to find the correct HLB value for a given oil [Shin69].

Determining the HLB Value of an Oil

The method for determining the optimum HLB value for a paraffin requires mixing two emulsifiers. Two emulsifiers, one lipophilic (with a high HLB) and one hydrophilic (with a low HLB), must be used to prepare different emulsion with HLB values over a broad range. When mixing the emulsifiers the new HLB value is determined using the equation 11 [Moll01, pg. 76].

$$HLB_{Oil} = \frac{m_A * HLB_A + m_B * HLB_B}{m_A + m_B}$$

Equation 11: Equation for finding the optimum HLB value [Moll01, pg. 76]

Once several solutions have been prepared, then the stability of the different solutions should be determined. The more stable emulsions are closer to the optimum HLB value. The HLB value range can then be narrowed between the more stable HLB values until an optimum value is found [Moll01, pg. 73-76]. It should be noted that previous works indicate temperature has an influence on the HLB values. There are several methods for determining the optimal HLB value. One method is to prepare the emulsions and then leave the emulsions to stand for a time and then compare the emulsions for transparency, creaming, sedimentation, and turbidity [Moll01, pg. 73]. In this method one must rely on visual signs of emulsion instability. For experimentation optimum HLB value was decided upon by preparing emulsions over a range of HLB values and then testing the droplet size. Kinetic stability can be directly linked to the droplet size, as will be discussed further in the section 2.2.4 Emulsion Stability.

Previous studies conducted by Orafidiya and Oladimeji have estimated the HLB value of paraffin to be between 11.8 and 12 [Oraf02]. Xu tested emulsions of Tween and Span 60 for storage life and showed that kinetically stable emulsion with a shelf life of at least 1 week could

be produced [Xu05]. Lu was also able to show that by using Tween 60 in conjunction with a co-emulsifier the subcooling effect can be reduced [Lu12]. Lui also found that when working with paraffin o/w nano-emulsions composed of 20 wt. % paraffin and 5 wt. % emulsifier (Tween 80 and Span 80 mixture), the optimum HLB value decreased as the emperature was increased [Liu06].

Phase Inversion Temperature

Another newer method of relating physical and chemical characteristics is to use the phase inversion temperature (PIT) method. It has been shown that the phase version temperature has an almost linear correlation with the HLB value. Phase inversion temperature method is based on the fact that rate of coalescence increases, and stability increases as temperature of an emulsion increases. The rate is influenced by factors such as the size and type of hydrophilic and hydrophobic groups, emulsifier concentration, length of hydrocarbon chain, and other chemical characteristics. With nonionic emulsifiers, as the temperature is raised, the hydrophilic group becomes less hydrophilic and the emulsifier is prevented from creating a stabile interface between water and the oil. In the PIT method, emulsions are prepared over a range of HLB values at room temperature. The emulsion is then subjected to heat until it inverts. For oil in water emulsion, this means converting to water in oil emulsions and vice versa. The temperature at which this inversion occurs is the phase inversion temperature, and should be observable visually. Since the interfacial tension reaches a minimum in the region of the PIT, the emulsion with the lowest PIT should also have the corresponding optimal HLB value [Moll01, 87]. However, the PIT method relies on visual indicators.

Chemical Structure

When selecting an emulsifier the chemical structure is important. The chemical structure of an emulsifier can be divided into the lipophilic tail and the hydrophilic head group. Both of these sections of the emulsifier can impact the stability of the emulsion. Previous research has indicated that selecting an emulsifier with a lipophilic tail with a similar number of hydrocarbons as the oil can improve the emulsion stability. Literature also suggests that the selection of the hydrophilic head group can impact the emulsion stability. As shown in figure 15 the stability of an emulsion can significantly increase depending on the chemical structure of the emulsifier [Moll01, pg. 76-77]. In the figure, all emulsions exhibit a peak stability at HLB value 12, but structure A has a much higher stability, indicating that different chemical structures impact

kinetic stability. It can also be observed that different structures can have a stability over a greater or smaller range of HLB. For example in figure 15, emulsifier B exhibits stability over the largest range of HLB values, while C exhibits stability over a very narrow range of HLB values.
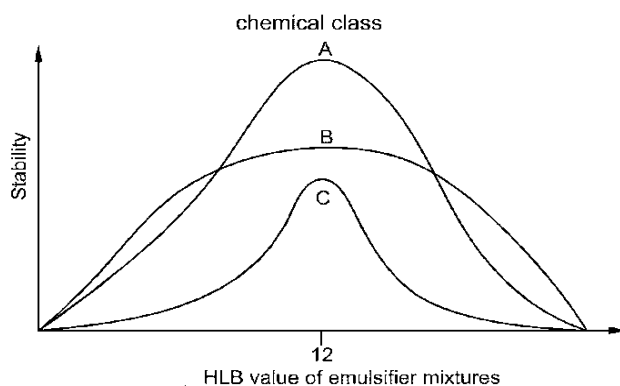
Figure 15: Emulsion stabilization by different chemical classifications as a function of the HLB value of the emulsifier [Moll01, pg. 77]

Temperature

A variety of previous works suggest that temperature has a profound influence on the formulation of a stable emulsion. The exact influence temperature has and the reasons for this influence vary greatly. Shinoda and Saito studied the emulsification temperatures influence on the mean volume diameter of oil and water emulsions. In this study emulsions were prepared using 3 wt. % emulsifier. Shinoda and Saito showed that as an emulsion approaches the phase inversion temperature (PIT) the droplet diameter rapidly decreases. PIT of an emulsion varies with the type of oil and the nonionic emulsifier chain length [Shin69]. This research suggests that if emulsions are prepared near the PIT will produce the smallest droplets. Shindoa and Arai found that PIT increased with increasing hydrocarbon chain length of the oil and emulsifier. Shindoa and Arai also found that the cloud point and the PIT are parallel values, thus the cloud point increases with increased hydrocarbon chain length or moles of ethylene oxide (EO) [Shin64]. According to Shinoda and Saito, emulsion components should be heated to a temperature within 2-4°C below the PIT, shaken and then rapidly cooled to obtain minimize droplet size, however as the PIT is approached the rate of coalescence increases [Shin69]. Mitsui suggests that the reason for the temperature influence is related to the moles of EO. For emlsifiers with more than 10 moles of EO, as the temperature increases the droplet diameter

decreases. For emulsifiers with less than 10 moles of EO the exact opposite is true and for emulsifiers with 10 moles EO there is little to no influence with temperature variations [Mits72].

2.2.4. Emulsion Stability

With PCS emulsions there are two main types of stability: kinetic stability and mechanical-thermal load stability. Kinetic stability is related to the stability of emulsion during storage periods. PCS emulsions should have the ability to be stored for long periods. Mechanical-thermal load stability is associated with the ability to maintain stability during phase changes and pump cycles. PCS emulsions must be stable through repeated freezing and melting phase changes and during circulation. Stability of an emulsion is measured by studying droplet size, droplet dispersion, subcooling, and/or phase separation.

Kinetic Stability

Emulsion stability is directly linked to the chemical compounds used in producing the emulsion, specifically the emulsifier its similarity to the paraffin. Figure 16 is a pictorial representation of the six different types of instability of emulsions due to five mechanisms [Todr05]. Creaming and sedimentation present in emulsions when the dispersed and continuous phases have density differences. As the emulsions set for long periods of time gravity acts upon the emulsion and it becomes unstable. Flocculation is exhibited when droplets aggregate without rupturing the stable protective layer of the emulsifier. Creaming, sedimentation and flocculation are reversible and do not contribute to a change in droplet size distribution. Coalescence is when two or more droplets form one single droplet due to droplet density. Ostwald ripening is due to solubility differences between the oil droplets of different sizes. Ostwald ripening and coalescence result in an overall increase in droplet size, an increase in droplet dispersion, and a decrease in interfacial area. Both forms of instability are irreversible. Phase inversion where the original continuous phase inverts and becomes the dispersed phase, while the dispersed phase becomes the continuous phase [Huan09b].
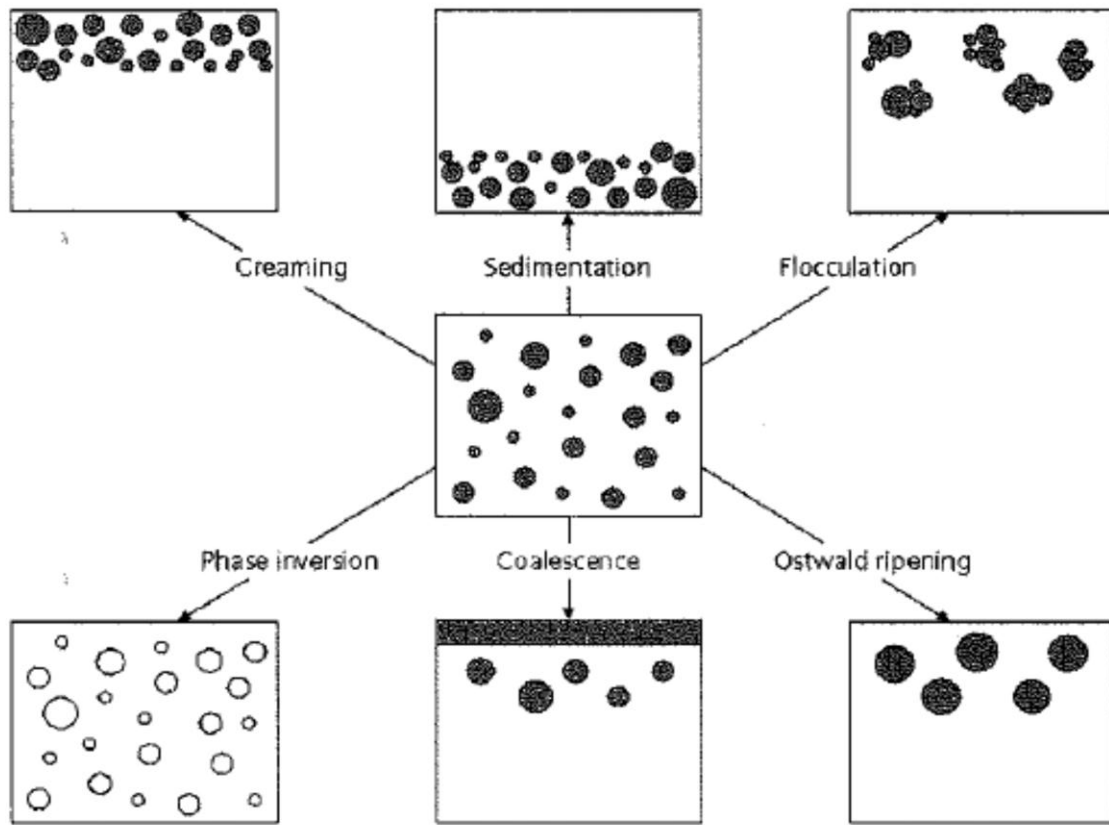
Figure 16: Types of emulsion instability [Todr05]

