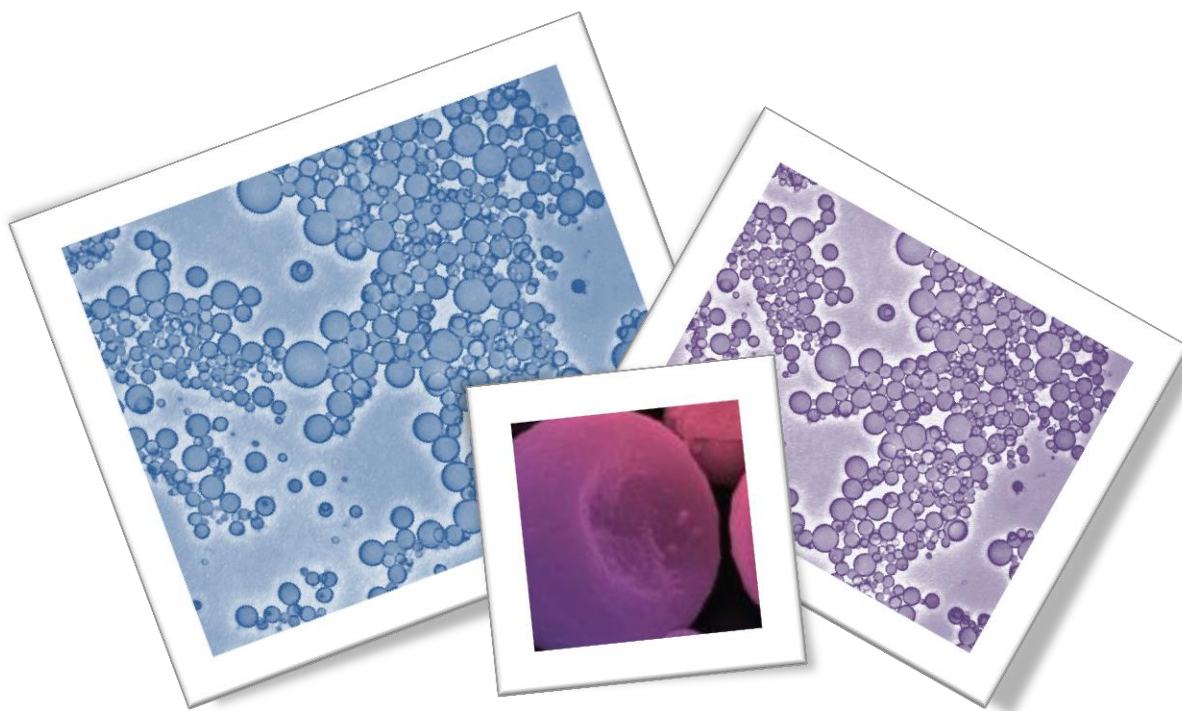


# CHALMERS



## Stabilization of organic solvent droplets using surface modified silica particles

**Master of Science Thesis in the Master Degree Programme, Materials Chemistry and Nanotechnology**

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Gothenburg, Sweden, 2014

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Cover: Microscopic pictures of silica and emulsions.

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## Abstract

Since early 20th century, it has been well known that colloidal particles may play an important role as emulsion agents to stabilize emulsions. In this master thesis work have two colloidal silica systems been compared; ii) pre-aggregated silica, with system iv) non-aggregated silica surface modified with both hydrophobic and hydrophilic groups as stabilizers in Pickering emulsions.

This work show that pre-aggregated silica relies on electrostatic stabilization, it have a poor pH stability and can thereby only could be used around a pH 4.5. The system also stabilizes larger droplets when using the same amount and size of silica particles than the system with modified silica. In the pre-aggregated system we see that a higher creaming is an indication of larger droplets in the system. With higher hydrophobicity of the dispersed phase, i.e. more isooctane, the creaming increased. This shows that the system with pre-aggregated silica, relying on electrostatic stability, is more sensitive towards the oil phase composition.

