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EFFECT OF SILICA NANOPARTICLE AGGRE-GATE STATE ON PICKERING EMULSION FOR-MATION AND STABILITY

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EFFECT OF SILICA NANOPARTICLE AGGREGATE STATE ON PICKERING EMULSION FORMATION AND STABILITY

BY

MAXIMILIAN SENDER

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OF

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ABSTRACT

During the Deepwater Horizon Oil Spill in 2010 approximately 210 million gallons of crude oil was released into the Gulf of Mexico. To enable bacterial degradation the oil had to be dispersed into small oil droplets, which was achieved using 1.84 million gallons of chemical surfactants. As these surfactants have questionable environmental impacts, the idea of this research project is to use silica nanoparticles as a model particle to form Pickering emulsions and to study oil-mineral aggregate (OMA) formation. Pickering emulsions typically consist of oil droplets stabilized by solid particles instead of surfactants. Silica might be suitable for this as it already occurs in the ecosystem ocean, e.g. as sand. Furthermore it is known that seawater, oil and particulate matter form OMAs, but the interactions between particles, OMAs, and surfactants are still poorly understood. This is why the commercial available surfactant Aerosol OT (AOT) as a model surfactant was used to estimate the interactions between surfactant and OMAs.

To determine the suitability of silica nanoparticle as oil dispersants, defined silica aggregates were created and fractionated to yield distinct size fractions. These aggregates were mixed with ethyl acetate, octanol and octane as model oils to determine the aggregate adhesion to oil/water interfaces and the formation of Pickering emulsions or OMAs. The reason for choosing these oils is their different polarity. With these results the formation of Pickering emulsions and OMAs are determined using silica agglomerates of three different sizes. The theory suggests that that the stability of Pickering emulsion in DI-water increases with increasing particle size. During the experiments an optimum particle size for Pickering emulsions in DI-water was observed. Furthermore it was observed that the formation of a significant OMA layer requires seawater. As soon as the surfactant Aerosol OT was added, the thickness of the sedimentation layer was reduced. AOT is believed to bind to the silica nanoparticles through

divalent cation bridging, but the exact nature of this interaction is still unknown. BP/The Gulf of Mexico Research Initiative Grant No. SA 12-05/GOMRI-002 supports this project.

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CHAPTER 1. INTRODUCTION

During the Deepwater Horizon Oil spill in the Gulf of Mexico in 2010, 1.84 million gallons of the chemical dispersants COREXIT® 9500 and 9527 were applied to the oil slick or injected at the wellhead [Hertsgaard, 2013]. They were used to disperse the crude oil within the water column. This process supports bacterial degradation in order to reduce the toxicity and the environmental impacts that result from oil migrating into costal ecosystems. However, the toxicity of such dispersants and their influence on the marine ecosystem is questionable and under intense debate [CNN, 2010a; George-Ares & Clark, 2000; Hemmer et al., 2010; Rico-Martínez et al., 2013]. The potential hazards associated with dispersant use have led to intense interest in identifying new biocompatible dispersant systems.

One new approach is to use silica nanoparticles solely or in combination with chemical dispersants as an emulsifier. Nanoparticles are particles of any shape with one dimension between 1 to 100 nanometer [Vert et al., 2012]. A container with silica nanoparticles is shown in Figure 1.1.

Figure 1.1: Silica nanoparticles as a dry powder [LHcheM, 2012]

Silica is very suitable for the usage as emulsifier as the formation, stability and structure of emulsions stabilized by colloidal silica has been investigated since the discovery of

Pickering emulsions[1] in 1906 [Aveyard et al., 2003]. Additionally, silica is available in nature and accounts for about 75 weight percent of the Earth's crust for example as quartz sand [Iler, 1979]. This means nature is accustomed to dealing with silica as bounded structures. Furthermore this availability makes silica inexpensive [Iler, 1979]. The proposed idea driving this research project is that silica nanoparticles will adhere to oil/water interfaces and can be used to disperse oil as Pickering emulsions. This dispersion will increase the bacterial degradation of an oil slick in comparison to one that is undispersed. Apart from the usage as an oil spill dispersant, silica nanoparticles might be able to replace surfactants in other areas where emulsions are sought such as in soaps, foods and cosmetics, or wastewater treatment.

The motivation for this project was two-fold. The first was to examine the use of silica nanoparticles as oil spill dispersants, and to study the underlying mechanisms that determine the physical properties and stability of the dispersions. The second was to use silica nanoparticles as a model mineral particle to study the formation and sedimentation behavior of oil-mineral aggregates (OMAs). Previous research showed that silica nanoparticles flocculate and form oil mineral aggregates [e.g. Midmore, 1999; Vignati et al., 2003]. These two aspects can be studied in tandem because the same physical phenomena that allow for the formation of Pickering emulsion also lead to OMA formation. Based on this knowledge the following hypothesis is identified: **The size of silica nanoparticles has a significant influence on the formation and stability of Pickering emulsions and the formation of oil mineral aggregates with oil in deionized and seawater.**

In order to test this hypothesis the following objectives were identified:

1) Create and fractionate silica nanoparticle aggregates to yield distinct size fractions with narrow size distributions.

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[1] In Pickering emulsions the stabilizing molecule around the dispersed droplets is replaced by an envelope of solid particles [Thieme et al., 1999]

2) Examine aggregate adhesion to oil/water interfaces and demonstrate the formation of Pickering emulsions for different oils (e.g. organic solvents, gasoline, crude oil).
3) Determine the influence of particle size on the formation of aggregates consisting of oil, silica and minerals in seawater.

In order to complete these objectives, the theoretical principles are discussed followed by choosing the three different oils to form Pickering emulsions with three different size fractions of silica particles. Later, the anionic surfactant Aerosol OT (AOT) was added to probe the emulsion formation and stability while adding a commercial available surfactant and the results are compared.

Results from this thesis project have been presented as a poster for the University of Rhode Island Chemical Engineering Research Symposium in April 2014, and as an oral presentation for the Colloid & Surface Science Symposium hosted by the American Chemical Society in June 2014 held in Philadelphia, PA. These can be found in appendix 6.9.

CHAPTER 2. **BACKGROUND**

In the following section the theoretical principles that form the basis for the conducted research are discussed. First, dispersants and their functionality are presented. The next section outlines natural oil degeneration with a focus on seawater and weathering of crude oil. This is followed by an explanation of Pickering emulsions and oil mineral aggregates (OMAs). After that the effects of reagglomeration and filtration are disclosed followed by a description of silica and silica nanoparticles. At the end of this chapter the measurement equipment used is explained.

2.1. Dispersants

A very general definition of dispersants is given by Heusch and Reizlein: Dispersants are “products that are able to promote or stabilize the formation of a dispersion” [Heusch & Reizlein, 2008, p. 1]. In a dispersion are two or more insoluble components finely distributed into each other [Heusch & Reizlein, 2008]. The U.S. codes for Federal Regulations describe dispersants as “chemical agents that emulsify, disperse, or solubilize oil into the water column or promote the surface spreading of oil slicks to facilitate dispersal of the oil into the water column” [CFR, 2001]. This means dispersants are a key for an effective oil spill response in order to minimize environmental damage. Conventional dispersants are detergent-like products [Lessard & DeMarco, 2000]. Using them is one of the limited practical available responses to offshore oil spills [Fiocco & Lewis, 1999]. Dispersants are used to reduce the oil water interfacial tension [Gong et al., 2014].

The usage of dispersants is necessary as only a small part of an oil slick can be removed by traditional mechanical response. Lessard and DeMarco estimate that this mechanical response rarely results in a recovery of more than 20% of the spilled oil [Lessard & DeMarco, 2000]. The reason one would use dispersants is to disperse the oil into the water.

This supports natural oil degeneration due to an increase of the specific surface area of the oil. The effective use of dispersants during the early phases of oil spill response may prevent or reduce impacts on coastal habitats, wildlife, and property [George-Ares & Clark, 2000]. Furthermore the usage of dispersants is cheaper than conventional methods like the mechanical removal of the spilled oil [Etkin, 1998]. The National Research Commission stresses that dispersants are one potential first response to oil spills [NRC, 1989].

Before dispersants can be applied to the oil slick their potential benefits and risks have to be evaluated. The potential benefit is that the dispersed spilled oil is removed from the sea surface and will not drift into shallow water or ashore. This is important as most damage is done by spilled, undispersed oil in shallow water or on the shore [EMSA, 2009]. But it has to be considered that the use of dispersants might expose some marine organisms to a higher level of dispersed oil than would happen without the usage of dispersants. Unfortunately it is difficult to predict the degree of harm for marine organisms exposed to dispersed oil [EMSA, 2009]. One reason for that is because it is difficult to predict oil toxicity [French-McCay, 2002]. Furthermore the quality and composition of crude oil varies depending on the type of crude oil (e.g. *Brent* or *West Texas Intermediate)* [EIA, 2012]. Dispersants are not a silver bullet for treating oil spills as they are not recommended for all spills and for all conditions [George-Ares & Clark, 2000]. Before their use, the net environmental benefit needs to be weighed against other spill response options. Fiocco and Lewis suggest for this an oil spill response decision tree [Fiocco & Lewis, 1999]. This tree is stated in appendix 6.1.

2.1.1. Application of dispersants

The application of dispersants to the surface is possible in many oil spills whereas the application at the wellhead is only possible at higher depths. Because of this are the fact that during the Deepwater Horizon oil spill more dispersants were applied on the surface then at the wellhead [Kujawinski et al., 2011], the following section will focus on the application of the dispersant at the surface.

There are three different ways to apply dispersants to oil slicks on the surface of the ocean [Fiocco & Lewis, 1999]. All ways have in common that their main principle is similar to crop spraying in agriculture, where a plane or a tractor sprays pesticides over a large area. The three different ways of application are:

1) **Using ships and boats:** The usage of ships and boats is relatively easy as ships can carry high loads in comparison to helicopters and planes. Their main disadvantages are their slow speed and the fact that they cross the oil slick. If a ship's bow wave is too large, it might push the oil out of the range of the dispersant spray unit. [Fiocco & Lewis, 1999]
2) **Using helicopters:** Helicopters are useful for spraying dispersants for smaller oil spills. One big advantage is that they are quickly equipped with the spraying bucket. The maximum capacity per helicopter varies between one ton of dispersant for a small helicopter such as MBB-105 and three tons for a larger helicopter such as Sikorsky S61-N, which is shown in Figure 2.1. [EMSA, 2009; Fiocco & Lewis, 1999]

Figure 2.1: A Sikorski 61N helicopter reloading dispersant spray bucket from a support vessel [EMSA, 2009]

3) **Using fixed wing aircrafts**: Many different types of aircrafts can be used for spraying dispersants. This starts with small, single engine crop spraying aircrafts, which carry less

than one ton of dispersant [Fiocco & Lewis, 1999]. The United States have developed their own dispersant spray system, called the Aerial Dispersant Delivery System. This system is based on the Lockheed Hercules C-130 and enables, depending on the exact configuration of the machine, a capacity of 13.250 to 15.000 liters chemical dispersant, which is limited in comparison to ships. A C-130 spraying a chemical dispersant over the Gulf of Mexico in 2010 is shown in Figure 2.2. The major problem with this plane type is that the C-130 was developed in the early 1950s, which means it is at the end of its product life. The main advantage of aircrafts compared to surface vessels is their much higher speed that enables them to reach a spill site faster than a ship and enables them to quickly spray large areas of an oil slick with dispersants. But planes are limited to low flying which is required in order to spray dispersant accurately. [EMSA, 2009; Fiocco & Lewis, 1999; IPIECA & OPG, 2012]

Figure 2.2: An US-Air Force plane drops an oil dispensing chemical into the Gulf of Mexico [Cadiz, 2010]

In case of a leakage at a wellhead, as with the Deepwater Horizon oil spill, it is possible to inject the dispersant close to the wellhead (subsurface injection). This has the advantage that oil and dispersant can mix ascending the water column. In case of the Deepwater Horizon oil spill the injection at the wellhead was not possible at all times because the conditions in terms of current and visibility varied. [Kujawinski et al., 2011]

2.1.2. Structure and functionality

Before dispersants can be applied, it must be determined whether the dispersant is suitable for treating an oil spill under the predominant conditions. Therefore the exact composition of the dispersants is important. Dispersants consist of three different types of chemicals: Solvents, additives and surfactants [Gong et al., 2014]. Solvents are added to promote the dissolution of surfactants, to reduce the viscosity of the dispersant and to affect its solubility in spilled oil [Gong et al., 2014]. Additives are used to improve the dissolution of the surfactants into an oil slick and to increase the long-term stability of dispersant formulation [NRC, 2005]. Surfactants (*surface active agents*) are the active components and have a ‘soap-like’ molecular structure. This structure has both, water-loving hydrophilic and oil-loving hydrophobic or lipophilic groups [Fiocco & Lewis, 1999]. Using a surfactant lowers the interfacial tension between oil and water and enables the formation of oil droplets [Gong et al., 2014].

For surface applications the dispersant is sprayed onto the oil slick (see step 1 in Figure 2.3). In the next step, the dispersant diffuses through the oil and patrons at the oil-water interface (see step 2 in Figure 2.3). As it is more difficult to diffuse through high viscosity oils, it is more difficult to disperse oils with a high viscosity than light oils [Sun & Zheng, 2009]. At the oil-water interface the dispersant adjusts itself so that the lipophilic end of the dispersant is attached to the oil phase and the hydrophilic end reaches in the water phase. With this the interfacial tension between water and oil is reduced. External energy input, e.g. by waves, wind or current, disperses the oil into the top 5-10 meters of a water column as tiny, 1-70 micrometer large droplets (see step 3 in Figure 2.3). [Lessard & DeMarco, 2000]

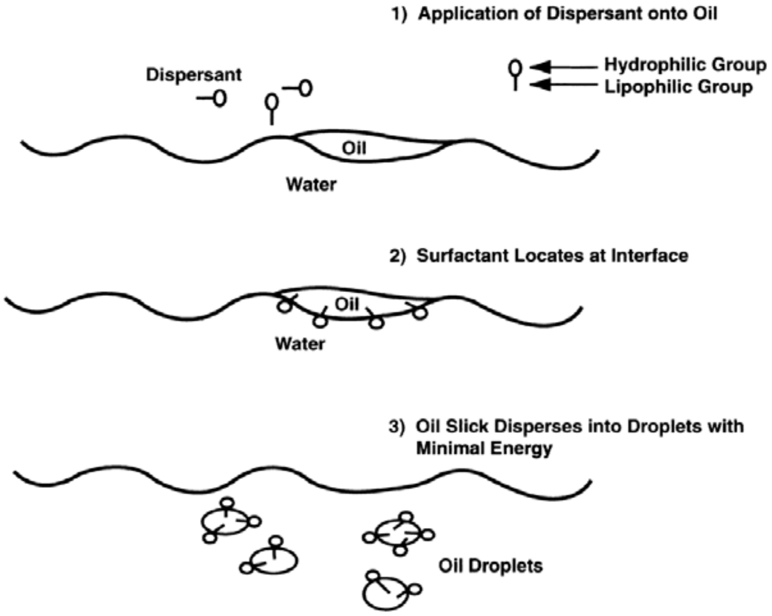


Figure 2.3: Working mechanism of dispersants to create oil droplets [Lessard & DeMarco, 2000]

2.1.3. Common Dispersants

First generation dispersants, which were developed in the early 1970s, were in some cases so toxic to the marine environment that the adverse effects of the dispersed oil were much greater than the effects of the untreated oil [Brochu et al., 1987]. Since then the dispersants have been improved. During the Deepwater horizon oil spill the surfactants COREXIT® 9500A (for surface applications and wellhead injections) as well as COREXIT® 9527 (for surface applications) were applied [Kujawinski et al., 2011].

One difficulty using dispersants during oil spills is to evaluate if dispersant treatment was successful and to estimate the toxicity if the dispersant on the marine environment. One example is the first usage of COREXIT® 9500 after the Sea Empress oil spill in the United Kingdom in February 1996 [Lessard & DeMarco, 2000]. The single hull tanker Sea Empress ran aground at the entrance to Milford Haven and exposed an estimated 72,000 tons of Forties Blend crude oil and 360 tons of fuel oil to the North Sea [Harris, 1997]. For the treatment of this oil spill 445 tons of dispersant were used [Harris, 1997]. Lessard and DeMarco as well as Lunel et al. describe the dispersant use as overall successful [Lessard & DeMarco, 2000;

Lunel et al., 1997]. There is some proof in the literature that there has been no significant effect on the plankton of the Southern Irish Sea [e.g. Batten et al., 1998]. Furthermore there are no reports of the mortalities of commercially-exploited crustaceans or fish as a result of the oil spill [Law & Kelly, 2004]. But other studies show that the oil spill had negative effects. For example Lyons et al. showed that the Sea Empress oil spill resulted in significantly higher self-reported illness in terms of anxiety, depressions, headache, sore eyes and sore throat of people living in towns exposed to the Sea Empires oil spill [Lyons et al., 1999]. But it is difficult to conclude if the oil spill or the dispersant are the cause of this.

Furthermore it was determined that the use of COREXIT® during the Deepwater Horizon oil spill supported the penetration of polyaromatic hydrocarbons into the sandy beach sediments of the Northeastern Gulf of Mexico [Zuijdgeest & Huettel, 2012].

Rico-Martinez et al. determined the toxicity of a mixture of Macondo crude oil, seawater and the dispersant COREXIT® 9500. They report that the toxicity of this mixture is up to 52 times higher to B. manjavacas than Macondo crude oil and seawater [Rico-Martínez et al., 2013]. Macondo crude oil was spilled during the Deepwater Horizon oil spill. Studies which were conducted by the COREXIT® manufacturer, oil companies like British Petroleum and the United States Environmental Protection Agency, do not view these dispersants as being extremely toxic [CNN, 2010a; Hemmer et al., 2010].

Such different toxicity results may occur as for testing dispersants it has to be considered that the laboratory aquatic toxicity varies with the test species and the experimental conditions [George-Ares & Clark, 2000]. This means factors like temperature, salinity, oil type and concentration, as well as concentration of the dispersant, might have an influence on the toxicity.

As of April 2014 the U.S. Environmental Protection Agency (EPA) lists 19 different dispersants in the National Contingency Plan’s Product Schedule. The EPA has effectiveness and heavy metal/chlorinated hydrocarbon content data available for the listed dispersants. This data can be found in the National Contingency Plan's Product Schedule Technical Notebook [US EPA, 2014a]. These dispersants are listed in Table 2.1.

Table 2.1: Dispersants on the National Contingency Plan Product Schedule as of April 2014 [US EPA, 2014b]

Product Name	Manufacturer	Listed since
COREXIT® EC9527A (formerly COREXIT 9527)	Nalco Environmental Solutions	1978
NEOS AB3000	Neos Company	1985
MARE CLEAN 200 (formerly MARE CLEAN 505)	Taiho Industries Co.	1988
COREXIT® EC9500A (formerly COREXIT 9500)	Nalco Environmental Solutions	1994
DISPERSOT SPC 1000™	U.S. Polychemical Corp.	1999
JD-109	GlobeMark Resources	2000
JD-2000™	GlobeMark Resources	2001
NOKOMIS 3-F4™	Mar-Len Supply	2002
BIODISPERS (formerly PETROBIODISPERS)	Petrotech America Coperation	2002
SEA BRAT #4	Alabaster Corp.	2002
FINASOL® OSR 52	TOTAL FLUIDES	2003
SAF-RON GOLD	Sustainable Environmental Technologies	2005
ZI-400	Z.I. Chemicals	2005
NOKOMIS 3-AA	Mar-Len Supply	2008
SUPERDISPERSE™ WAO2500	Baker Petrolite Corporation	2011
ACCELL CLEAN® DWD	Advanced BioCatalytics Corporation	2011
FFT-SOLUTION®	Fog Free Technologies	2011
MARINE D-BLUE CLEAN™	AGS Solutions	2012
COREXIT® (EC9500B)	Nalco Environmental solutions	2013

These dispersants have different toxicities and efficacies. The LC_{50}-value for Mysidopsis bahia (a kind of shrimp) after 48 hours depends on the concentration of the dispersant and oil. The LC_{50} value is the median lethal dose where half of the members of the tested population were killed. As an example the LC_{50} value for Mysidopsis bahia with COREXIT® 9527A is stated in Table 2.2.

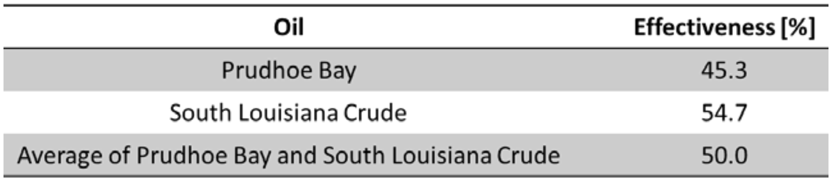
Table 2.2: LC_{50}-value for Mysidopsis bahia after 48h [US EPA, 2014a]

Material tested	LC 50 [ppm]
COREXIT® EC9527A	24.14
Benchmark Oil	16.12
COREXIT® EC9527A & Benchmark oil (1:10-ratio)	6.60

From this table it can be seen that the dispersant COREXIT® EC9527A alone has a much higher LC_{50} value than a benchmark crude oil. The combination of COREXIT® EC9527A and benchmark crude oil has a lower toxicity then the oil alone. This means that COREXIT® EC9527A has to be used carefully so that dispersant is only dispensed over the oil slick.

The efficacy of dispersants is varying depending on the crude oil. The effectiveness of COREXIT® EC9527A when applied to Prudhoe Bay and South Louisiana Crude oil is stated in Table 2.3.

Table 2.3: Effectiveness COREXIT® EC9527A [US EPA, 2014a]



Oil	Effectiveness [%]
Prudhoe Bay	45.3
South Louisiana Crude	54.7
Average of Prudhoe Bay and South Louisiana Crude	50.0

The varying effectiveness shows that the dispersant has to be chosen in consideration of the spilled oil.

One component of COREXIT® EC9527A is Aerosol OT (AOT), Dioctyl sodium sulfosuccinate or Butanedioic accid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester [US EPA, 2014c]. This organic, negatively charged surfactant AOT is used as a wetting agent in cosmetic products, gelatin, and beverages [Schor, 2010; Sigma-Aldrich, 2014; US EPA, 2013]. Furthermore AOT is registered as an insecticide in pet shampoos [US EPA, 2013] and a registration as a pesticide has been filed [US EPA & Keigwin, 2010]. AOT is ranked in the Hazardous Material Identifier System as inflammable and stable, but temporary minor injury may occur for humans after contact [Sigma-Aldrich, 2014]. Additionally AOT is listed on the WHO Model List of Essential Medicines as a drug in palliative care [WHO, 2013]. The structure formula for AOT is shown in Figure 2.4.

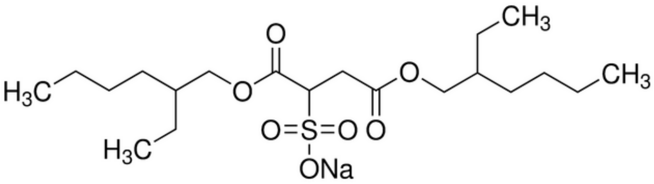


Figure 2.4: Chemical structure Aerosol OT [Sigma-Aldrich, 2014]

In the *Agreement for cooperation in dealing with pollution of the North Sea by oil and other harmful substances* from 1983 (“Bonn Agreement”) many European states limit the usage of dispersants [Bonn Agr. Secr. et al., 2009]. For example Sweden is not using dispersants at all. In Germany the usage of dispersants in shallow water with less than 10 meter depth is not allowed. Between 10 and 20 meter depth the usage of dispersants has to be permitted by official administration (Havariekomando in Cuxhaven). [Bonn Agreement, 2005]

While choosing the right dispersant, it has to be considered that under certain conditions like special emulsions or heavier oils the dispersion rate might be slow as the chemical agents need time to penetrate the oil [Lessard & DeMarco, 2000].

2.2.Natural oil degeneration

The effect of oil degradation in the ocean is a natural process and is necessary because natural oil spills take part without human action. The total worldwide input of hydrocarbons into the ocean is estimated at 1,300,000 tons per year between 1990 and 1999. The input from natural seeps is about 600,000 tons per year, which is 46% of the total input [NRC, 2003]. The other sources are stated in Table 2.4.

Table 2.4: Average, annual releases of petroleum by source (1990-1999) [NRC, 2003]

Source	Tons per year	Percentage
Natural seeps	600,000	46
Activities related with consumption of petroleum	480,000	37
Accidental spills and operational discharges of cargo oil occurring during transportation	160,000	12
Extraction processes	38,000	3
Total	**1,276,000**	**100**

At the Sea Empress Oil spill in 1996 were 72,000 tons crude oil exposed to the sea. During the Gulf War 1,500,000 tons of oil were exposed to the sea during the largest oil spill in history [CNN, 2010b; The Telegraph, 2014]. During the Deepwater Horizon oil spill 210 million gallon of crude oil was spilled in the Gulf of Mexico [The Telegraph, 2014]. Assuming a density of $\rho_{oil\ Deepwater\ Horizon} = 0.84\frac{kg}{L}$ [Liu et al., 2012] this equals about 670,000 tons crude oil. This is about the average annual release from natural seeps (compare Table 2.4).

Crude oil consists of four types of hydrocarbon molecules, called the hydrocarbon series. The percentage of each hydrocarbon series varies depending on the type of crude oil controlling the chemical and physical properties of that oil. These hydrocarbon series are paraffines, naphthens, aromatics and asphaltics. If a hydrocarbon has only single bonds between carbon atoms, they are called saturated. If they have at least one double bond, they are unsaturated. Paraffin or alkane molecules are saturated linear chains of carbon atoms. If paraffin has more than 17 carbon atoms, it is a wax and forms a waxy crude oil. A naphthalene or cycloparaffin molecule is a closed circle with saturated bonds between the carbon atoms. As soon as one of these bonds is unsaturated, it is an aromatic or a benzene molecule. An asphaltic molecule has more than 40 carbon atoms. These asphaltic molecules are brown to black and determine the color of crude oil. The average and range of hydrocarbon series molecules is shown in Table 2.5 [Hyne, 2012, pp. 2–4].

Table 2.5: Average and range of hydrocarbon series molecules in crude oil [Hyne, 2012, p. 4]

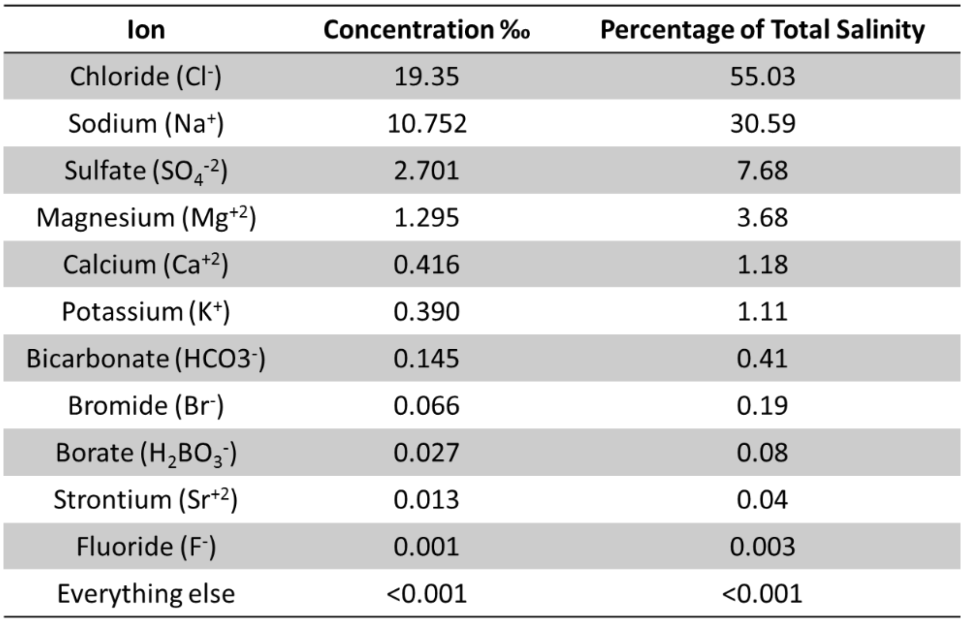
	Average weight percent	Percent range
Paraffins	30	15-60
Naphthenes	49	30-60
Aromatics	15	3-30
Asphaltics	6	remainder

It has to be considered that the chemical composition of crude oils from different producing regions and even from within one formation can vary tremendously [NRC, 1985, p. 17]. The process of degradation takes place in an ocean surrounding, which consists of seawater.

2.2.1. Seawater

According to the Encyclopedia Britannica seawater is a mixture consisting of water, salts and some small amount of dissolved inorganic and organic materials, particulates and dissolved atmospheric gases [Mackenzie et al., 2014]. The salt concentration is defined as salinity, which is the total amount of salt dissolved in seawater. Salinity is expressed as grams of salt left behind after 1,000 grams of seawater are evaporated [Castro & Huber, 2003]. It is interesting that the percentage of different salt ions present in the solution remains constant and the absolute amount of salt, the salt concentration, varies. This salt concentration is in a range between 33 ‰ and 37 ‰ with an average about 35 ‰ in the open ocean [Castro & Huber, 2003]. That means that vaporizing 1,000 g seawater will leave in average 35 g salt, which is a salt concentration of about 1148 mM [Pilson, 1998, p. 59]. The composition of seawater under the assumption of 35 ‰ salinity is shown in Table 2.6.

Table 2.6: The composition of seawater of 35 ‰ salinity [Castro & Huber, 2003, p. 48]



Ion	Concentration ‰	Percentage of Total Salinity
Chloride (Cl^{-})	19.35	55.03
Sodium (Na^{+})	10.752	30.59
Sulfate (SO_4^{-2})	2.701	7.68
Magnesium (Mg^{+2})	1.295	3.68
Calcium (Ca^{+2})	0.416	1.18
Potassium (K^{+})	0.390	1.11
Bicarbonate ($HCO3^{-}$)	0.145	0.41
Bromide (Br^{-})	0.066	0.19
Borate ($H_2BO_3^{-}$)	0.027	0.08
Strontium (Sr^{+2})	0.013	0.04
Fluoride (F^{-})	0.001	0.003
Everything else	<0.001	<0.001

The temperature of seawater varies between -2°C and +30°C. Temperatures below 0°C are possible as seawater is saltwater which freezes colder than ordinary water [Castro & Huber, 2003, p. 48]. Temperature and salt concentration are a key parameter for the density as seawater gets denser as it gets saltier or colder [Castro & Huber, 2003]. The range of pH 7.4 to pH 9.6 covers most pH water on earth [Marion et al., 2011]. In this surrounding of seawater takes the natural oil degeneration part.

2.2.2. Weathering and natural oil degeneration

Within 24 to 48 hours after an oil spill the properties of the oil change significantly. This effect is called "weathering". Even after 48 hours this process of weathering continues, but the early changes are the most significant. The word "weathering" includes the processes of evaporation, dissolution, photo oxidation and emulsion formation [US EPA, 1993]. The type of oil and environmental factors like temperature, sea state and wind speed have an influence on the weathering process. The weathering process may reduce the dispersant effectiveness under extreme situations within two to four hours. This results in the loss of volatiles in the oil slick through evaporation, which causes an increase in oil density, viscosity and surface tension. Within 48 to 72 hours after the oil spill, the oil slick loses nearly all aromatic hydrocarbons that are lighter than naphthalene. [US EPA, 1993, p. 41]

The oil itself is generally degenerated by bacteria [Das & Chandran, 2011]. The first study of the utilization of hydrocarbons by organisms was conducted in the early 1900 [Bushnell & Haas, 1941]. In these studies the oxidation of methane was observed [Fuhs, 1961]. The general mechanism follows this reaction formula:

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O \tag{2.1}$$

But there are no general bacteria that consume all types of crude oil as the biodegradation is a selective utilization of certain types of hydrocarbons by microorganisms [Speight, 2006, p. 100]. The temperature has an influence on the degeneration rate of oil [Atlas, 1975; Garrett et al., 2003]. Another factor on the degeneration rate is the oil type. Garrett et al. determined that n-alkanes degenerate before iso-alkanes and smaller aromatic molecules are degraded before larger ones [Garrett et al., 2003].