Subcooling

For PCS emulsions subcooling effects are a concern. Subcooling is when a liquid can be cooled below its melting point without showing crystallization, thus to counterbalance this phenomenon in emulsions nucleating agents are used. Previous studies have indicated that the droplet size has a direct effect on the subcooling of an emulsion. It has been shown that a decrease in the droplet
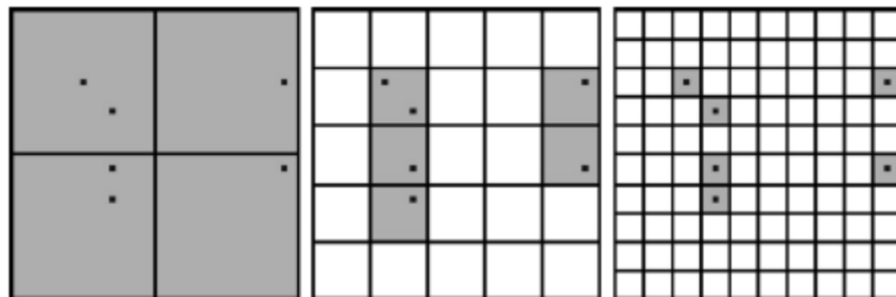
Figure 17: Example of small droplets lacking nucleation sites decreasing the overall ability of the emulsion to crystalize [Günt11]

size is drastically impacts the melting and nucleation temperature of an emulsion. Reductions in droplet size decrease both temperatures in comparison with pure PCMs. The effect on melting temperature is in the range of 2K, whereas the impact on nucleation temperature can reach as high as 15K. This large subcooling effect should be avoided because it leads to an extended charging/discharging temperature range of the PCM [Huan10b]. However, decreased droplet size leads to more stable emulsions. In a stable emulsion there is no direct contact between droplets. This affects the ability of nucleation of the droplets through two main mechanisms. The first is that small droplets isolate the nucleation sites, in contrast to bulky situations were one nucleation site causes the whole volume to solidify through crystal growth. In an emulsion individual droplets must be nucleated in order for solidification of the whole volume. If the number of nucleation sites is low in comparison with the droplet volume then only some of the droplets will contain nucleation seeds and these will be virtually deactivated. This is visually represented in figure 17, where the smaller squares represent the small droplet size present in kinetically stable emulsions [Günt11]. The other effect is the deactivation of primary nucleation seeds through solid impurities [Günt11]. This can cause the nucleation mechanism to shift to secondary seeds that are not found in pure bulk situations. In the worst case scenario, all the heterogeneous seed sites are deactivated and nucleation is solely dependent on homogenous nucleation at much lower temperatures. To combat this wider range of nucleation temperature due to a decrease in nucleation sites, new nucleation sites can be created on the increased surface are of the droplets in emulsions. The possibility of this increase inner surface to improve the nucleation rate
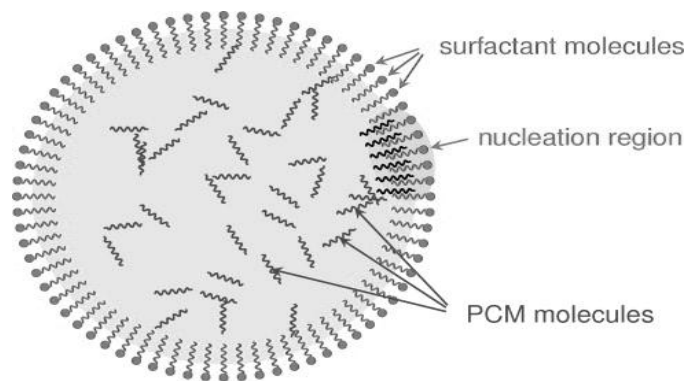

Figure 18: Increase nucleation sties on droplet surface due to emulsifier [Günt11]

depends on the interface energy between the emulsifier and the solid of the dispersed phase. As shown in figure 18 the pattern of the hydrophobic tails on the inner surface of the droplet could act as a crystal template to facilitate crystallization of the PCM molecules [Günt11]. This effect

is suspected to be highly dependent on the PCM and the emulsifier used. Other influencing factors include the paraffin, emulsifier and nucleating agent used [Günt11]. Effective nucleating agents have higher phase change temperatures than the PCM [Huan10b]. Nucleating agents used in previous studies include using paraffin wax with a higher freezing temperature [Huan10a].

Thermal Mechanical Stability and viscosity

Studies on the mechanical-thermal load stability for paraffin/water emulsions have shown that

(a) Droplet size distribution of RT20 mixture before and after mechanical-thermal testing

(b) Droplet size distribution of RT10 mixture before and after mechanical-thermal testing
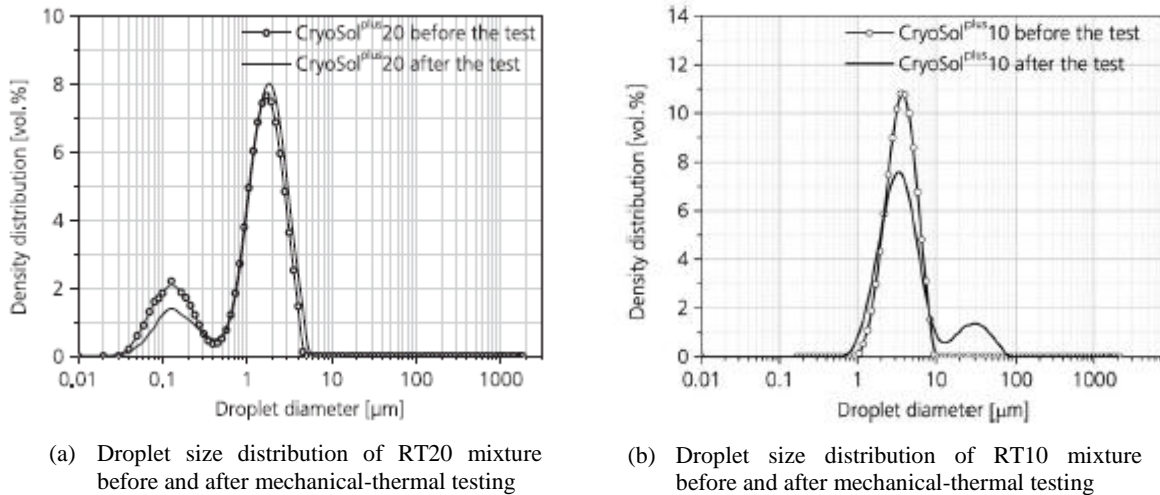
Figure 19: Variation in droplet size after mechanical-thermal testing [Huan10a]

emulsion stability is linked with the emulsifier. This means that here is no one optimal emulsifier for all paraffins; each paraffin has an optimal emulsifier. Huang tested two emulsions using RT10 and RT20 for mechanical-thermal stability. Both of these are trademarked paraffin blends from the company Rubitherm Technologies GmbH. In this experiment the different emulsions are called Cryosol 20 for the emulsion using RT20 and Cryosol 10 for the emulsion containing RT10. The same emulsifier and nucleating agent and wt. %[6] were used in creating the emulsions. The experiments showed that RT20 showed very little change in droplet size distribution, while the RT10 emulsion showed slight increases in droplet sizes due to the mechanical-thermal repetitions, as pictured in figure 19 [Huan10a].

Viscosity is another important parameter of emulsions. With CTES technology the emulsion will be continually pumped through a storage system, while undergoing heating and cooling cycles. It is important that the viscosity of the fluid be minimized in order for the pump energy to remain low. It is also a sign of stability for the emulsion to exhibit a stable viscosity afer many pump

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[6] Wt. % is an abbreviation for weight percentage, or a percentage of the whole based on weight

cycles. This shows that the heating/cooling cycles are not causing kinetic instability. Further studies should be done to understand how to properly match a paraffin with the best emulsifier, by studying the physical and chemical characteristics (i.e. chemical structure, HLB value, cloud point) in order to achieve kinetic stability, a stable viscosity and minimal subcooling.

2.5. Previous Phase Change Slurry Studies

Table 5: Previous PCS studies [Huang 10a]

No.	PCS form	Paraffin	Interface Component*	Interface Component Concentration	Reference
1	Emulsion	Tetradecane $C_{14}H_{30}$	Surfactant: polyethylene glycostearylether and alkylbenzene-sulfanate (10:1)	Tetradecane 5-40%	[Inab94]
2	Shape-stabilized paraffin	Paraffins C_{12}-C_{15}	Support material: SEBS (Styrene-butadiene-styrene)	PCM 75% SEBS 25%	[Royo98 & Royo11]
3	Emulsion	Hexadecane $C_{16}H_{34}$	Surfactant: Titron X-100	Hexadecane 10-70%	[Clar03]
4	Shape-stabilized paraffin	Pentacosane $C_{22}H_{52}$	Support material: HDPE (high density poly-ethylene)	PCM 74% SEBS 26%	[Inab03]
5	Paraffin micro-capsules	Nonadecane $C_{19}H_{40}$	-	Nonadecane 10-40%	[Inab03]
6	Paraffin micro-capsules	Tetradecane $C_{14}H_{30}$	Capsule material: PMMA (polymethyl methacrylate) or PEMA (polyethyl methacrylate)	Tetradecane capsule 5-40%	[Yang03]
7	Paraffin micro-capsules	Hexadecane $C_{16}H_{34}$	Capsule material: PMMA (polymethyl methacrylate)	Hexadecane capsule 10-40%	[Gsch05]
8	Paraffin micro-capsules	Tetradecane $C_{14}H_{30}$	-	Tetradecane capsule 10-30%	[Poll05]
9	Emulsion	Tetradecane $C_{14}H_{30}$	Surfactant: mixture of Span and Tween 60	Span 32.4 wt.% Tween 67.6 wt.%	[Xu05]
10	Paraffin micro-capsules		Support material: HDPE (high density poly-ethylene) Surfactant material: Styrene Maleic Anhydride (SMA)	SMA 5 wt.%	[Lee06]
11	Shape-stabilized paraffin	Paraffin with a melting point of 29 °C	Support material: Inorganic silica gel	Paraffin: 65%	[Miao07]

12	Emulsion	Paraffin with melting temperatures between 0 - 20 °C		Paraffin 2.5-15 wt.%	[Huan09a]
13	Emulsion	Paraffin with melting temperatures between 0 - 20 °C		Paraffin 30-50 wt.%	[Huan09b]
14	Emulsion	Paraffin with melting temperatures between 0 - 20 °C	Surfactant: Alcohol ethoxylates	Surfactant 1.5wt.% Nucleating Agent 2.5wt.% Paraffin 30 wt.%	[Huan10a & Huan10c]
15	Emulsion	Paraffin with melting temperatures between 0 - 20 °C	Surfactant: sodium dodecyl sulfate (SDS) Tween40 polyethylene glycostearylether and alkylbenzene-sulfanate (10:1) Nucleating Agent: paraffin with freezing peak of 50 °C		[Huan10b]
16	Paraffin nano-capsules	Hexadecane C16H34	Capsule material: Urea-formaldehyde resin Surfactant material: Sodium dodecyl sulfate	Surfactant .5-2 wt.%	[Li11]
17	Emulsion	Tetradecane C14H30 Pentadecane C15H32	Surfactant : Tween60 Hexadecanol	Tween 60 2.5% Hexadecanol 0.5%	[Lu12]

 *Interface component refers to the substance that creates a stable interface between the paraffin and the continuous phase carrier fluid

**Most of these studies use paraffins with phase changes between 0°C and 30°C

Paraffin PCSs as a viable solution for CTES began to be investigated in the mid-90s. Table 5 lists the major research data available on the topic of PCSs for use in CTES [Huan10a]. Over the last fifteen years, the area of PCSs has become an increasing topic of interest. Although many studies have been conducted on paraffin emulsions, there is not much data on the selection process for components of paraffin/water dispersions. In recent years, more data has been published; however, the selection process for suitable emulsifiers is still not well understood.

3. Experimental Procedure and Apparatus
3.1. Experimental Set-up

All experiments are designed around producing a variety of emulsions by varying the following parameters seen in table 6. Emulsions were produced using the following apparatus and methods

Table 6: Experimental dynamic parameters

Parameters
Emulsifier concentration
Paraffin concentration
Preparation temperature
HLB value
Hydrophilic head group structure
Lipophilic tail group structure
Mixing speed
Mixing time

described in sections 3.1.1 Preliminary Preparation Method and 3.1.2 Emulsion Preparation Method. After the emulsion is produced, it will be processed using the testing instrumentation described in section 3.3 Evaluation Apparatus and Methods. All emulsions are prepared based on weight percentages.

3.1.1. Preliminary Preparation Method

Emulsions were prepared using a variety of equipment. For initial experiments designed to characterize emulsion kinetic stability, a simple mixing set-up consisting of an IKA RW11B stirrer, beakers and IKA heating plate were used. The IKA RW11B, shown in figure 20 (a) stirrer is capable of a 0-2000 rpm and producing emulsions with droplet sizes ranging from 10-100 μm. The IKA RW11B was used to remove influences on droplet stability from high mixing energy. This also allowed for smaller sample quantities to be produced, 150g, and thus limited excess material consumption. For a preliminary sample, the water and oil amounts are weighed in separate beakers using IKA balances. The emulsifier is added to either the oil or water, depending on the HLB value. More hydrophilic emulsifiers are added to the water, whereas more lipophilic emulsifiers are added to the oil. Both the oil and water beakers are placed on the IKA hot plates and then heated to the mixing temperature. The oil phase is then added to the water phase and then stirred for a specific time.