The surface modified silica system show the following result, a higher amounts of silica stabilize emulsions with smaller droplets in a narrow size distribution and smaller silica particles will result in an emulsion with smaller droplets which is a useful for size control in future emulsions. The surface functionality showed to be less important than expected, as long as the surface is modified with both hydrophobic and hydrophilic functionalities the particles stabilizes emulsion droplets well. This work show that it is possible to store the emulsions in order to grow the droplets. This is a possible way to control the particles size by simply leaving the emulsions to rest. Last but not least the modified silica resulted in Pickering emulsions with great pH stability than the pre-aggregated system, since it seems possible to use in the pH range of 4-10.

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## 1. Introduction

Since early 20th century, it has been well known and well established that colloidal particles may play an important role as emulsion agents to stabilize emulsions. When substituting classical emulsifiers such as surfactants, by small solid colloidal particles, which adsorb at the water/oil-interface, you create emulsions called Pickering emulsions. In the literature we find several systems where colloidal silica are used as particles in Pickering emulsions; i) aggregated silica, ii) pre-aggregated silica, iii) non-aggregated silica and iv) non-aggregated silica surface modified with both hydrophobic and hydrophilic groups (1).

B.P. Binks and S.O. Lumsdon (2) have shown that the ii) pre-aggregated silica Pickering emulsion systems stability are dependent on salt concentration, salt type and the amount of flocculated silica particles. A weaker flocculated silica particle gives a more stable Pickering emulsion and a complete flocculation results in a destabilized Pickering emulsion.

Hassander et al (3) studied non-aggregated and aggregated silica particles with and without co-stabilizers, to create oil in water emulsions. The results showed excellent stability towards coalescence for the Pickering emulsions with co-stabilizers. Hassander et al suggest the use of a two-step stabilization mechanism, i) agglomeration of silica particles and ii) adsorption of aggregated silica particles to the oil/water-interface.

Pickering emulsions stability is dependent of a variety of parameters on the stabilizing colloidal particle such as size, shape, and surface properties. Therefore the idea of tailor made modified silica particles for the “right” applications is of great interest. There is not much literature on non-aggregated silica surface modified with both hydrophobic and hydrophilic groups, but the attractiveness for this type of Pickering emulsions is significant (4).

### 1.1 Project aim

In this master thesis work we have decided to compare system ii) pre-aggregated silica, with system iv) non-aggregated silica surface modified with both hydrophobic and hydrophilic groups as stabilizers in Pickering emulsions. The project will mainly focus on investigating the ability to control emulsion properties with different surface modified silica. These systems will further on be called the reference system (ii) and the novel system (iv).

### 1.2 Limitations

This work will compare the new novel system with various recipes to a predetermined composition of the reference system previously known at the university. The novel system will be studied in order to acquire a toolbox in tailoring emulsions and the reference system will only be used for comparison. Therefore the reference system will only briefly be characterized and no deep studies regarding flocculation and charge stabilization will be done.

## 2. Background

### 2.1 Colloidal Silica

#### 2.1.1 General

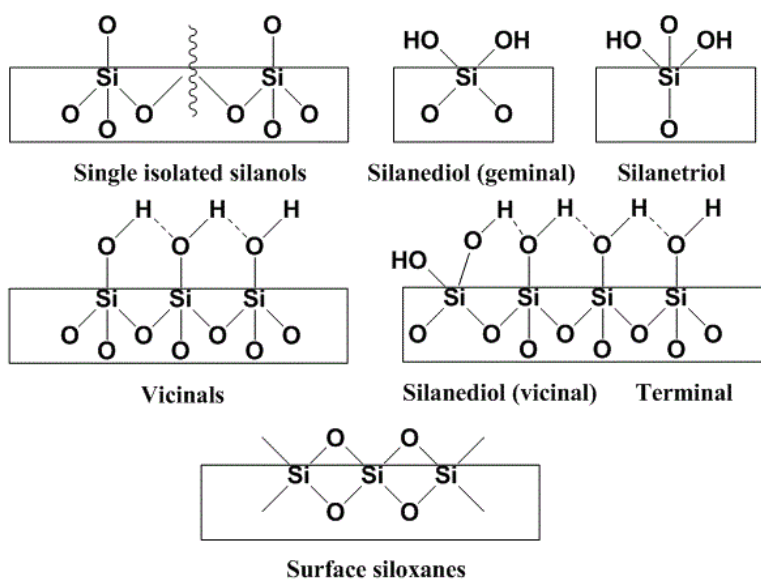
Silicone oxides are commonly known as silica and found in nature as sand or quartz, it is also one of the main components of the earth crust. It is not to be confused with “silicones” which are synthetic compounds of silicone-carbon structures. Silica is important in plants and algae and can be found in the cell-walls, these organisms where the first to produce oxygen for the earth’s atmosphere (5) (6).