As this chemical decomposition takes part as soon as the oil is spilled on the sea, the U.S. National Research Council notes that experiments designed to access the impact of crude oil should consider weathering effects [NRC, 1989]. These chemical and biological weathering processes reduce the toxicity and amount of oil residue and its potential effect to wildlife [Jahns & Bragg, 1991]. Weathering effects are supported by waves and tides as well as other cleanup activities [Jahns & Bragg, 1991]. Another supporting factor is the dispersion effect.

2.2.3. Dispersion effect

Lessard and DeMarco define the dispersion effect as an ongoing mixing of crude oil and seawater in the water column which results in very low concentrations of crude oil, less than 1 part per million in most cases. According to Lessard and DeMarco this dilution is the key to a successful dispersant application. Furthermore this process makes the oil droplets highly accessible to hydrocarbon-degrading bacteria, promoting removal from the environment by natural processes [Lessard & DeMarco, 2000]. The result of the dispersion effect is shown in Figure 2.5:

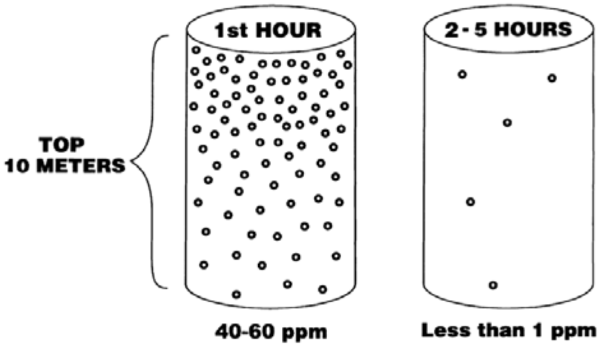


Figure 2.5: Dispersion effect [Lessard & DeMarco, 2000]

The idea of this research project is to disperse the oil using Pickering emulsions with silica instead of traditional surfactants.

2.3.Pickering Emulsions

A Pickering emulsion is an emulsion of two liquids with solid particles as the emulsifier. The general concept of Pickering emulsions is to replace the surfactant and form a classical emulsion with a solid particle. This creates a solid particle envelope around the dispersed droplets [Thieme et al., 1999]. The particles do not lower the oil/water interfacial tension like a conventional surfactant, but they are strongly absorbed at the interface and cannot easily be removed. This is shown in Figure 2.6.

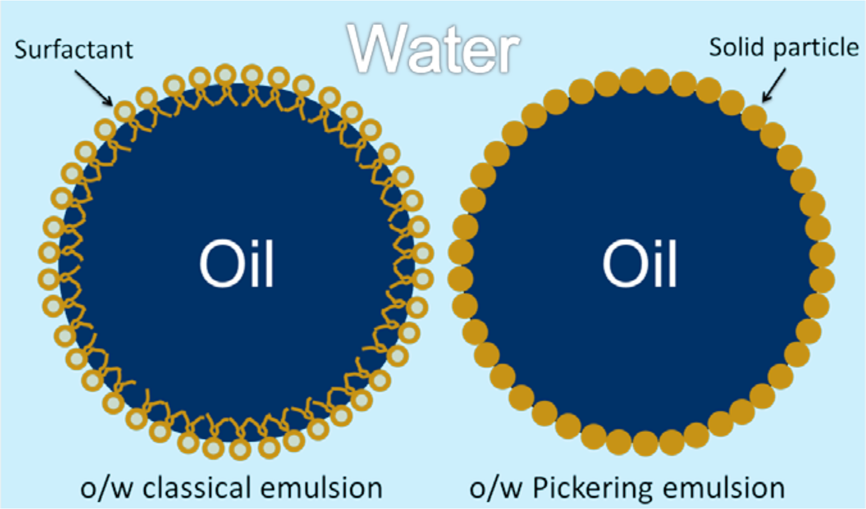


Figure 2.6: Sketch of a Pickering emulsion and a classical (surfactant-based) oil in water emulsion [c.f. Chevalier & Bolzinger, 2013]

This means Pickering emulsions are “emulsifier free”, which makes them attractive for applications where surfactants might have a negative influence, especially for applications with living matter for health and body care applications [Frelichowska, Bolzinger, & Chevalier, 2009].

Pickering Emulsions were discovered at the beginning of the 19th century [Pickering, 1907; Ramsden, 1903]. Even though Walter Ramsden discovered the effect first in 1903, this kind of emulsions is called after Spencer U. Pickering, who reported this emulsion in 1907.

2.3.1. Formation

Classical emulsifiers have similarities with Pickering emulsions [Midmore, 1998]. One important point is that the production is exactly the same. Particles are dispersed in the water or oil phase the same as emulsifiers [Chevalier & Bolzinger, 2013].

But Pickering emulsions show specific properties: The particle acts as barrier against formation and material transfer through the interface. This offers the possibility of forming stable millimeter sized emulsions as well as very stable double emulsions [Chevalier & Bolzinger, 2013] and is usable for drug release [Frelichowska, Bolzinger, Valour, et al., 2009].

The number of droplets formed in a Pickering emulsion strongly correlates with the viscosity, temperature, and asphaltene content of the two liquids [Khelifa et al., 2002]. Viscosity and asphaltene content are depending on the type of crude oil. Consequently is the number of droplets in a Pickering emulsion depends on the oil type. In this study Pickering emulsions are prepared with a vortex mixer. The basic principles of vortex mixing are explained in appendix 6.3.

2.3.2. Stability

For the stability the following equation is given for solid spherical particles, which are dispersed in an aqueous phase [Levine et al., 1989]:

$$\Delta G = \pi r_p^2 \gamma_{ow} (1 - |cos\Theta|)^2 \qquad 2.2$$

In this equation r_p stands for the radius of the particle, γ_{ow} is the interfacial oil/water tension and Θ is the contact angle. The interfacial tension is the work that is required to increase the surface area divided by that area [IUPAC, 2014, p. 1499]. If one of the media is water, it is called surface tension. The contact angle is defined as the angle between the two interfaces at the three-phase line of contact [IUPAC, 2014, p. 327]. The contact angle is defined as stated in Figure 2.7:

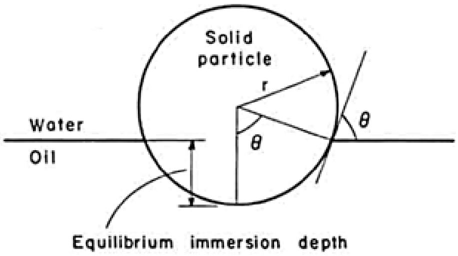


Figure 2.7: Isolated solid spherical particle at a planar oil/water interface [Levine et al., 1989 edited]

Furthermore it is assumed that the particles are so small so that the effect of gravity is negligible [Aveyard et al., 2003]. The equation *2.2* expresses the Gibbs free energy while a solid spherical particle is detaching the oil-water layer. The larger the ΔG-value the more stable the emulsion.

Additionally the effectiveness of the solids in forming a stable emulsion depends on the size, shape and concentration of the particles as well as on the interactions between particles [Binks, 2002; Giermanska-Kahn et al., 2002].

2.3.3. Pickering Emulsions with silica

There has been a significant amount of research on silica particles and Pickering emulsions. The main observations and results are stated below:

- The less polar the oil, the larger amount of silica is required to form a stabile Pickering emulsions. [Frelichowska, Bolzinger, & Chevalier, 2009]
- An increasing silica concentration causes a significant decrease in emulsion droplet size. [Frelichowska, Bolzinger, & Chevalier, 2009]
- Silica Pickering emulsions are pH dependent as the stability of the emulsion layer changes with changing pH. [Binks & Whitby, 2004; Dyab, 2012]
- Very hydrophobic or hydrophilic silica particles form emulsions with large droplets (>100µm). These droplets are unstable to coalescence [Binks & Lumsdon, 2000] except if a very polar oil is used [Frelichowska, Bolzinger, & Chevalier, 2009].
- Droplets formed by silica particles with a medium hydrophobicity are smaller than a micrometer and stable to coalescence indefinitely. [Binks & Lumsdon, 2000]
- If sodium chloride is present, emulsions with silica particles are unstable to creaming at all salt concentrations (0 to 5 M) and at pH values between 2 and 10. [Binks & Lumsdon, 1999]
- The average drop diameter of O/W-emulsions increases with increasing silica particle size. [Binks & Whitby, 2005]
- Pickering Emulsions with silica become less stable as sedimentation occurs. [Binks & Lumsdon, 1999]

Furthermore research has been conducted on the interactions between emulsions stabilized by silica nanoparticles and surfactants, but those interactions are still poorly understood [Whitby et al., 2009].

As the Pickering emulsions in this research project were formed using a vortex mixer, the function of a vortex mixer is explained in appendix 6.2.

2.4. Oil mineral aggregates

Oil can be present in the water column in two physical forms: As dispersed droplets and as dissolved components. These dispersed droplets or dissolved components can interact with sediments through [Gong et al., 2014]:

1) Direct aggregation to form oil mineral aggregates (OMAs)
2) Adsorption or incorporation in the sediment phase

The first reported interactions between oil droplets and minerals suggested that the factors which have an influence on the amount of oil connected to the solid phase include the type of oil (viscosity, composition), type of solid (mineralogy, grain size distribution, organic matter content), amount of turbulent energy and water salinity [Owens & Lee, 2003]. It has been suggested that the formation of OMAs play a major role in the natural cleaning of oiled shorelines and may be the basis for the development of oil spill countermeasure technologies [Khelifa et al., 2005].

There are three different structural types of OMA known [Gong et al., 2014; Stoffyn-Egli & Lee, 2002]. Examples for this are shown in Figure 2.8:

Droplets: Droplet OMAs appear as dispersed oil (spherical droplets) with mineral particles attached to their surface only (see Figure 2.8 A and B). Droplet OMAs are the most common type. Sometimes more than one droplet can be found within one OMA.

Flakes: Flake aggregates are thin sheets in which solid and oil particles are arranged in an ordered configuration in a scale up to millimeter (see Figure 2.8 C).

Solid: Solid mineral aggregates are typically a non-spherical mixture of oil and solid bodies of various shapes with irregular fluorescent contours (see Figure 2.8 D).

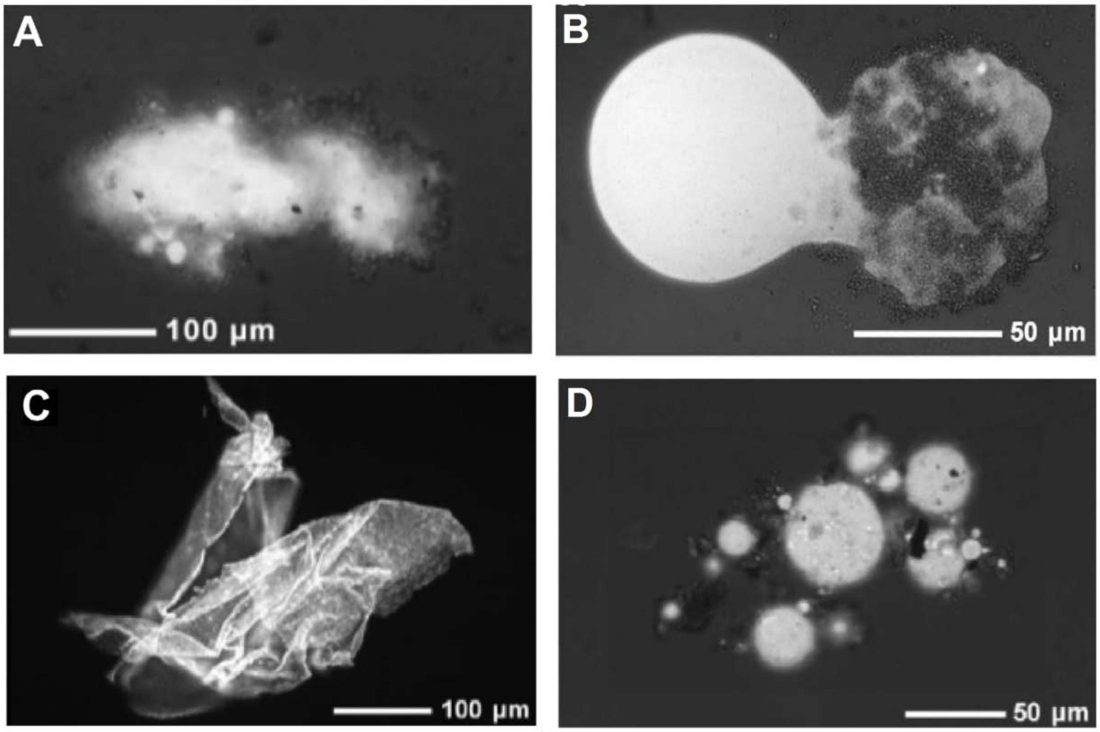


Figure 2.8: Three different types of OMAs [Gong et al., 2014 edited; Stoffyn-Egli & Lee, 2002 edited]. (A) Single droplet or multiple droplets (B) Droplet OMA from which particle free oil has leaked out leaving at right its mineral casing, (C) flake aggregates (D) solid OMA. All images seen by combined bright-field and UV Epi-fluorescence. Oil appears as bright areas and the mineral particles are dark

These structures can form rapidly in presence of oil-droplets, mineral fines and sea-water with an adequate amount of energy [Weise et al., 1999]. This flocculation stimulates the natural rates of oil biodegradation due to an increase in the oil-water interface area. This makes the oil more accessible to bacteria [Bragg et al., 1994; Weise et al., 1999]. An aggregation of solid material was observed in Pickering emulsions. This should be similar to the above-discussed droplet OMA [Thieme et al., 1999].

The typical formation of OMAs takes place in two steps. At first the oil slick is dispersed into oil droplets. The energy for that can be introduced in two different ways – external disturbing forces, which are mainly produced by the flow field, and internal restoring forces such as interfacial tension to maintain the shape of the droplet. In this step the mixing energy, the oil viscosity and the interfacial tension between oil and seawater are important. In the second step the oil droplets interact with suspended particulate matter. This interaction is mainly between the polar compounds within the oil and the suspended particulate matter. This is one of the main causes for destabilization of Pickering emulsions as this aggregation causes a transformation of particles into compact clusters. The particle in these solid clusters cannot create new Pickering emulsion droplets [Juárez & Whitby, 2012].

Salinity, oil type and concentration as well as sediment type and particle concentration have an effect on this second step. Afterwards, denser heavy OMAs settle while less-dense lighter OMAs are suspended in the water and rinse up to the surface. This effect is shown in Figure 2.9:

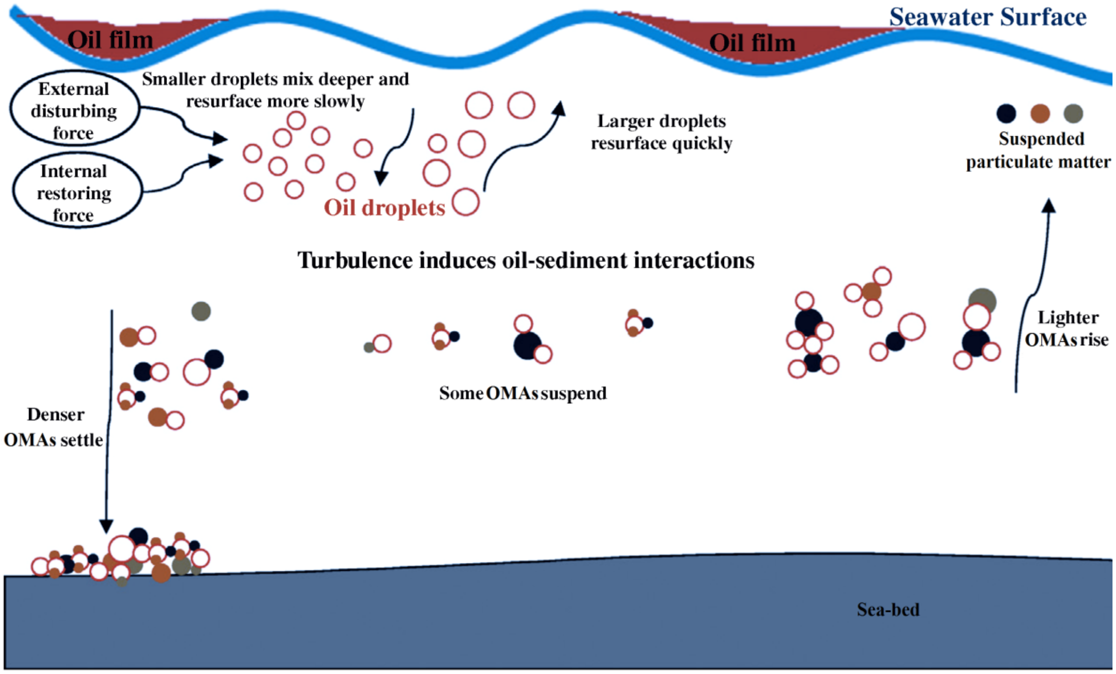


Figure 2.9: Formation and movement of various types of OMAs in the ocean [Gong et al., 2014 edited]

According to a review article written by Gong et al. the following factors have an influence on the formation of OMAs: [Gong et al., 2014]

1) **Oil characteristics** (viscosity, droplet size, composition, density, concentration)

2) **Physical properties of the solids** (mineralogy, grain size distribution, organic matter content, density, concentration)
3) **Environmental conditions** (temperature, pH, water salinity, pressure, hydrodynamic conditions)

Stoffyn-Egli and Lee state that fumed silica do not form OMAs in real seawater to any significant degree with IF30 fuel oil and different types of crude oil. *"Both mineral particles and oil droplets have a negative surface charge. In an electrolyte such as seawater, an electrical double layer forms, where cations are attracted to the surface of the particle, and this higher local concentration of cation in turn attracts more anions. […] It can be concluded that very fine particles cannot stabilize oil droplets because they cannot keep them at a distance large enough to overcome the hydrophobic bonding that cause oil droplets to re-coalesce."* [Stoffyn-Egli & Lee, 2002, p. 42]

2.5.Reagglomeration

One problem with silica nanoparticles is that they tend to agglomerate during drying in the production process [Maskara & Smith, 1997]. This aggregation involves adhesion between the colloidal particles via interparticle attraction [Iler, 1979; Visser, 1976]. It occurs when the particle becomes smaller than 10 µm in at least one direction [Visser, 1989] – sand on a beach has no real adhesion to a dry towel or the swimming suit as it can be shaken off easily, but chalk stays on the blackboard after writing on it. This effect is possible because the chalk particles are much smaller and have more specific surface area than the sand particles [Visser, 1995]. "Aggregation" is involved in the following phenomena for colloidal silica [Iler, 1979, p. 364f]:

1) **Gelling**: In gels are the particles linked together in branched chains that fill the whole volume of sol. This is why there is no increase in concentration of silica in any region

macroscopic region of the medium possible. The overall medium becomes viscous and is solidified by a coherent network of particles that can retain liquid by capillary action.

2) **Coagulation**: Coagulation is where the particles come together into relatively close-packed clumps in which silica is more concentrated than in the original sol. This is why the coagulum settles as a relatively dense sedimentation.
3) **Flocculation**: Flocculation means that the particles are linked together by bridges of the flocculating agent, which are sufficiently long that the aggregated structure remains open and voluminous. This flocculation occurs during the formation of OMAs [Omotoso et al., 2003].

As silica particles form agglomerates while drying, they have to be dispersed or "de-agglomerated" in order to make them smaller. These agglomerates are similar to the above described coagulates.

There are three possible methods to deagglomerate suspended nanoparticles [Sato et al., 2008]: (1) Ball milling, (2) Bead milling and (3) Sonication. Unfortunately the energy density is not high enough to break most of the colloid agglomerates [Müller et al., 2004]. This is why sonication was chosen for this study:

Sonication, ultrasonication or ultra-sonication is defined by the Royal Society of Chemistry as the irradiation of a liquid sample with ultrasonic (>20 kHz) waves resulting in agitation. Other references define a range of around 15 kHz to tens of MHz. These sound waves dispersed into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During the high pressure phases the sonication waves generate small vacuum bubbles in the liquid, which collapse violently during compression and break the agglomerates into smaller fragments. This collapse is called cavitation and is shown in Figure 2.10. Furthermore sonication can be used for heating solutions. [Bensebaa, 2013; RSC, 2014; Suslick, 1995]

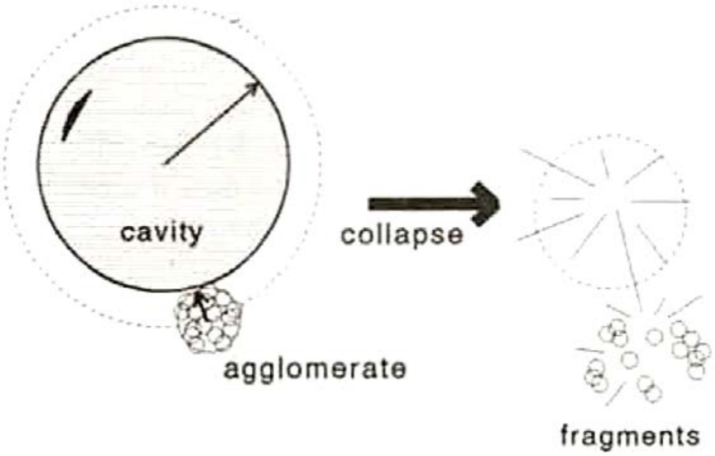


Figure 2.10: Mechanism of cavitation during sonication [Kusters & Pratsinis, 1993 edited]

For processing nanoparticles it is known that the extent of particle breakage by ultrasound is a function of the ultrasound energy delivered to the unit volume of the sample [Gibson et al., 2009; Yong et al., 2008]. Generally there are three different techniques available to deliver the energy to the sample [Santos & Capelo, 2007]: (1) Bath sonication, (2) probe sonication and (3) cup sonication.

1) **Bath sonication**: The ultrasonic bath is a common piece of equipment in chemical laboratories [Santos & Capelo, 2007] and shown in Figure 2.11. One major disadvantage is that the intensity distribution inside an ultrasonic bath is not homogeneous [Santos & Lodeiro, 2009]. That means that the efficiency varies depending on the position of the sample in the bath. One way of determining the efficiency in a bath sonicator is the aluminum foil test. This is defined in the ASTM-Standard B548. In order to enable a better intensity distribution some manufactures developed ultrasonic baths with sonication units at the bottom and at the walls [Bandelin, 2014; Santos & Lodeiro, 2009].

Figure 2.11: Picture of bath sonicator Branson 1510

Nevertheless bath sonication is not a powerful tool as a common bath only has a specific power between 1 and 5 $\frac{W}{cm^3}$.

2) **Probe sonication**: For probe sonication the probe is immersed directly into the solution, where the sonication takes place. This is why the ultrasonic power with a probe is about 100 times higher than bath sonication [Santos & Capelo, 2007]. A normal probe sonicator consists of four major parts: A generator, an ultrasonic converter, a standard or booster horn and a probe. The generator converts the voltage from the electricity grid to a high frequency (most likely 20 kHz). This electrical energy is transformed by the ultrasonic converter to mechanical energy, which is increased by the horn. Finally the mechanical energy is leaded into the sample by the probe. [Santos & Capelo, 2007]

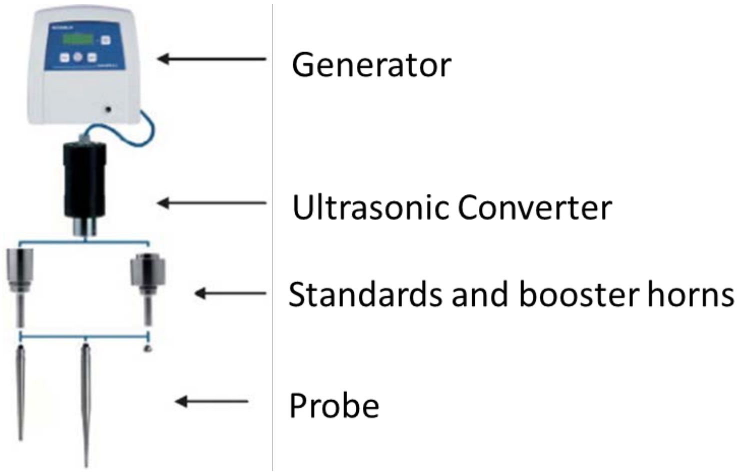


Figure 2.12: Comprehensive scheme of an ultrasonic probe [Santos & Capelo, 2007 eddited]

A challenge while using probe sonication are the dead zones as the ultrasonic intensity rapidly decreases radially and axially from the tip. This is why the distance between the tip and container should be minimized. But a contact between the wall and the probe should be avoided as this might break the probe. [Santos & Lodeiro, 2009]

3) **Cup sonication**: In a cup horn the probe is held within an acrylic cup filled with the sonication medium. Such a sonication cup is shown in Figure 2.13. The average cup sonication is about 50 times more intense than an ultrasonic bath. Furthermore cup sonication enables the processing of sealed tubes or vials. This is why they are ideal for sterile or dangerous pathogenic samples. [Santos & Capelo, 2007]

Figure 2.13: Cup horn probe [Nano Lab, 2012]

Due to the high costs of cup sonication only bath and probe sonication were possible treatments for nanoparticles in this study. As the processing of nanoparticles requires high sonication power [Qsonica, 2014], probe sonication was chosen for this study.

2.6.Filtration

Filtration is a unit operation designed to separate suspended particles from a fluid media by passing the solution through a porous membrane or medium [Cheremisinoff, 1998]. Other operations to separate suspended particles from fluid media include centrifugation [Akbulut et al., 2012] and, if possible, magnetic separation [Kelland, 1998].

In order to conduct a filtration, liquid feed with solid particles is delivered to the filter medium (e.g. a filter paper). This filter medium prevents larger particles from passing. These large particles are collected on the filter and form the filtration cake. If the cake is thick enough, it supports the effect of the filter medium. The filtrate passes the filter. A schematic of this is shown in Figure 2.14:

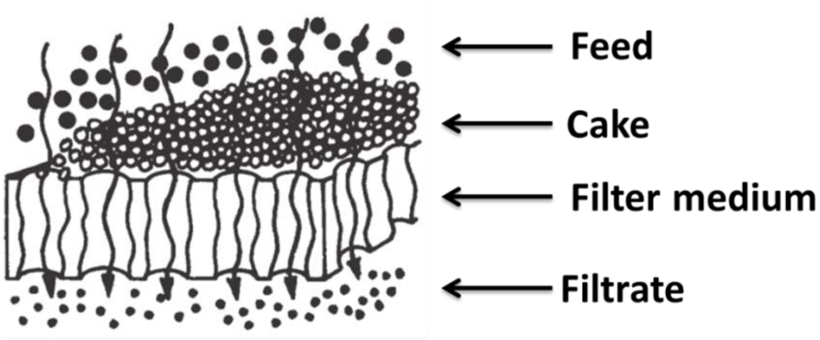


Figure 2.14: Schematic of cake filtration [Sutherland, 2008, p. 20 edited]

For the pressure drop Δp through a filter is the following known [Rushton et al., 1996]:

$$\Delta p = v \cdot \mu \cdot (R_c + R_m) \tag{2.3}$$

From this equation it can be seen that the pressure drop is proportional to the velocity through the filter medium v, the viscosity of the following fluid μ as well as the sum of the resistance of the cake R_c and the resistance of the filter medium R_m. That means the pressure drop can be reduced by reducing the velocity of the feed or by reducing the resistance respectively to the thickness of the cake.

2.7. Silica and Silica Nanoparticles

Silica, silicon dioxide or SiO_2, is a major constituent of rock-forming minerals [Flörke et al., 2008]. Furthermore it is an important component of sediments and soils [Castro & Huber, 2003]. Free silica makes about 12-14 wt% of the upper earth surface [Flörke et al., 2008]. The US and the European countries declared silica as a hazardous chemical [Flörke et al., 2008]. The National Institute for Occupational Safety and Health suggests a exposure limit of 0.05 $\frac{mg}{m^3}$ respirable crystalline silica as a time-weighted average for up to 10 hour workdays during a 40-hr workweek [NIOSH, 2002]. While dealing with respirable crystalline silica (e.g. quartz dust) it has to be considered that it is labeled as a carcinogenic substance by the US Department of Health and Human Service, World Health Organization and the International Agency for Research on Cancer [HHS, 2011; WHO, 1997].

Silica nanoparticles are used as an additive for rubber and plastics, a strengthening filter for concrete and other construction composites as well as a drug delivery system [AZoNano, 2013; Tang & Cheng, 2013]. Silica nanoparticles received the first step of the Food and Drug Administration (FDA) approval for a first-in human clinical trial testing [Benezra et al., 2011]. The worldwide annual production of silica is 138,000,000 metric tons, grown crystal silica was about $170 per kilogram in 2011 [Dolley, 2013].

Adams et al. found out that in water suspended silica nanoparticles have antibacterial properties towards the bacteria *B. subtilis* and to a lower extend to *E. coli* [Adams et al., 2006]. However other studies found out that silica has no effect on *B. subtilis* [Liang et al., 2005]. These results show that silica nanoparticles might be toxic against some cell types.

According to Iler silica is not “soluble to any appreciable degree in any other liquid than water” [Iler, 1979]. If this silica is amorphous silica, it can form combined structural bounds while being in water [Zhuravlev, 2000]. There are some silica particles already in the ocean. Anderson et al. assumed for the Bering Strait a silica concentration of 23 ±9 µM and for the Fram Strait a concentration of 5 ±1 µM [Anderson et al., 1983].

The surface properties of pure silica are determined mainly by two factors: [Zhuravlev, 2000]

1) The chemical activity on the surface, which depends on the concentration and distribution of different types of OH groups and the presence of siloxane bridges. OH groups on

the silica surface become deprotonated above the isoelectric point (pH 2-3), leading to a negative surface charge. The OH surface concentration and pH ultimately determine the charge and colloidal stability of silica dispersed in water.

2) The porosity of the silica nanoparticles as this has an influence on the specific surface properties of the silica nanoparticles.

2.8.Measurement equipment

In this chapter the theory behind the used measurement equipment is described. At first Dynamic Light Scattering is discussed followed by a brief description of optical microscopy and an introduction in scanning electron microscopy.

2.8.1. Dynamic Light Scattering

Dynamic light scattering (DLS, sometimes referred to as Photon Correlation Spectroscopy or Quasi-Elastic Light Scattering) measures the size of dispersed particles in the submicron region. Therefore it measures with a laser the Brownian motion and relates it to the size of particles. This is possible because the larger the particle, the slower the Brownian motion is if temperature is kept constant. Malvern Instruments Ltd., a manufacturer of DLS systems gives in a technical note a more detailed explanation of DLS systems [Malvern Instruments, 2014a], Berne & Pecora derive the relevant equations [Berne & Pecora, 2003]. For the usage of a DLS system the following terms have to be defined:

1) **Polydispersity Index (PDI):** The PDI is calculated from a regression of correction data for the intensity distribution. The PDI is dimensionless and scaled. Values smaller than 0.05 are highly monodisperse and rarely seen. Values greater than 0.7 show a very broad distribution, which is not suitable for DLS [Malvern Instruments, 2011]. The exact calculations are defined in ISO standard 13321:1996 E and ISO 22412:2008.