Experimental Procedure and Apparatus

The preliminary preparation method was used for HLB, concentration, and chemical structure experiments. Since the mixing speed has the largest influence on droplet size ranges, by preparing at a slower speed this influence was removed and the smaller influence on droplet stability exhibited by the concentration, the HLB and the chemical structure could be observed. All emulsions prepared with the preliminary preparation method exhibit droplet sizes from 15-50 μm.
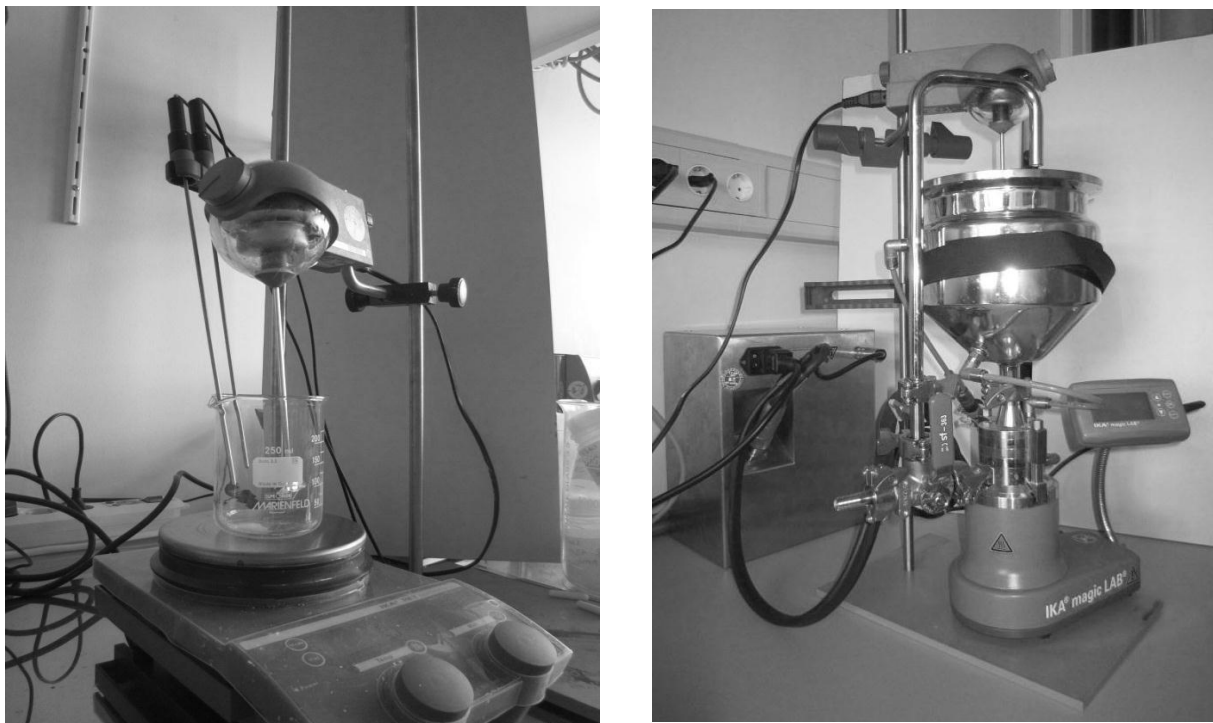

Figure 20: (a) Preliminary set-up with IKA RW11B (b) IKA magic LAB with IKA RW 11B

3.1.2. Emulsion Preparation Method

For studies on the effect droplet size and distribution have on subcooling, an IKA magic LAB with an IKA RW 11B were used. In combination these mixers produce emulsions with droplet diameters ranging from 1-10 μm. Emulsions were prepared using the same method as previously described in the 3.1.1 Preliminary Preparation. However, after reaching the desired mixing temperature on the heating plate, the oil and water were mixed in the holding container pictured in figure 20 (b). The water was added first and then the oil and emulsifier mixture. The temperature during mixing in the IKA magic LAB set-up was kept constant using a LAUDA Integral T 2200. The IKA magic LAB produces speeds ranging from 10,000rpm to 24,000 rpm.

3.2. Evaluation Apparatus and Methods

This research focuses on the kinetic and thermal mechanical stability of emulsions. Therefore, machines and evaluation methods are based on testing these properties and relating the chemical and physical properties of the emulsifier to optimum stability properties.

3.2.1. Cloud Point

The cloud point of a emulsifier is important in determining the optimum preparation temperature. Shinoda and Saito suggest that mixing an emulsion within a few degrees below the PIT and then rapidly cooling to room temperature, smaller droplets or a more kinetically stable emulsion can be formed [Shin69]. Through temperature experiments Mistui explains this phenomenon. In these temperature experiments emulsifiers with more than 10 moles of ethylene oxide the interfacial tension decreases as the temperature rises, until there is a phase inversion. Therefore, the lowest interfacial tension would be close to a phase inversion temperature of the emulsifier, either at the PIT or the cloud point. The cloud point of nonionic emulsifiers is the temperature at which the a mixture of water and emulsifier start to exhibit phase separation. Nonionic emulsifiers containing polyoxyethylene chains exhibit decreased solubility with temperature in water. These emulsifiers slowly go from hydrophilic to lipophilic as the temperature increases. Therefore, right before this phase inversion takes place, the interfacial tension will be at the lowest and small kinetically stable droplets can be formed. Therefore, the cloud points of the various emulsifiers were determined using IKA Werke thermal bath. Solutions of water and the 1,5 wt.% emulsifier were heated from 27°C to 98°C at a rate of 1°C/min and then left for 2 min before increasing the temperature again.

3.2.2. Kinetic Stability

Figure 21: Beckman Coulter LS 13 320 [Beck09]

Experimental Procedure and Apparatus

For determining kinetic stability several different methods can be used. First, kinetic stability can be visually observed. By determining the amount of flocculation, sedimentation, and creaming or by observing phase inversion, kinetic stability can be determined. However, a more quantitative approach will be used, so that degree of coalescence and Oswald ripening can be determined. This quantitative approach involves using a particle size analyzer machine to determine the average droplet size of different emulsions. A Beckman Coulter LS 13 320 particle size analyzer machine, pictured in figure 21, will be used to determine the average droplet size of emulsion samples. The LS 13 320 Series is a laser diffraction particle size analyzer. For measurements the multi-wavelength system of Polarization Intensity Differential Scattering technology was used. This system allows for measurements within the range of 0.017 μm to 2,000 μm [Beck09]. The light scattering technique is the most widely used for measuring size distribution of particles. The method of measurement is as follows. A laser light is used to illuminate particles within a
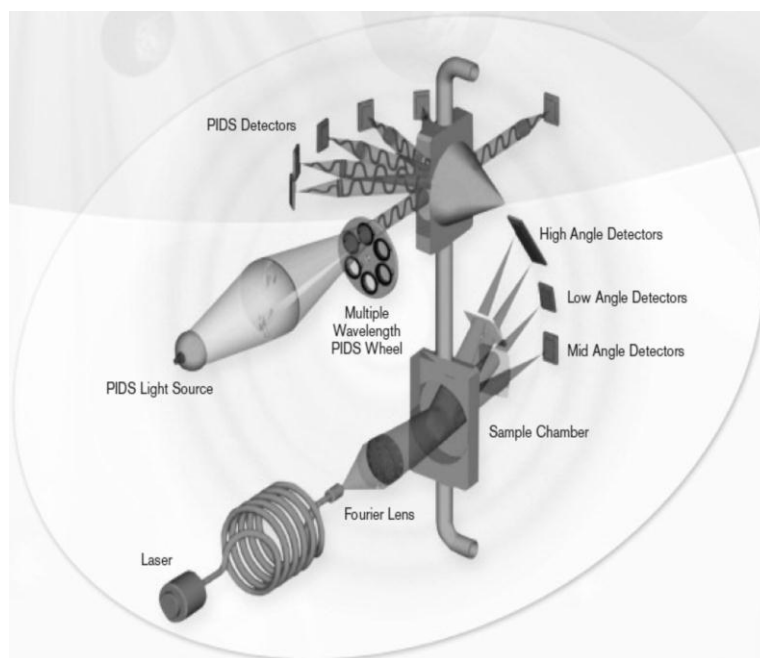

Figure 22: Laser diffraction particle size analyzer [Beck09]

sample chamber, as shown in figure 22. The scattered light is then detected by a set of silicon photo-detectors. The detectors measure the intensity of the light as a function of the angle of refraction. Then using a complex inversion matrix algorithm, the particle distribution is displayed as a volume % in a discrete size class. The PIDS is used for sizing small particles since sub-micron particles scatter light in similar patterns, thus making it difficult to distinguish the differences between the patterns. This leads to inaccurate sizing with low resolution. PIDS relies

on the transverse nature of light. The sample is illuminated with a light of a given polarized wavelength. This causes the electrons of the sample to oscillate in the same plane of polarization at the light source. The oscillating dipoles in the particles radiate light in every direction except that of the light source. PIDS measures the light at different angles as light from three different wavelengths (450 nm, 600 nm, and 900 nm) irradiate the sample. The PIDS measures the difference between the horizontal and vertical light from each wavelength and is able to gain accurate information on the particle size distribution [Beck09].

3.2.3. Heat Capacity/Subcooling

Materials have a physical property called specific heat capacity, this is the amount of energy/heat required to raise a certain mass of the material by one degree and is expressed in units of J /

Figure 23: Setaram micro DSC III

kg*K. A differential scanning calorimeter (DSC) can be used to determine the specific heat capacity of a substance. In all heat capacity and subcooling experiments a Micro DSC III by
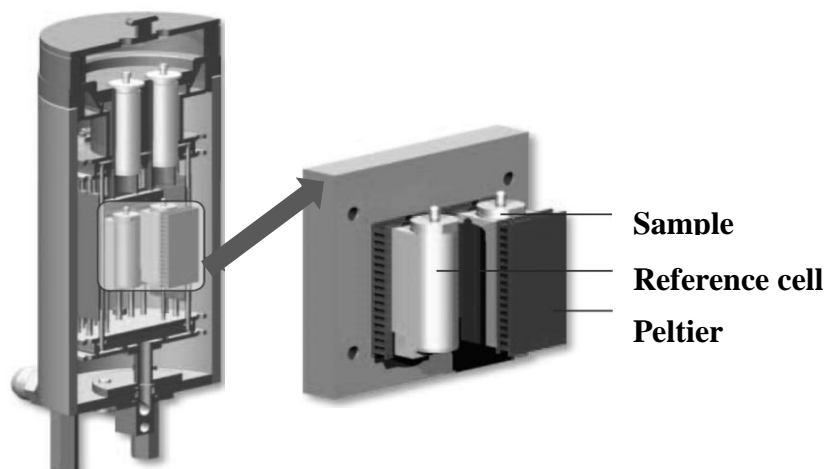

Sample

Reference cell

Peltier

Figure 24: Internal sample chamber of micro DSC [Seta]

Experimental Procedure and Apparatus

Setaram was used, as shown if figure 23. A DSC operates by recording information on the thermal changes of a sample during heating and cooling alongside an inert reference. The sample chamber of a micro DSC is shown in figure 24. Theoretically a DSC operates in one of two ways. The first is by measuring the differential thermal power input. The DSC monitors the temperature of the inert reference cell and the sample cell. When a temperature difference occurs then the DSC uses power to eliminate this temperature difference. The DSC records the power input required over a heating and cooling period. From this the heat capacity of the sample can be calculated. DSCs can also operate by measuring the temperature difference of the sample and the reference during a heating and cooling period and then uses software to convert the temperature difference into a heat flux [Laye 02]. When taking measurements it is important to select a proper heating/cooling rate. High heating rates of materials with low thermal conductivity causes error in the measurements due to temperature differences between the outside of the chamber and the material within. Temperature readings are taken by a sensor attached to the outside of the chamber, thus the readings are not accurate. This phenomenon causes the slopes of the melting and freezing curves to widen and the freezing and melting points to shift. In terms of PCMs and PCSs a DSC can be used to determine the degree of subcooling.

Figure 25 is an example of a DSC reading, labeled with the freezing and melting points of the emulsion. The difference between the two points represents the degrees of subcooling. Typically
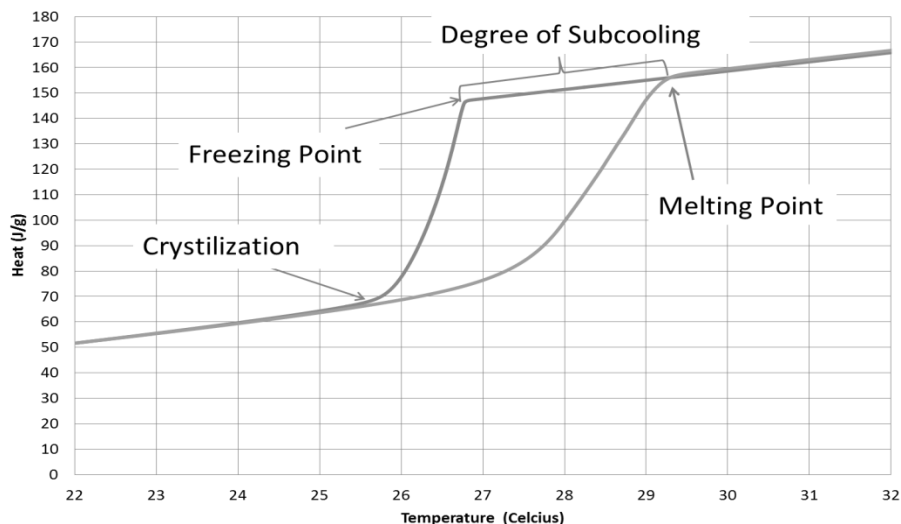

Figure 25: DSC measurement

the heat capacity of a paraffin/water emulsion depends heavily on the paraffin concentration.