Silica exists in both crystalline and amorphous forms. Its most stable and common crystal structure is quartz with a tetrahedral conformation where silicone is bonded to four oxygen atoms and oxygen is bonded to two silicone atoms. The quartz structure is based on  $\text{SiO}_4$  tetrahedrons, and the total formula is  $\text{SiO}_2$ . Si-O bonds are very strong bonds with a radius of about 0.162 nm, smaller than the sum of the oxygen and silicone covalent radius, which make the bond partially ionic in character. Amorphous silica can be regarded as random stacking of  $[\text{SiO}_4]^{4-}$  which create an anisotropic structure with differences in bond-angle compared to the crystal structure (6) (7).

Colloidal silica is a dispersed system where sub-micron particles of amorphous silica are dispersed in a continuous liquid phase, and are also known as silica sols. The range of particle size is about 5-1000 nm, small enough to not be subjected to gravitational forces and thereby segregate, and large enough to be untrue solutions (7). Production of colloidal silica starts with dissolution of sodium silicate followed by neutralization by acid. Nucleation of the silica sol is done by this neutralization which also induces particle growth and the result is a silica particle dispersion with sodium as counter ions. Nucleation and particle growth is normally carried out at temperatures above 60°C in presence of alkali (pH 8-10.5). Several ways of removing the sodium ions have been developed where ion-exchange is the most used (8).

#### 2.1.2 The surface of colloidal silica

The surface of silica particles has been studied for a long time and in 1934 the presence of hydroxyl groups on the silica surface (silanol groups) was confirmed. Research later showed that several conformations with oxygen and hydrogen on the surface are possible. Different amounts of silanol groups on the same silicone atom exist and are named accordingly. Siloxane bridges may be formed by Si-O-Si bonds outside of the particle; in the figure below Figure 1 are some of these Si-O-Si bonds and silanol groups illustrated (7). Furthermore, hydroxyl groups can be situated inside the silica particle and are called structurally bound water (9).



**Figure 1.** The surface structure of colloidal silica with different conformations of Si-O bonds. The picture is redrawn from the reference (7).

The structure of the surface is important for the properties of the colloidal silica and can be modified to tune the silica performance.

### 2.1.3 Surface modified colloidal silica

Surface modification of the colloidal silica can be used to tune the properties of the particles when dispersed in fluids. Tuning the hydrophilicity-hydrophobicity of the silica would expand the possibilities for the field of applications. In early experiments polymers have been connected to the silica to act as sterical stabilizers via esterification of the silanol groups with Poly ethylene oxide (10). Rickey et. al.(11) summarizes several ways to modify the silica to make it stable in organic solvents. They discuss hydrophobic polymers on the silica surface that alters the hydrophobicity of the silica. The polymers are attached at the silanol groups, via surface chlorosilanes or by anionic initiation groups pre-attached to the silica surface. The purpose of these experiments was to take advantage of the high surface area of the colloidal silica and use it as support for catalysis in nonpolar solvents. The properties of these modified silica particles is interesting as stabilizers of emulsions with better interaction with the oil phase than regular silica (11)

## 2.2 Stability

Particles in a dispersed liquid will show a Brownian motion, a random motion where the particles collide frequently with each other. To determine stability in a system where particles are dispersed in liquid; we need to study the interactions between particles during collision. There are attractive forces or repulsive forces that act when two particles collide. If the case is that we have more attractive forces, the particles will adhere and coalesce. When the repulsive forces dominate, the particles will repel each other and the system will be stable. The primary source of attractive forces between particles are Van der Waals forces, and are forces that are present when we have particles of the same or similar composition in a liquid. To stabilize a dispersion it is of importance to have a sufficient strong repulsive force that can counteract the Van der Waal attractive forces.