2) **Z-average**: The Z-average, sometimes called cumulates mean, can be expressed as the intensity based harmonic mean and is computed with this expression: [Horiba Scientific, 2014; Malvern Instruments, 2014a]

$$D_Z = \frac{\sum S_i}{\left(\sum \frac{S_i}{D_i}\right)} \tag{2.4}$$

Here is S_i the scattered intensity and D_i the diameter of particle i. For sufficient small particles occurs the Rayleigh scatters, which means $S_i \sim D_i^6$. With this follows:

$$D_Z = \frac{\sum D_i^6}{\left(\sum D_i^5\right)} \tag{2.5}$$

3) **Distribution**: The DLS system measures the intensity. Based on this results can the intensity distribution computed. Using the intensity distribution and the Raylingh approximation the number and the volume distribution can be computed. There is a 1:1,000,000 ratio between the number and intensity distribution because the intensity is proportional to d^6 due to the Rayleigh approximation. Between the number and volume distribution is the ratio 1:1,000 because the volume is proportional to the diameter to the power of three due to the volume of a square. This effect is shown in Figure 2.15 with a bimodal mixture of 5 and 50 nm particles present in equal numbers:

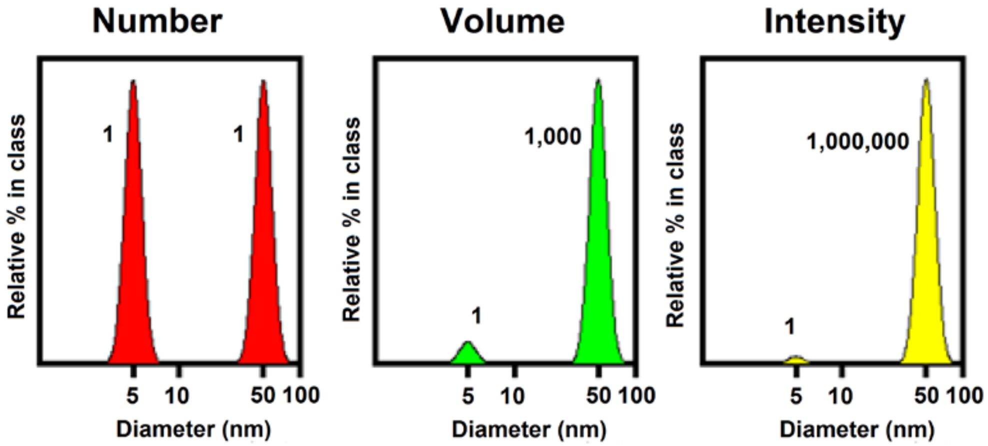


Figure 2.15: Number, volume and intensity distribution of a bimodal mixture of 5 an 50 nm particles in equal numbers [Malvern Instruments, 2014a, p. 11 edited]

2.8.2. Optical Microscopy

Optical microscopy is a relatively old technique, but in recent years much of progress made was in terms of digital imaging [Davidson & Abramowitz, 1999]. As optical microscopy is standard, well known equipment, it is not discussed here. A detailed introduction is given by Tkaczyk [Tkaczyk, 2010].

2.8.3. (Cryogenic) Scanning Electron Microscope

A cryogenic scanning electron microscope (cSEM) is a normal scanning electron microscope (SEM) equipped with a cold stage. This cold stage is cooled with liquid nitrogen or helium to freeze the sample in order to determine bubbles or other liquid samples. An extremely low temperature is necessary to avoid degassing of the sample as the SEM is operated under a high vacuum that reduces the freezing point of liquids. [Greiser, 2009]

A SEM consists of two major components: The electron column and the control console. The column consists of an electron gun and two or more lenses, which influence the electrons moving down the evacuated tube. The gun generates electrons and accelerates them with energy between 0.1 and 30 keV and sends them down the column which has a vacuum about 10^{-4} to 10^{-5} Pascals. In the column the electrons pass through lenses that focus them on the sample. The electrons enter the sample to a depth of approximately 1µm. During this contact is the signal generated which is used by the detector to generate the image, which is shown on the control console. This control console consists of a viewing screen and a computer to control the electron beam and lenses. A detailed introduction into scanning electron microscopy is given by Goldstein et al. [Goldstein et al., 2003]. A schematic of this process is shown in Figure 2.16:

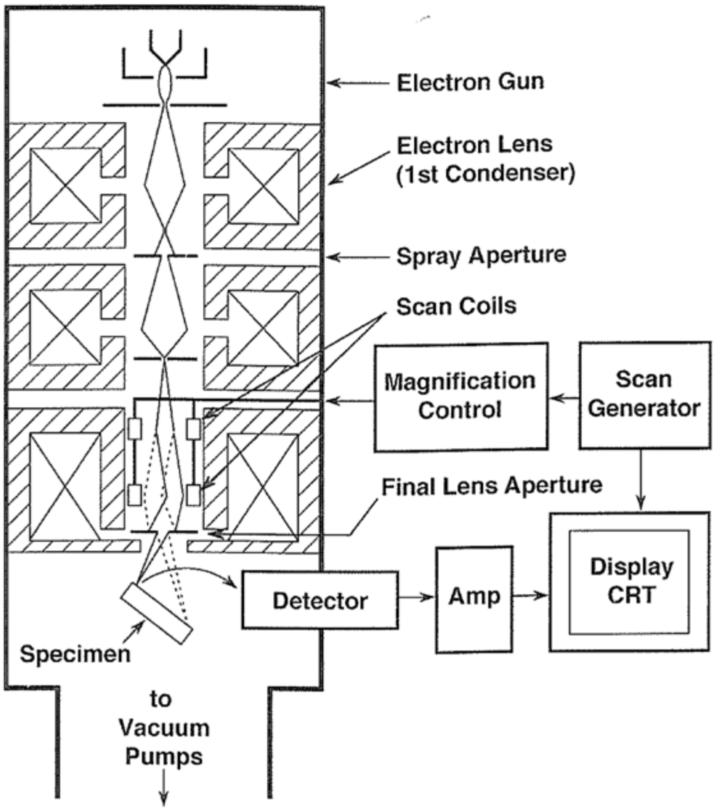


Figure 2.16: Schematic drawing of the electron column in an SEM [Goldstein et al., 2003, p. 23]

The highest commercially available magnification of a field emission SEM is done with a Hitachi SEM. This instrument allows a 0.4 nm resolution with an accelerating voltage of 30 kV. [Hitachi, 2011]

Some SEM systems are connected to an Energy-dispersive X-ray spectroscopy (EDS or EDX). This is an analytical technique used for the elemental analysis of a sample. The sample is shot with electrons inside the SEM. The sample emits electrons with certain energy. Based on the energy is it possible to estimate the atoms which are in this sample. A more detailed description of EDS systems is given by Garratt-Reed and Bell [Garratt-Reed & Bell, 2003].

CHAPTER 3. MATERIALS AND METHODS

In the following section the setup of the conducted experiment and its procedures are described. All silica nanoparticles used are 99.5% purity, 20nm primary particle size nonporous nanoparticle provided by SkySpring Nanomaterials Inc, Huston USA, Lot #6808-072110.

3.1.Probe Sonication

For the probe sonication a Fisher Scientific FB 120-Sonicator with a $^1/_8$“ horn is used. This sonicator has a power rating of 120 watts and an operating frequency of 20 kHz. This machine enables a change of the amplitude. With this it is possible to vary the vibration of the horn and change the cavitation [Santos & Lodeiro, 2009].

As the probe sonication heats a 16 mL sample up, which results in vaporization, a Lauda Ecoline RE 106 cryostat is used to keep the sample at a constant temperature of 15° Celsius. Furthermore the probe sonication is done in the pulsation modus. That means each interval of 15 seconds probe sonication is followed by a 15 seconds break. This supports the heat exchange between the sample and the cooling medium. The total sonication time is 90 minutes plus a 90 minute break per 16 mL sample. The whole setting is shown in Figure 3.1, a picture of the probe sonicator is stated in appendix 6.6.3.

Figure 3.1: Setting probe sonication with probe, cryostat and sample

The used standard operating procedure is stated in appendix 6.5.1.

3.1.1. Calibration

For the calibration of the probe sonicator is a 1 L Pyrex beaker insulated and filled with 521 g water. A magnetic stir bar rotates with 60 rpm, a thermometer and the tip are placed in the beaker. The important thing is that the tip is at a depth of exactly 20 mm in the water, because the transferred energy is dependent on how much the horn is covered with water. The setting is shown in Figure 3.2:

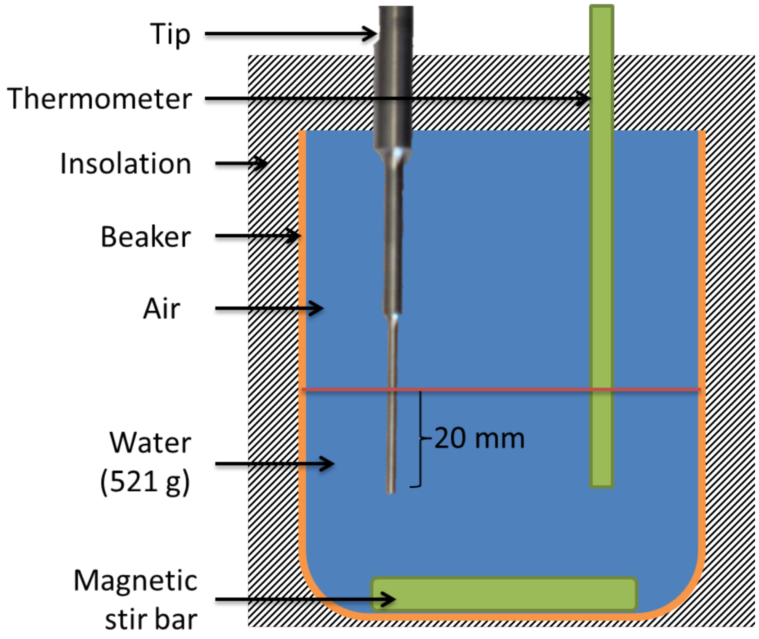


Figure 3.2: Setting Calibration probe sonicator

For the calibration of the probe sonicator a procedure is suggested by the National Institute of Standards and Technology (NIST) adapted to the special needs of this type of experiment [Taurozzi et al., 2012].

At the beginning the water temperature is equilibrated to the room temperature. This reduces heat losses to the environment. Before the measurement run is started, the probe sonicator is set at the given amplitude for 5 minutes on the needed level of amplitude. This enables a better heat mixture in the water. Then is the temperature T_0 at the temperature at the beginning of the experiment is noted. The measurement itself lasts for 15 minutes. After this time period the end temperature T_1 was noted.

Under the assumption that water has a constant heat capacity of $c_p(water, T = 30°C) = 4.180 \frac{kJ}{kg \cdot K}$ [VDI, 2010] and the absolute heat capacity of the magnetic stir bar is able to neglect in comparison to the water follows:

$$\begin{aligned} P &= \frac{dT}{dt} \cdot m\ (water) \cdot\ c_p(water) \\ &= \frac{\Delta T}{\Delta t} \cdot m\ (water)\ \cdot c_p\ \ (water) \end{aligned} \quad 3.1$$

In this equation P is the resulting power of the probe sonicator in kW, ΔT the temperature difference in K, Δt the time difference in s, m the mass of the water in kg and c_p the heat capacity of the water in $\frac{kJ}{kg \cdot K}$. As this experiment was repeated with different amplitude settings, the following graph is computed:

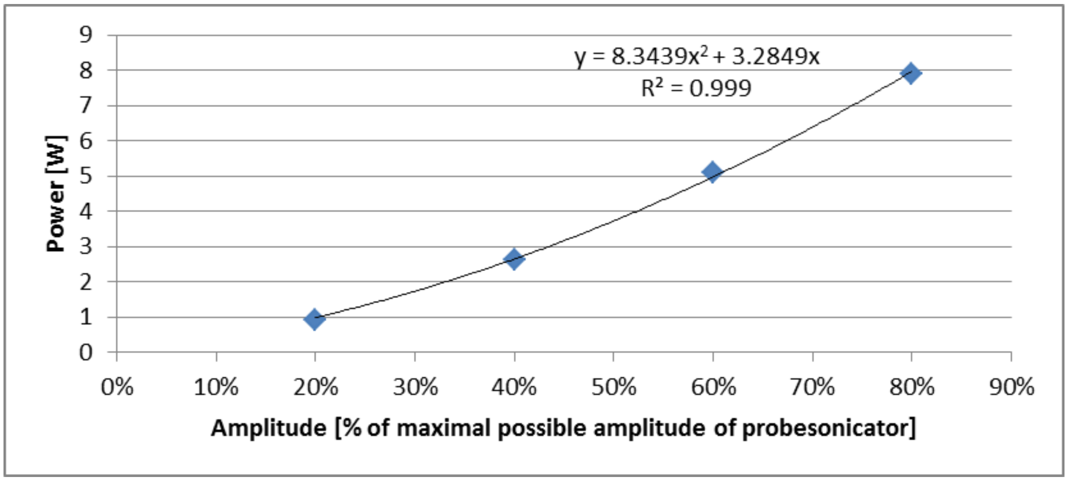


Figure 3.3: Power as a function of amplitude for a 16 mL sample

For the data points plotted in Figure 3.3 the following regression equation is computed with Microsoft Excel® 2010, whereas x the variable for the amplitude is:

$$P = (8.3439\, x^2 + 3.2849\, x)W \quad 3.2$$

In this equation the regression coefficient or coefficient of determination $R^2 = 0.999$. This quantity is a measure of the proportion of variability explained by the fitted model [Walpole et al., 2007]. As this value is almost 1, the regression function can be considered as valid. As stated in the standard operating procedure for probe sonication probe sonication is done with 75% amplitude to disperse the nanoparticle. This means the following sonication energy is introduced in the system:

$$P_{sonication} = (8.3439 \cdot 0.75^2 + 3.2849 \cdot 0.75)W = 7.98\ W \qquad 3.3$$

As 16 mL samples are used and the sonication time $t_{sonication}$ equals to 90 minutes, the following represents the energy density $\hat{E}$:

$$\hat{E} = \frac{P_{sonication}}{V_{sample}} \cdot t_{sonicaion} = \frac{7.98\ W}{16\ mL} \cdot 5400\ s = 2693.25 \frac{W \cdot s}{mL} \qquad 3.4$$

$$= 2.7 \cdot 10^6 \frac{J}{L} = 2.7 \cdot 10^3 \frac{J}{m^3}$$

This is a relatively high energy density [Böhm et al., 2000], which is necessary to disperse nanoparticles [Qsonica, 2014].

3.1.2. Reproducibility

To show the reproducibility for the probe sonication a 90 minutes sonication is repeated three times with a 75% amplitude according to the standard operating protocol stated in Appendix 6.5.1. In Figure 3.4 the intensity distribution of this experiment is shown:

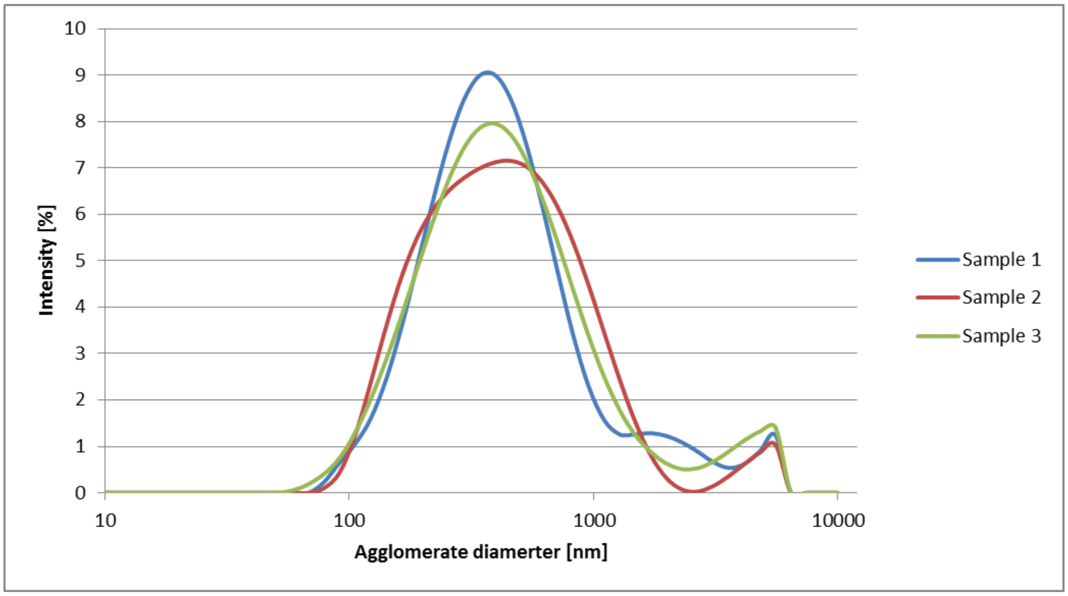
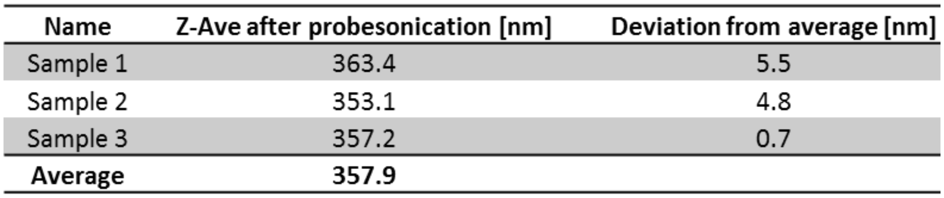


Figure 3.4: Intensity for probe sonication reproducibility with 90 min sonication according to SOP

The different values of the Z-average are stated in Table 3.1:

Table 3.1: Z-average after probe sonication



Name	Z-Ave after probesonication [nm]	Deviation from average [nm]
Sample 1	363.4	5.5
Sample 2	353.1	4.8
Sample 3	357.2	0.7
Average	**357.9**	

Based on these results it can be stated that the probe sonication is reproducible. Unfortunately is the distribution very wide, which means a filtration is necessary.

3.2.Filtration

As stated above the size distribution of the silica nanoparticle after the probe sonication is broad. This is why a filtration becomes necessary. For the filtration a Teledine Isco 500D syringe pump and Fisher Scientific, Fisherbrand™, nitrocellulose filtration paper with a 220 nm, 450 nm and 800 nm pore size are used. The diameter of the filter is 47 mm and the thickness 150 µm. Nitrocellulose is an ester of cellulose and used for a wide range of analytical procedures [Cheremisinoff, 1998, p. 22; Purchas & Sutherland, 2002, p. 356]. The pump is shown in Figure 3.1. The standard operating procedure used is described in appendix 6.5.2.

Figure 3.5: Teledine Isco 500D syringe pump

According to the standard operating procedure for probe sonication three batches were sonicated for 90 minutes and filtered with the 800nm, 450 nm and 220 nm filter. After each filtration step the particle size was measured with the DLS system. The resulting Z-averages are stated in Table 3.2.

Table 3.2: Z-average for filtration reproducibility

[nm]	Sample 1	Sample 2	Sample 3	Average	Standard-deviation
Before Filtration	363.4	353.1	349	355.2	7.4
800 nm filtrate	244.1	253	260	252.4	8.0
450 nm filtrate	200	206.7	206.5	204.4	3.8
220 nm filtrate	165.5	168.5	180.3	171.4	7.8

Since the standard deviation is low and non-spherical aggregates were measured with the DLS, this result is considered as reproducible.

3.3.Forming Emulsions

For this experiment a sole with a 0.25 wt% silica solution was chosen. This equals a concentration of approximately 1 mM. This is about 43 times the silica concentration of the Bering Strait, which is about 23 ±9 µM [Anderson et al., 1983]. In this experiment, some of the samples were prepared in artificial seawater, which was created after adding salt provided by Lake Products Inc., Missouri, USA. This was prepared according to the ASTM standard practice for the *Preparation of Substitute Ocean water* [ASTM, 2003].

To create the emulsion, the silica solution is set to pH 7 with hydrochloric acid. Then the sample for the DI-water experiments is poured and 1 mL of each is placed in 15x45 mm glass vials with Teflon caps provided by FisherBrand™. Afterwards the sea salt is added to the rest of the pH 7 sample, stirred with a magnetic stir bar and 1 mL of each is placed in glass vials. Following this 0.25 mL of oil is added to the sample and the mixture is vortexed for 30 seconds on a Fisher Scientific™ Mini Vortex Mixer at 2800 rpm to create an emulsion.

A reciprocating shaker with a speed higher than 70 cycles per minute causes enough agitation to form oil droplets [Weise et al., 1999]. This is why the sample vials were placed after the visual and microscope evaluation for 5h on a New Brunswick R-2 reciprocating shaker at 100 rpm. This table shaker is shown in Figure 3.6:

Figure 3.6: New Brunswick R-2 table shaker with samples

3.4.Stability Control

As the idea was to use one single batch of solution consisting of DI-water and silica, it had to be shown that the particles are stable over a long time period. For the long term stability one sample was sonicated according to the sonication SOP. The particle size is measured with DLS at different times after the probe sonication. To allow an equal distribution of particles in the solution the sample was placed on an orbital moving shaking table for five minutes before each measurement. Furthermore every DLS measurement is repeated three times and the average of these three measurements is reported. In Figure 3.7 the mean of the Z-averages are shown.

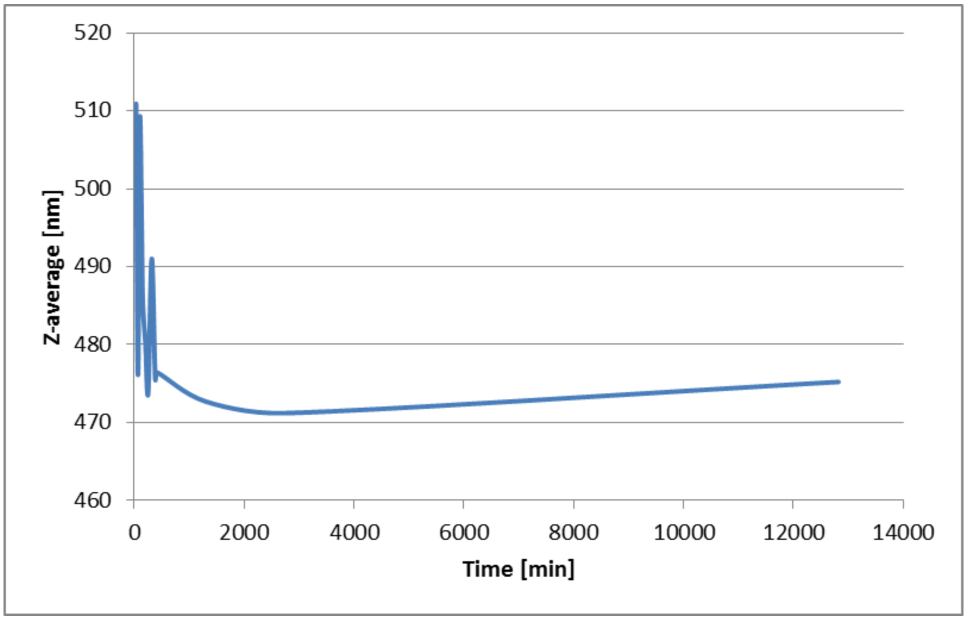


Figure 3.7: Z-average for long-term stability measurement

The different number-distributions are stated in Figure 3.8:

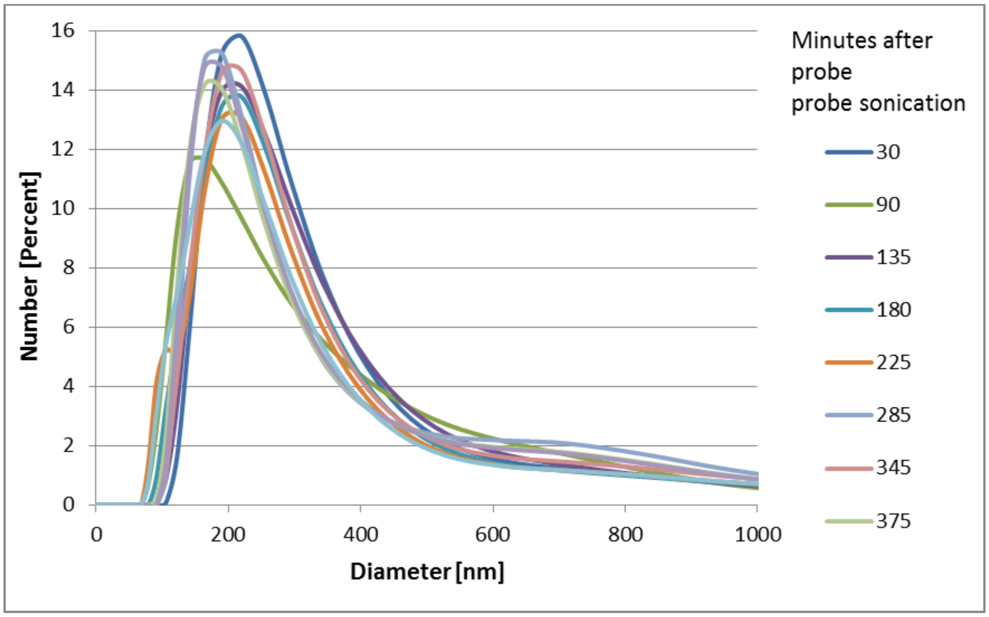


Figure 3.8: Number distribution for long-term stability measurement

As the manufacture of the DLS-system gives a range of ±2% based on NIST traceable standards [Malvern Instruments, 2014b] for the Z-average and the computation is based on spherical or near-spherical particles [Malvern Instruments, 2011], these results can be considered as stable.

3.5.Concentration

One difficulty is to determine the particle concentration after the filtration. Three different approaches were used to try to measure the concentration:

1) **Ultraviolet-visible spectroscopy**: This approach is good if the particle size is constant and uniform. Furthermore there has to be a set of samples with known concentration available in order to calibrate the system. Unfortunately both variables are unknown.
2) **Weighing the filter paper**: The silica in the sample before filtration is known. After the filtration, a part of the silica is in the filtrate and the rest of the silica is in the filter cake. This filter cake should consist only of silica as the original sample consists of DI-water and silica. This is why the following balance should be valid:

$$\begin{aligned} &m_{silica\ in\ sample\ before\ filtration} \\ &= m_{silica\ in\ filtrate} + m_{filter\ cake} \end{aligned} \tag{3.5}$$

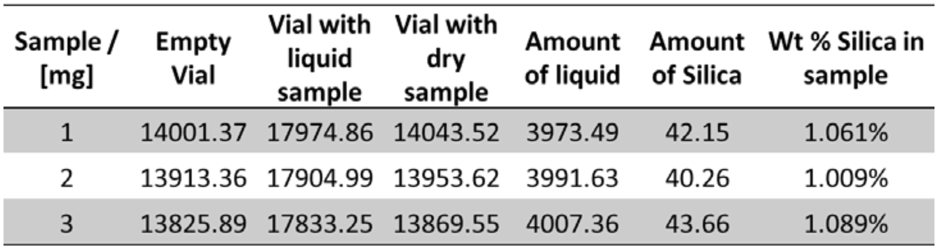
Unfortunately this balance was not true, because the used scales were not precise enough or the filter paper interacts with water.

3) **Vaporization:** The idea is to vaporize a small amount of sample and measure the weight difference and the silica residuals. This was the only suitable approach which is explained in the following section:

3.5.1. Measuring

A small amount of sample (4 mL) is poured into vials. Previously these vials were flushed twice with ethanol and only handled with gloves to avoid fatty residuals that influence the results. After the sample are poured into the vials, the vials are placed for 24 hours in a 75°C warm Isotemp Icubator manufactured by Fisher Scientific to vaporize the water. With the weight differences the silica concentration is computed. The detailed standard operating procedure is stated in Appendix 6.5.3. To show the reproducibility of this approach, the experiment is repeated three times with a 1 wt% DI-water/silica solution. The results from this are shown in Table 3.3.

Table 3.3: Reproducibility Silica measurement



Sample / [mg]	Empty Vial	Vial with liquid sample	Vial with dry sample	Amount of liquid	Amount of Silica	Wt % Silica in sample
1	14001.37	17974.86	14043.52	3973.49	42.15	1.061%
2	13913.36	17904.99	13953.62	3991.63	40.26	1.009%
3	13825.89	17833.25	13869.55	4007.36	43.66	1.089%

This shows that the measured weight concentration is similar to the original weight concentration. The samples after the measurement are shown in Figure 3.9:

Figure 3.9: Samples after weight concentration measurements

Based on these results it is assumed that the conducted way of concentration measurement is reproducible.

3.5.2. Changing Concentration

For the increase of the concentration in the solution some of the water from the solution is vaporized. Procedures like this have been generally used for stable sols like colloidal silica. Another idea for increasing the concentration is centrifugation. Unfortunately requires a particle size smaller than 30 nm very high speeds. [Iler, 1979]

The solution is placed in an Isotemp Icubator manufactured by Fisher Scientific. The temperature is set to 75°C. The weight of the beaker is frequently measured. As the silica remains in the solution while the water is vaporizing and the silica concentration at the beginning of the experiment is measured according to Chapter 3.5.1, the desired weight of the solution can be computed.

Figure 3.10: Fisher Scientific Isotemp Incubator

To show that the increase of the concentration has no effect on the agglomeration size, one sample was vaporized. During the vaporization the particle size was measured with DLS. The results are stated in Figure 3.11:

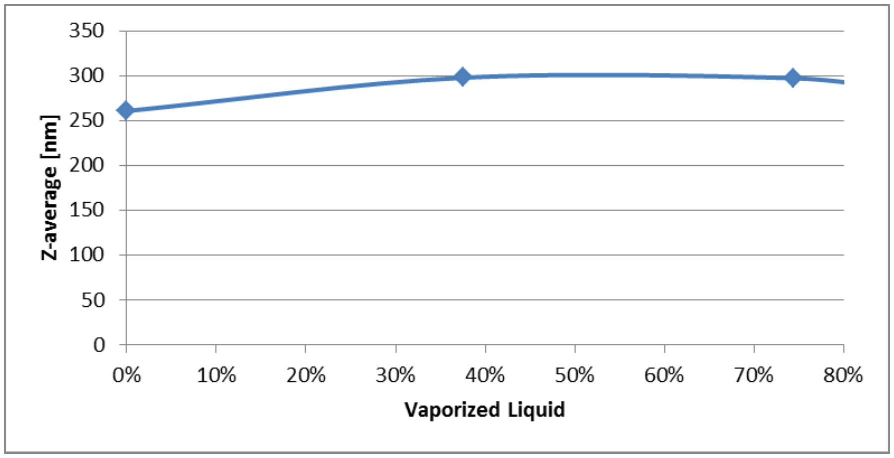


Figure 3.11: Z-average during vaporization

Based on this result and the results in chapter 3.6.1 which discussed measurement errors, the Z-average can be assumed to be constant.

3.6.Measurement Techniques

This chapter describes the used measurement procedures. At first Dynamic Light Scattering is discussed. Then optical and (cryogenic) scanning electron microscopy is introduced. Finally the methods of video recording and visual evaluation are described.