3.2.4. Viscosity

Thermal mechanical stability is very important in PCS systems. During the life of a PCS the emulsion will be continuously heated and cooled as it is pumped through a storage system. Due to the stress of pumping and the heating and cooling cycles over time the emulsion properties change and begin to degrade. A Anton Paar Modular Compact Rheometer MCR 502, as shown in figure 26, was used to test the thermal mechanical/pump stability. Experiments were conducted only on emulsions that showed potential as kinetically stable emulsions with minimal

Figure 26: Anton Paar Modular Compact Rheometer MCR 502 [Anto12]

degrees of subcooling. The Anton Paar Rheometer was programed to complete a heating and cooling cycle.

4. Experimental Results and Discussion
4.1. Kinetic Stability
4.1.1. Hydrophile-lipophile Balance

With many commercially available non-ionic emulsifiers, choosing an emulsifier requires the use of a systematic method. The most commonly used method is the Hydrophilic-lipophilic balance system (HLB). Created in 1948 by William C. Griffin, the HLB arbitrarily quantifies the ratio of the lengths of the hydrophilic head group and the lipophilic tail group. Emulsions with an HLB of less than 10 are lipophilic, while HLB values over 10 indicate a hydrophilic emulsifier. The HLB value of paraffin 18-97 was determined by measuring the kinetic stability of emulsions prepared with a range of HLB values. Emulsions were prepared by mixing two ionic emulsifiers, Tween 60 and Span 60. From reference sheets provided by Sigma Aldrich, the HLB value of Tween 60 was determined to be 14.9, while the HLB value of Span 60 was determined to be 4.7. Using equation 10, emulsions were prepared with HLB values ranging from 10-14.

Tween 60 was selected due to its use in several previous works. Span 60 due to literature suggestions that a co-emulsifier improves stability and its appearance in Xu's previous study. In
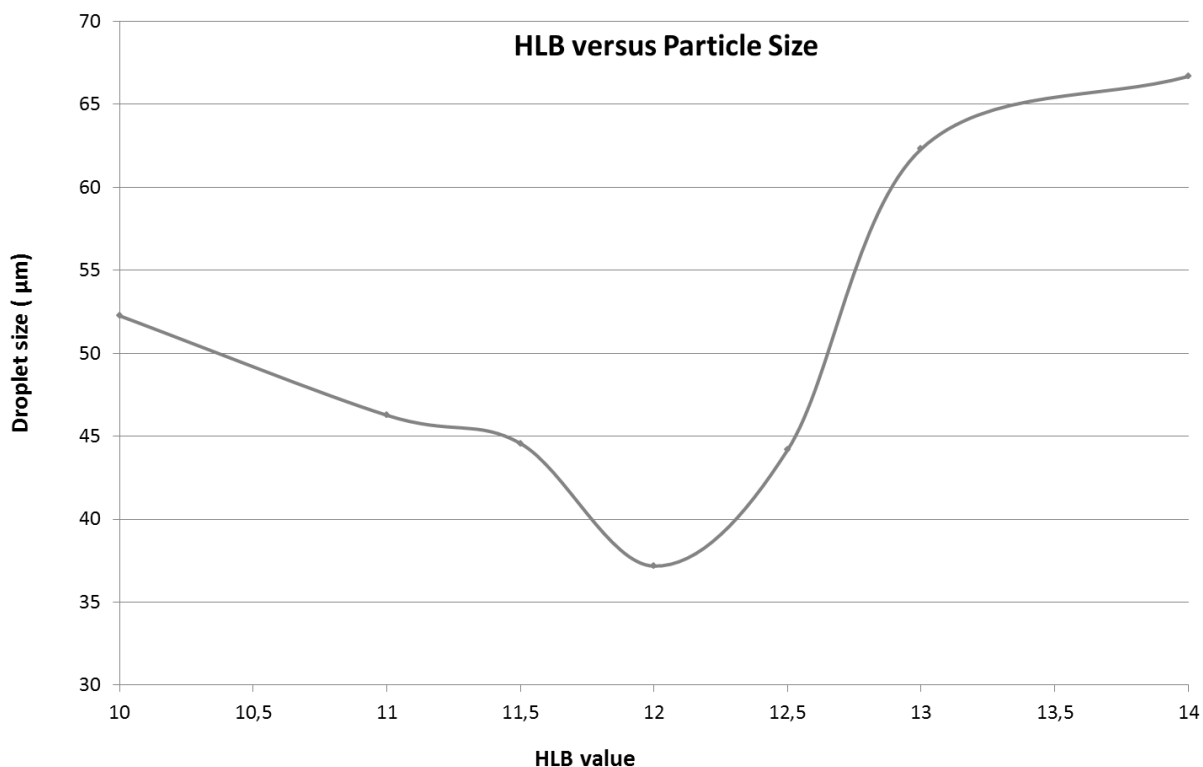

Figure 27: HLB versus droplet size

Experimental Results

Xu work a mixture of Tween and Span 60 were used to create an emulsifier mixture. Xu's lists the emulsifier concentration as 67.6 wt. % Tween 60 and 32.4 wt. % Span 60. Using equation 11 this mixture would result in an HLB value of 11.5.

In the experiment each of the emulsions was measured for kinetic stability. Kinetic stability was determined by measuring the droplet diameter, and the emulsion with the smaller droplet diameter is considered more kinetically stable. For this experiment emulsions were prepare using the preliminary preparation method at a temperature of 50°C. As shown in figure 27 a minimum droplet size or maximum stability was found at HLB 12.

 In order to determine whether the HLB value varied with preparation temperature and/or
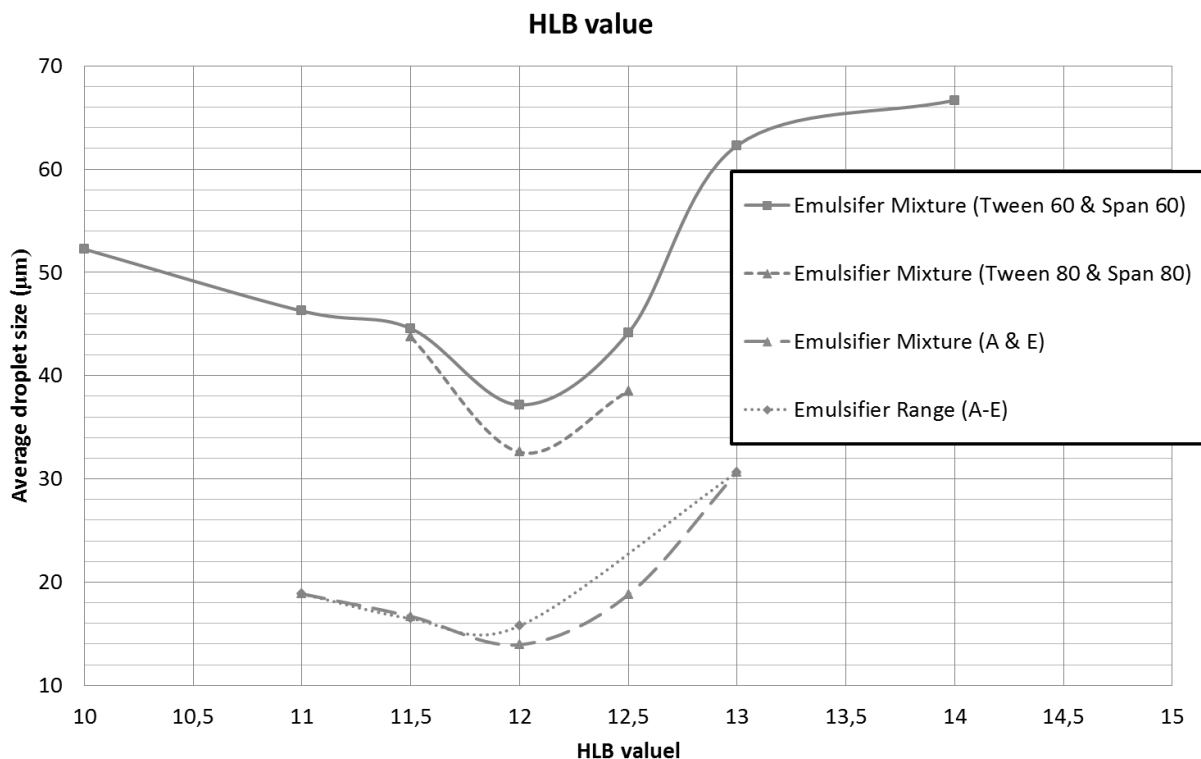
Figure 28: HLB dependency emulsifier and temperature

emulsifier, emulsions were prepared using the method as previously, but varying the emulsifier and adjusting the preparation to 80°C. For these experiments two Tween/Span mixtures were compared with another group of commerically available nonionic emulsifiers with HLB ranges from 11 to 13. The HLB values of the emulsifiers are as follows; Emulsifier A – 11 , Emulsifer B – 11.5 Emulsifer C – 12, Emulsifier D- 12 and Emulsifier E – 13. Using Emulsifier A and E, and equation 11 emulsions with HLB values ranging from 11-13 were prepared and compared as

well. It can be observed in figure 28, that all HLB curves exhibit a minimum at a HLB of 12. However, similar to figure 16 the structural differences in emulsifiers is reflected with changes in stability. The emulsifier mixture A & E with an HLB value of 12, exhibited the best droplet size stability. It should be noted that Emulsifier D is actually a mixture of two emulsifiers

Both Tween/Span emulsifiers were mixed at a temperature of 50°C, while emulsifier mixtures of A & E and emulsifier ranges A-E were prepared at a temperature of 80°C. Figure 28 shows that the HLB value of paraffin does not change with preparation temperature. However, it can be observed that the temperature has a large influence on the droplet size created. By preparing at a temperature of 80°C the average droplet size can be decreased by a magnitude of about two.

Another aspect that is important with the HLB scale is the mixing/blending of emulsifiers. It is important to note that Emulsifier D is a mixture of two nonionic emulsifiers. The emulsifier blend of A & E with an HLB of 12 can be compared with Emulsifier D. A & E have an HLB difference of 2, while the emulsifiers mixed to form Emulsifier D have a HLB gap of 5. Emulsifier A & E is exhibited a slightly smaller droplet size than that of Emulsifier D. This can be explained by research conducted by Shinoda, Yoneyama, and Tsutsumi. Shinoda, Yoneyama, and Tsutsumi found that when mixing emulsifiers, better solubility behavior is exhibited when the HLB difference in the emulsifiers is small [Shin80].

4.1.2. Temperature / Cloud point

The emulsifiers that were tested for cloud point were emulsifiers A, C, D ,E, G and a mixture of A & E. The mixture of A & E has an HLB value of 12. The cloud point was determined by averaging the initial separation temperature and the temperature at complete separation. The cloud point for the various emulsifiers was as following: Emulsifier A = 82°C, Emulsifier D = 91°C, Emulsifier = 92°C, and Emulsifier C, E and mixture of A & E > 98°C. Since Emulsifiers C, E and mixture A & E all exhibited cloud points of greater than 98°C, a preparation temperature above 98°C would be improbable. Therefore, it was deemed appropriate that when preparing emulsions with droplet sizes of less than 10μm a preparation temperature of at least 80°C should be used. However, further experimentation on the exact effect of preparing emulsions with different emulsifiers at different preparation temperatures closer to the cloud point should be conducted.

Experimental Results

4.1.3. Chemical Strucutre

It is an established principle of chemistry that the when mixing two solvents the chemical structure of the solvents can affect the physical properties of the solution. This principle is applicable when mixing emulsifiers with oils to form emulsions. Since emulsifiers have two distinct sections, the hydrophilic head and the lipophilic tail, the chemical structures of both of these sections have an effect on the stability of an emulsion.