Van der Waals forces consists of three different forces, i.e. permanent dipole - permanent dipole (Keesom-forces), permanent dipole – induced dipole (Debye- interactions) and transitory dipole - transitory dipole (London-forces). Both Keesom and Debye forces are short-range interactions,

although London forces are long-range interactions. This means that the London forces will contribute to the long-range attraction between particles, and to get a stable system it need to have not only repulsive forces, they also need to be long-range repulsive forces. The DLVO-theory describes the range of van der Waals – London forces and determines strategies for stabilizing dispersed particles (12).

Methods to stabilize a dispersion is:

1. Particles with an electrical double layer which creates an electrostatic or charge stabilization. Counterbalancing the Van der Waals attraction with Columbic repulsion, to either neutralize or to negatively charge the surface of the particle.
2. Polymeric molecules attached to the particle (steric stabilization). Is achieved by grafting or adsorbing e.g. polymeric macromolecules to the particle surfaces. The macromolecule at the surface will sterically hinder other particles to adhere or attach to the surface, and the dispersion will be stable.
3. Polymers in dispersion – not attached to the particles surface (depletion stabilization). Similar as number two, but with one important difference, the macromolecules are free in solution.
4. Combination of number one and two (electrosteric stabilization). A combination of number electrostatic and steric stabilization give a very stable dispersion.

## 2.3 Surface Tension

Surface tension is the sum of all cohesive forces that act between molecules at a surface or an interface. When observing a molecule in the middle of a bulk of liquid, the net force is zero, since the molecule is equally pulled in each direction by neighbouring molecules. When the surface or the interface is observed it is clear that the surface molecules do not have the identical neighbouring molecules in every direction, compared to the example above. Instead the surface/interface molecules have different neighbouring molecule, which result in a positive or negative net force for one of the phases. This positive/negative net force is for example responsible for how droplet shapes are formed. For example droplets of water in air are formed as a spherical shape by all the cohesive forces. The shape of the water droplet minimizes the surface tension according to Laplace's law. It is also possible to describe the same phenomenon in terms of energy. A single molecule is in a higher state of energy than a molecule in contact with a neighbour molecule. This means that molecules that are on the surface have a higher energy than the molecules in the bulk. To minimize a liquids energy state, the number of high energy molecules on the surface needs to be minimized. This results in a minimized surface area, and the water droplet gets a spherical shape.

There are different surface-active molecules that have an impact on the surface tension; surfactants, surface-active polymers and colloidal solid particles. The surface-active molecules go to the surface/interface and lower the surface-/interfacial tension (13).

## 2.4 Emulsions

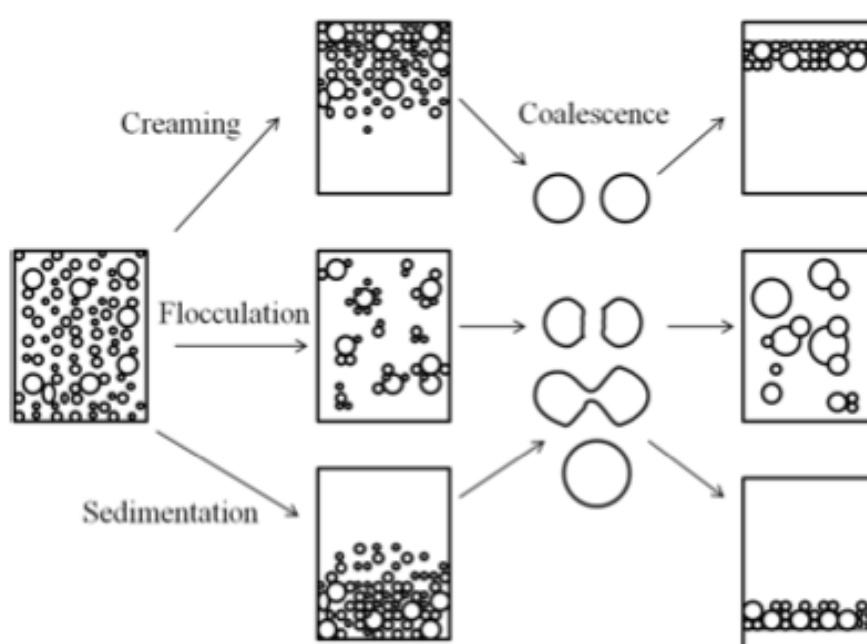
### 2.4.1 Classic Emulsions

An emulsion is a dispersion of one or more liquids, in an additional liquid. The liquids are immiscible, which means that they when mixed they will stay as two separate phases. Emulsions often consist of one liquid that is water (called water phase) and another liquid that is an organic solution (called oil phase). In a classical emulsion system there are two phases, a dispersed phase and a continuous phase. When considering the dispersed phase, we refer to the droplets in the emulsion. The continuous phase