3.6.1. Dynamic Light Scattering

For the DLS measurements a Zetasizer ZS manufactured by Malvern Instruments PLC, Malvern, UK is used. This system has a 173° Backscatter measurement angle with a He-Ne laser with a 633 nm frequency. For this frequency the refractive index of silica is 1.450 [Waxler & Cleek, 1971], the absorption is assumed to be zero. The dispersant is set to water at a temperature of 25°C with a viscosity of 0.8872 and a refractive index of 1.330. The equilibrium time is set to 120 seconds. The measurement is conducted in DTS0012-style Polyethylene disposable cuvettes. The measurement duration is set to automatic and the number of measurements per sample is three. From these three measurements an average is computed, which is the reported value. The accuracy of this equipment is better than +/- 2% on NIST traceable latex standards. A picture of the equipment is shown in Figure 3.12.

Figure 3.12: Dynamic Light Scattering system and PC- setting

3.6.2. Optical Microscopy

Optical microscopy is conducted with a Fisher Scientific Micromaster II optical microscope connected to an office computer. The software package Micron II by Westover Scientific is used as the imaging software. The setting, shown in Figure 3.13, features 10x-, 20x-, 40x- and 100x objective images at a size of 1024x768 pixels. For the imaging concave microscope slides without a cover slide and the 20x- objective are used.

Figure 3.13: Optical microscope with attached PC

Unfortunately the imaging of emulsions is very sensitive to vibrations and a keyboard entry or a mouse click might result in a blurry image. This is why a mouse is taped on the floor and used as foot pedal.

3.6.3. (Cryogenic) Scanning Electron Microscope

For the cSEM an Alto 2500 cryo stage manufactured by Gatan, Oxon, U.K., is used. This device is connected to a Sigma VP SEM manufactured by Carl Zeiss AG, Jena, Germany. For all imaging an electron voltage between 1 and 5 eV is used. The higher the electron voltage, the better the quality of the pictures is. Unfortunately such a high electron voltage results often in surface charging.

Before the sample is prepared, the microscope is cooled to -170°C and the preparation chamber to -130°C with liquid nitrogen. To prepare samples for cSEM imaging about 10µL of a sample is placed in the holder shown in Figure 3.14 – the blue arrow points to the holder on which the sample is placed.

Figure 3.14: cSEM sample holder. Blue arrow points to holder which is used for placing the sample

In the next step the sample is cooled with slushed liquid nitrogen to freeze the droplet. It is important that this step is done under a nitrogen atmosphere because the air moisture freezes on the sample as soon as the sample comes in contact with air. After this the sample was placed in the sample preparation chamber. In this chamber three steps were performed:

1) The sample was fractured. This means a part of the frozen droplet was removed with a blade to create an internal surface that shows the inside of the droplet.

2) Sublimation was conducted. The sample was warmed to -100°C to sublime the water at a controlled rate. This should expose OMAs or droplets to make them visible. The sample is left for about 2 minutes at -100°C. Afterwards the preparation chamber was cooled down back to -130°C.
3) Before the sample was placed in the microscope chamber, it was sputtered for 60 seconds with platinum in an argon atmosphere. This sputtering is a coating that reduces charging and improves the quality of imaging.

A cSEM sample can be treated as an ordinary SEM sample as soon as it is in the microscope chamber.

For some samples was an EDS with an X MAX-System manufactured by Oxford Instruments PLC, Abington, England, used.

3.6.4. Video Recording

To determine the emulsion stability over time the emulsions are filmed directly after vortexing. This is done with a Nokia® Lumia 520 cell phone using WVGA quality with 30 frames per second. This setting is shown in Figure 3.15. For a good light distribution two independent light sources are used. Afterwards the videos are edited with Microsoft® Movie Maker Version 2012 to generate a fast motion film and Free Video to JPG Converter v. 5.0.40 to extrapolate the frames for the time stability analysis.

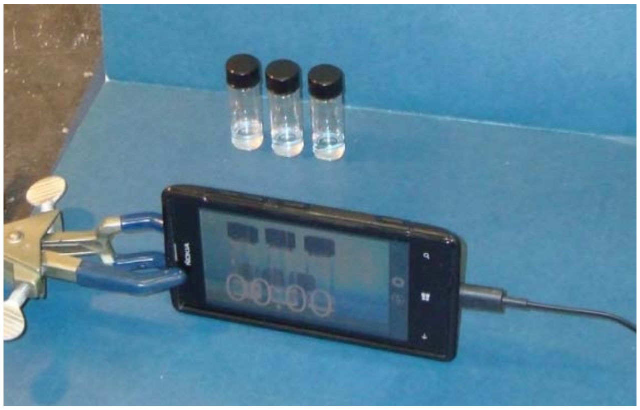


Figure 3.15: Setting for video recording

3.6.5. Visual Evaluation

For the visual evaluation pictures of the sample are taken with a Sony® DSC-W80 digital camera. Apart from the activated macro modus all settings kept are in the automatic modus. Based on these images the thickness of the sedimentation and the emulsion layer is measured with the imaging processing software ImageJ 1.48v provided by the National Institutes of Health. For the thickness of the sedimentation layer, the emulsion layer and the total thickness 10 measurements are conducted, for the time stability 5. For the scale the 14.88 mL diameter of the vials is measured with a Mitutoyo® ABSOLUTE caliper. This procedure gives a good estimation and a trend between the different samples.

CHAPTER 4. RESULTS AND DISCUSSION

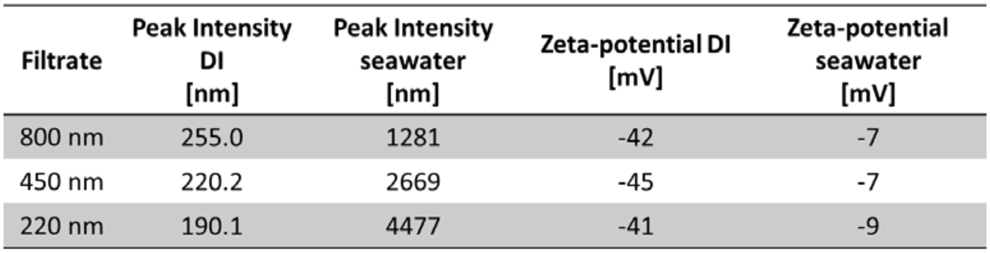
One batch of silica solution is used for the conducted studies. This chapter describes the properties during the preparation of the batch. In the following the results of the emulsion formation are stated and discussed. This description consists of a qualitative and quantitative evaluation of the emulsion and the sedimentation phase. Additionally, this chapter consists of a measurement of the time stability and wave experiments.

4.1.Preparation Silica batch

4.1.1. Filtration

The silica solution is prepared according to the prior discussed standard operating procedure with 1 wt% silica powder and probe sonicated for 90 minutes. Afterwards the solution is filtered twice. Similar to Viganti et al. DLS and SEM are used for the determination of the particle size [Vignati et al., 2003]. The results for the peak of the intensity distribution in DI- and seawater as well as the zeta potential in DI- and seawater are stated in Table 4.1, the intensity distribution in DI-water is shown in Figure 4.1.

Table 4.1: Distribution of silica solution after second filtration at pH=7



Filtrate	Peak Intensity DI [nm]	Peak Intensity seawater [nm]	Zeta-potential DI [mV]	Zeta-potential seawater [mV]
800 nm	255.0	1281	-42	-7
450 nm	220.2	2669	-45	-7
220 nm	190.1	4477	-41	-9

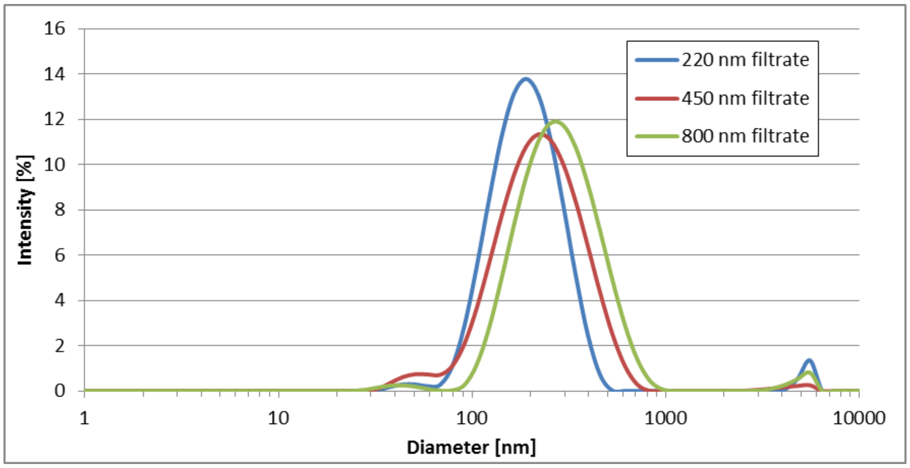


Figure 4.1: Intensity distribution after second filtration without pH adjustment

From the above stated Table 4.1 and Figure 4.1 it can be seen that the size of the silica aggregates in terms of the z-average and the intensity peak is varying. The intensity peaks in DI-water, which have differences about 30 nm in size, will be used as size in the evaluation. The smallest silica agglomerates in DI-water form the largest silica-sea salt agglomerates and the largest silica agglomerates in DI-water form the smallest silica-sea salt agglomerates. Additionally it can be observed that the small agglomerates in DI-water form the largest agglomerates in seawater and the other way around. Furthermore it can be seen from the intensity distribution that the distributions of the silica filtrate are narrow – the PDI for all distributions in DI-water is approximately 0.25.

The zeta-potential, which is a value for the surface charging of the particles, is at pH=7 for the particles in DI-water solution between -41 and -45 mV, in seawater it decreases to -7 to -9 mV. This decrease occurs because the cations in seawater absorb onto the surface of the silica particles.

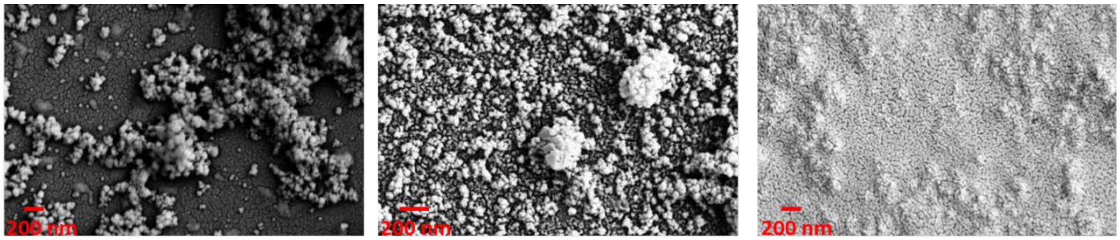
4.1.2. Measuring and increasing concentration

As the filtration removed an unknown amount of silica from the solution, the concentration of silica has to be measured and adjusted. A concentration measurement according to standard operating procedure stated in appendix 6.5.3 is conducted before the concentration of silica is increased. The results of this measurement are stated in Table 4.2:

Table 4.2: Results concentration measurement

[mg] Filtrate	Empty Vial	Vial w. liquid sample	Vial w. dry sample	Amount liquid	Amount Silica	Weight %
800 nm	13852.01	17314.52	13853.33	3462.51	1.32	0.038%
450 nm	13854.09	17830.97	13855.95	3976.88	1.86	0.047%
220 nm	13963.7	17926.88	13964.63	3963.18	0.93	0.023%

The low and varying amount of silica in solution makes an adjustment necessary in order to achieve the desired 0.25 wt% silica in solution. This is done with the described standard operating procedure for adjusting the silica concentration. After the concentration adjustment SEM images are taken (see Figure 4.2). In these images it can be seen that the particle still form aggregates. This is reasonable as the primary particle size is 20 nm, which is one order of magnitude smaller as the measured Z-averages, which are stated in Table 4.1.



220 nm filtrate 450 nm filtrate 800 nm filtrate

Figure 4.2: Scanning electron microscope images of the silica filtrate

The EDS shows that the silica solution consists of silica and oxygen atoms. In ure 4.3 the red dots represent detected silica and the green ones detected oxygen atoms. This is reasonable as the solution consists of silicon dioxide (SiO_2), which consists of silica and oxygen atoms.

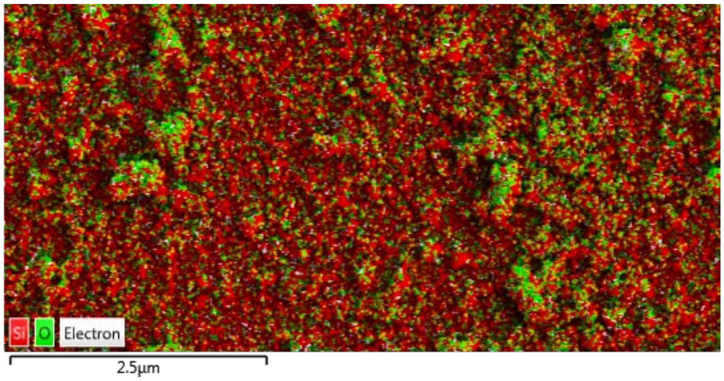


Figure 4.3: EDS map of 450nm filtrate

The silica solution described above is the one used during the emulsion experiments.

4.2.Emulsion

4.2.1. Type of Oil

The oil types for the final batch are chosen after a screening experiment. 1.2 mL of 10 different oils are mixed with a 6 wt% silica solution with DI-water and real seawater. The pH value of the DI-water-silica solution is brought to pH 2, 4 and 6. The real seawater was taken from the Narragansett Bay on February 7th 2014.

The silica solution is not probe sonicated. That means the solution consists as received silica nanoparticles in DI- or seawater. The samples are vortexed and their stability is visually observed. Afterwards the samples are bath sonicated and evaluated again. The results of this screening experiment are stated in Appendix 6.6.

For samples forming an emulsion optical microscopy is conducted. In Figure 4.4 an optical microscopy image of octanol in seawater at a 20x magnification 15 hours after vortexing is shown. This sample is bath sonicated for 10 hours.

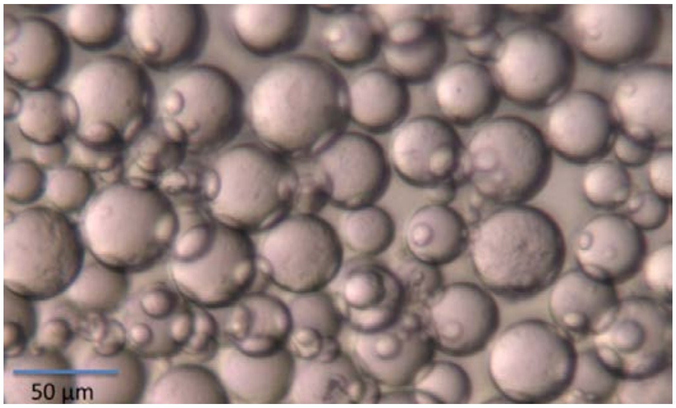


Figure 4.4: Microscope image of octanol in seawater (15h vortex; 10 h bath sonication)

In this image silica particles are at the side interface between oil and water. As the droplets are stable for at least 10 hours, these droplets are Pickering emulsion droplets. Based on this result the following three oils for the final experiment are chosen: n-octane, octanol and ethyl acetate.

The following nomenclature is used:

Table 4.3: Used nomenclature

Coding	Meaning
EA	Ethyl acetate
ON	Octane
OL	Octanol
220	Silica filtered with 220 nm filter
450	Silica filtered with 450 nm filter
800	Silica filtered with 800 nm filter
SW	Emulsion in seawater
DI	Emulsion in DI-water

4.2.2. Experiment

In the main experiment the filtrate is brought to pH 7 with hydrochloric acid (HCl). If necessary, sea salt is added. For the final formation of the emulsion 1 mL of this solution is mixed with 0.25 mL oil to achieve an oil to water ratio of 1:4 or 20 volume percent. These samples are evaluated with visual observation, optical microscopy and cSEM. Furthermore their time stabilities are measured. After this evaluation 0.05 mL of an oil/AOT solution are added in order to achieve an AOT concentration of 0.5 mM.

In this subchapter the results for emulsion formation with the above chosen oils and the silica filtrate are discussed. The pictures of the visual and microscopically evaluation without AOT are shown in appendix 6.7, those with AOT are shown in appendix 6.8.

4.2.2.1. Without AOT

The following trends can be observed with the samples before AOT are added:

Emulsion

One way to compare the emulsion stability between the different oils as well as DI- and seawater is to express the relative emulsion layer thickness as a function of particle size. The relative thickness of the emulsion layer is defined as the ratio between the height of the emulsion layer and the total sample:

$$relative\ thickness\ emulsion\ layer = \frac{h_{Emulsion}}{h_{Total\ sample}}\ [\%] \qquad 4.1$$

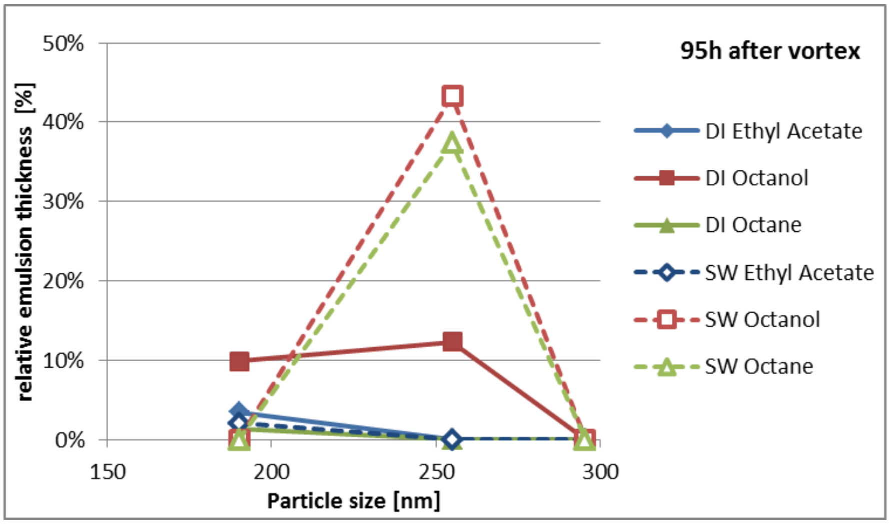


Figure 4.5: Relative emulsion thickness over intensity peak 95h after vortex without AOT

From the visual evaluation of the emulsion and the measurements of the relative emulsion thickness (Figure 4.5) the following are observations drawn:

1) Octanol and octane in seawater with silica form a thick emulsion layer especially for the 450 nm filtrate. Octanol forms water in oil emulsions (W/O), while octane forms oil in water emulsion (O/W). A W/O emulsion means that water droplets are present within the oil phase, oil in water emulsions are oil droplets in the aqueous phase. As an example is octanol in seawater with 450 nm silica filtrate shown in Figure 4.6 A. With the optical microscope is visible that the emulsion layer consists of droplets (Figure 4.6 B). Some of these droplets show nanoparticle aggregate and/or OMA deposition (see blue mark in Figure 4.6 B). It seems to be reasonable that the seawater samples with the small particle size have no or a small emulsion layer as the silica particles sedimented. The largest particle form in all cases no emulsion, which is not following the accepted theory. This is discussed in chapter 4.3.

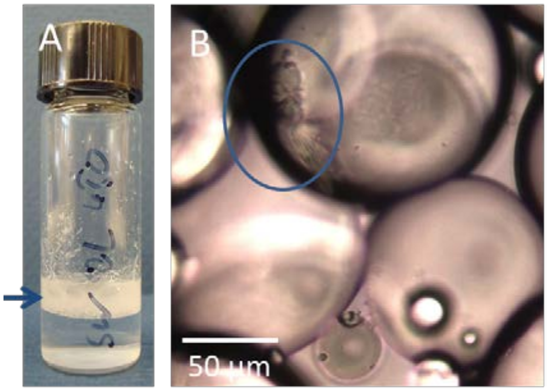


Figure 4.6: Water in oil emulsion phase of SW OL 450 without AOT. (A) picture of the sample, blue mark is pointing on emulsion phase. (B) 10x optical microscopy image, blue mark points on OMA.

2) Only octanol forms an emulsion in DI-water (O/W). Neither octane nor ethyl acetate forms an emulsion to a significant degree in DI-water.

3) Ethyl acetate with silica filtrate does not form visible emulsions in DI- or seawater to a significant degree. As an example is the SW EA 450 sample shown in Figure 4.7 A. At the optical microscope some droplets and a kind of inverted droplets are visible at the interface. These droplets are shown in Figure 4.7 B. This is according to the literature as Binks and Lumsdon observed that Toluene in a DI-water silica solution with

the presence of Sodium Chloride unstable towards creaming [Binks & Lumsdon, 1999]. Frelichowska et al. observed that Ethyl Acetate with fully hydrophilic fumed silica nanoparticles forms a stabile emulsion using 6 wt% silica nanoparticle [Frelichowska, Bolzinger, & Chevalier, 2009]. It seems to be reasonable that ethyl acetate do not form a stable emulsion in this study as the stability of Pickering emulsion is depending on the concentration of nanoparticles [Binks, 2002] and this study uses 0.25 wt%.

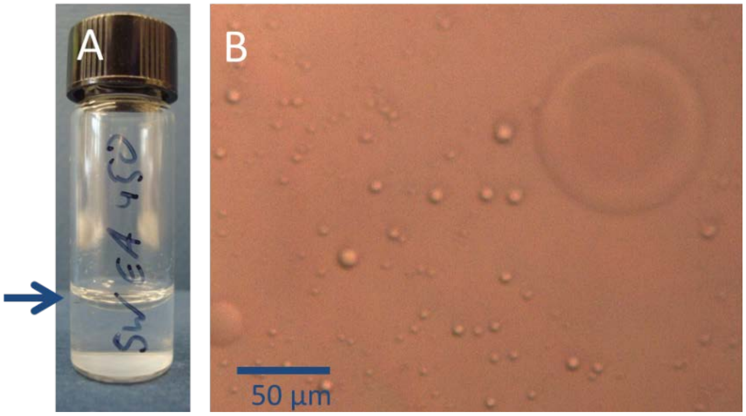


Figure 4.7: SW EA 450 without AOT

Sedimentation

Samples in DI-water show little sedimentation. What sedimentation that is present is deposited on the bottom of the vial and not measurable with ImageJ. As an example is the sedimentation of octane in DI-water with decreasing particle size shown in Figure 4.8. From this figure can be seen that the sedimentation phase accumulates at the bottom of the vial and decreases with decreasing particle size.

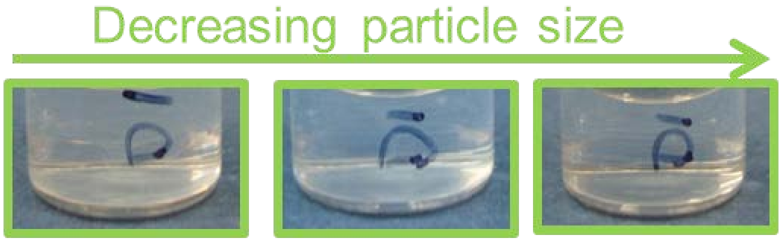


Figure 4.8: Sedimentation of octane in DI-water without AOT

With the optical microscope is some sedimentation visible. An exemplary microscopy image of octanol in DI-water with 800 nm filtrate is shown in Figure 4.9. The blue marks show solid deposition in the bottom phase, which are very likely to be OMAs.

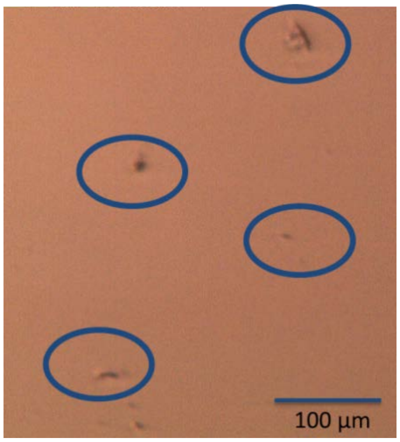


Figure 4.9: Solid depositions in bottom phase of DI OL 800 without AOT

Another example for the OMAs is octanol in DI-water with 450 nm filtrate (see Figure 4.10 A). Even if the sedimentation phase is relatively small in comparison with other samples, there is a small sedimentation visible. This is with the cSEM visible (see Figure 4.10 B), where a cut through the frozen sedimentation phase droplet is shown. Furthermore it is possible to see the OMA with optical microscopy (see Figure 4.10 C). This OMA look like flake aggregates, which are reported by Stoffyn-Egli and Lee and stated in Figure 2.8 C [Stoffyn-Egli & Lee, 2002].

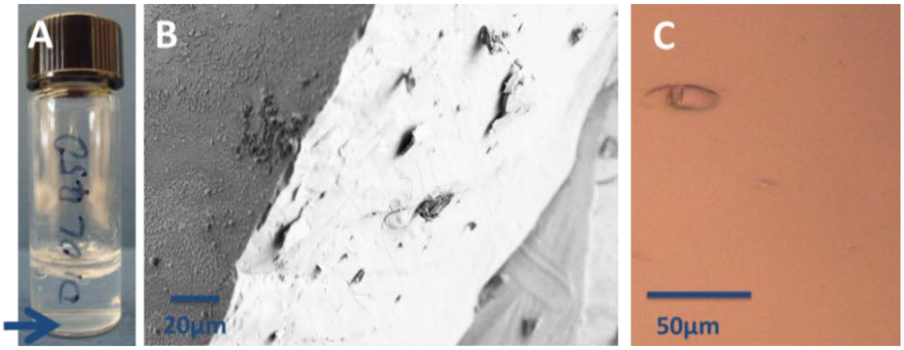


Figure 4.10: OMA in DI OL 450 sedimentation without AOT. (A) picture of the sample, blue mark points on the sedimentation phase (B) cSEM image of the sedimentation phase (C) optical microscopy image of the sedimentation phase at a 20x magnification.

Both, the OMAs shown Figure 4.9 in and Figure 4.10, are relatively small. Based on these images it can be concluded that the OMAs in DI-water have only a small amount of oil trapped. Furthermore almost all oils in DI-water show few oil droplets using an optical microscope. These oil droplets might be created during pouring the sample with the pipet from the vial onto the microscope slide. This is why they are not further discussed.

This sedimentation is following the literature as Binks and Lumsdon have discovered sedimentation (they call it flocculation) in samples with Toluene in DI-water with 0.5 wt% silica nanoparticles for all concentrations of sodium chloride [Binks & Lumsdon, 1999]. As they used a twice as high silica concentration, they might have recognized a thicker flocculation layer than it is visible in Figure 4.10 A. Toluene has a similar relative polarity as ethyl acetate [Freed et al., 1990].

The amount of sedimentation is much higher in seawater than in DI-water. In seawater the sedimentation phase is visible and measurable for all three different oils. In Figure 4.11 is the relative thickness of the sedimentation phase in seawater over the particle size shown. The relative thickness of the sedimentation is defined as the ration of the sedimentation height and total sample height:

$$relative\ thickness\ sedimentatoion = \frac{h_{Sedimentation}}{h_{Total\ sample}}\ [\%] \qquad 4.2$$

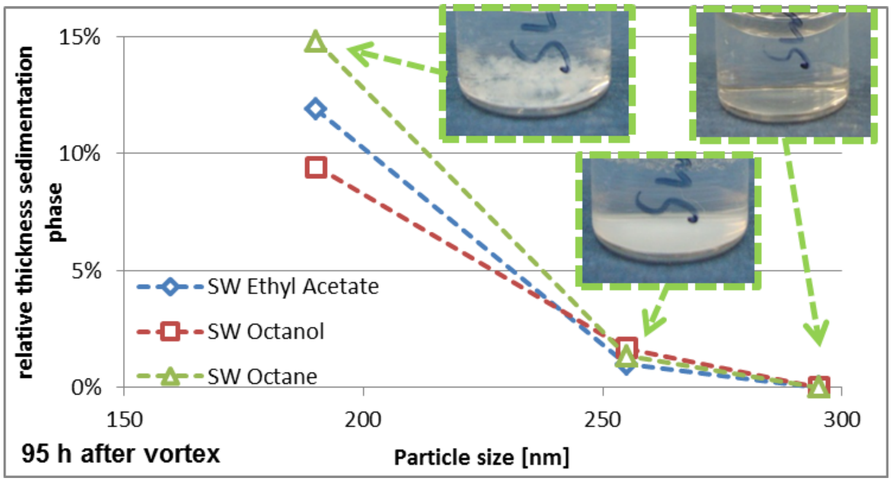


Figure 4.11: Relative thickness sedimentation phase over particle size without AOT 95h after vortex

This means smaller silica agglomerates in seawater form a significantly thicker sedimentation layer than larger silica agglomerates. This is reasonable as the small silica agglomerates form the largest silica-sea salt agglomerates.

With the cSEM it can be seen that the sedimentation for octane in seawater and the 220 nm filtrate consists of OMAs consisting of silica, oil, oxygen and the minerals in sea salt (see Figure 4.12 A). Using an optical microscope it can be seen that the sedimentation layer floats as a blurry phase within the sample (see mark in Figure 4.12 B). Furthermore this sedimentation layer is visible at the bottom of the vial (see mark in Figure 4.12 C). This OMA looks similar to the droplet OMAs which are reported by Stoffyn-Egli and Lee and stated in Figure 2.8 A [Stoffyn-Egli & Lee, 2002].

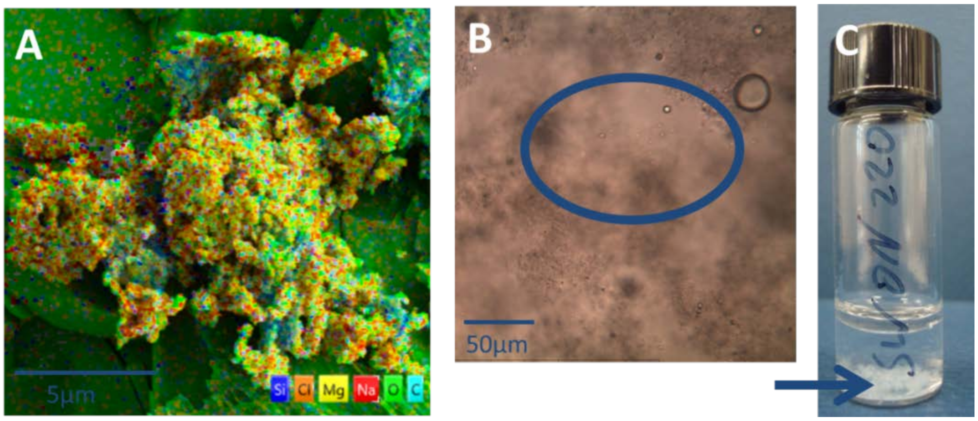


Figure 4.12: OMA in SW ON 220 sedimentation without AOT. (A) EDS/cSEM image of sedimentation phase, light cyan represents carbon, green oxygen and blue silica, other colors are minerals from the seawater. (B) optical microscopy image of the sedimentation phase at a 20x magnification, blue mark is a floating sedimentation phase. (C) picture of the sample, the blue mark points on the sedimentation phase.

The presence of OMAs follows Le Floch et al's results [Le Floch et al., 2002]. They observed the formation of OMAs with different crude oils in seawater at changing salinities. Their results indicate that some salt presence is needed for the formation of OMAs. Furthermore it is observed by Guyomarch et al. that the amount of salt concentration has an influence on the size of OMAs [Guyomarch et al., 2002]. Both, Le Floch et al. and Guyomarch et al., support with this the hypothesis that OMAs are stabilized among others with charges on mineral surfaces [Bragg & Yang, 1995]. These charges are present as charged salt ions.