Lipophilic Tail Group

To determine the impact the lipophilic tail group has on the overall emulsion kinetic stability three emulsion mixtures with an HLB value of 12 were prepared using the preliminary preparation method with a mixing temperature of 50°C. Figure 29 shows the droplet distribution for three non-ionic emulsifiers with the same hydrophilic head group, but with various lipophilic tail lengths. Emulsifier A is an ester with a chain length of 14 hydrocarbons. Emulsifier B is an ester with a chain length of 18 hydrocarbons and emulsifier C is an unsaturated ester with a chain
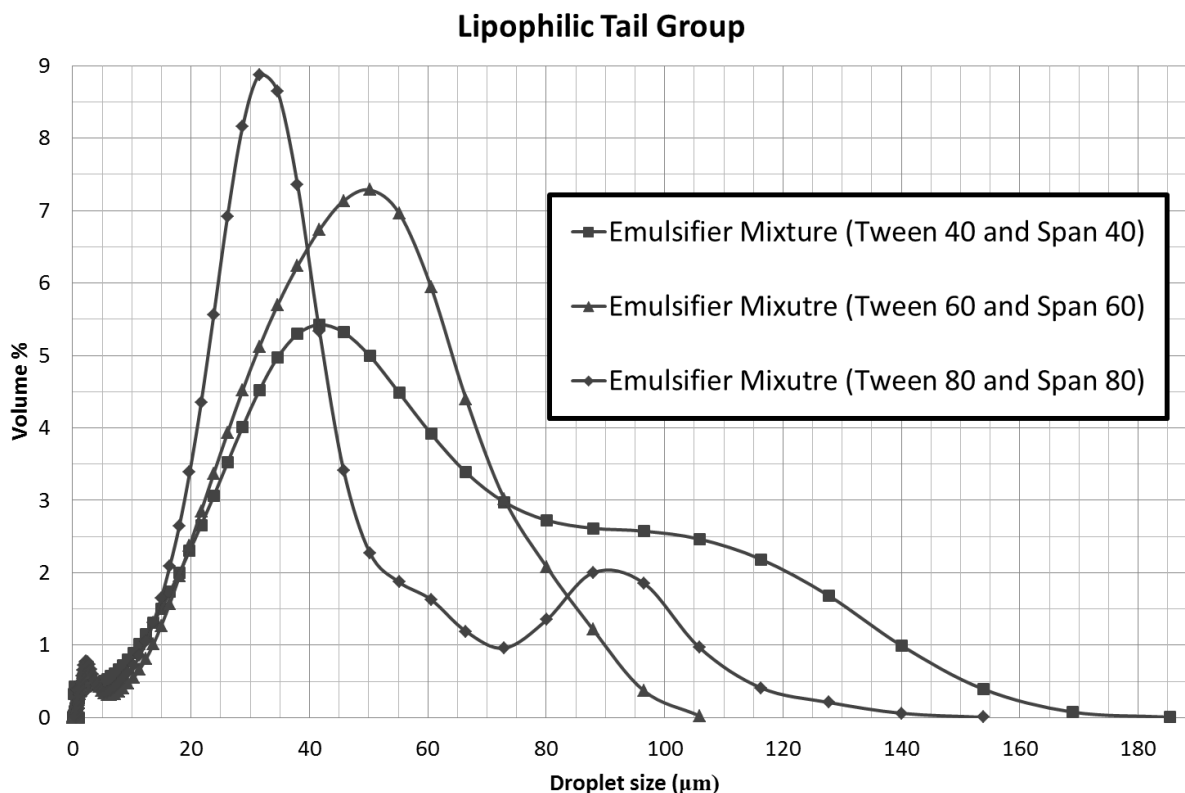

Figure 29: Lipophilic tail group droplet size and distribution

length of 18 hydrocarbons. It was hypothesized that emulsifiers with hydrocarbon chains similar

Experimental Results

in length to the paraffin would exhibit better stability properties. Contrary to the hypothesis emulsifier C with an unsaturated chain length exhibited the smallest average droplet size. However, emulsifier B with a saturated carbon chain exhibits a more stable monodispersed droplet formation. As hypothesized emulsifier A with a shorter chain length exhibits a larger average droplet size and is heterodispersed.

Hydrophilic Head Group

To measure the effect of the hydrophilic head group, two different head groups were compared. In this experiment both emulsions were prepared using the preliminary preparation method with a mixing temperature of 50°C. It is also of importance to note that all emulsions have an HLB value of 12. Emulsifiers F- H have an ether head group in comparison with the Tween/Span mixtures which area all esters. To eliminate effects from the lipophilic chain length, comparisons should be made between Emulsifier F and Tween/Span 40, Emulsifier G and Tween/Span 60, and Emulsifier H and Tween/Span 80. In figure 30 it can be immediately noticed that the average
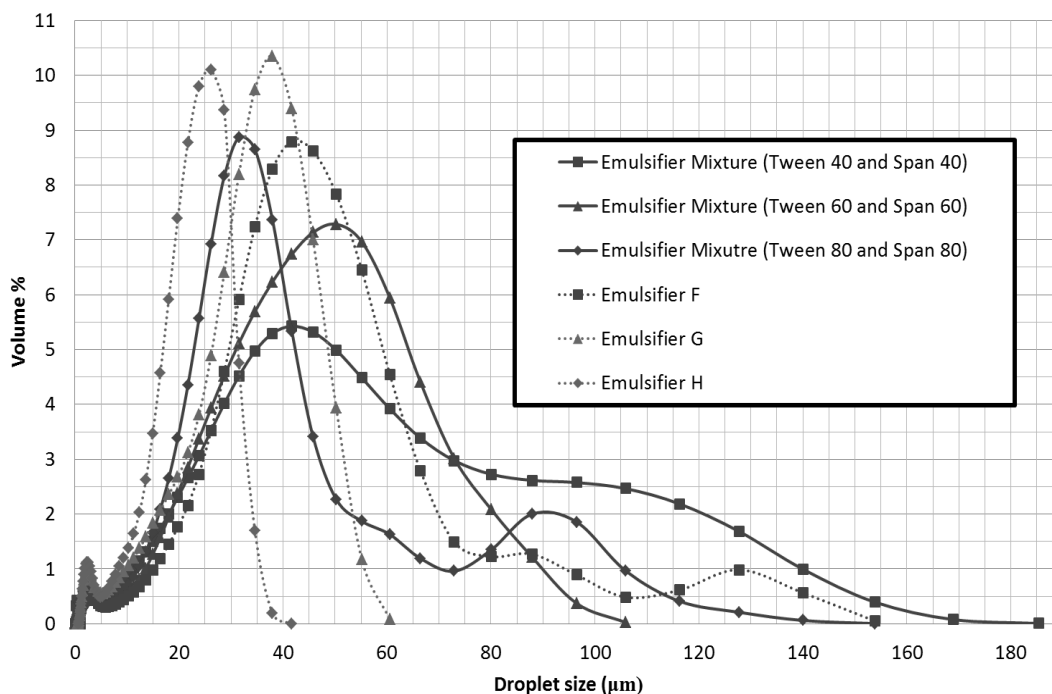
Figure 30: Hydrophilic head group droplet size and distribution

droplet size of the emulsions is decreased by using the emulsifiers with an ether hydrophilic head group. When comparing the emulsions with similar lipophilic tail groups (i.e. Emulsifier F and Tween/Span 40), it can be observed that they exhibit similar droplet distributions. This indicated that the droplet size is more dependent on the head group, while the droplet distribution

influences the droplet distribution. However, the droplet distribution of Emulsifier H, an ether with an unsaturated hydrocarbon chain composed of 18 carbons shows a more monodispersed droplet distribution than its ester counterpart (Tween/Span 80). Further investigation is needed to determine the cause of the shift between heterodispersion and monodispersion.

4.1.4. Concentration

For emulsions, concentrations of the emulsifier were based on a weight percentage of the paraffin phase. All emulsifier concentration emulsions were prepared using the preliminary preparation method at a mixing temperature of 50°C.

Emulsifier Concentration

In these experiments the paraffin and water concentrations were considered constants. The paraffin maintained a 30 wt. % concentration, while the emulsifier concentration was varied from 0.5-6 wt. % of the paraffin total mass. 0.5 wt. % was chosen as the lower limit for the
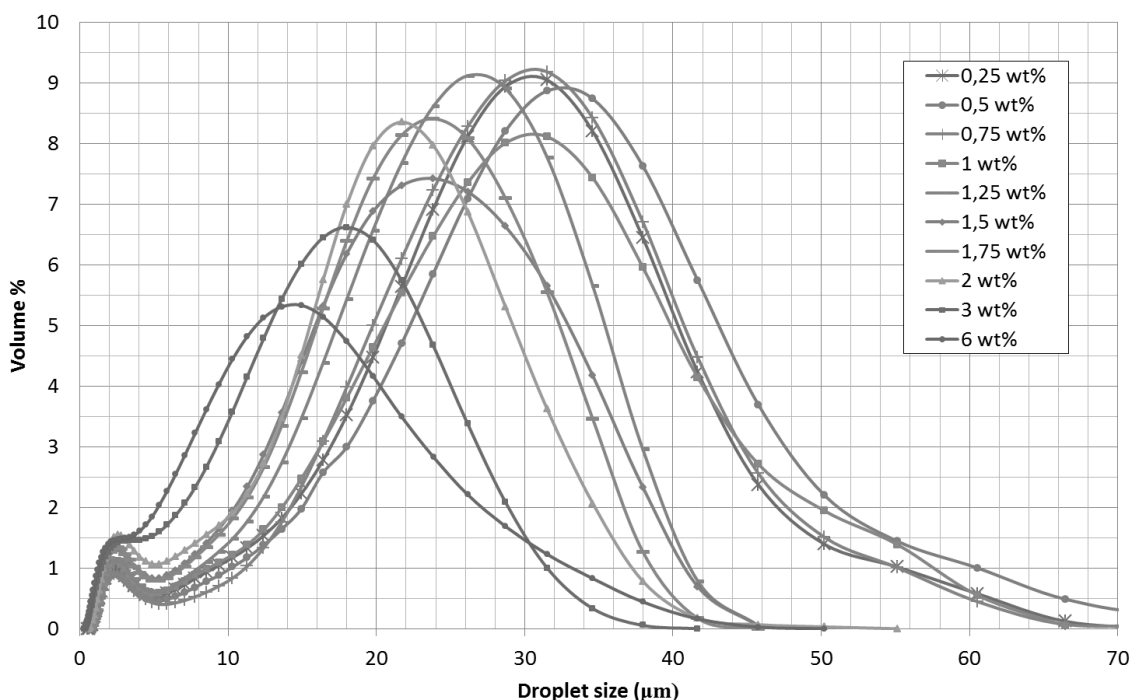

Figure 31: Concentration particle dispersion and droplet size

concentration based on the critical micelle concentration in literature. The critical micelle concentration is the minimum concentration of an emulsifier that must be used in order for stable micelles to be formed. This is the minimum concentration required for the emulsifier to complete cover the droplet surface and produce a stabile droplet. From figure 31 it can be observed that as the emulsifier concentration increases it impacts the average droplet size and droplet distribution.

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Experimental Results

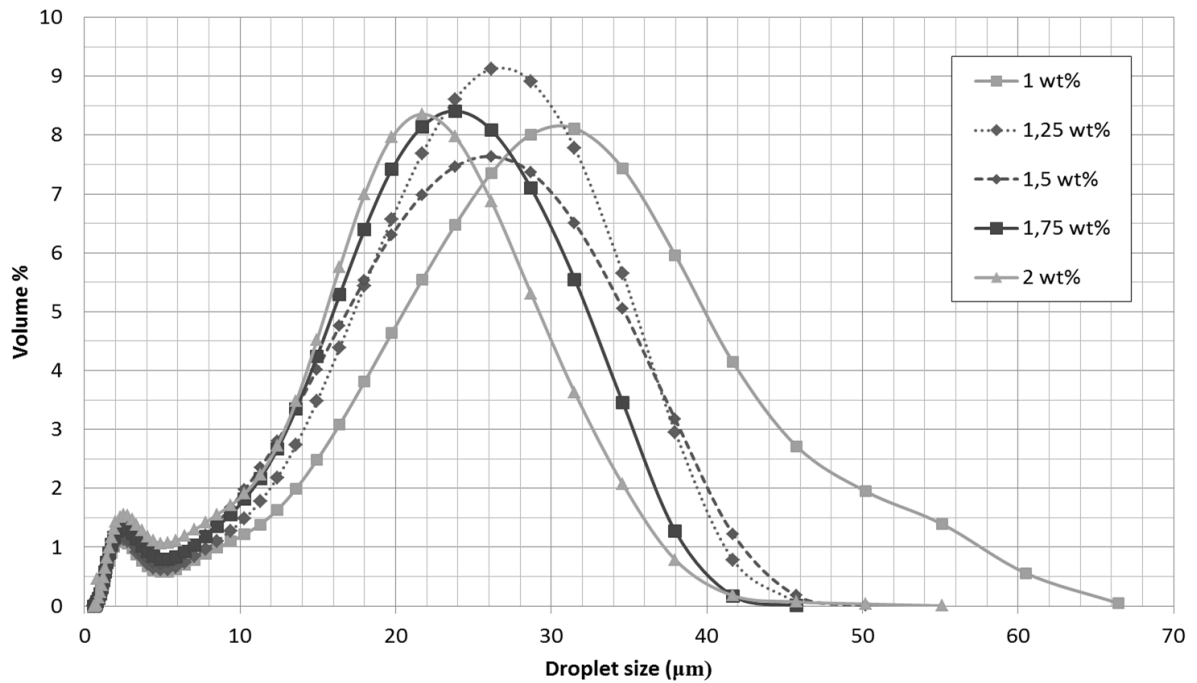Figure 32: Concentration versus droplet size (narrow range)