is referred to as the surrounding liquid between the droplets in the emulsion. The dispersed phase could be either an oil phase (o) or a water phase (w), and the continuous phase could also be either an oil phase (o) or a water phase (w), but in the system there need to be at least one oil and one water phase. There are different types of emulsions, water-oil phase (w/o), oil-water phase (o/w) or multiple emulsions as water-in-oil-in-water (w/o/w) or oil-in-water-in-oil (o/w/o) (13) (4).

Thermodynamical properties of emulsions show that they are unstable. In practice this means that they will break down with time. How long time depends on the type of emulsion, and the timeframe could be everything from seconds, hours, to weeks or even longer (4).

Emulsions have four common breakdown mechanisms; creaming or sedimentation, flocculation, coalescence and Ostwald ripening. They could all occur simultaneously, and destabilize the emulsion. Coalescence and Ostwald ripening are irreversible processes, whereas creaming or sedimentation and flocculation are reversible processes (13).



**Figure 2** Scheme of different breakdown mechanism for emulsions including creaming, coalescence, flocculation and sedimentation (13).

The prospect of applications for emulsions are enormous, because of its possibility to solubilize and transport hydrophobic substances (oil phase) in a water phase. In practice this means that organic solvents, that often are harmful to the environment, can be avoided in the formulation. Examples of emulsions can be found in paint, road surfacing, paper coating, but can also be a possible way to create improved drug delivery systems (14).

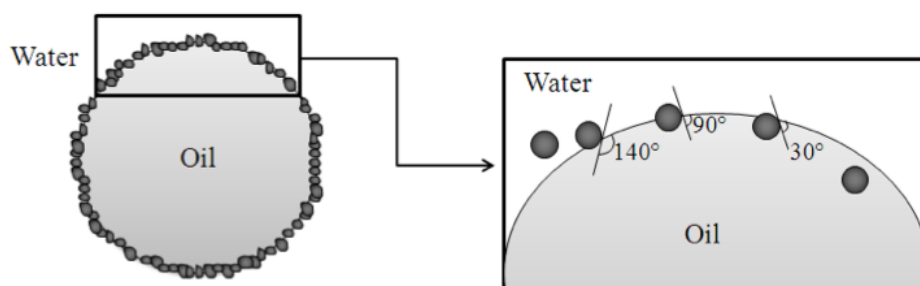
When creating emulsions the interface tension often need to be decreased to get a proper dispersion. A good way to decrease the interface tension is to use an emulsifier. An emulsifier could be a surface-active polymer, surface-active molecule or solid particle that has the main function to lower the interfacial tension between the oil- and water phase. The two most common groups of emulsifier are electrostatic stabilizing- and steric stabilizing emulsifiers. The emulsion system decides what kind of emulsifier that should be used or if a combination of the two would be a better option. An emulsifier decreases the interfacial tension, but it doesn't necessarily give the emulsion a long-term stability.

When it is desirable to have a long-term stable emulsion, a stabilizer usually needs to be added. A stabilizer is commonly a water-soluble polymer (o/w emulsion), which slowly diffuses to the interface and stabilizes the emulsion (15) (13) .

### 2.4.2 Pickering emulsions

A Pickering emulsion is an o/w, w/o or a multiple emulsion, which use small solid particles instead of surfactant to stabilize the emulsion. The name Pickering emulsion comes from S.U. Pickering (1) who was the scientist that described the phenomenon early as in 1907, even though he wasn't the first man to describe it.