4.2.2.2. *With AOT*

Emulsion

After the samples without AOT are evaluated, AOT is added to these samples. As the necessary amount of AOT dissolved in 0.05 mL oil, the total amount of oil is assumed as constant. The samples with DI-water with AOT form a thick O/W emulsion layer. This is shown in Figure 4.13, where the relative thickness of the emulsion layer is shown:

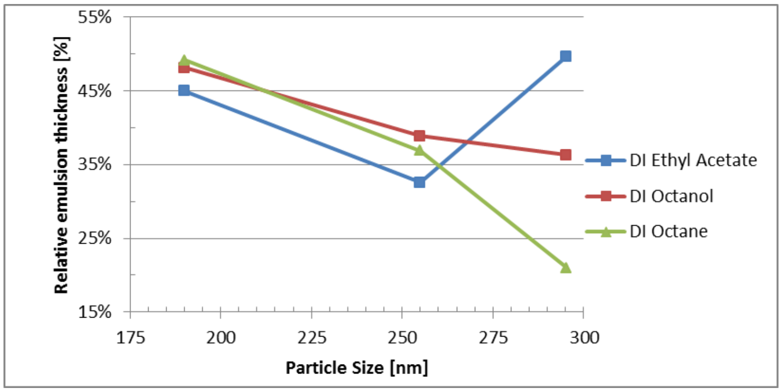


Figure 4.13: Relative emulsion thickness DI-water samples with AOT 48h after vortex

From this figure and from the visual observations it can be seen that the thickness of the emulsion layer is decreasing with increasing particle size. Only ethyl acetate in DI-water samples with silica particles do not follow this trend. In Figure 4.14 a picture, a microscopy image and a cSEM image of the DI ON 450 with AOT sample are shown.

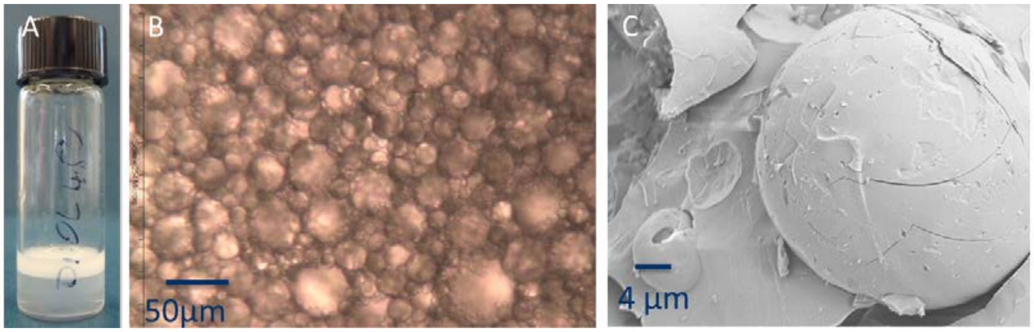


Figure 4.14: Octanol in 450 nm silica filtrate and DI-water with AOT. (A) Picture of DI OL 450 (B) optical microscopy image of emulsion phase at 20x magnification (C) cSEM image of the emulsion phase

Apart from some relatively large droplets at the interface of the SW OL 220 sample no emulsion is visible in seawater. Unfortunately these droplets were too large to be imaged with optical microscopy or cSEM as pipets destroy those large droplets. Furthermore these droplets are really unstable towards vibration, which might be the reason why they were not reproducible. All in all it can be summarized that silica, oil and DI-water form a larger emulsion than without AOT. This effect becomes visible in the time stability.

Sedimentation

Samples with DI-water do not form visible sedimentation to any significant degree. The mixtures with seawater form a visible sedimentation layer except for the samples with 800 nm filtrate particles. The general trend of this is similar to the experiment without AOT. Unfortunately these sedimentation layers were too small to measure with ImageJ in order to achieve a valid result. Only the emulsions with ethyl acetate in seawater form visible sedimentation to a significant degree, but this is less than in the samples without AOT. Pictures of this series are shown in Figure 4.15 A-C. The corresponding images of the bottom phase show emulsion and OMAs to a different degree. In the SW EA 220 sample are clearly OMAs with some inverted droplets visible. The larger the particles the less distinct are the OMAs in this series.

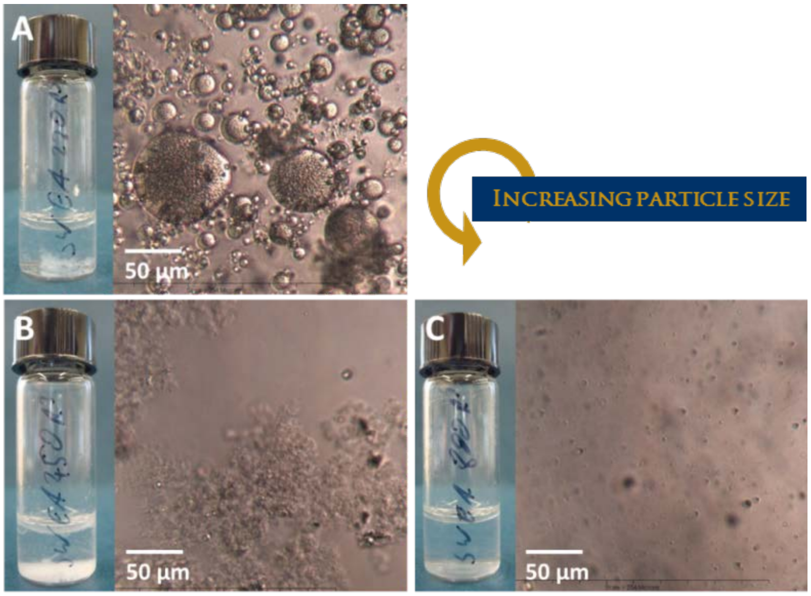


Figure 4.15: Sedimentation of ethyl acetate in seawater with AOT. (A) Picture of SW EA 220 and a 20x microscopy image of the bottom phase. (B) Same as (A), but for SW EA 450 . (C) Same as (A), but for SW EA 800.

4.2.2.3. Time stability

For this experiment the samples are vortexed for 30 seconds. Directly after vortexing videos are recorded as described in chapter 3.6.4. Based on these videos the thickness of the emulsion layer is measured every 10 minutes according to chapter 3.6.5. The results are stated in Figure 4.16. The thickness of the emulsion layer is expressed as relative thickness of the emulsion layer, which is defined in equation 4.2.

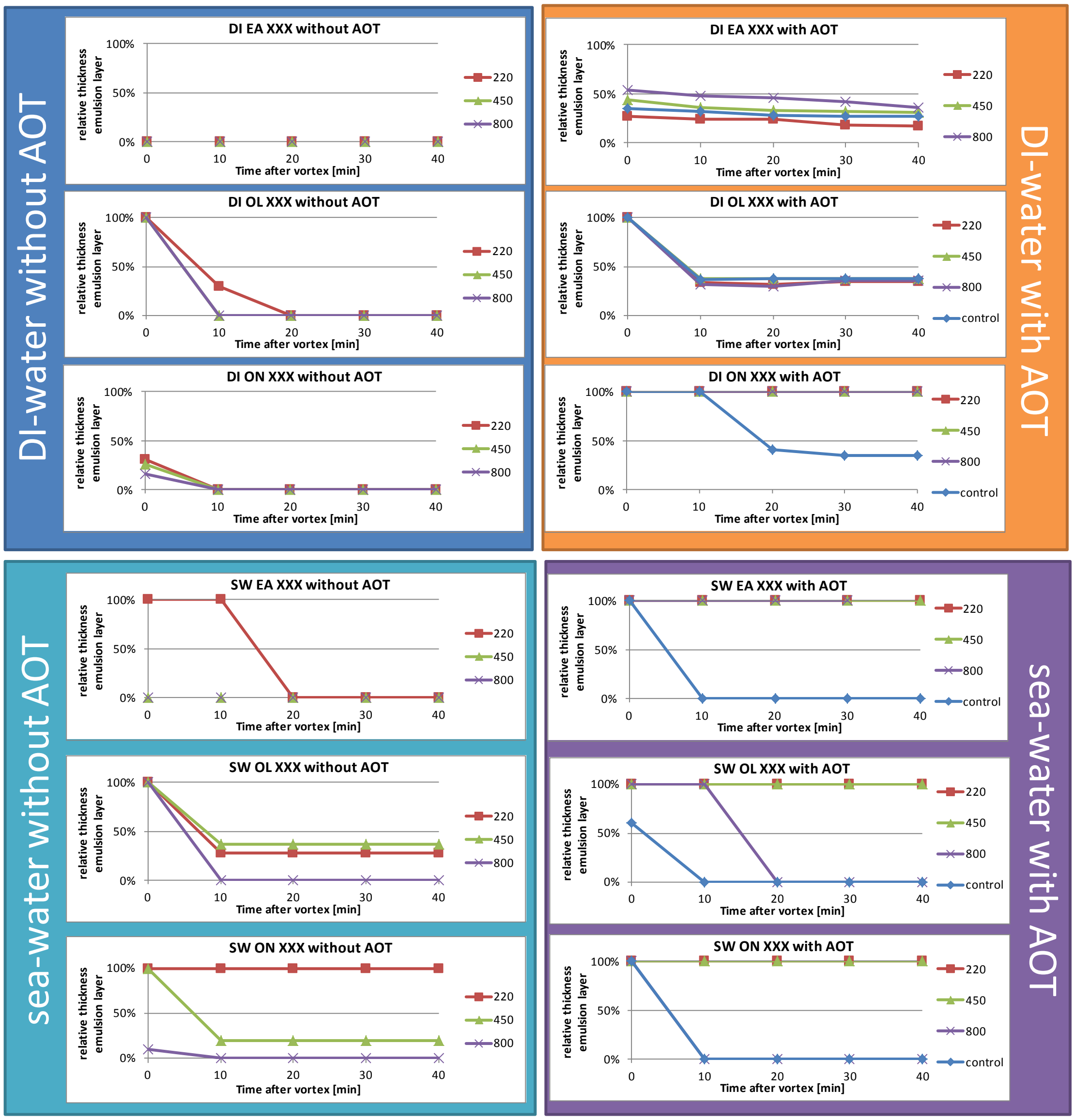


Figure 4.16: Thickness of the emulsion phase over time after vortexing

It was not possible to observe the formation of OMAs within 40 min after vortexing. During this experiment the following was observed for the emulsion phase:

1) Samples with AOT form larger and longer stable emulsion layer then samples without AOT. Adding AOT results in a better emulsion performance in all cases. This is reasonable as AOT is used as a surfactant. This effect was previously observed by Binks and Whitby with the cationic surfactant Dodecyltrimethylammonium bromide (DTAB) [Binks & Whitby, 2005].
2) Ethyl acetate forms no emulsion in DI-water regardless of the particle size. In seawater it forms only the 220 nm filtrate emulsion, but these emulsions are not stable for a long time. After adding AOT the emulsion layer is much more stable.
3) There is a general trend that samples with smaller particles form larger and more sustainable emulsions. Only samples with ethyl acetate in DI-water and AOT do not follow this trend. But this difference is not significant and could have been resulted because of measurement inaccuracies.
4) Octanol in DI-water without AOT results in the largest and most sustainable emulsion layer regardless of the particle size. Ethyl acetate forms no emulsions for all combinations with seawater and DI-water/with AOT.
5) After comparing the relative emulsion layer thicknesses of the samples without AOT with the one with AOT and with the controls it becomes obvious that AOT and silica nanoparticle have an influence on the emulsion layer. This means interactions between the cationic surfactant AOT and silica nanoparticles are possible. Unfortunately a proof of statistical significance is not possible using the available. Worthen et al. suggest for an opposite charge of nanoparticle and surfactant a strong surfactant adsorption on the nanoparticles [Worthen et al., 2014].

4.2.2.4. Waves

As it is stated in the literature that a reciprocating shaker with more than 70 revolutions per minute can break the oil/water interfacial tension [Weise et al., 1999], the vials without AOT were placed on a reciprocating table shaker. The scale was set to 100 rpm and the samples were shaken for five hours. The change of the samples was compared with visual evaluation. As an example the visual comparison of the DI OL 220 is shown in Figure 4.17:

Before shaking

After shaking

Figure 4.17: DI OL 220 comparison before and after 5h shaking without AOT

From the comparison of these pictures it can be seen that the shaking destroyed some droplets and reduced the cloudiness at the interface. This effect occurred in all samples. None of the tested samples showed a larger emulsion phase, which is goes against what was expected and the reported by Weise et al [Weise et al., 1999].

The reason for that could be that in this study only 1 mL DI or seawater is used. Weise et al. use Erlenmeyer flasks filled with 300 mL of solution to test dispersant efficiency [Weise et al., 1999]. This leads to the assumption that the used vial is too small to develop waves which would mix the sample in order to lead to emulsion formation. Unfortunately there was not enough silica solution available to repeat the experiment with a larger sample size. This is why detailed determination with optical microscopy and replication with AOT was not conducted.

4.3. Theoretical computations

In order to use equation 2.2 for the used oils, the values for oil/water interfacial tension and the contact angle have to be taken form the literature. These values are shown in Table 4.4.

Table 4.4: Surface tension, O/W interfacial tension, contact angle and density of the used oils [Carré & Lacarriere, 2006; CRC, 2010; Frelichowska, Bolzinger, & Chevalier, 2009; Grifalco & Good, 1957; Kwok & Neumann, 1999; VDI, 2010]. Dipole moment for 1-octanol is measured in the gas phase.

	Oil Surface tension $[\frac{mN}{m}]$	Oil water interfacial tension $[\frac{mN}{m}]$	Contact angle silicon waver [°]	Density [kg/m³]	Dipole Moment [D]
Ethyl acetate	22.6	5.84	142	900.1	1.78
N-octane	21.8	50.8	51	702.3	0
1-octanol	27.5	8.5	75.1	826.8	1.76

As expression 2.2 depends on the contact angle between oil, water and silica, the contact angle measured on a silicon waver cannot be used. Unfortunately for this contact angle are no literature values available. This is why the Gibbs free energy divided by $(1 - \cos(\theta))^2$ is shown in Figure 4.18.

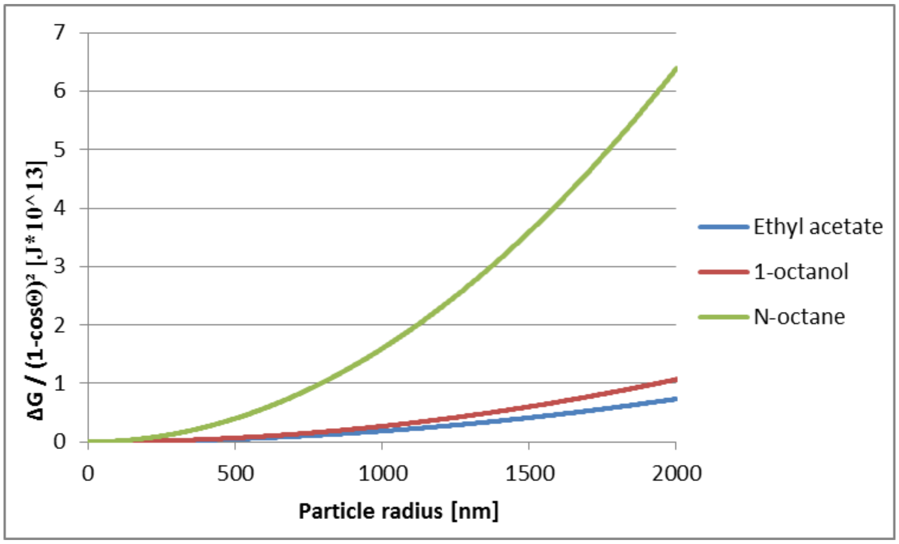


Figure 4.18: Theoretical computations for Gibbs free energy of particle adsorption at different oil/water interfaces.

All of the computed values are positive and the expression $(1 - \cos(\theta))^2$ is positive for all contact angles, all oils should be able to form stable Pickering emulsions in theory.

From this figure it can be shown that the Gibbs free energy grows quadratically with increasing particle size. This effect could not be observed with the above evaluated experiments. It looks like there is an optimum particle size where the droplets are most stable. This might be because in the derivation of the equation 2.2 it was assumed that gravity has no influence on the particle. Also it neglects the rate of diffusion of the particles from the bulk phase (water) to the oil/water interfaces once droplets are formed.

From Figure 4.18 it can be seen that octane forms the most stable emulsions in theory as the Gibbs free energy is highest. This seems reasonable as n-octane has the lowest dipole moment out of the three chosen oils. The dipole moment is a measurement for the charge distribution of polyatomic molecules [VDI, 2010, p. 130]. The higher the dipole moment, which is usually expressed in the dimension Debye, the more asymmetric is the charge distribution within the molecule. As octane is a non-polar molecule, the dipole moment is zero. Consequently octane forms no hydrogen bonds with water, which supports the formation of sustainable emulsions. This is why it seems to be reasonable that octane forms the most stable emulsions in DI-water without AOT (compare Figure 4.11). Ethyl acetate and octanol, having dipole moments around 1.8 and, do not form stable emulsions in DI-water because the required energy to break the emulsion is low and can be brought up by the hydrogen bonds.

CHAPTER 5. SUMMARY AND OUTLOOK

This study hypothesized that the size of silica nanoparticles has a significant influence on the formation and stability of Pickering emulsions and the formation of oil mineral aggregates with oil in deionized- or seawater. In order to proof this hypothesis silica nanoparticle aggregates were created and fractionized in distinct size fractions. Then the aggregate adhesion to oil/water interfaces was examined and the formation of Pickering emulsions and oil mineral aggregates of ethyl acetate, octane and octanol with the fractionized silica nanoparticles in deionized- and seawater with and without the surfactant Aerosol OT determined. The following results were gained:

- Without Aerosol OT the sedimentation in seawater is higher than in deionized water. Furthermore the sedimentation thickness decreases with increasing particle size.
- It could be shown that the sedimentation layer in seawater consists of silica, oil and salt minerals. With Aerosol OT only small primary silica aggregates form significant sedimentation layer. The reason for that is that the smallest silica agglomerates form the largest silica-sea salt agglomerates.
- Emulsions with Aerosol OT are more stable then without. Surprising is that octanol and octane in seawater and octanol in DI-water form the largest emulsion layer with the medium sized particles. This is not according to the conventional theory, which assumes increasing stability with increasing particle size. Based on this can be assumed that there is an optimum particle size.

Based on this result can be concluded that the aggregate has a significant influence on the formation of emulsions and sedimentation layers. In order to use this effect and to develop a silica nanoparticle based dispersant, the following questions have to be answered:

1) **What is the interaction of silica nanoparticles and a surfactant on a molecular level?**

The understanding of this interaction on a molecular level is important in order to understand the formation of OMAs in an ocean surrounding. Based on the conducted study the following can be hypothesized in seawater without the surfactant Aerosol OT:

The silica agglomerates are negatively charged. This negatively charge attracts the sea salt-cations, which stick to the silica agglomerates due to cation bridging. Evidence for this is provided by the drop of the surface charge from around 43 mV to around 8 mV while adding sea salt (see Table 4.1). These silica-sea salt agglomerates have positive charge. This is why they are attracted by the negative charged oil and form oil mineral aggregates. Depending on the specific weight of the mineral aggregate, the oil mineral aggregate floats up to the emulsion phase or saddles down and forms the sedimentation phase. The amount of silica bounded to the oil has a large influence on the specific weight as the density of amorphous silica is about 2.2 $\frac{g}{cm^3}$ [Flörke et al., 2008] and much higher than the density of the used oils (compare Table 4.4). A schematic of the whole process is shown in Figure 5.1.

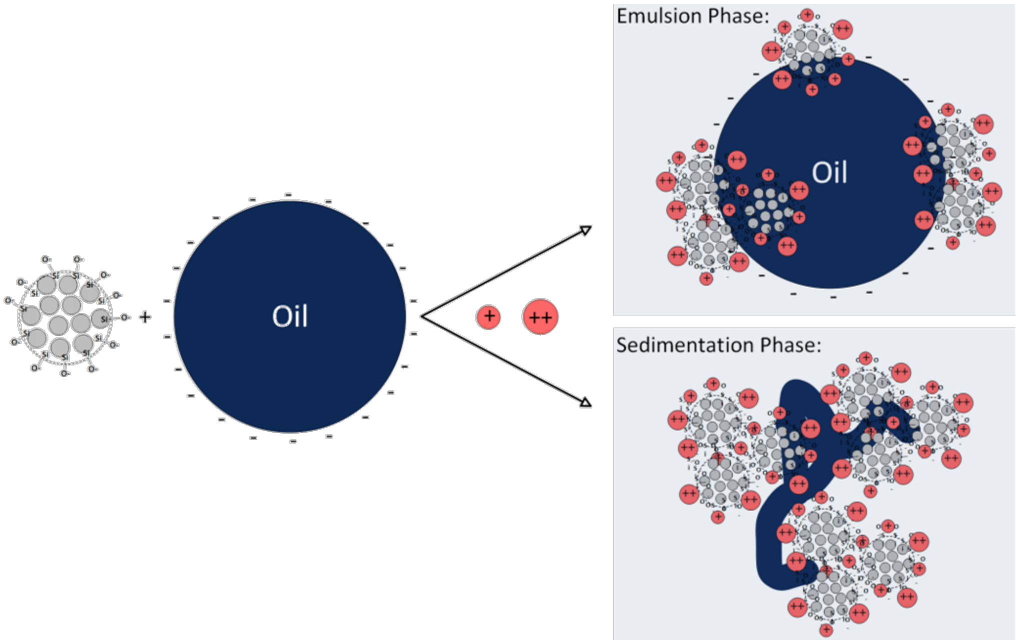


Figure 5.1: Hypothesized interactions between silica, sea salt and oil

After adding Aerosol OT, it surrounds the silica-sea salt agglomerates with a micelle like structure. This is because the negative charge in the head group of Aerosol OT is attracted to the positive charge of the salt cations. The tale groups of such micelle like structures and the ones of free Aerosol OT molecules act like ordinary surfactant. This is shown in Figure 5.2.

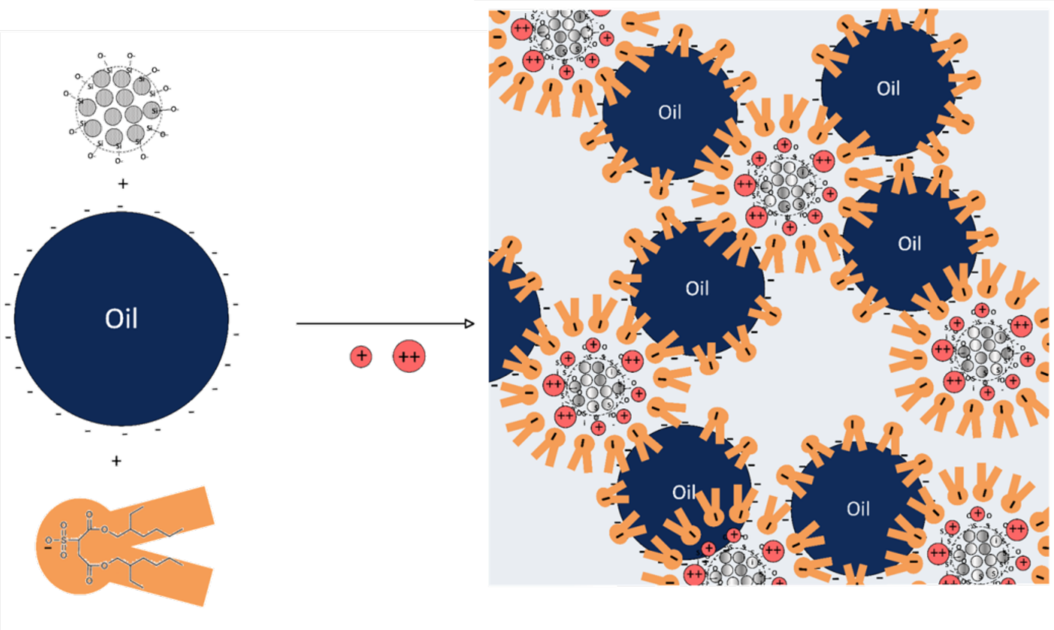


Figure 5.2: Hypothesized interactions between silica, sea salt, oil and Aerosol OT

However, future research has to identify the interactions of silica, sea salt and Aerosol OT.

2) **What is the toxicity of silica nanoparticles in an ocean surrounding?**

Conventional dispersants might be toxic towards marine species. In order to use silica nanoparticles solely or additional to conventional dispersants, it has to be proven that they have no or less toxicity then conventional treatments. Furthermore has the influence of oil mineral aggregates to be determined.

3) **What is the behavior of silica based dispersants at different temperature ranges?**

Offshore oil spills can occur everywhere in the ocean. This means the effectiveness of silica based dispersants has to be evaluated in a temperature range between -2°C to 30°C as this the range of ocean temperature [Castro & Huber, 2003].

4) **Can the silica nanoparticles be coated with nutrients in order to have optimal conditions for oil-degrading bacteria?**

   If it is possible to enrich emulsion with nutrition to support oil-degrading bacteria, the process of oil degradation can be speed up. With this effect is the presence time of crude oil in the ocean reduced. This would reduce the environmental impact of crude oil spills.

If these questions are answered and the interaction between silica nanoparticles, dispersants, seawater and oil are understood, silica nanoparticle based dispersants might be a useful tool for treating future oil spills.

CHAPTER 6. APPENDIX

6.1. Oil spill response decision tree

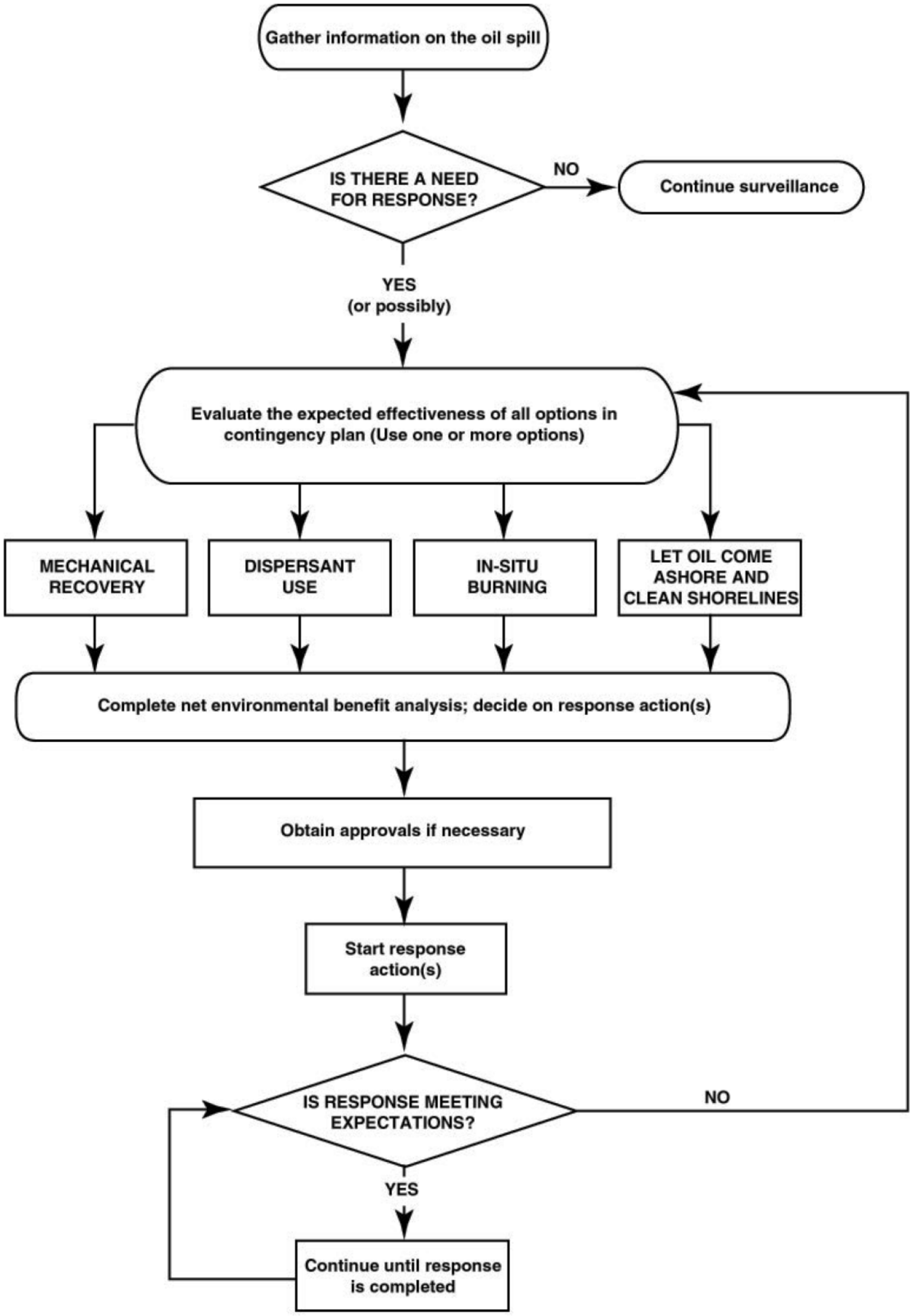


Figure 6.1: Oil spill response decission tree [Fiocco & Lewis, 1999]

6.2. Vortex

Little research about vortex mixing and its reproducibility can be found within the scientific community. The invention of an *apparatus for mixing fluent material*, which is similar to today’s vortex mixer, goes back to the 1950s. The Kraft brothers invented a small scale mixer especially for laboratory use and filed it as a patent in 1959 [Kraft & Kraft, 1959]. Their mixer consists of a vertically oriented, electrically powered drive shaft which is attached to a cupped rubber piece. As the rubber cup is mounted slightly off-center, it oscillates in a circular motion when the motor is switched on. Pressing a vial on this rubber cup creates a vortex in the solution. This enables an effective mixing of the liquid. [Buie, 2011]

A drawing of this mixer is shown in Figure 6.2:

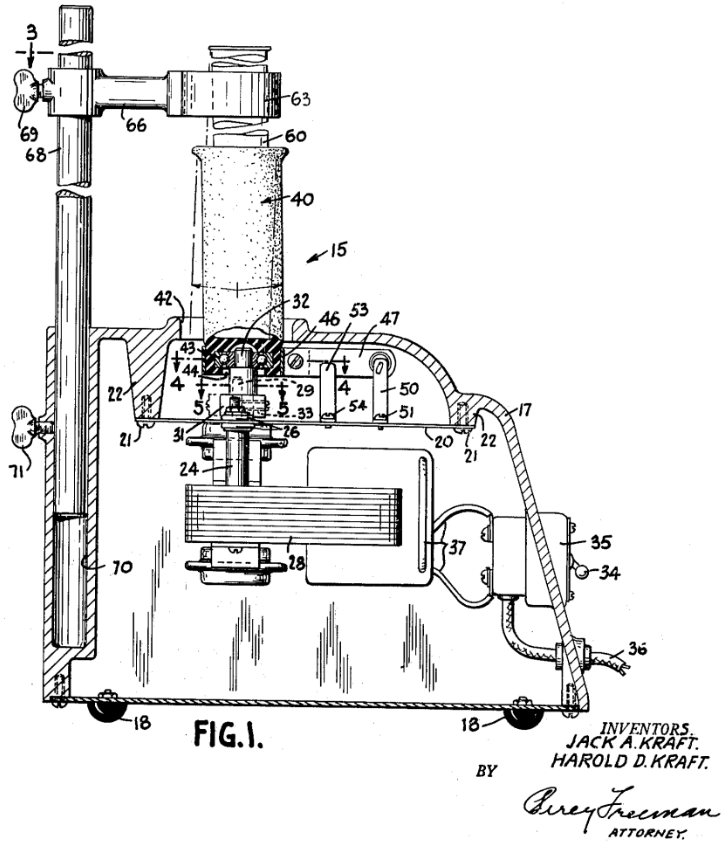


Figure 6.2: Technical drawing of the first vortex mixer [Kraft & Kraft, 1959, p. 1 edited]

Today companies like Scientific Industries offer vortex mixers which do not need a manual pressing against the rubber cup as the vials can be mechanically fixed to the vortex mixer [Scientific Industries, 2014a, 2014b]. This setting should be more reproducible than the conventional vortex mixing [Buie, 2011].