Low and high concentrations tend to exhibit a more heterodispersed droplet distribution, with tails, that denote the existence of larger droplets. The increasing concentration does tend to decrease the average droplet size. However, to determine droplet stability, the dispersion and the
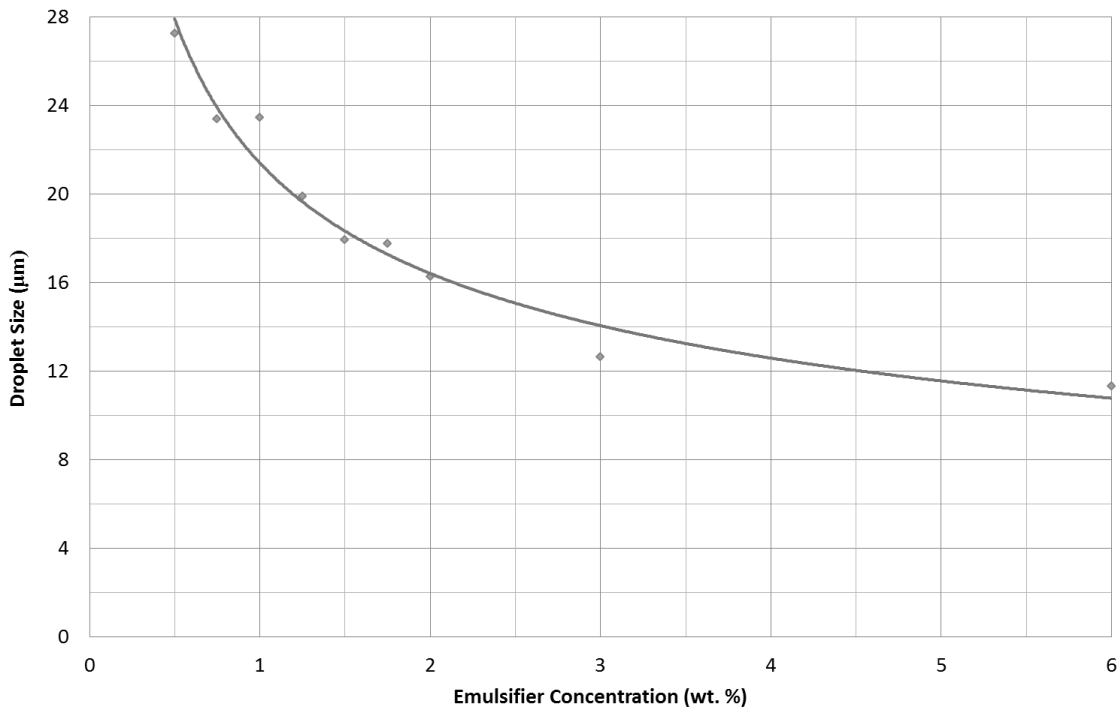

Figure 33: Average droplet diameter versus Concentration

50

droplet size must both be considered. In the instance of concentration, since other parameters can be varied to decrease the average droplet size, the most stable concentration would be around 1.5 wt. %. Figure 32 shows emulsions with concentrations within the range of 1-2 wt. % to better determine a more precise optimum concentration. From figure 32 it can be determined that the best droplet dispersions are monodispersed between ranges of 1.25-1.75 wt. %. However, with a concentration ranging from 1.25 – 1.5 wt. % appear to have the best droplet distribution. By plotting the average droplet size for the different concentrations, as seen in figure 33, it can be observed that as the concentration increases from 0.5 – 2 wt. % there is a large decrease in the droplet diameter. However, after reaching 3 wt. %, the droplet size decrease with concentration reaches a plateau. This indicates that using the concentration to influence droplet size not efficient. Emulsifier concentrations over 3 wt. % should not be used because they do not significantly improve the droplet stability.

4.2. Subcooling/heat capacity

Paraffin/water emulsions tend to exhibit subcooling effects. Subcooling is when a liquid can be cooled below its melting point without showing crystallization. To counterbalance subcooling nucleating agents can be used. However, previous research has indicated that by optimizing the
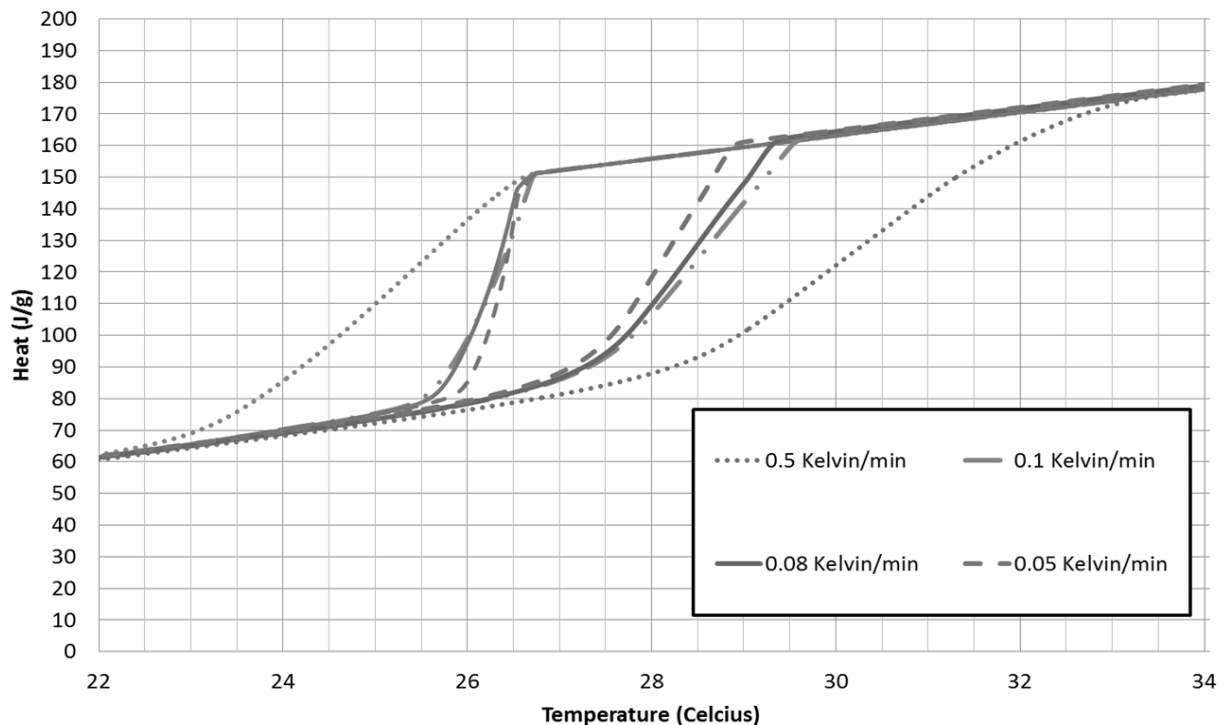

Figure 34: Temperature heating/cooling rate
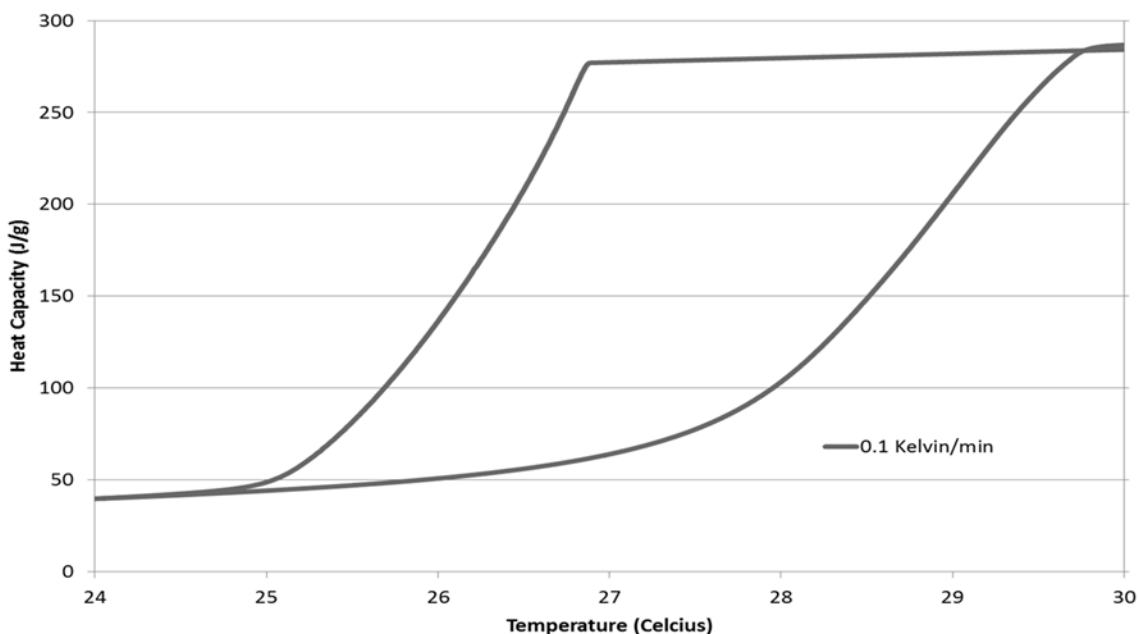
Experimental Results

Figure 35: Pure paraffin (baseline) subcooling

emulsifier the degree of subcooling can be minimized. An initial testing was done on the different heating /cooling rates to determine the maximum heating/cooling rate to be used to gain accurate data. The degrees of subcooling are determined by observing the degrees difference in the heat capacity curve of the heating cycle with that of the cooling cycle. Figure 34 shows a graph where the same emulsion went through repeated measurements on the micro DSC, where only the heating/cooling rate was changed. From this graph it was determined that the maximum heating/cooling rate that would achieve an accurate subcooling measurement was 0.1 Kelvin/min. The 0.5 Kelvin/min rate showed signs of being too quick and causing a temperature difference between the inside of the sample chamber and the outside. The slower heating/cooling rate of 0.05 Kelvin/min shows a deviation from the 0.1 Kelvin/min rate, but the time duration for one measurement was considered too long for the large number of samples. However, it could be considered if more accurate readings are necessary. Figure 35 shows the subcooling associated with a pure sample of paraffin. The subcooling was determined to be around 3°C. Figure 35 will be used as a baseline for all other subcooling graphs. All other subcooling graphs can be compared for similar melting, freezing temperatures, and degrees of subcooling.

Throughout the subcooling results, there are variances in the heat capacity of different samples. This can be explained by either two main causes. The first is that over time as samples were left

out they may have been subject to evaporation. As the water content in the sample decreases, the paraffin concentration would increase and result in a larger heat capacity. The other possible explanation would be that many samples showed signs of physical separation within hours. When left standing overnight, samples tended to separate and the paraffin phase would re-solidify. Since measurements were taken sometimes day or weeks after samples were prepared, the emulsions had to be reheated and shaken. It is possible that emulsions were not completely re-liquefied and that this caused variations in the paraffin concentration.