Solid particles in Pickering emulsions have similar properties as “classical” surfactants in a liquid; it is therefore possible to replace many surfactants with this type of solid particles. The difference is though that the diffusion velocity to the interface will be lower with particles compared to surfactants, due to its greater size and shape. The larger the particles, the slower diffusion it has (16). The advantage with Pickering emulsion compared to classical emulsions is the resistance to coalescence. The solid particles will adhere to the interface as a mono-layer of particles, and sterically hinder droplets from coalescence. This will stabilize the emulsion and make it more robust towards coalescence. To fulfil stabilization with Pickering emulsions the particle size need to be substantial smaller than the droplet size, so wetting could occur (17) (18). The best stabilization effect is developed when the particles form a  $90^\circ$  contact angle with the droplets of the emulsion (19), see Figure 3 below (13).



**Figure 3.** Particle stabilized droplet showing schematically different the contact angles at the water-oil interface in an emulsion (13).

There are many properties of the stabilizing particles that affect the stability of an emulsion, such as hydrophobicity, size and shape. To characterise the hydrophobicity of the system, the particles contact angles could be determined (19).

## 2.5 Solvation

Solvation is the process of interaction of a solute with the solvent. The interaction will generate a stabilization of the solute species in the solution, where ions in the solution are surrounded by solvent. This phenomenon is usually entitled “solvated state”. A polar solvent molecule contains dipoles and is structured in an appropriate partially charged way with the molecule towards the ion, in response to electrostatic attraction. This creates a solvation shell and stabilizes the system. Solvation involves different types of intermolecular interactions: hydrogen bonding, ion-dipole, and dipole-dipole attractions or van der Waals forces. The interactions will only occur if the net Gibbs energy of the solution will be decreased (20) (21).

## 2.6 Stokes law

The properties of a particle in a continuous phase were described in the 1800s by George Gabriel Stokes (22). From Stokes law the drag force that a small sphere is subjected to in a continuous liquid can be calculated. The law uses fundamental assumptions such as no particle interference, spherical particle and smooth surfaces. To determine the force the densities and buoyancy of the particle and continuous liquid are needed as well as the gravity and the particle radii. The formula to calculate the force is shown in Equation 1 (16).

$$F_g = (\rho_P - \rho_L)g \frac{4\pi}{3} R^3 \quad \text{Equation 1}$$

In equation 1  $\rho$  = the density of the particle and liquid,  $g$  = the gravity and  $R$  = the radius of the particle. This equation describes the force exerted by the particle in the direction of the gravity. The friction force or Stokes Drag is calculated with Equation 2 (23).

$$F_d = 6 \pi \mu R v \quad \text{Equation 2}$$

Where  $\mu$  is the dynamic viscosity of the liquid and  $v$  is the velocity of the sphere. The settling velocity can be calculated by force balance for the density force (Equation 1) and friction force (Equation 2) which yields Equation 3:

$$v = \frac{2(\rho_P - \rho_L)}{9\mu} g R^2 \quad \text{Equation 3}$$

The final velocity has a positive value if the particle density is higher than the liquid density, resulting in a sedimenting particle. A higher liquid density results in a negative directed velocity and a rising particle, i.e. creaming (16).

## 2.7 Characterization methods

### 2.7.1 Light Optical Microscopy

Microscopy is a versatile instrument to study small objects and have been used hundreds of years. Today there are several types of microscopes, the traditional light optical microscope is used in this master thesis work. The instrument consists of a body, that holds a number of convex lenses, a sample stage, a foot and a limb that hold the other three parts. An operator and/or a camera looks through the microscope body where the lenses manipulate the light through the body which creates a virtual image that appears larger than it is. The magnification is depending on the lenses shape and distance from each other. To increase the image quality the sample is lit up by a light from underneath. An optical microscope is calibrated with length standards (24).

### 2.7.2 Dynamic light scattering (DLS)

Measurement of particle size and particle size distribution of dispersed particles can be performed with dynamic light scattering. The concept of light scattering has been known since 1802 but the method is highly developed since. Today the method can be used for determination of molecular weight, radius of gyration and much more. Particles scatter light differently; by comparing the scattered light with the incoming light many properties of the sample can be determined. The advanced methods used is made possible by the invention of laser light over 50 years ago (25) (26). When particles diffuse, the light intensity changes and these fluctuations can be used to determine the diffusion constant of a specie.