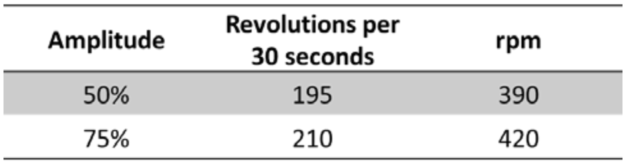
6.3.Picture Probesonicator

Figure 6.3: Probesonicator

6.4.Calibration Shaking Table

The calibration of the rotating New Brunswick® Excella E-1 Classic Platform shaker is conducted with an video camera recording 29 frames per seconds. That means the camera creates a video with 29 pictures per second. Such videos are recorded at a 50% and at a 75% intensity. With these video files frame by frame analyses are conducted and the revolutions for 30 seconds counted. Based on this number the following revolutions per minute (rpm) number are computed:

Table 6.1: Calibration New Brunswick® Excella E-1 Classic Platform shaker



Amplitude	Revolutions per 30 seconds	rpm
50%	195	390
75%	210	420

Surprising in these results is that the technical specifications in the manual give a maximum speed of 400 rpm.

6.5.Standard Operating Protocols

6.5.1. Probe Sonication

1) Water bath 15°C
2) Mix 17 ml DI-water and 0.17 g non porous nanoparticle
3) Shaking table for 5 minutes on 75% (while this prepare DLS so that only the start measurement button has to be pushed, check 20 mm mark on horn)
4) DLS (120 s temperature time, 3 runs, 25°C) with 1 mL → **This is necessary because all reported values will be the average from the three measurements!!!**
5) Probe sonification at 75% (15 seconds pulsation and 15 seconds break) in the water bath. Time is the variable

6) Remove from the water bath

7) Wait for 30 Minutes (prepare the DLS during this time)

8) Shaking table for 5 Minutes on 75%

9) DLS (120 s temperature time, 3 runs) with 1 mL

10) Cleaning the probesonicator with Ethanol and a kimwipe

6.5.2. Filtration

1) Fill pump with DI-water

2) Set refill speed to 20 ml/min

3) Empty pump

4) Set pump speed to 0.5 ml/min

5) Put filter in case (the small diameter sieve has to be the one next to the filter paper) and mount case together

6) Vortex sample

7) Fill sample in the pump (20 mL/min)

8) Mount case to pump

9) Pump (0.5 mL/min)

10) Refill 4 mL DI-water in pump to empty pipes

11) Pump (0.5 mL/min)

12) Demount case

13) Vortex Sample

14) DLS sample (120 s temperature time, 3 runs, 25°C) with 1 mL

→ **This is necessary because all reported values will be the average from the three measurements!!!** → **Put DLS sample back in sample container**

15) Clean case (flush all parts with DI-water, put it in DI-water and Bath sonication, flush all parts again)

16) Flush pump two times with DI-water

Filtration of sample >20 mL: Filter batches 20 mL each. Cleaning between the batches not necessary, repeat steps 5-9 as long as all sample is filtered.

6.5.3. Concentration measurement

1) Set oven to 70 degree Celsius
2) Clean 20 mL vial (Flush it with DI-water twice, than with Ethanol once)
3) Dry vial with a Kimwipe
4) Place it in the oven for at least 2h
5) Let it cool down
6) Weight it (**wait until the scale is balanced and the value remains constant!!!**) → Empty vial weight
7) Fill 4 mL sample in it, weight it again → Weight liquid sample + vial
8) Put it for at least 24 h in the oven
9) Turn the oven of and let the sample cool down for 2h
10) Weight sample → Weight dry sample + vial

The sample should look like this:

Figure 6.4: Sample after concentration measurement

6.6. Results pre experiment

6.6.1. Without sonication, 80h after Vortex

80 hours after Vortexing without Sonication		pH=2	pH=4	pH=6	Seawater
1	1-Butanol	oil phase and water phase, sedimentation within the waterphase	one micele, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	no oil droplets, seperation between the oil and water phase, sedimentation, even for silica is the sedimentation layer is very large
2	n-octane	few oil droplets, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase
3	hexadecane	oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase
4	Ethyl Acetate	one micele, oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase	one micele, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase
5	Dodecane	oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase	few, realy large oil droplets, oil phase and water phase, sedimentation within the waterphase
6	vegetable oil	oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	mixture Gas, Oil - really large oil droplets, no seperation within oilphase, large oil droplets in the silica phase
7	gas	many oil droplets, oil phase and water phase, sedimentation within the waterphase	many oil droplets, oil phase and water phase, sedimentation within the waterphase	many oil droplets, oil phase and water phase, sedimentation within the waterphase	emulsion in the top phase, many oil droplets - there are many silica particles in the top phase but still sedimentation occures
8	1-4. Dioxane	one phase, sedimentation	one phase, sedimentation	one phase, sedimentation	one phase, sedimentation
9	Cylohexane	few oil droplets, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase	few oil droplets, oil phase and water phase, sedimentation within the waterphase, two oil droplets in the silica sedimentation at the bottom of the sedimentation	oil phase and water phase, sedimentation within the waterphase
10	Octanol	few oil droplets, oil phase and water phase, sedimentation within the waterphase	many oil droplets, oil phase and water phase, sedimentation within the waterphase	two little oil droplets, oil phase and water phase, sedimentation within the waterphase	few oil droplets at the interface, large silica phase and oil droplets in the silica phase
					For all Saltwater combinations is the silica layer at the ground large in comparison with the DI-water Emulsions

6.6.2. With 3h bathsonication, 80h after vortex

3 h Bathsonication 80 hours after vortex		pH=2	pH=4	pH=6	Seawater
1	1-Butanol	oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase, clear interface	oil phase and water phase, sedimentation within the waterphase, clear interface between the two phases	no oil droplets, seperation between the oil and water phase, sedimentation, even for silica is the sedimentation layer is very large, clear interface between the two phases
2	n-octane	few oil droplets at the interface, interface seems to be cloudy, oil phase and water phase, sedimentation within the waterphase	many really small oil droplets at the cloudy interface, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase, cloudy interface between the two phases	few really small droplets at the interface, oil phase and water phase, sedimentation within the waterphase, cloudy interface between the two phases
3	hexadecane	interface seems to be cloudy, oil phase and water phase, sedimentation within the waterphase	many really small oil droplets at the cloudy interface and in the water phase, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase, cloudy interface between the two phases	no oil droplets, oil phase and water phase, sedimentation within the waterphase, clear interface, frozen sample
4	Ethyl Acetate	no oil droplets, clear inteface between oil phase and water phase, sedimentation within the waterphase	no oil droplets, clear inteface between oil phase and water phase, sedimentation within the waterphase	no oil droplets, oil phase and water phase, sedimentation within the waterphase, cloudy interface	small droplets at the interface, clear interphase between the oil phase and water phase, sedimentation within the waterphase
5	Dodecane	some oil droplets in the water phase, oil and water phase, sedimentation within the waterphase	many really small oil droplets at the cloudy interface and in the water phase, oil phase and water phase, sedimentation within the waterphase	few, big oil droplets in the water phase, oil phase and water phase, sedimentation within the waterphase, cloudy interface	no droplets, two phases with clear surface
6	vegetable oil	vegetable oil got coludy, phase seperation and sedimentation within the waterphase	vegetable oil got coludy, few big oil droplets in the waterphase, oil phase and water phase, sedimentation within the waterphase	vegetable oil got coludy, phase seperation and sedimentation within the waterphase	mixture Gas, Oil - really large oil droplets, no seperation within oilphase, large oil droplets in the silica phase, cloudy surface between the two interphases
7	gas	many small oil droplets at the interface and in the water phase, interface seens to be cloudy, oil phase and water phase, sedimentation within the waterphase	many oil droplets at interface and in water phase, cloudy interphase between the phases, oil phase and water phase, sedimentation within the waterphase	few oil droplets at the interface, oil phase and water phase, sedimentation within the waterphase, cloudy interface	few small droplets at the interphase - there are many silica particles in the top phase but still sedimentation occures, cloudy interphase between the two phases
8	1-4. Dioxane				
9	Cylohexane	many oil droplets at the interface and in the water phase, oil phase and water phase, sedimentation within the waterphase, clear interface bet ween the phases	oil phase and water phase, sedimentation within the waterphase, cloudy interphase	few oil droplets at the interphase and in the water phase, oil phase and water phase, sedimentation within the waterphase, many oil droplets in the silica sedimentation at the bottom of the sedimentation, little cloudyness at the interface	oil phase and water phase, sedimentation within the waterphase, cloudy interphase
10	Octanol	few oil droplets at the surface, oil phase and water phase, sedimentation within the waterphase, clear interface between the phases	many oil droplets in the water phase and at the interface, oil phase and water phase, sedimentation within the waterphase, cloudy interphase	many small little oil droplets at the cloudy interface, oil phase and water phase, sedimentation within the waterphase	few oil droplets at the interface, large silica phase and oil droplets in the silica phase
					For all Saltwater combinations is the silica layer at the ground large in comparison with the DI-water Emulsions

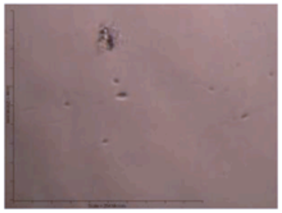
6.6.3. With 6h Bathsonication, 11 h after vortex

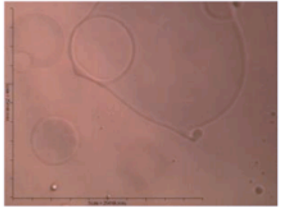
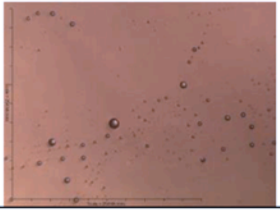
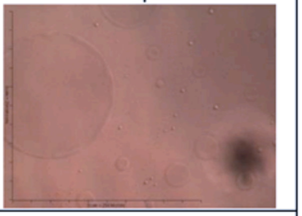
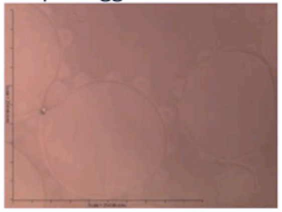
6 h Bathsonication 11h after vortex		pH=2	pH=4	pH=6	Seawater
1	1-Butanol	two phases, all waterphase is grey, few little droplets at the interface, grayish waterphase	few really small dropletts at the interface between oil and water phase. Grayish waterphase	oil phase and water phase, sedimentation within the waterphase, grayish interphase	no oil droplets, seperation between the oil and water phase, sedimentation, even for silica is the sedimentation layer is very large, clear interface between the two phases
2	n-octane	few big droplets at the interface, two phases, all waterphase is grey, grayish waterphase	oil phase and water phase, sedimentation within the waterphase, cloudy waterphase	oil phase and water phase, sedimentation within the waterphase, grayish interphase	many bigger droplets at the interface, oil phase and water phase, sedimentation within the waterphase, clear interface between the two phases
3	hexadecane	many small dropletts at the interface, two phases, all waterphase is grey, grayish waterphase	oil phase and water phase, sedimentation within the waterphase, cloudy waterphase	one at the interface, sedimentation within the waterphase, cloudy interface between the two phases, grayish waterphase	many bigger droplets at the interphase, oil phase and water phase, sedimentation within the waterphase, clear interface, grayish waterphase
4	Ethyl Acetate	many realy small droplets in the oil phase, two phases, grayish waterphase	many really small oil droplets at the cloudy interface and in the water phase, oil phase and water phase, grayish waterphase	many small droplets at the interface, sedimentation within the waterphase, cloudy interface between the two phases, grayish waterphase	big dropletts at the interface, sedimentation within the waterphase, grayish waterphase
5	Dodecane	big droplett at the interface, grayish waterphase, two phases	few really small oil droplets at the cloudy interface and in the water phase, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase, grayish interphase, small oil droplets at the glass wall of the water phase	big dropletts at the interface, sedimentation within the waterphase, grayish waterphase
6	vegetable oil	vegetable oil got coludy, phase seperation and sedimentation within the waterphase, one big dopletts under the interface in the water phase , clear waterphase, but deposition of silica particles at the tube	vegetable oil got coludy, droplettts, but silica particle deposition at the interface oil phase and water phase, sedimentation within the waterphase, grayish waterphase	vegetable oil got coludy, phase seperation and sedimentation within the waterphase, few small droplets at the interface	mixture Gas, Oil - really large oil droplets, no seperation within oilphase, large oil droplets in the silica phase, cloudy surface between the two interphases, seperation in the water phase
7	gas	many small and big oil droplets at the interface and in the oil phase, silica seperation in the water phase, interface seems to be cloudy, oil phase and water phase, grayish waterphase	many oil droplets at interface and in oil phase, cloudy interphase between the phases, oil phase and water phase, grayish waterphase	one big droplets at the interface, silica deposition at the interface, oil phase and water phase, sedimentation within the waterphase, cloudy interface, grayish waterphase	many droplets at the interphase - there are many silica particles in the top phase but still sedimentation occures, cloudy interphase between the two phases
8	1-4. Dioxane				
9	Cylohexane	few really small oil droplets at the interface, oil phase and water phase, grayish waterphase	oil phase and water phase, sedimentation within the waterphase, gray waterphase, one medium sized droplett at the wall at the oil phase	few oil droplets at the interphase, oil phase and water phase, sedimentation within the waterphase, many oil droplets in the silica sedimentation at the bottom of the sedimentation, little cloudyness at the interface, grayish waterphase	two big droplet, oil phase and water phase, sedimentation within the waterphase, cloudy interphase
10	Octanol	many oil droplets at the interface, phase and water phase, sedimentation within the waterphase, grayish emulsion phase	many oil droplets in the water phase and under the interface, oil phase and water phase, sedimentation within the waterphase, grayish waterphase	many small little oil droplets at the cloudy interface, oil phase and water phase, sedimentation within the waterphase, grayish waterphase, thick emulsion layer	almost everything looks like one phase, many oil droplets at the interface, large silica phase and oil droplets in the silica phase, sedimentation in the water phase
					For all Saltwater combinations is the silica layer at the ground large in comparison with the DI-water Emulsions

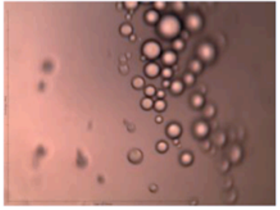
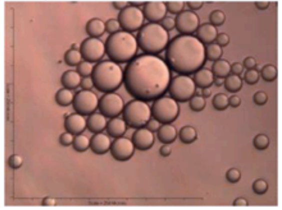
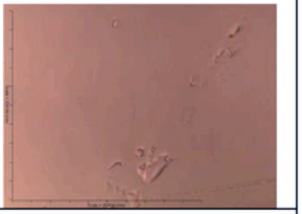
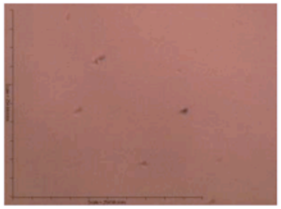
6.6.4. With 10 h bathsonication, 15h after vortex

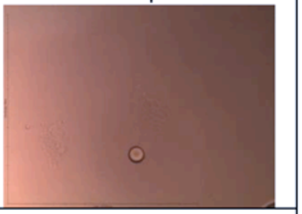
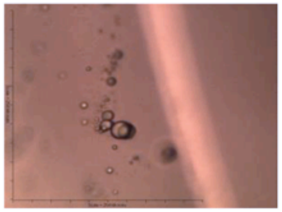
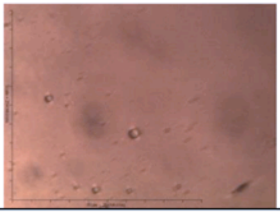
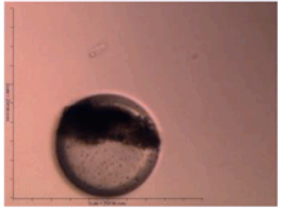
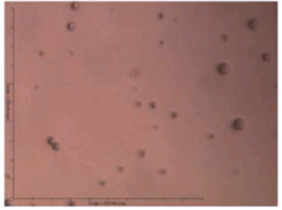
10 h Bathsonication 15h after vortex		pH=2	pH=4	pH=6	Seawater
1	1-Butanol	two phases, all waterphase is grey, no droplets at the interface, grayish waterphase	two phases, all waterphase is grey, no droplets at the interface, grayish waterphase	oil phase and water phase, sedimentation within the waterphase, grayish interphase	no oil droplets, seperation between the oil and water phase, sedimentation, even for silica is the sedimentation layer is very large, clear interface between the two phases
2	n-octane	few big and small droplets at the interface, two phases, all waterphase is grey, grayish waterphase	oil phase and water phase, sedimentation within the waterphase, cloudy waterphase	oil phase and water phase, sedimentation within the waterphase, grayish interphase, some silica depositon at the wall of the interface	one bigger and few smaller droplets at the interface, oil phase and water phase, sedimentation within the waterphase, clear interface between the two phases
3	hexadecane	many medium sized droplets at the interface, two phases, all waterphase is grey, grayish deposition at the wall of the oil phase	oil phase and water phase, sedimentation within the waterphase, cloudy waterphase and silica deposition at the wall of the oil phase	no droplett at the interface, sedimentation within the waterphase, cloudy interface between the two phases, grayish waterphase, silica deposition at the interface	many bigger droplets at the interphase, oil phase and water phase, sedimentation within the waterphase, clear interface, grayish waterphase
4	Ethyl Acetate	few realy small droplets in the oil phase, two phases, grayish waterphase	oil phase and water phase, sedimentation within the waterphase, cloudy waterphase	some small droplets at the interface, sedimentation within the waterphase, cloudy interface between the two phases, grayish waterphase	big droplets at the interface, sedimentation within the waterphase, grayish waterphase
5	Dodecane	big droplets at the interface, grayish waterphase, two phases	few really small oil droplets at the cloudy interface and in the water phase, oil phase and water phase, sedimentation within the waterphase	oil phase and water phase, sedimentation within the waterphase, grayish interphase, small oil droplets at the glass wall of the water phase	big droplets at the interface, sedimentation within the waterphase, grayish waterphase
6	vegetable oil	vegetable oil got coludy, phase seperation and sedimentation within the waterphase, few medium sized droplets at the interface in the water phase , clear waterphase, but deposition of silica particles at the tube	vegetable oil got coludy, droplettts, but silica particle deposition at the interface oil phase and water phase, sedimentation within the waterphase, grayish waterphase	vegetable oil got coludy, phase seperation and sedimentation within the waterphase, few small dropletts at the interface, silica deposition on the interface	mixture Gas, Oil - really large oil droplets, no seperation within oilphase, large oil droplets in the silica phase, cloudy surface between the two interphases, seperation in the water phase
7	gas	few small and big oil dropletts at the interface and in the oil phase, silica seperation in the water phase, interface seems to be cloudy, oil phase and water phase, grayish waterphase	many oil droplets at interface and in oil phase, cloudy interphase between the phases, oil phase and water phase, grayish waterphase	no dropletts at the interface, silica deposition at the interface, oil phase and water phase, sedimentation within the waterphase, cloudy interface, grayish waterphase	many dropletts at the interphase (the droplets are above the interface - this seems to be unusual in comparisson with the other measurements)- there are many silica particles in the top phase but still sedimentation occures, cloudy interphase between the two phases
8	1-4. Dioxane				
9	Cylohexane	many really small oil droplets at the interface, oil phase and water phase, grayish waterphase	two phases, all waterphase is grey, one or two small droplets at the interface, grayish waterphase	few small oil droplets at the interphase, oil phase and water phase, sedimentation within the waterphase, many oil droplets in the silica sedimentation at the bottom of the sedimentation, little cloudyness at the interface, grayish waterphase	few big droplets, oil phase and water phase, sedimentation within the waterphase, cloudy interphase
10	Octanol	many oil droplets (small and big) at the interface, phase and water phase, sedimentation within the waterphase, grayish emulsion phase	few small oil droplets in the water phase and under the interface, oil phase and water phase, sedimentation within the waterphase, grayish waterphase	many small little oil droplets at the cloudy interface, oil phase and water phase, sedimentation within the waterphase, grayish waterphase, thick emulsion layer	many oil droplets at the interface, large silica phase and oil droplets in the silica phase, sedimentation in the water phase
					For all Saltwater combinations is the silica layer at the ground large in comparison with the DI-water Emulsions

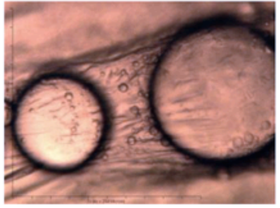
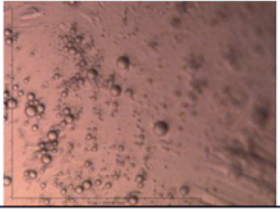
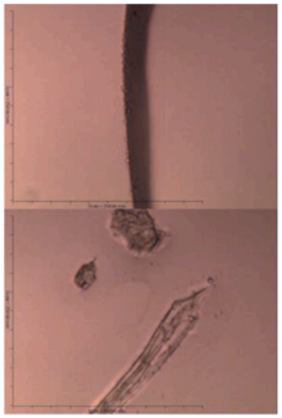
6.7.Results microscopy and visual evaluation without AOT

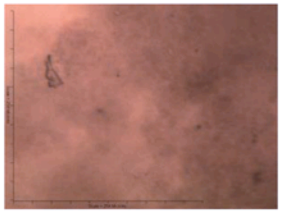
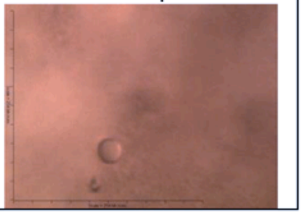
	PICTURE	OBSERVATION	TREND	O/W INTERFACE (THE SCALE BAR MIGHT VARY!).	BOTTOM PHASE/SEDIMENT (THE SCALE BAR MIGHT VARY!)
DI EA 220		Visual evaluation: • Little grey shadow as sedimentation phase • Some really small, visible droplets at the interface (it is difficult to say if that are w/o or o/w droplets) Optical microscopy: • Some small droplets at the interface. These droplets look like they are three dimensional and have particles around them. The not spherical particles look like not miscible water ethyl acetate phases • Some honeycombs lice structures in the bottom phase. I suspect this phases being non miscible Ethyl Acetate phases. Additionally are some silica depositions there. The explanation for this is that Ethyl acetate has the closest density to water.	• DI EA XXX-series shows decreasing sedimentation with increasing particle size. Unfortunately is it too small to measure with photos [1] • DI EA XXX series shows decreasing visible emulsion with increasing particle size [3]	Interface: Little spherical, three dimensional droplets and non-miscible Ethyl Acetate phases  	Bottom: Honeycomb like structure:  Silica sedimentation: 

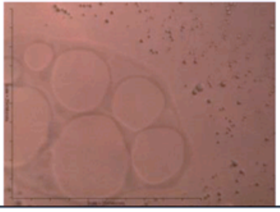
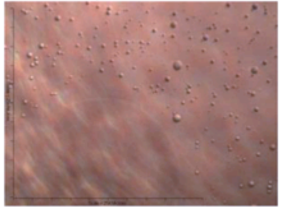
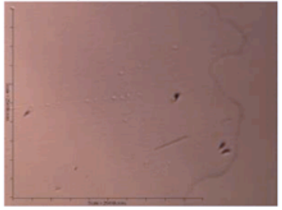
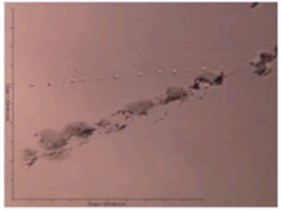
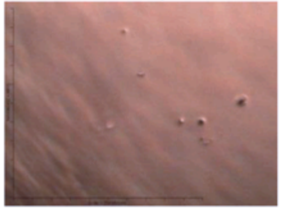
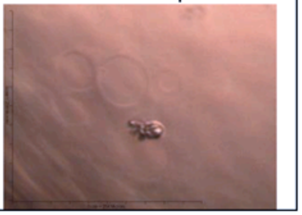
DI EA 450		Visual evaluation: • Very little grey shadow as sedimentation phase (it is less than DI EA 220) • One or two little droplets at the interface Optical microscopy: • Interface and Bottom have not miscible Ethyl Acetate phases • At the interface are little 3D droplets (Silica Pickering Emulsions) • At the Bottom phase are silica residuals	• DI EA XXX-series shows decreasing sedimentation with increasing particle size. Unfortunately is it too small to measure with photos [1] • DI EA XXX series shows decreasing visible emulsion with increasing particle size [3]	Interface: Non miscible phase:  Little 3D droplets: 	Bottom: Silica sedimentation:  Non miscible phases 
DI EA 800		Visual evaluation: • No visible sedimentation • No visible emulsion phase Optical microscopy: • At the interphase and in the bottom phase are not miscible EA/water droplets • For interphase: strange droplet agglomeration • In bottom phase: Silica deposition and 3D silica droplets	• DI EA XXX-series shows decreasing sedimentation with increasing particle size. Unfortunately is it too small to measure with photos [1] • DI EA XXX series shows decreasing visible emulsion with increasing particle size [3]	Interface: Droplet agglomeration:  Non miscible: 	Bottom: Non miscible:  3D-droplets and silica: 

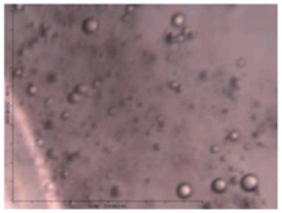
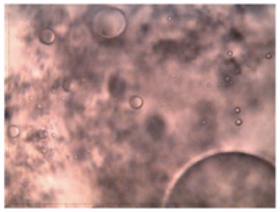
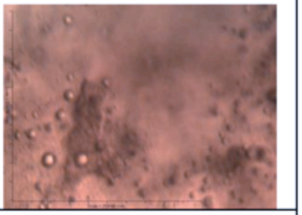
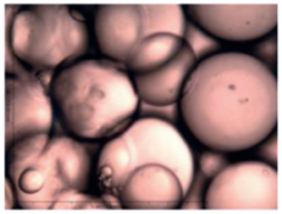
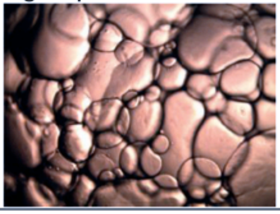
DI ON 220		Visual evaluation: • Some really small droplets at the wall • o/w emulsion • Little grey shadow as sedimentation phase (too small to make it visible on photos) Optical microscopy: • Droplets on interphase and bottom phase • Interface sample was fast moving • Silica sedimentation in bottom phase	• DI ON XXX-series shows decreasing sedimentation with increasing particle size. Unfortunately is it too small to measure with photos [7]	Interface: Droplets: 	Bottom: Droplets:  Silica sedimentation: 
DI ON 450		Visual evaluation: • No visible emulsion phase • Less little grey shadow as sedimentation phase then DI ON 220 (too small to make it visible on photos) Optical microscopy: • Clear interface • Droplets in the bottom phase and silica deposition	• DI ON XXX-series shows decreasing sedimentation with increasing particle size. Unfortunately is it too small to measure with photos [7]	Interface:  The interface seems to be clear, no particles or droplets visible - unstable emulsion – I suspect that that what is seen is dirt.	Bottom: Droplet:  Silica sedimentation 

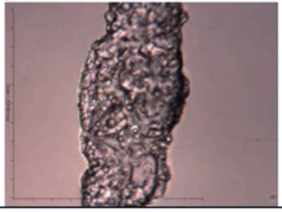
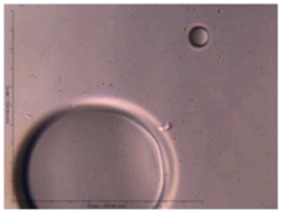
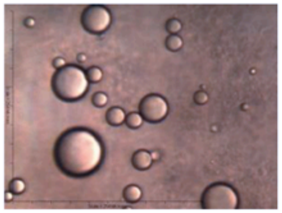
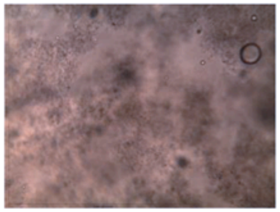
DI ON 800		Visual evaluation: • No visible emulsion phase • No visible sedimentation phase Optical microscopy: • Rally few droplets at the interface, mostly clear • Almost no droplets in the bottom phase, some silica deposition	• DI ON XXX-series shows decreasing sedimentation with increasing particle size. Unfortunately is it too small to measure with photos [7]	Really few droplets at the interface:  Really few droplets. This is an unstable emulsion	Almost no droplets. Clear water with few droplets:  Some silica deposition: 
DI OL 220		Visual evaluation: • Large visible emulsion phase with large droplets • o/w emulsion Optical microscopy: • Silica sedimentation and some little silica droplets. • Some droplets in the bottom phase are covered. • In the interface some silica clouds visible (see video DI EA 800) • Smaller droplets in the Interface	• DI OL XXX series shows decreasing visible emulsion phase with increasing particle size [2]	Some sedimentation clouds visible  Sedimentation clouds: 	Covered droplet:  Smaller particles: 

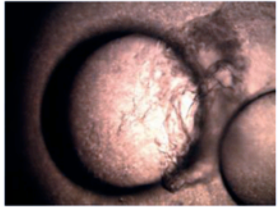
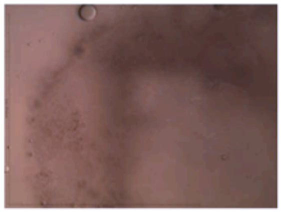
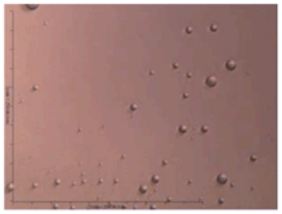
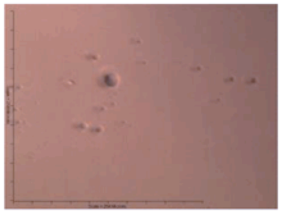
DI OL 450		Visual evaluation: - Some small droplets in the emulsion phase - o/w emulsions Optical microscopy: - some (but very few) silica deposition in the bottom phase - no droplets at the interface - small and large droplets in at the interface - silica deposition at the interface	- DI OL XXX series shows decreasing visible emulsion phase with increasing particle size [2]	Interface: Larger droplets:  Smaller droplets: 	Bottom: the bottom phase was clear and nothing can be seen under the optical microscope, but some silica deposition 
DI OL 800		Visual evaluation: - No visible emulsion phase in water phase - One droplet in the oil phase (w/o emulsion) Optical microscopy: - No droplets but some silica deposition in the bottom phase - At the interface silica deposition and some really small droplets	- DI OL XXX series shows decreasing visible emulsion phase with increasing particle size [2]	Interface:  Really small droplets + solids.	Bottom:  The Bottom phase was clear and nothing can be seen under the optical microscope but some silica deposition

SW EA 220		Visual evaluation: • Some small droplets at the interface • o/w emulsion • highest sedimentation for SW EA XXX series Optical microscopy: • non miscible parts and silica deposition at the interface • cloudy bottom phase (see video) • some droplets in the sedimentation phase	• Similar to [1] and [4] shows SW EA XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [6]	Interface: Non miscible droplets and silica deposition:  Silica at the interface, different shapes of droplets	Bottom:  Clouds / sedimentation can be seen under the optical microscope. Some droplets in the sedimentation phase: 

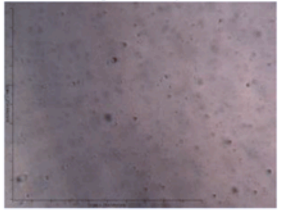
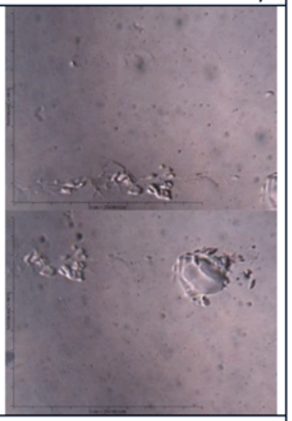
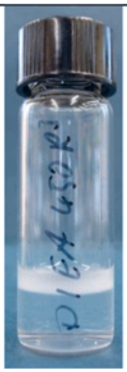
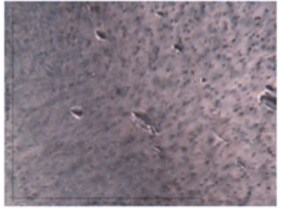
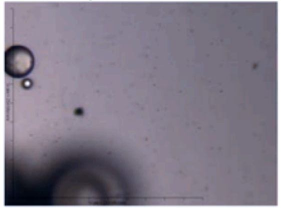
SW EA 450		Visual evaluation: • Few (and one large) droplet at the interface • o/w emulsion • significantly less sedimentation then SW EA 220, but still visible Optical microscopy: • non miscible Water EA phase at the interface and in the bottom phase • different droplets at the interface and in the sedimentation phase	• Similar to [1] and [4] shows SW EA XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [6]	Different sizes of droplets at the Interface:  Non miscible phase: 	Small droplets and non-miscible phase 
SW EA 800		Visual evaluation: • Few (but significantly less than SW EA 450) droplets at the interface • o/w emulsion • no visible sedimentation Optical microscopy: • silica deposition in the bottom phase • non miscible phase in the bottom phase • silica deposition at the interface	• Similar to [1] and [4] shows SW EA XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [6]	No droplets and particles:  Silica deposition: 	Very few particles in the sedimentation phase:  Non miscible droplets: 

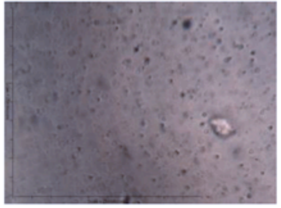
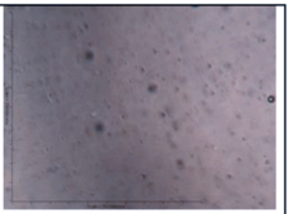
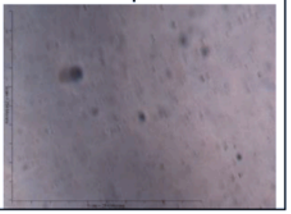
SW OL 220		Visual evaluation: • One droplet at the interface • No visible emulsion phase • Some grayish clouds at the o/w interface in water • Whole water phase seems to be cloudy • Cloudiness in sedimentation phase (most for SW OL XXX series) Optical microscopy: • Some silica deposition in emulsion and sedimentation phase visible • Droplets in different sizes in sedimentation and emulsion phase • Generally are the droplets in the sedimentation phase larger than at the interface	• Similar to [1] and [5] shows SW OL XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [4]	Interface:  Difficult to take images from the interface, droplets in different sizes, some silica depositions visible	Bottom:  Droplets in different sizes at the interface, cloudiness is visible 
SW OL 450		Visual evaluation: • From visibility: it looks like a w/o and o/w emulsion • Large visible emulsion phase at the sides of the sample • no visible emulsion and it is clear in the middle of the vial • deposition of emulsion at the vial wall above the sample (this effect has neither DI nor OL alone) • some visible cloudiness (significantly less than SW OL 220) Optical microscopy: • large droplets in the emulsion phase • clear bottom phase	• Similar to [1] and [5] shows SW OL XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [4]	Interface:  Big droplets visible: 	Bottom Clear as the sedimentation phase is too small to get pipette particles.