4.2.1. Hydrophile-Lipophile Balance

Emulsions over a variety of HLB values were tested to determine if the HLB value had any significant effect on the subcooling. For this experiment emulsions made from a Tween/Span 60 mixture with a mixing temperature of 50°C were used. The subcooling as shown in figure 36, was for all samples deemed to be between 2.5-3°C, and unaffected by the HLB value of the
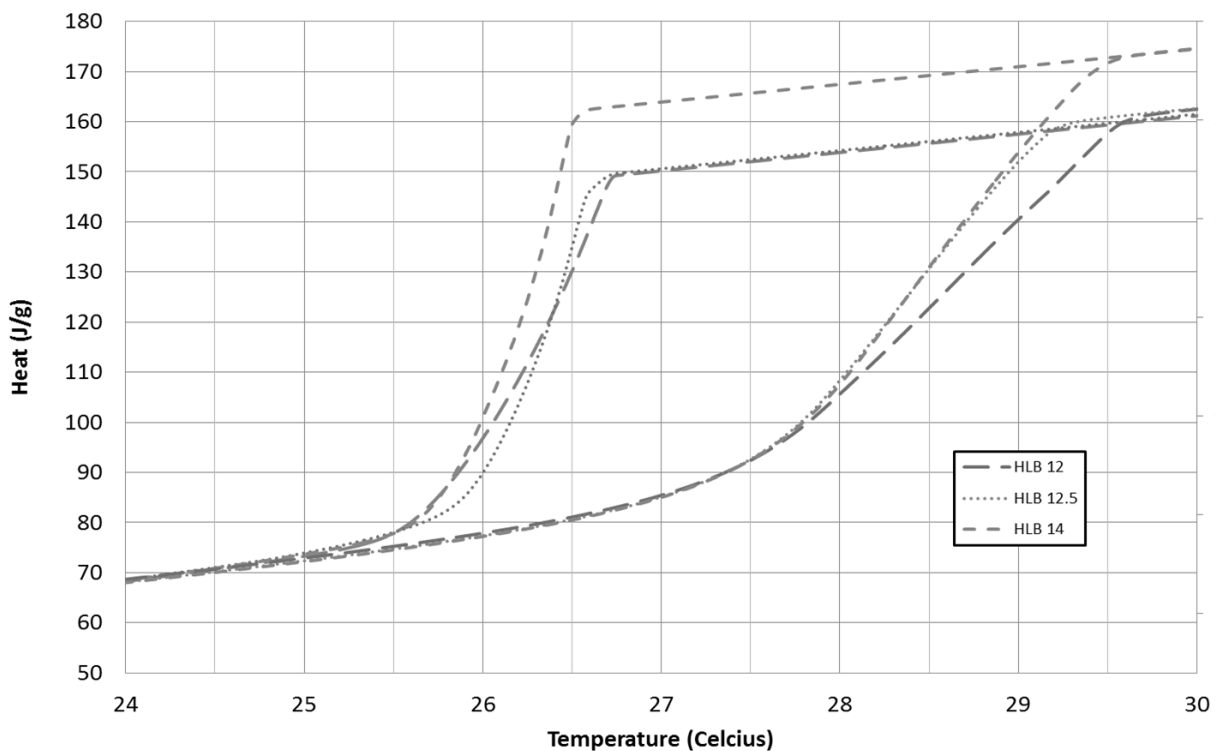

Figure 36: HLB subcooling

emulsion. The melting point for all emulsions was seen at being near 29.5°C and the freezing point around 26.5°C.

Experimental Results

4.2.2. Chemical Structure

Lipophilic Tail

Figure 37 shows the subcooling variation related to different tail lengths. Subcooling is observed to be between 1-3 degrees Celsius for all samples, showing that the chemical structure of the emulsifier does not greatly impact the degree of subcooling. For this experiment the melting
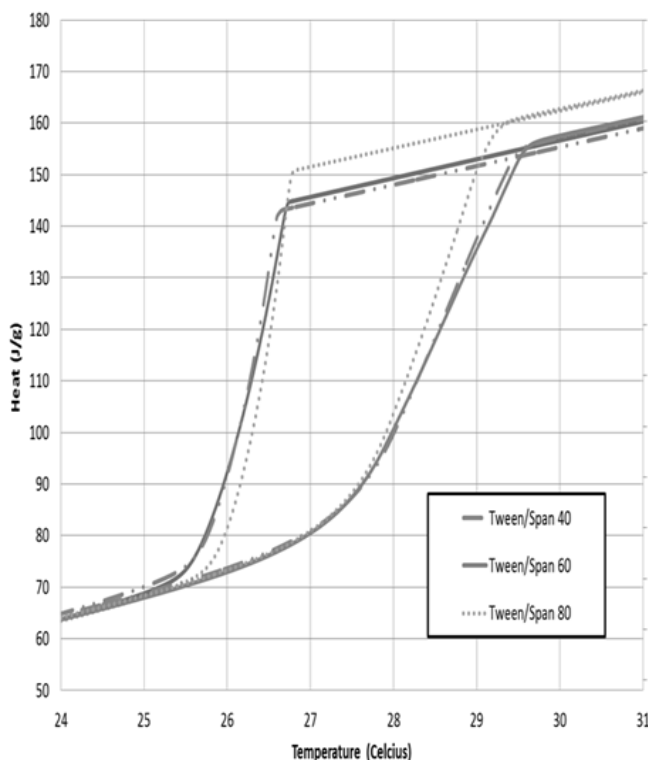
Figure 37: Lipophilic tail group and

point was determined to be at 29.5°C, while the freezing point was between 26 and 26.5°C.

4.2.3. Concentration

The subcooling of the emulsion in connection with variations of concentration can be observed in figure 38. There is a slight variation in the freezing temperature; it is not a significant change. The melting temperature is observed to remain for all concentrations at 29.5°C and the freezing point was determined to be between 26.3 and 26.7°C. The degree of subcooling ranges from about 2.5-3°C. This shows that varying the concentration does not significantly impact the subcooling.

Figure 38: Subcooling due to Concentration

4.2.4. Dispersion

In previous studies it has been observed that as the droplet size of an emulsion decreases the degrees of subcooling increases. Therefore, experiments were conducted on the droplet size and

Figure 39: Droplet dispersion

distribution of different emulsions to determine influence on the subcooling of the emulsion.
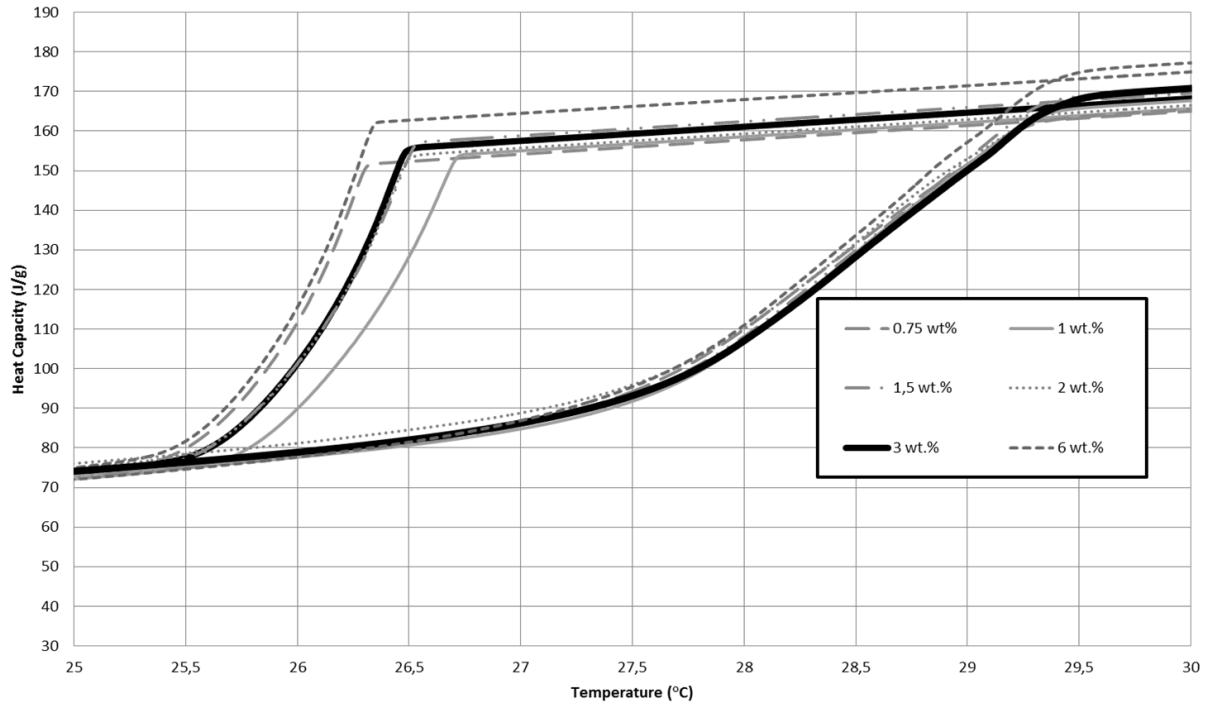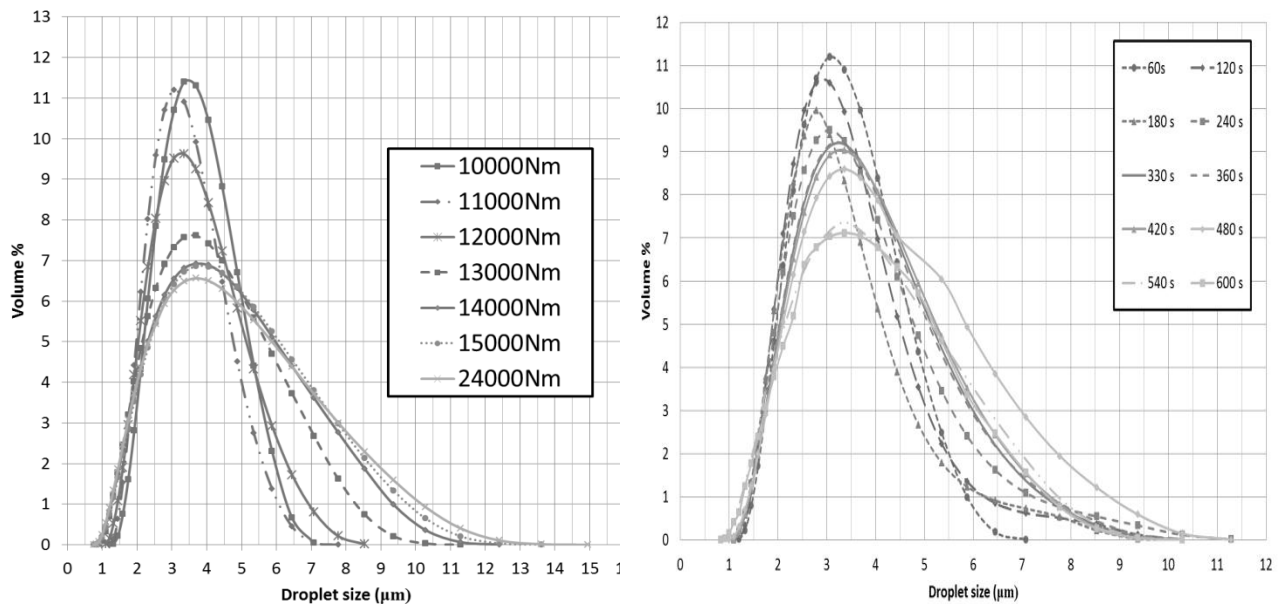
Experimental Results

Two experiments were conducted, both using the emulsion preparation method. The first experiment the speed of mixing was varied from 10,000 rpm to 24,000 rpm and the other the time of mixing was varied. The droplet dispersions were recorded, figure 39. It can be observed that as the mixing time and the speed increase the droplets become less monodispersed. The subcooling was measured for emulsions with narrow distributions (60 seconds) against that of an emulsion with a broad distribution (600 seconds). The subcooling for these different droplet
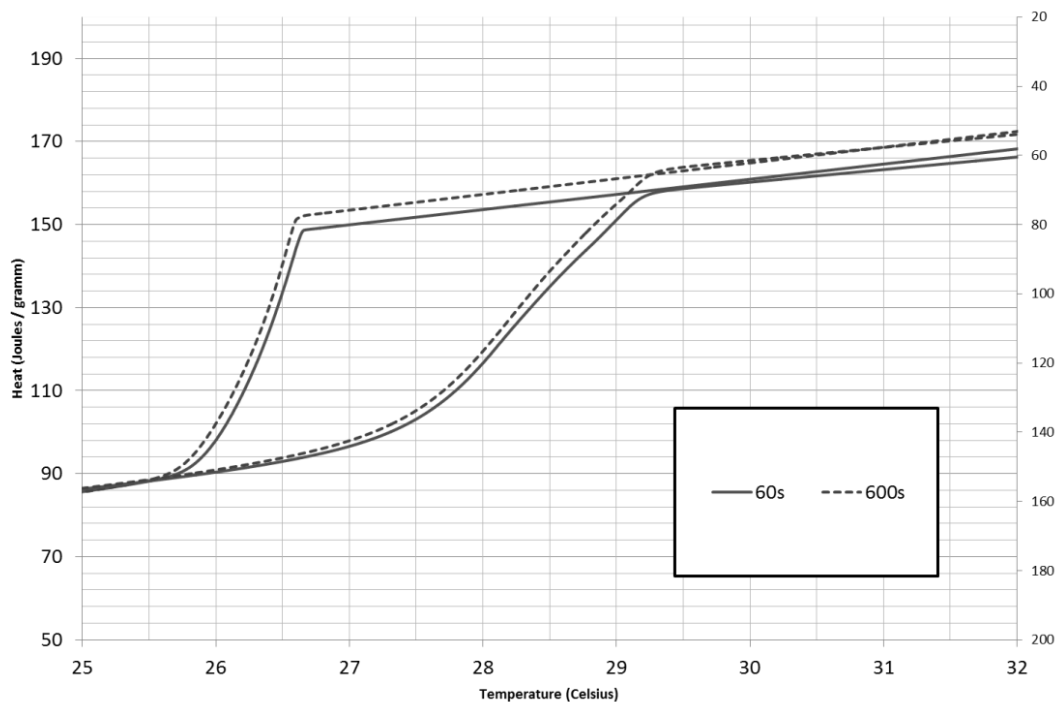
Figure 40: Droplet dispersion subcooling

dispersions was measured, shown in figure 40.