This constant is used to get the spherical radius of the particles by using the Stokes-Einstein relationship, see Equation 4 (27).

$$D = \frac{k_B T}{6\pi\eta r} \quad \text{Equation 4}$$

Where  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature,  $\eta$  is the viscosity and  $r$  is the particle radius (28). The equation only applies for low Reynolds numbers and the viscosity of the continuous medium is required. This technique can measure samples with particles less than 1  $\mu\text{m}$  in diameter (27).

### 2.7.3 Laser diffraction

Laser diffraction measures particle size by measuring scattered light from the particles. A laser beam passes through a dispersed sample and a particle in the range of 100 nm to 3.5 mm scatters the beam. By measuring the angle and intensity of the scattered light the size of the particle can be calculated. Small particles create a large scattering angle and larger particles create a narrow angle towards the incoming light. The intensity data is used to calculate the size approximated for a sphere which makes the characterizing of irregular particles difficult (29).

Laser diffraction uses two different techniques to calculate size distribution, i.e. the Mie theory and the Fraunhofer approximation. The Mie Theory requires data of the optical properties for both the continuous phase and the dispersed particles. If the particles have a rough surface this data is not easy available. The Fraunhofer approximation which does not need any optical data of the samples; however this technique is less accurate for particles smaller than 50 microns (29) (30). Fraunhofer approximation is the method used in this work.

A batch of monodispersed particles should when analysed give data with a single continuous peak of size distribution. Two peaks would therefore indicate the presence of two types of particles, different sizes (bimodal distribution) or possible aggregation. When analysing a particle dispersed in a liquid, gaseous bubbles in the continuous media is regarded as unwanted data (normally) and should therefore be excluded from the interpretation. Air bubble peaks are commonly around 100-300 microns and the peak is therefore easy to identify given that your sample is expected to be far less or far greater in size than that range (30).

### 3. Materials

#### 3.1 Oil phase

The oil phase consisted of the model solvent MMA and isooctane. MMA was chosen as solvent, due to its fairly nontoxic properties, and together with isooctane constituted a good model system.

##### 3.1.1 MMA

Methyl methacrylate (99 %), purchased from Sigma Aldrich.

##### 3.1.2 Isooctane

2,2,4-trimethyl pentane (>99.8 %), purchased from Sigma Aldrich.

#### 3.2 Water phase

The water phase was based on water buffer solutions containing acetic acid and sodium hydroxide. Into the water phase is also the colloidal silica added. These are the main ingredients, for the reference system there is also a condensation oligomer and a metal ion to aid in the colloidal silica flocculation and hence improve the stability of the emulsion.

#### 3.3 Colloidal silica

Colloidal silica of different sizes and surface modification were received from AkzoNobel PPC. The 14 different types of colloidal silica are presented in table 1 below.

**Table 1.** *The names, sizes and properties of the colloidal silica evaluated.*

Name	Size (nm)	Specific Surface Area	
		(m <sup>2</sup> /g)	Surface modification
Ref	12	220	-
CS 1	7	360	85:15
CS 2	7	360	67.5:32.5
CS 3	7	360	60:40
CS 4	12	220	85:15
CS 5	12	220	67.5:32.5
CS 6	12	220	60:40
CS 7	21	130	85:15
CS 8	21	130	67.5:32.5
CS 9	21	130	60:40
CS 10	60	45	85:15
CS 11	60	45	67.5:32.5
CS 12	60	45	60:40
CS 13	7	360	100:0

## 4. Methods

### 4.1 The reference system

The water phase of the emulsion is prepared in a buffer with 4.5 pH and the colloidal silica particles are added. The flocculent is added and the solution is stirred. The oil phase is prepared with a polar solvent (MMA) and hydrophobicity is tuned with addition of isooctane. The two phases are mixed, together with an electrolyte containing multivalent metal ions and homogenized to create the emulsion.

### 4.2 The novel system

The water phase for the novel system is prepared with the same buffer as in the reference system together with the surface modified colloidal silica particles, no further ingredients. The oil phase is the same for this system and the mixing and homogenization is equal, excluding the addition of the multivalent ions.

### 4.3 Preparation of emulsions

#### 4.3.1 Water phase

The buffer solution is prepared by mixing NaOH (38.8 g, 1M) and HAc (18.8 g, 10%) with deionized water to a final volume of 500 ml. The buffer is dispensed by using a Dosimat. Water phases are mixed with a constant buffer amount of 25 ml. The added amount of silica varies with the experiments. To 25 ml buffer colloidal silica is added drop wise on a scale and the solution is stirred.