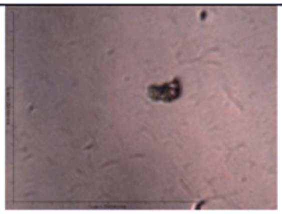
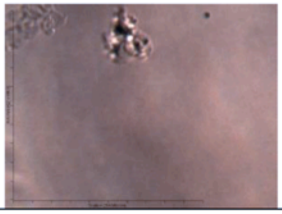
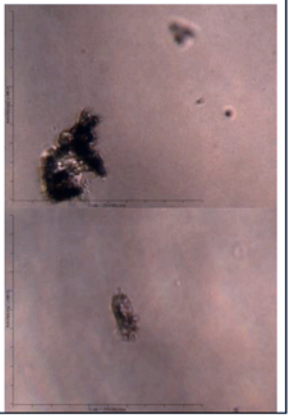
SW OL 800		Visual evaluation: - Few (half a dozen) droplets at the interface, one bigger droplet - No visible sedimentation - Some grayish sedimentation at the interface? Optical microscopy: - Few particles visible in the bottom phase (some large, are the small silica particles or little droplets?) - Silica deposition at the interface?	- Similar to [1] and [5] shows SW OL XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [4]	Interface:  Some silica particles at the interface. Or is that junk? 	Bottom:  Few particles visible, or are that little droplets?
SW ON 220		Visual evaluation: - Some small visible droplets at the interface (significantly less than SW ON 450) - Difficult to determine if o/w emulsion or not - Cloudiness in the sedimentation phase (the most for the SW ON XXX series) Optical microscopy: - Different droplets visible at the interface - Some droplets and cloudiness visible in the bottom phase - video sedimentation clouds	- Similar to [1] and [4] shows SW ON XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [5]	Interface:  Different droplet sizes at the interface, some silica cloudiness	Bottom:  Different droplet sizes in the sedimentation phase, silica cloudiness is visible

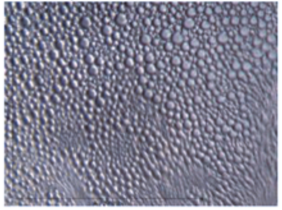
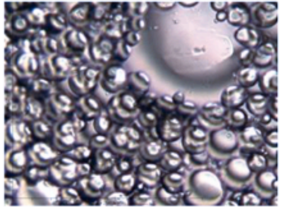
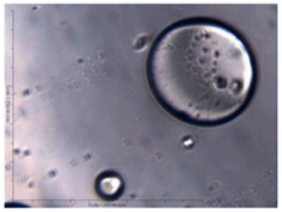
SW ON 450		Visual evaluation: • Thick visible emulsion phase • o/w emulsion • some grayish, visible emulsion phase (significantly less than SW ON 450) Optical microscopy: • cloudiness and some droplets in the sedimentation phase visible • extremely large droplets in at the interface • some silica at the interface	• Similar to [1] and [4] shows SW ON XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [5]	Interface: 10x picture  Extremely large droplets, silica particles visible	Bottom:  Some droplets and cloundines visible in the sedimentation phase
SW ON 800		Visual evaluation: • No visible emulsion phase • No visible sedimentation Optical microscopy: • Some droplets at the interface visible • Few droplets in the bottom phase	• Similar to [1] and [4] shows SW ON XXX decreasing sedimentation phase with increasing particle size. This time it is measurable with photos [5]	Interface:  Some droplets visible at the interface	Bottom:  few droplets visible, no silica clouds

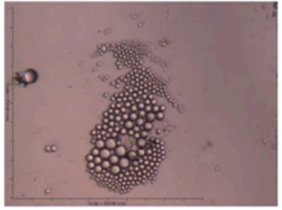
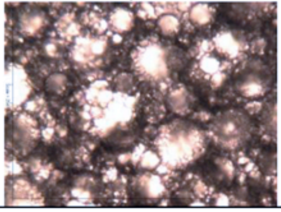
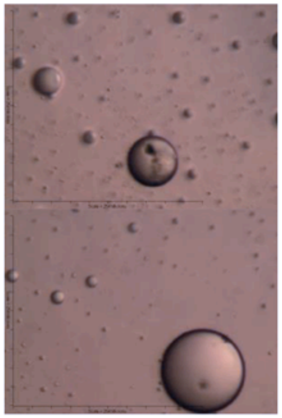
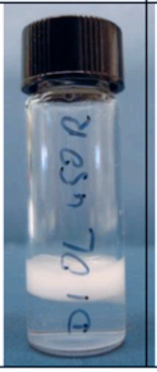
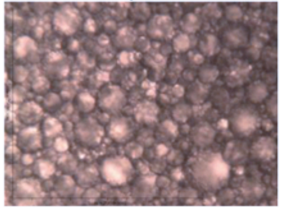
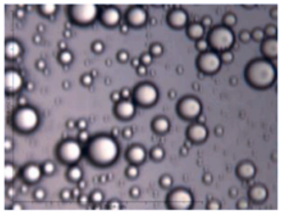
6.8.Results microscopy and visual evaluation with AOT

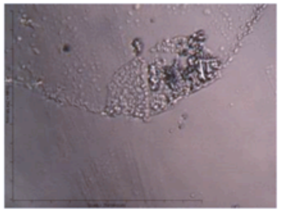
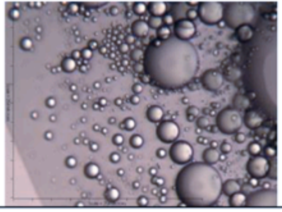
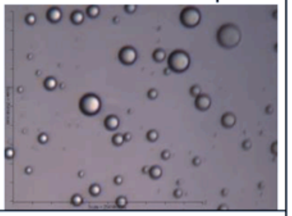
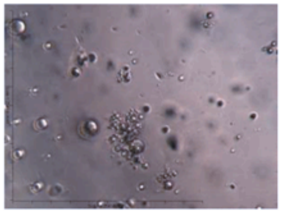
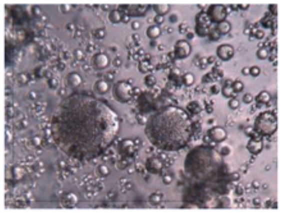
	PICTURE	OBSERVATION	TREND	O/W INTERFACE (THE SCALE BAR MIGHT VARY!).	BOTTOM PHASE/SEDIMENT (THE SCALE BAR MIGHT VARY!)
DI EA 220		• Looks like Experiment has less oil in it. Reason for that: Already did the microscopy experiments with the experiment samples. • Less mixing energy? → **Evaluation with DI EA 220 R3** • Thick emulsion layer at the wall (only thin) • Looks like OMA deposition in the bottom phase. • Comparison between w and wo AOT: AOT is in charge for the formation of an emulsion	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	**Note**: The droplets were fast moving. This is why no clear Image was possible 	
DI EA 450		• Thick emulsion layer at the wall (only thin) • Looks like Experiment has less oil in it. Reason for that: Already did the microscopy experiments with the experiment samples. • Less mixing energy? → **Evaluation with DI EA 450 R3** • Comparison between w and wo AOT: AOT is in charge for the formation of an emulsion	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	**Note**: The droplets were fast moving. This is why no clear Image was possible  Some Silica deposition	Droplets and some, few sedimentation in the bottom phase: 

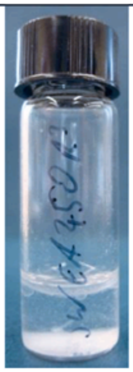
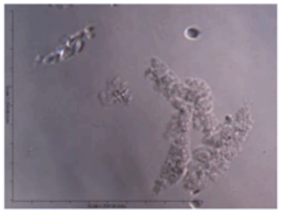
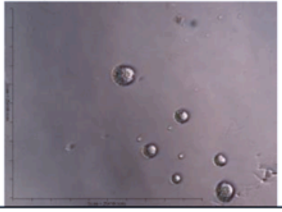
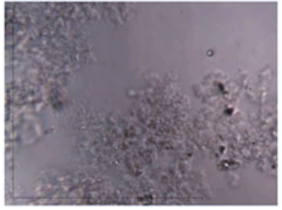
DI EA 800		• Looks like Experiment has less oil in it. Reason for that: Already did the microscopy experiments with the experiment samples. • Less mixing energy? → **Evaluation with DI EA 220 R3** • Thick emulsion layer at the wall (only thin) • Comparison between w and wo AOT: AOT is in charge for the formation of an emulsion	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	**Note**: The droplets were fast moving. This is why no clear Image was possible 	 Droplets in- droplets were with a sec. microscopy phase Inverted droplets: 

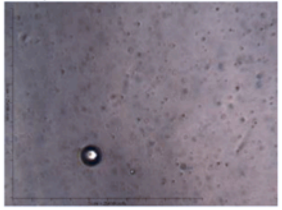
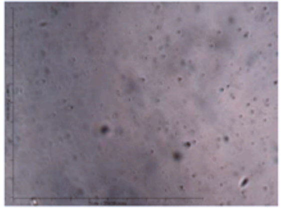
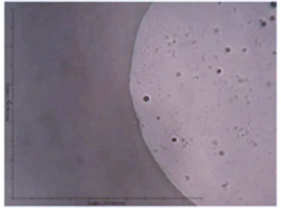
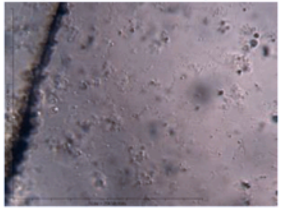
DI ON 220		• Thick emulsion layer • On the experiment is it nor right dispersed • Microscopy with DI ON 220 • Comparison between w and wo AOT: AOT is in charge for the formation of an emulsion	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	 OMAs: 	OMAs: 

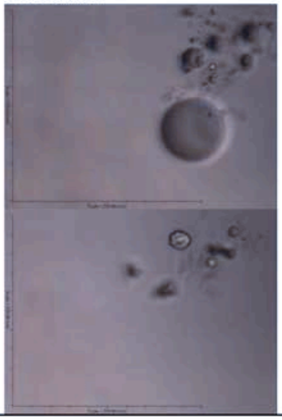
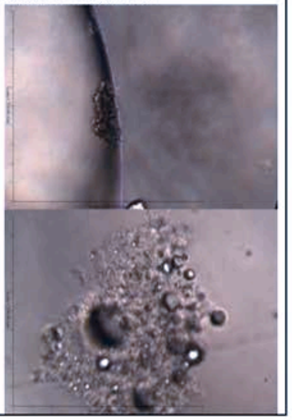
DI ON 450		• Reproducible • Microscopy with DI ON 450R2 • More droplets in the emulsion then in the bottom phase → seems to be reasonable • Deposition seems to be dirt as it occurred only once • Comparison between w and wo AOT: AOT is in charge for the formation of an emulsion	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	**Note:** plain slice  OMAs in Emulsion phase 	Tiny droplets 
DI ON 800		• Experiment not clearly dispersed • Different thickness of emulsion phase. Sample for imaging was taken from DI ON 800 → only different energy input can be reason for that • Microscopy imaging was done with DI ON 800 • One chaotic emulsion droplet in bottom phase. Or is that OMA?	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	Hugh amount of droplets in the emulsion phase: 	Chaotic em., droplets over each other or OMA?  Clearly droplets

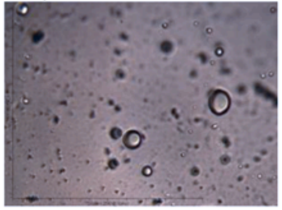
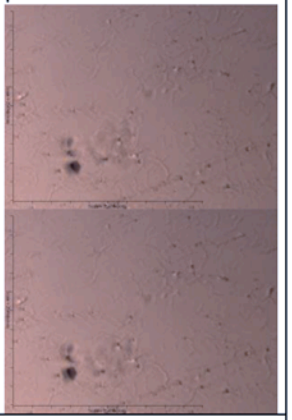
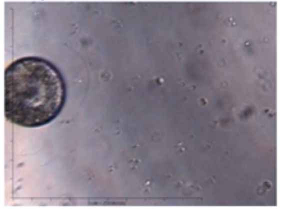
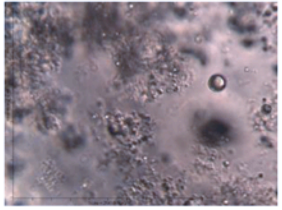
DI OL 220		- In reproducible: Thick droplet, apart from that replicate few thick droplets - AOT decreases the droplet size	- Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] - No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	Silica deposition in the emulsion phase:  Hugh amount of droplets in emulsion phase 	Silica deposition on the Interface 
DI OL 450	 	- Reproducible - Thick emulsion layer - Imaging DI OL 450 - Bottom phase is not as packet as the emulsion phase with the droplets - AOT decreases the droplet size	- Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] - No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	Hugh amount of Droplets in emulsion phase 	

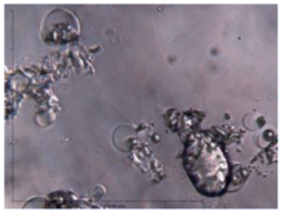
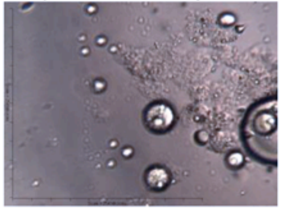
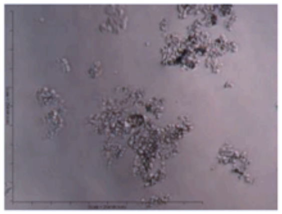
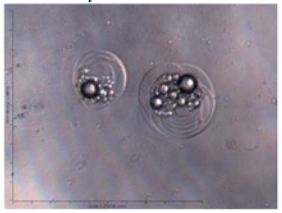
DI OL 800		• Doesn’t look reproducible • Imaging done with DI OL 800R • Comparison between w and wo AOT: AOT is in charge for the formation of an emulsion	• Silica, DI water, Oil and AOT cause a large emulsion layer then without AOT [1] • No influence of particle size for DI XX XXX on sedimentation and emulsion formation according to visible evaluation [4]	OMAs at the interface  DI OL 800: Many Droplets in the emulsion layer: 	Strange formation in water phase (or OMAs?)  DI OL 800: Some droplets: 
SW EA 220		• Clouds in both samples in the water phase • Reducible • Imaging done with SW EA 220 • No emulsion for w AOT • Amount of sedimentation is the same w / wo AOT	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplets at the interface, some silica deposition at the interface 	Droplets in the sedimentation phase: 

SW EA 450	 	• Clouds in both samples in the water phase • Reducible • Imaging done with SW EA 450R3 • For SW EA 450 R3: Silica deposition at the interface (can be seen from the optical microscopy • AOT increases the amount of sedimentation	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Silica deposition at the interface:  Droplets at the interface: 	Some droplets and sedimentation in the bottom phase 

SW EA 800		• Looks reproducible • Imaging done with SW EA 800 R3 • AOT increases the amount of sedimentation	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplets at the interface 	Some Droplets and sedimentation in bottom phase 
SW OL 220		• Droplets in the replicate. This aren't in the experiment • Imaging done with SW OL 220	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplets at the interface, two phase interface visible 	Sedimentation and droplets in bottom phase 

SW OL 450		• looks reproducible • imaging done with SW OL 450	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplets and OMA at the interface: 	Droplets and sedimentation 

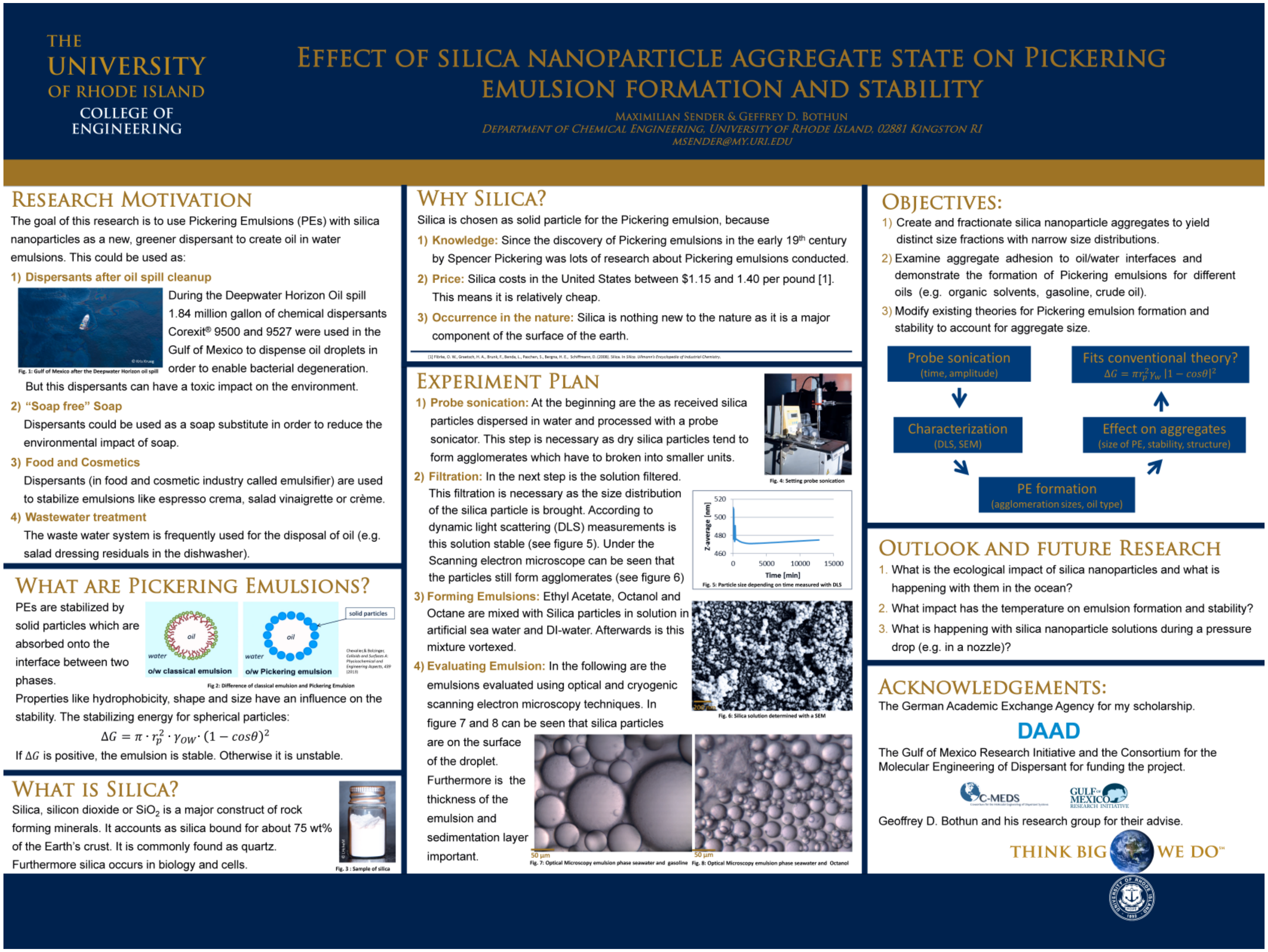
SW OL 800		- Reproducible - Imaging done with SW OL 800R	- Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] - Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] - AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplets in Interface 	OMA in the bottom phase: 
SW ON 220		- Reproducible - Imaging done with SW ON 220R - AOT reduces cloudiness	- Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] - Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] - AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplets in interface. Is there one inverted droplet? 	Sedimentation in bottom phase: 

SW ON 450		• Reproducible • Imaging done with SW ON 450 • AOT reduces cloudiness	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	Droplet and OMA in interface 	Droplet in bottom phase 
SW ON 800		• Reproducible • Imaging done with SW ON 800	• Decreasing visible sedimentation in the emulsion phase with increasing particle size for all SW XX XXX samples [2] • Decreasing optical microscopy sedimentation and OMA concentration for all SW XX XXX samples with increasing particle size [3] • AOT reduces cloudiness for SW ON XXX and SW OL XXX, but increases cloudiness for SW EA XXX [5]	OMA at interface 	Droplets and droplet aggregates (OMA?) in bottom phase 

6.9. Presentations / Manuscripts

6.9.1. Poster URI Chemical Engineering Research Symposium

This poster was presented during the URI CHE Research Symposium, April 25th 2014



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ENGINEERING

EFFECT OF SILICA NANOPARTICLE AGGREGATE STATE ON PICKERING EMULSION FORMATION AND STABILITY

MAXIMILIAN SENDER & GEFFREY D. BOTHUN
DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF RHODE ISLAND, 02881 KINGSTON RI
MSENDER@MY.URI.EDU

RESEARCH MOTIVATION

The goal of this research is to use Pickering Emulsions (PEs) with silica nanoparticles as a new, greener dispersant to create oil in water emulsions. This could be used as:

1) Dispersants after oil spill cleanup

During the Deepwater Horizon Oil spill 1.84 million gallon of chemical dispersants Corexit® 9500 and 9527 were used in the Gulf of Mexico to dispense oil droplets in order to enable bacterial degeneration.

© Kris Krug

Fig. 1: Gulf of Mexico after the Deepwater Horizon oil spill

But this dispersants can have a toxic impact on the environment.

2) "Soap free" Soap

Dispersants could be used as a soap substitute in order to reduce the environmental impact of soap.

3) Food and Cosmetics

Dispersants (in food and cosmetic industry called emulsifier) are used to stabilize emulsions like espresso crema, salad vinaigrette or crème.

4) Wastewater treatment

The waste water system is frequently used for the disposal of oil (e.g. salad dressing residuals in the dishwasher).

WHAT ARE PICKERING EMULSIONS?

PEs are stabilized by solid particles which are absorbed onto the interface between two phases.

Chevalier & Bolzinger, *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 439* (2013)

Fig 2: Difference of classical emulsion and Pickering Emulsion

Properties like hydrophobicity, shape and size have an influence on the stability. The stabilizing energy for spherical particles:

$$\Delta G = \pi \cdot r_p^2 \cdot \gamma_{OW} \cdot (1 - cos\theta)^2$$

If ΔG is positive, the emulsion is stable. Otherwise it is unstable.

WHAT IS SILICA?

Silica, silicon dioxide or SiO_2 is a major construct of rock forming minerals. It accounts as silica bound for about 75 wt% of the Earth's crust. It is commonly found as quartz. Furthermore silica occurs in biology and cells.

Fig. 3 : Sample of silica

WHY SILICA?

Silica is chosen as solid particle for the Pickering emulsion, because

1) **Knowledge:** Since the discovery of Pickering emulsions in the early 19th century by Spencer Pickering was lots of research about Pickering emulsions conducted.
2) **Price:** Silica costs in the United States between \$1.15 and 1.40 per pound [1]. This means it is relatively cheap.
3) **Occurrence in the nature:** Silica is nothing new to the nature as it is a major component of the surface of the earth.

[1] Flörke, O. W., Graetsch, H. A., Brunk, F., Benda, L., Paschen, S., Bergna, H. E., Schiffmann, D. (2008). Silica. In *Silica. Ullmann's Encyclopedia of Industrial Chemistry.*

EXPERIMENT PLAN

1) **Probe sonication:** At the beginning are the as received silica particles dispersed in water and processed with a probe sonicator. This step is necessary as dry silica particles tend to form agglomerates which have to broken into smaller units.

Fig. 4: Setting probe sonication

2) **Filtration:** In the next step is the solution filtered. This filtration is necessary as the size distribution of the silica particle is brought. According to dynamic light scattering (DLS) measurements is this solution stable (see figure 5). Under the Scanning electron microscope can be seen that the particles still form agglomerates (see figure 6)

Fig. 5: Particle size depending on time measured with DLS

3) **Forming Emulsions:** Ethyl Acetate, Octanol and Octane are mixed with Silica particles in solution in artificial sea water and DI-water. Afterwards is this mixture vortexed.

Fig. 6: Silica solution determined with a SEM

4) **Evaluating Emulsion:** In the following are the emulsions evaluated using optical and cryogenic scanning electron microscopy techniques. In figure 7 and 8 can be seen that silica particles are on the surface of the droplet. Furthermore is the thickness of the emulsion and sedimentation layer important.

Fig. 7: Optical Microscopy emulsion phase seawater and gasoline

Fig. 8: Optical Microscopy emulsion phase seawater and Octanol

OBJECTIVES:

1) Create and fractionate silica nanoparticle aggregates to yield distinct size fractions with narrow size distributions.
2) Examine aggregate adhesion to oil/water interfaces and demonstrate the formation of Pickering emulsions for different oils (e.g. organic solvents, gasoline, crude oil).
3) Modify existing theories for Pickering emulsion formation and stability to account for aggregate size.

Probe sonication
(time, amplitude)

Characterization
(DLS, SEM)

PE formation
(agglomeration sizes, oil type)

Effect on aggregates
(size of PE, stability, structure)

Fits conventional theory?
$\Delta G = \pi r_p^2 \gamma_w \, |1 - cos\theta|^2$

OUTLOOK AND FUTURE RESEARCH

1. What is the ecological impact of silica nanoparticles and what is happening with them in the ocean?
2. What impact has the temperature on emulsion formation and stability?
3. What is happening with silica nanoparticle solutions during a pressure drop (e.g. in a nozzle)?

ACKNOWLEDGEMENTS:

The German Academic Exchange Agency for my scholarship.

DAAD

The Gulf of Mexico Research Initiative and the Consortium for the Molecular Engineering of Dispersant for funding the project.

C-MEDS
GULF of MEXICO RESEARCH INITIATIVE

Geoffrey D. Bothun and his research group for their advise.

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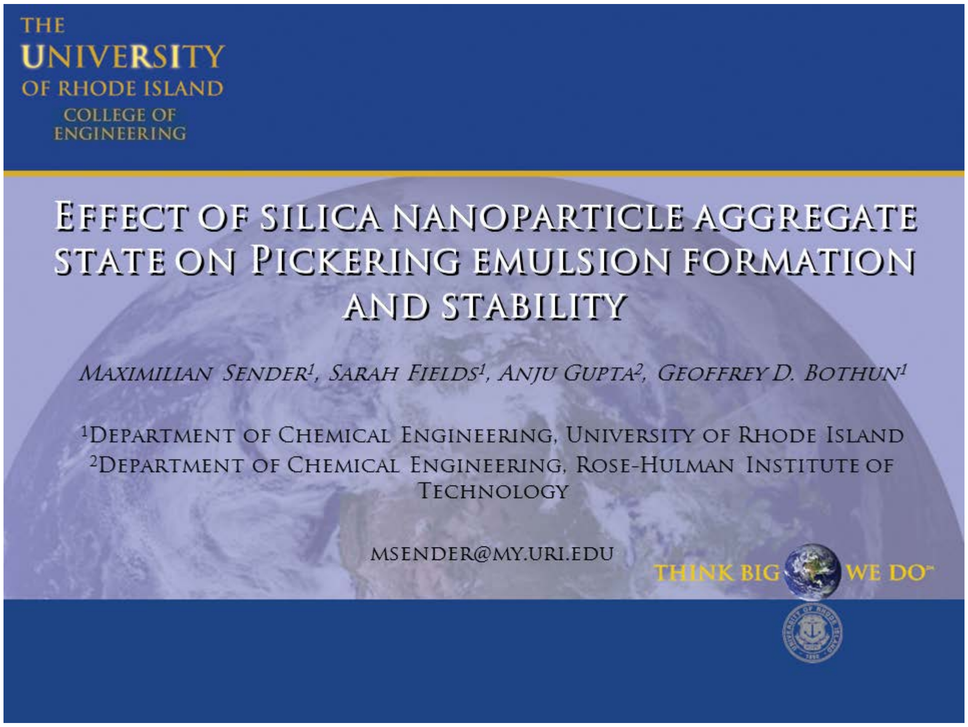
6.9.1.Presentation ACS Colloid & Surface Science Symposium

The following slides were shown during a presentation on the American Chemistry Society Colloid & Surface Science Symposium, Philadelphia PA, June 25th 2014.