It can be observed that even though the droplet dispersion varies, the subcooling does not. The subcooling again measured at roughly 3°C. The melting point and freezing point are observed at 29.5 and 26.5°C, respectively. The more heterodispersed emulsions do not significantly change the subcooling. However, the droplet size during these experiments does not vary greatly. Therefore, another comparison should be done where the droplet size not the distribution is varied.

4.2. Thermal Mechanical Stability / Viscosity

Experiments were conducted only on emulsions that showed potential as kinetically stable emulsions with minimal degrees of subcooling. The Anton Paar Rheometer was programed to complete a heating and cooling cycle. Short cycles were conducted of 20 heating and cooling

Experimental Results

cycles for emulsions. The Rheometer was programmed for longer cycles for emulsions that showed stable viscosities during the short cycles.
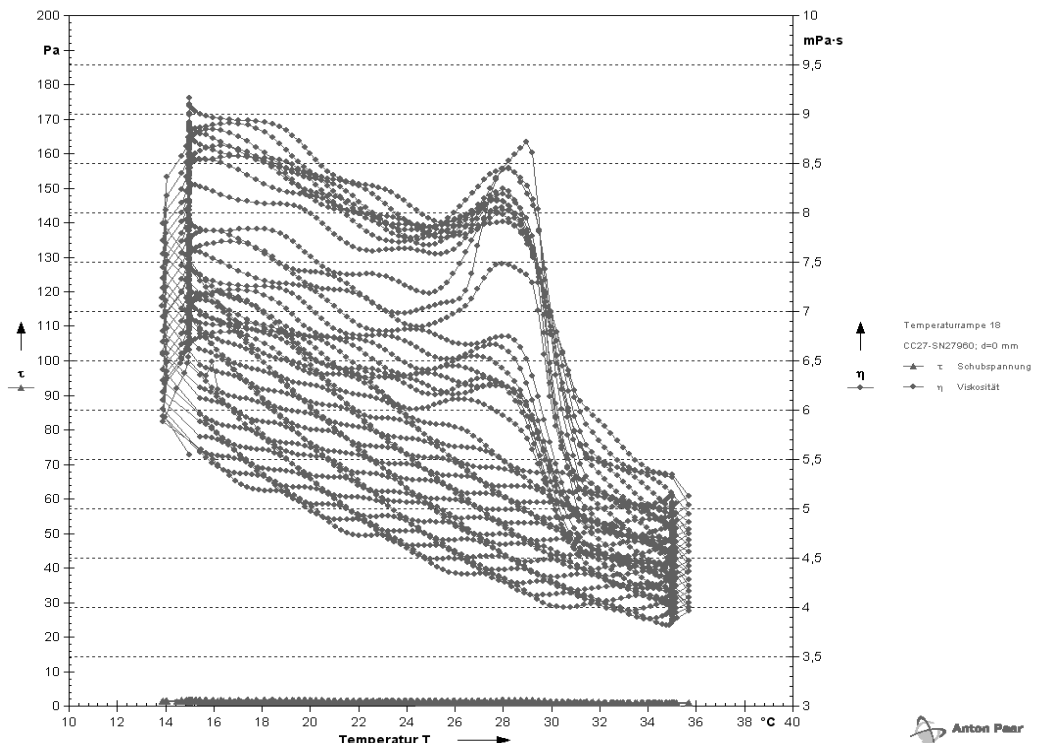
Figure 41: Viscosity profile of sampel TO6_8_1,5wt%_HLB12_11,000_rpm after short cycle

Results for the emulsifiers F, G, H and their derivatives exhibited unstable viscosities during the
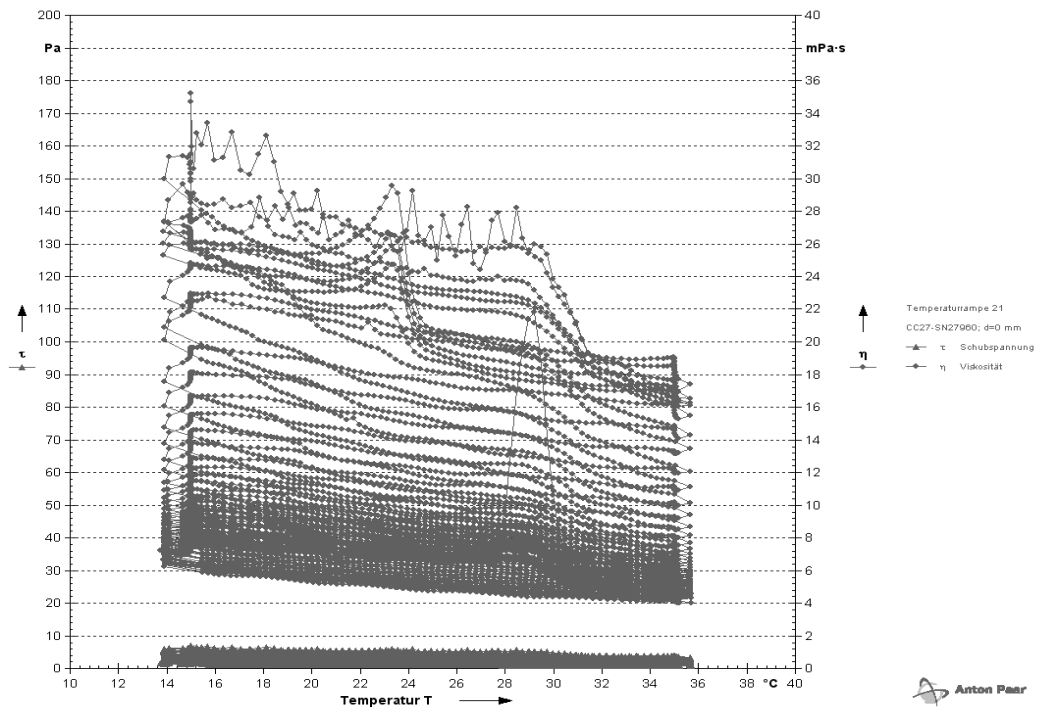
Figure 42: Viscosity profile of sample TO_6_8_1,5wt%_HLB12_11,000_rpm after long cycle

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short cycles, regardless of emulsifier concentration variations between 1,5wt% and 3wt%. Emulsifiers C and D also exhibited unstable viscosities during short cycles. Emulsifier mixture of emulsifiers A & E with a HLB value of 12, prepared at a mixing temperature of 80°C and
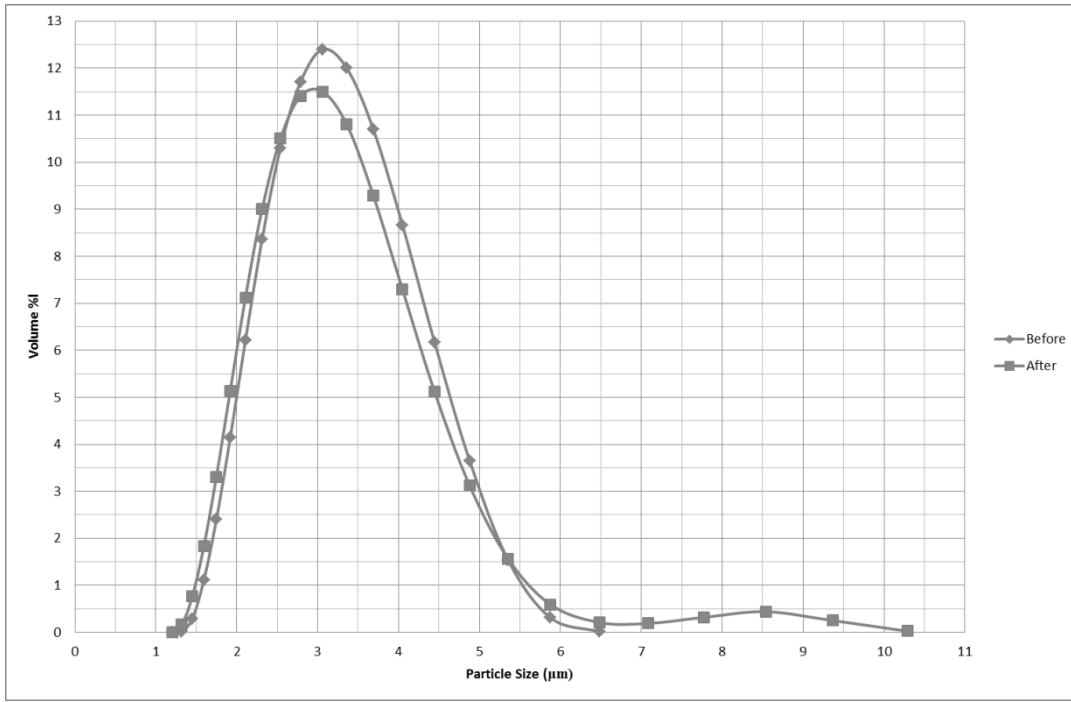
Figure 43: Droplet size and distribution before and after short cycle

speed of 11,000 rpm for 3 min, exhibited a stable viscosity for short cycles and a semi-stable viscosity over long cycles. It can be observed that the visocisty slowly increases during the long cycles, with the last few cycles showing an unpatterned unstability. Figures 41 and 42 show the viscosity profile of the short and long cycles, respectively, while figure 43 shows the droplet distribution and size before and after the short cycles.

5. Conclusion and Future Recommendations

From these experiments it can be concluded that the chemical structure, preparation method, emulsifier concentration, and HLB have a significant impact on the droplet size and distribution of an emulsion. These parameters greatly influence the kinetic stability of an emulsion; however, these parameters do not have a significant impact on the thermal properties of an emulsion. It should be also be noted that for all emulsions prepared with the preliminary emulsion method, clumping and separation were observed usually within 24 hours. However, for emulsions prepared with the emulsion preparation method, this clumping and separation was not always observed. Thus for future studies it is important to use the emulsion preparation method to avoid kinetic instability.

From the kinetic stability studies it can be concluded that the octadecane used has an optimal HLB value of 12. It can be concluded that to produce a kinetically stable emulsion the following parameters should be used. The emulsifier should have an HLB value of 12. The emulsifier concentration should be between 1.25 – 1.5 wt. %. The lipophilic chain length should be similar to the chain length of the oil, in this case 18 hydrocarbons. The stir time should not exceed 3 min and to produce emulsions with droplet diameters between 1-10 μm a pump speed no greater than 11,000 rpm should be used. It can also be concluded that the hydrophilic head group impacts the kinetic stability of an emulsion and that in these studies a ether head group produced more stable emulsions than an ester head group. However, since not every commercially available nonionic emulsifier head group was tested the best head group cannot be determined.

After analyzing the mechanical thermal stability, future research should be concentrated on determining the optimal properties exhibited by a mixture of emulsifiers A & E with a HLB of 12. This was the only emulsion that exhibited a stable viscosity after repeated cycles. By determining the properties of this emulsion that enable a stable viscosity and minimal degradation of droplets over cycles, other potential emulsifiers can be identified.

Although this research has characterized the impact of certain parameters on the kinetic stability and thermal properties of emulsions in an effort to improve the understanding of selecting a suitable emulsifier for use as a PCS, there are still significant gaps of knowledge. The following section discusses recommendations for future work in order to close these gaps of knowledge.

In the area of kinetic stability, further studies on different hydrophilic head groups should be conducted to better understand how each head group interacts in the emulsion. It should be noted

Future Recommendations

that several other types of head groups are available. Since it was observed that esters and ethers interact differently, it would be recommended to conduct further experiments on other head groups. It is recommended to conduct surface tension measurements in order to obtain the critical micelle concentration and determine the minimum concentration required to produce a stable emulsion.

In the area of thermal physical properties, it would be of interest to conduct experiments relating the subcooling. This would include conducting experiments on emulsions with smaller droplet sizes in order to know the smallest droplet size possible with the least amount of subcooling. It would also be of interest to conduct experiments on the effects emulsifiers have on the viscosity of emulsions. In these studies no experiments were conducted on the viscosity, but achieving emulsions with low viscosity is important for future use in a pump system and therefore would be of significant interest to future research works.

From the conclusions drawn from these experiments on how to optimize kinetic stability of an emulsion, emulsions with a droplet size of less than 10 μm should be produced and tested for rheological properties. Emulsions should also undergo testing for thermal-mechanical pump stability. Thermal-mechanical pump stability should first be tested in a laboratory setting and then in a pilot test apparatus to determine the difference between measurements in the lab and operational functionality.

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