THE UNIVERSITY OF RHODE ISLAND
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EFFECT OF SILICA NANOPARTICLE AGGREGATE STATE ON PICKERING EMULSION FORMATION AND STABILITY

MAXIMILIAN SENDER[1], SARAH FIELDS[1], ANJU GUPTA[2], GEOFFREY D. BOTHUN[1]

[1]DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF RHODE ISLAND
[2]DEPARTMENT OF CHEMICAL ENGINEERING, ROSE-HULMAN INSTITUTE OF TECHNOLOGY

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Figure: © Adrian Cadiz

MOTIVATION

An US-Air Force plane drops an oil dispensing chemical into the Gulf of Mexico

Deepwater Horizon Oil spill (210 million gallon oil)

1.84 million gallon Chemical surfactants

Oil – water emulsions

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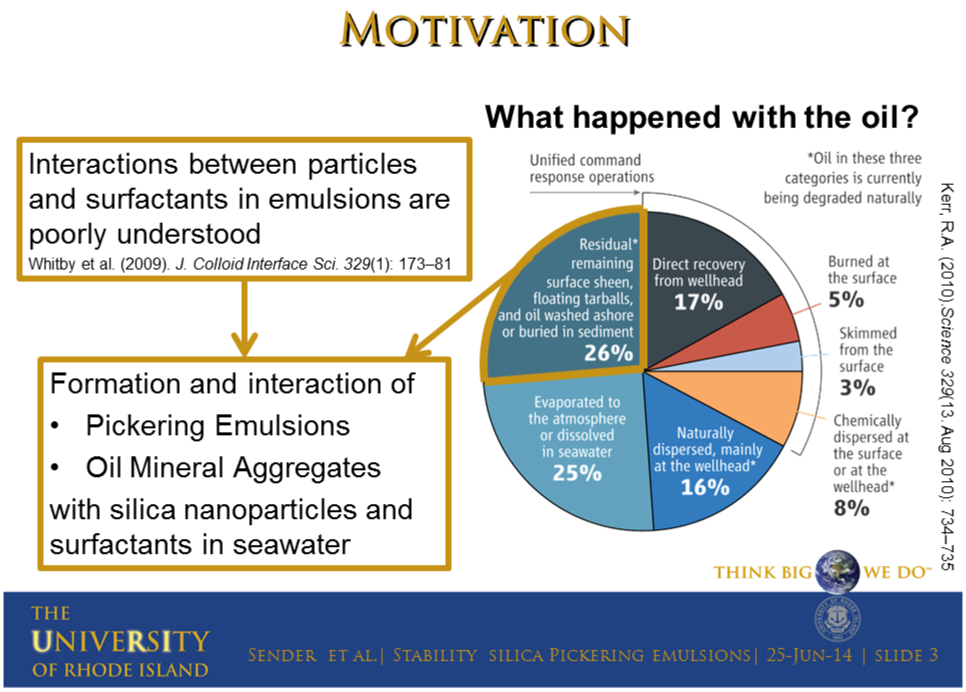
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 2



MOTIVATION

Interactions between particles and surfactants in emulsions are poorly understood

Whitby et al. (2009). *J. Colloid Interface Sci. 329*(1): 173–81

Formation and interaction of
- Pickering Emulsions
- Oil Mineral Aggregates

with silica nanoparticles and surfactants in seawater

What happened with the oil?

Kerr, R.A. (2010). *Science* 329(13. Aug 2010): 734–735

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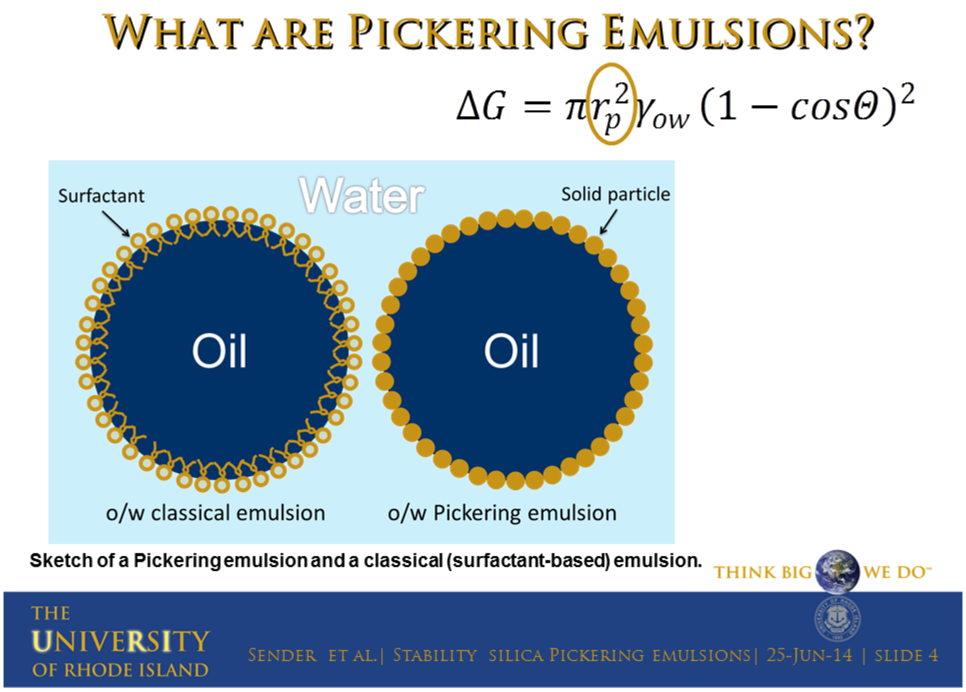
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 3



WHAT ARE PICKERING EMULSIONS?

$$\Delta G = \pi r_p^2 \gamma_{ow} (1 - cos\Theta)^2$$

Sketch of a Pickering emulsion and a classical (surfactant-based) emulsion.

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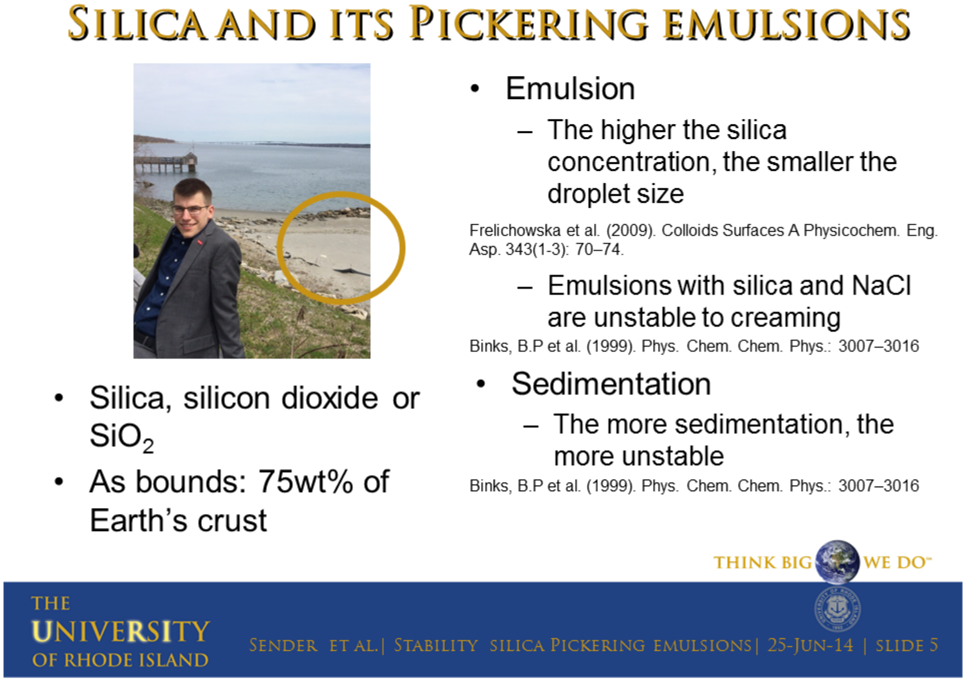
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 4



SILICA AND ITS PICKERING EMULSIONS

- Silica, silicon dioxide or SiO_2
- As bounds: 75wt% of Earth's crust

- Emulsion
  - The higher the silica concentration, the smaller the droplet size

Frelichowska et al. (2009). Colloids Surfaces A Physicochem. Eng. Asp. 343(1-3): 70–74.

  - Emulsions with silica and NaCl are unstable to creaming

Binks, B.P et al. (1999). Phys. Chem. Chem. Phys.: 3007–3016

- Sedimentation
  - The more sedimentation, the more unstable

Binks, B.P et al. (1999). Phys. Chem. Chem. Phys.: 3007–3016

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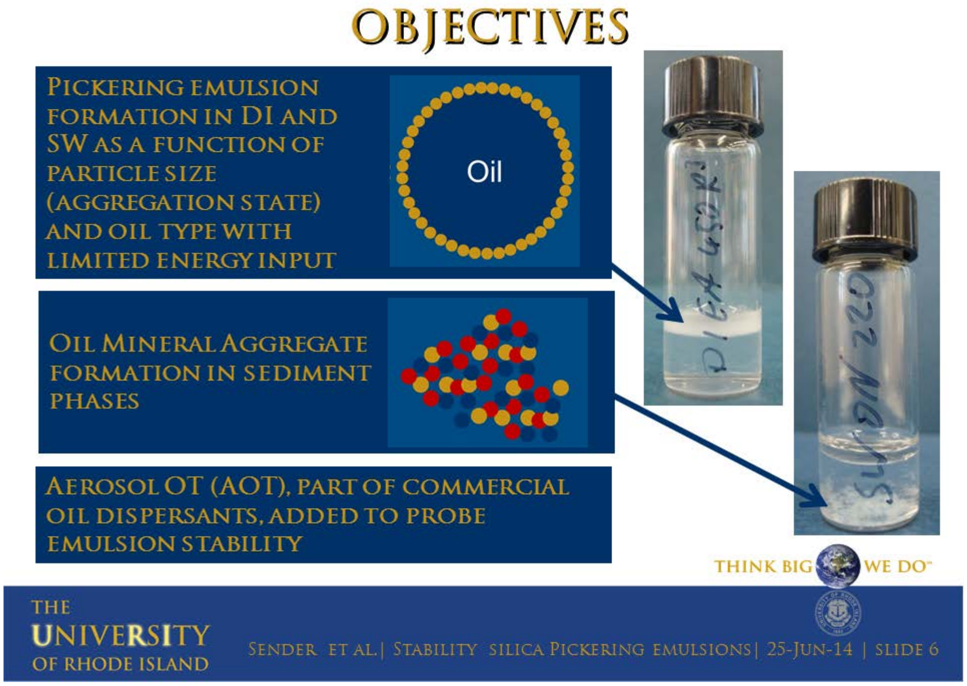

OBJECTIVES

PICKERING EMULSION FORMATION IN DI AND SW AS A FUNCTION OF PARTICLE SIZE (AGGREGATION STATE) AND OIL TYPE WITH LIMITED ENERGY INPUT

OIL MINERAL AGGREGATE FORMATION IN SEDIMENT PHASES

AEROSOL OT (AOT), PART OF COMMERCIAL OIL DISPERSANTS, ADDED TO PROBE EMULSION STABILITY

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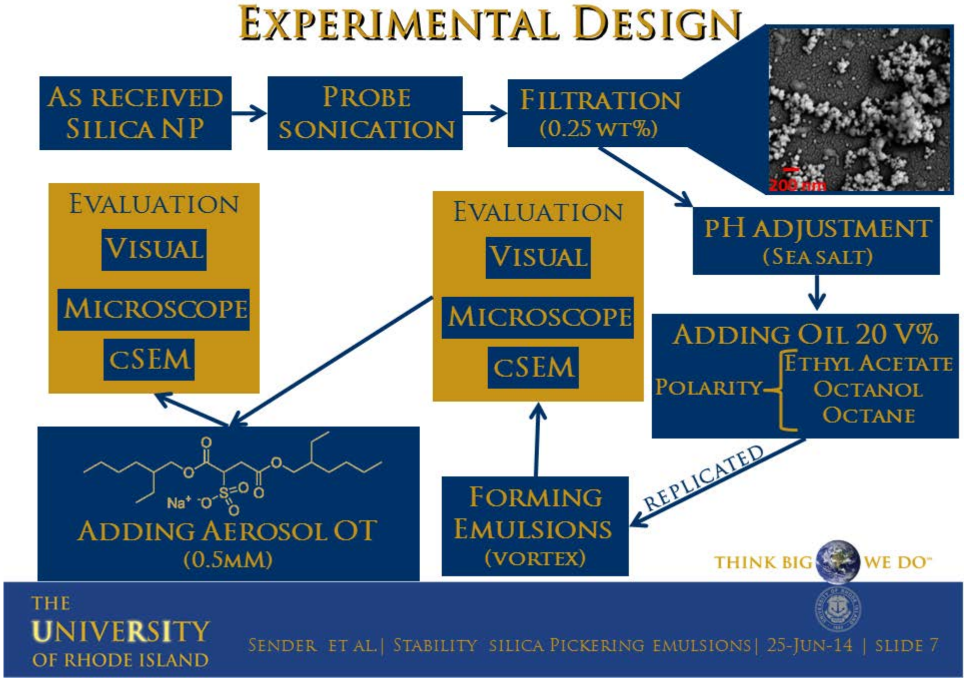

EXPERIMENTAL DESIGN

AS RECEIVED SILICA NP → PROBE SONICATION → FILTRATION (0.25 WT%) → PH ADJUSTMENT (SEA SALT) → ADDING OIL 20 V%

POLARITY – ETHYL ACETATE, OCTANOL, OCTANE

REPLICATED

FORMING EMULSIONS (VORTEX)

EVALUATION
VISUAL
MICROSCOPE
CSEM

ADDING AEROSOL OT (0.5MM)

EVALUATION
VISUAL
MICROSCOPE
CSEM

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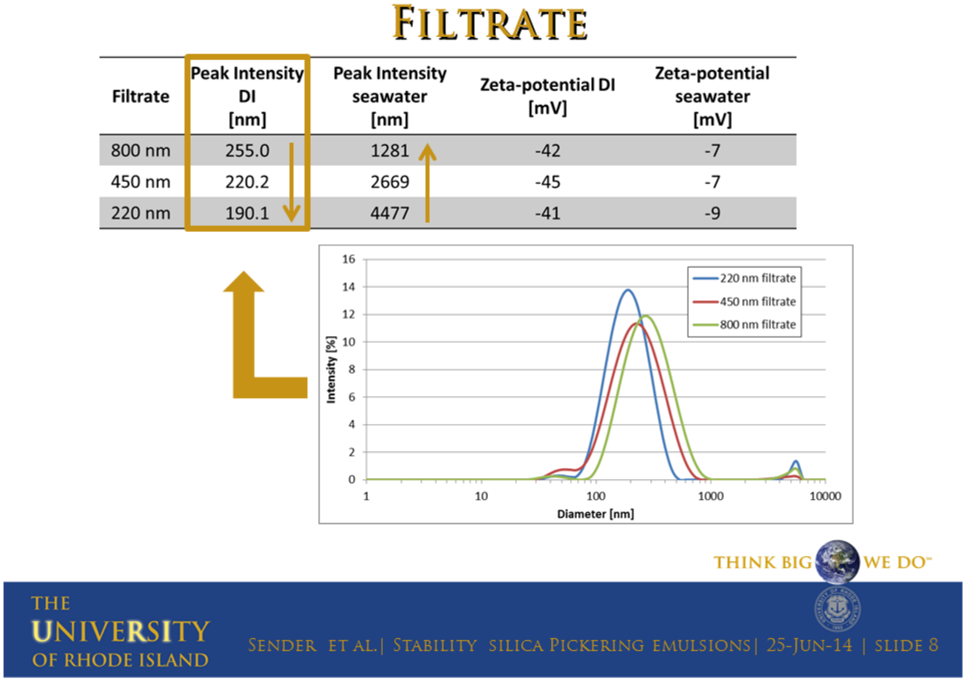
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 7



FILTRATE

Filtrate	Peak Intensity DI [nm]	Peak Intensity seawater [nm]	Zeta-potential DI [mV]	Zeta-potential seawater [mV]
800 nm	255.0	1281	-42	-7
450 nm	220.2	2669	-45	-7
220 nm	190.1	4477	-41	-9

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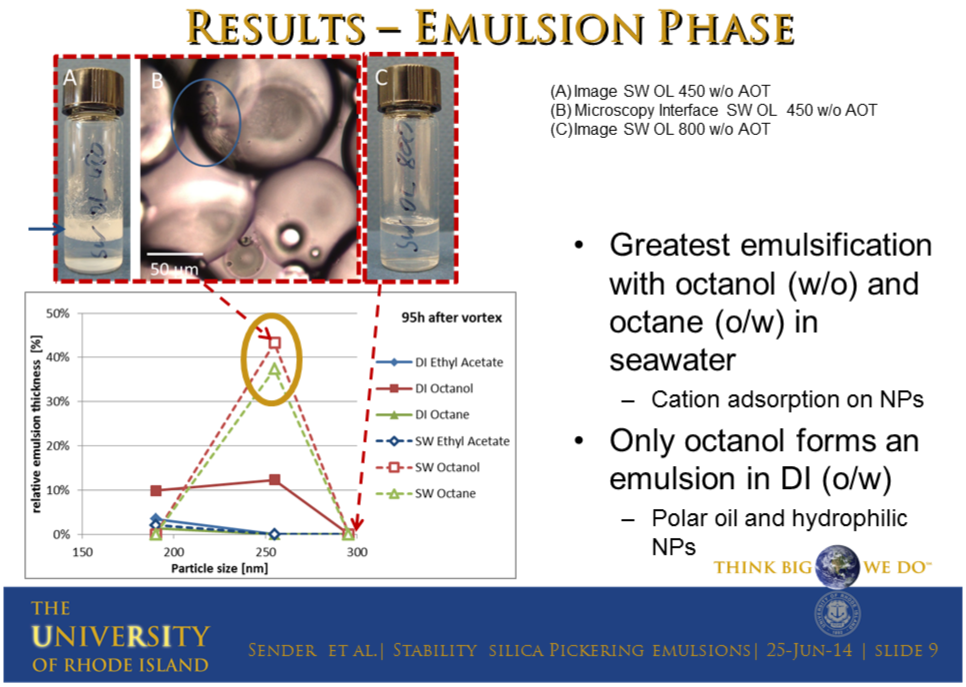

RESULTS – EMULSION PHASE

(A) Image SW OL 450 w/o AOT
(B) Microscopy Interface SW OL 450 w/o AOT
(C) Image SW OL 800 w/o AOT

- Greatest emulsification with octanol (w/o) and octane (o/w) in seawater
  - Cation adsorption on NPs
- Only octanol forms an emulsion in DI (o/w)
  - Polar oil and hydrophilic NPs

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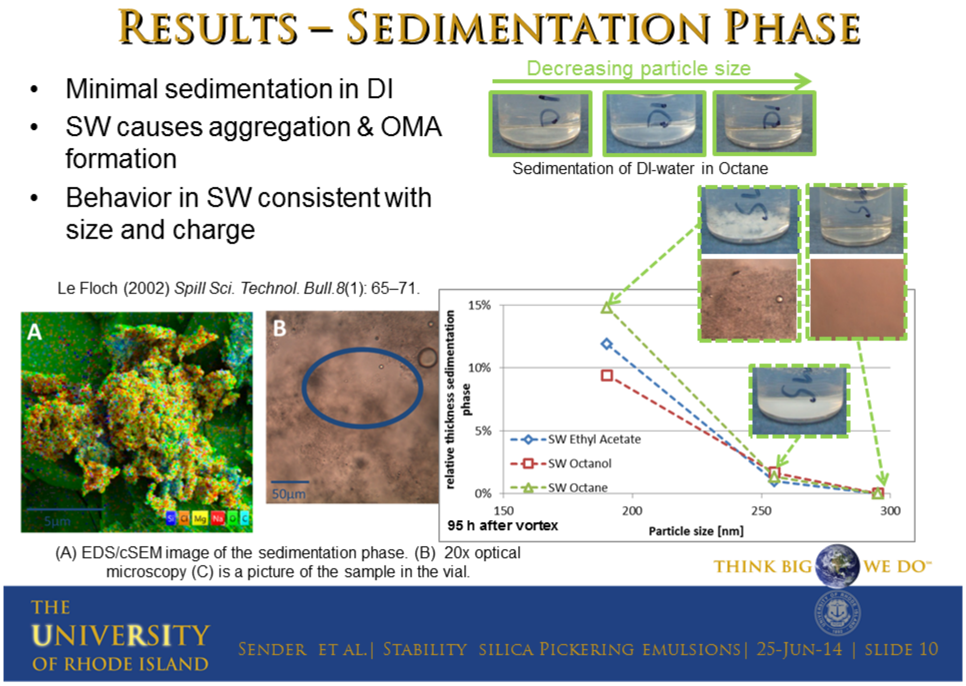

RESULTS – SEDIMENTATION PHASE

- Minimal sedimentation in DI
- SW causes aggregation & OMA formation
- Behavior in SW consistent with size and charge

Sedimentation of DI-water in Octane

Le Floch (2002) *Spill Sci. Technol. Bull.* 8(1): 65–71.

(A) EDS/cSEM image of the sedimentation phase. (B) 20x optical microscopy (C) is a picture of the sample in the vial.

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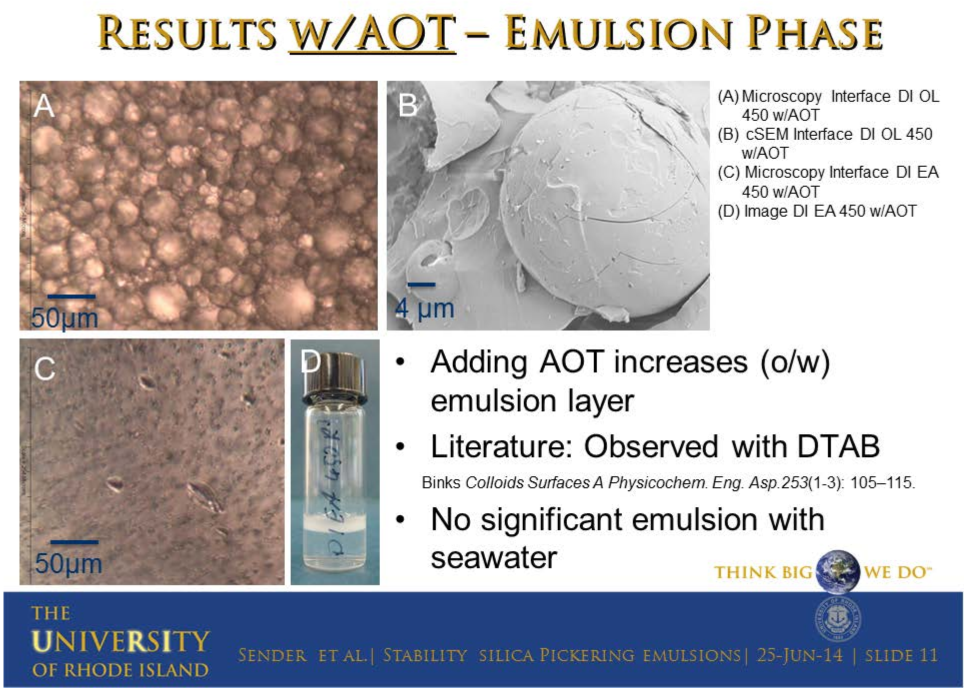
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 10



RESULTS W/AOT – EMULSION PHASE

(A) Microscopy Interface DI OL 450 w/AOT
(B) cSEM Interface DI OL 450 w/AOT
(C) Microscopy Interface DI EA 450 w/AOT
(D) Image DI EA 450 w/AOT

- Adding AOT increases (o/w) emulsion layer
- Literature: Observed with DTAB

Binks *Colloids Surfaces A Physicochem. Eng. Asp.253*(1-3): 105–115.

- No significant emulsion with seawater

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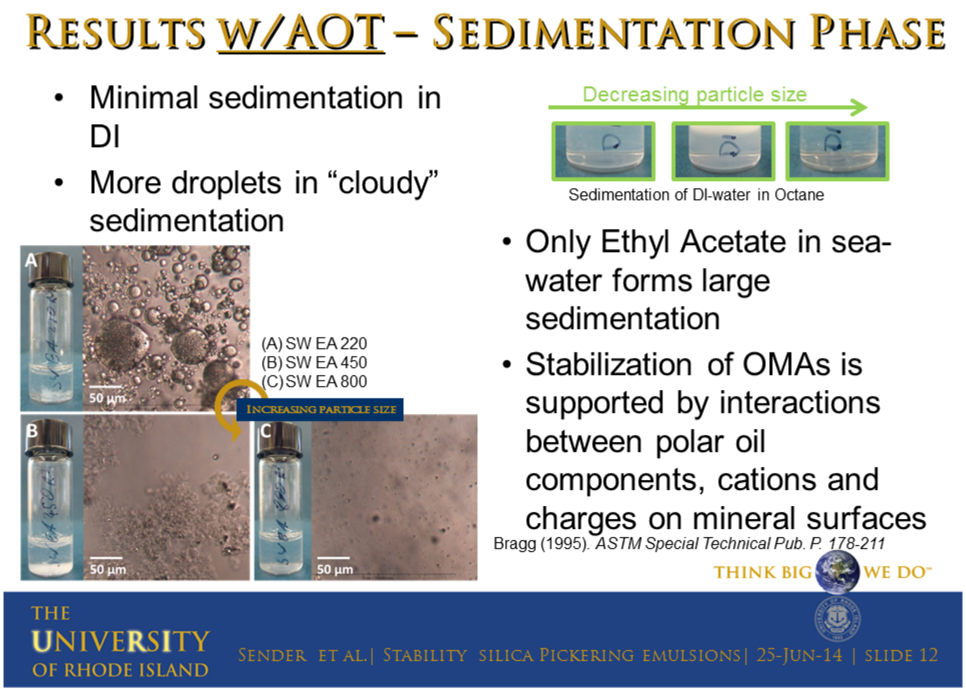
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 11



RESULTS W/AOT – SEDIMENTATION PHASE

- Minimal sedimentation in DI
- More droplets in "cloudy" sedimentation

Sedimentation of DI-water in Octane

(A) SW EA 220
(B) SW EA 450
(C) SW EA 800

- Only Ethyl Acetate in sea-water forms large sedimentation
- Stabilization of OMAs is supported by interactions between polar oil components, cations and charges on mineral surfaces

Bragg (1995). *ASTM Special Technical Pub. P. 178-211*

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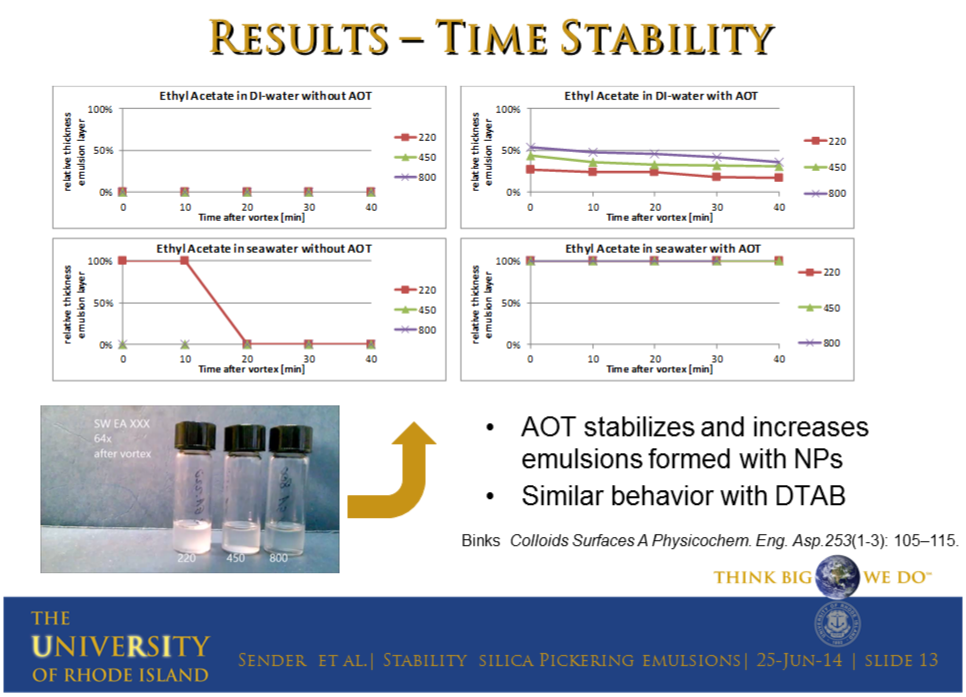
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 12



RESULTS – TIME STABILITY

- AOT stabilizes and increases emulsions formed with NPs
- Similar behavior with DTAB

Binks *Colloids Surfaces A Physicochem. Eng. Asp.253*(1-3): 105–115.

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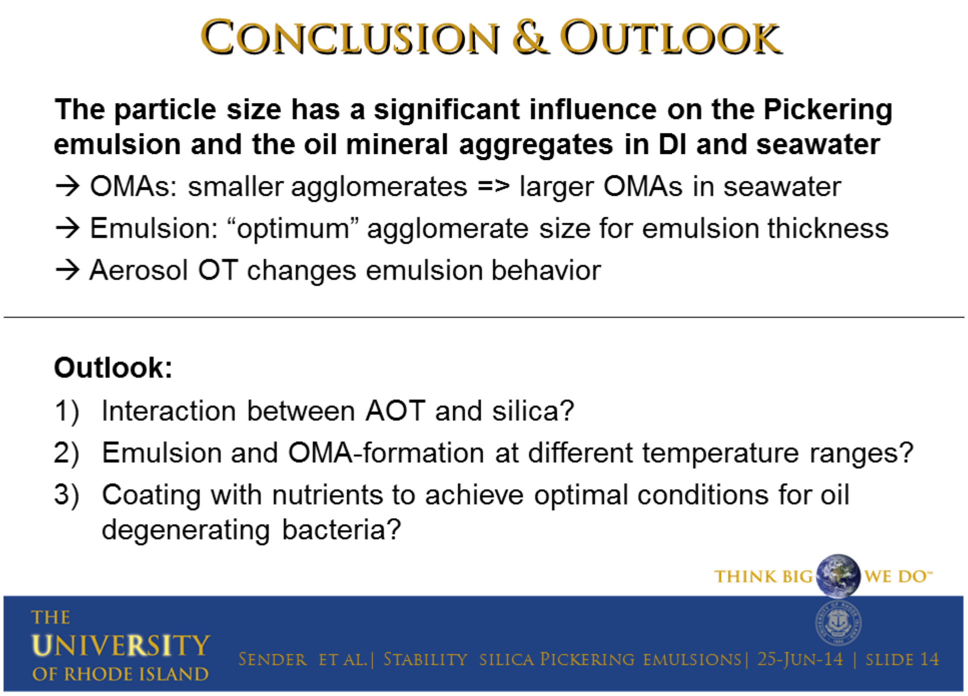
SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 13



CONCLUSION & OUTLOOK

The particle size has a significant influence on the Pickering emulsion and the oil mineral aggregates in DI and seawater

→ OMAs: smaller agglomerates => larger OMAs in seawater

→ Emulsion: “optimum” agglomerate size for emulsion thickness

→ Aerosol OT changes emulsion behavior

Outlook:

1) Interaction between AOT and silica?
2) Emulsion and OMA-formation at different temperature ranges?
3) Coating with nutrients to achieve optimal conditions for oil degenerating bacteria?

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SENDER ET AL.| STABILITY SILICA PICKERING EMULSIONS| 25-JUN-14 | SLIDE 14

ACKNOWLEDGEMENTS

- BP/The Gulf of Mexico Research Initiative Grant No. SA 12-05/GOMRI-002.

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Consortium for the Molecular Engineering of Dispersant Systems

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