The procedure is different for the reference system where a condensation oligomer is added to the solution after the addition of silica. The mixture is stirred for 30 minutes to give the flocculating silica a certain degree of shearing and hence aggregate size. Prior to oil phase introduction and further homogenization a ferric salt ( $\text{Fe(III)(NO}_3)_3$ , 1.43 % 0.35 g) is added to the solution.

A third water phase with chromium instead of the ferric salt is prepared in the same way as the ferric water phase. Chromium nitrate ( $\text{Cr(NO}_3)_3$ , 0.26 g of a 16.4 % solution) is added to the solution prior to flocculation. The mixture is stirred for thirty minutes.

#### 4.3.2 Oil phase

The oil phases is prepared by mixing methyl methacrylate and isooctane (2,2,4-trimethylpentane) of predetermined weight ratio (wt. % in the experiments) and 13.45 ml of the desired mixture is prepared with automatic pipettes for each emulsion.

#### 4.3.3 Homogenization

Homogenization is made with a vertically mounted Ultra Turrax DIAX 900 with a 10F tool mounted (10.0 mm). The instrument is introduced to the solution and the speed is gradually increased to desired speed, in our case 8000-22000 rpm. The various samples were exposed to 45 seconds of shearing at full speed and the instrument is turned off while still in the solution.

### 4.4 Microscopy

The instrument is an Axio Scope A1 from Zeiss and the resolutions used are 20x0.63 and 40x0.63 with transmitting light and no filters. The image is viewed with an AxioCam ICc 5 camera and the pictures are processed with the software included with the microscope. From each sample a 5  $\mu\text{l}$  droplet is collected from the centre of the dispersed phase and added on the glass slide with a micropipette and covered by a top-glass. The images are taken on the edges of the droplet to get a

good and even picture of single layer emulsions. Scale bars, calibrated by the manufacturer, are burned in to the images of the droplets but no further measurements of droplet size are in this report.

#### **4.5 Laser diffraction**

The laser diffraction measurements were carried out on a Malvern Mastersizer Micro Plus. The continuous flow loop was circulating deionized water from an 800 ml beaker and the stirring was set to 2000 rpm. The sample was extracted by pipette from the centre of the emulsion phase and dripped into the beaker until the signal was at about 20 % of maximum, corresponding to 2-3 ml of added emulsion. The laser strength of the instrument was 60 % of its initial power. The loop was rinsed three times with deionized water between each measurement and a fresh beaker was used for each new sample. Signals indicating considerably larger sizes than the emulsion droplet, i.e. air-bubbles, were removed from the data. The density of the oil phase was set to 1 g/cm<sup>3</sup> in all experiments. The measurements cannot be regarded as absolute determinations of droplet sizes (due to various degree of polydispersity, homoflocculation of silica etc.) and this investigation has focused on the relative differences between the different samples. By comparing laser diffraction data with the light microscope analysis the differences in droplet sizes were verified.

#### **4.6 Dynamic light scattering**

A Zetasizer Nano series ZS from Malvern was used to measure the size of the silica aggregates after addition of multivalent ions from the ferric and chromium salt. Three samples were prepared in water according to the procedure described in the beginning of this section. The aggregates were kept for 60 minutes without stirring before measurement and filtrated through a 43µm filter. The samples were diluted and transferred to cuvettes and analysed by the software included with the instrument.

#### **4.7 Creaming observations**

Emulsions were prepared according to the procedure described earlier. After extracting 5 µl for microscopy imaging the samples were left in their Falcon tubes for about 24 hours. The tubes were photographed and the lower level of the emulsion phase was recorded and the fraction of water phase to emulsion phase was calculated. The percentage of creaming used throughout this work is the amount of clear water phase per total amount of liquid.

#### **4.8 Thermal stability experiment**

Three emulsion samples stabilized by different modified colloidal silica were prepared by the previously mentioned methods. The colloidal silica had all different surface modifications but size and added amount was the same. The samples were sealed tight with Para film and submerged in a water bath holding 80 °C. The samples were left in the same temperature for three hours and then examined.

## 5. Results

### 5.1 Reference results

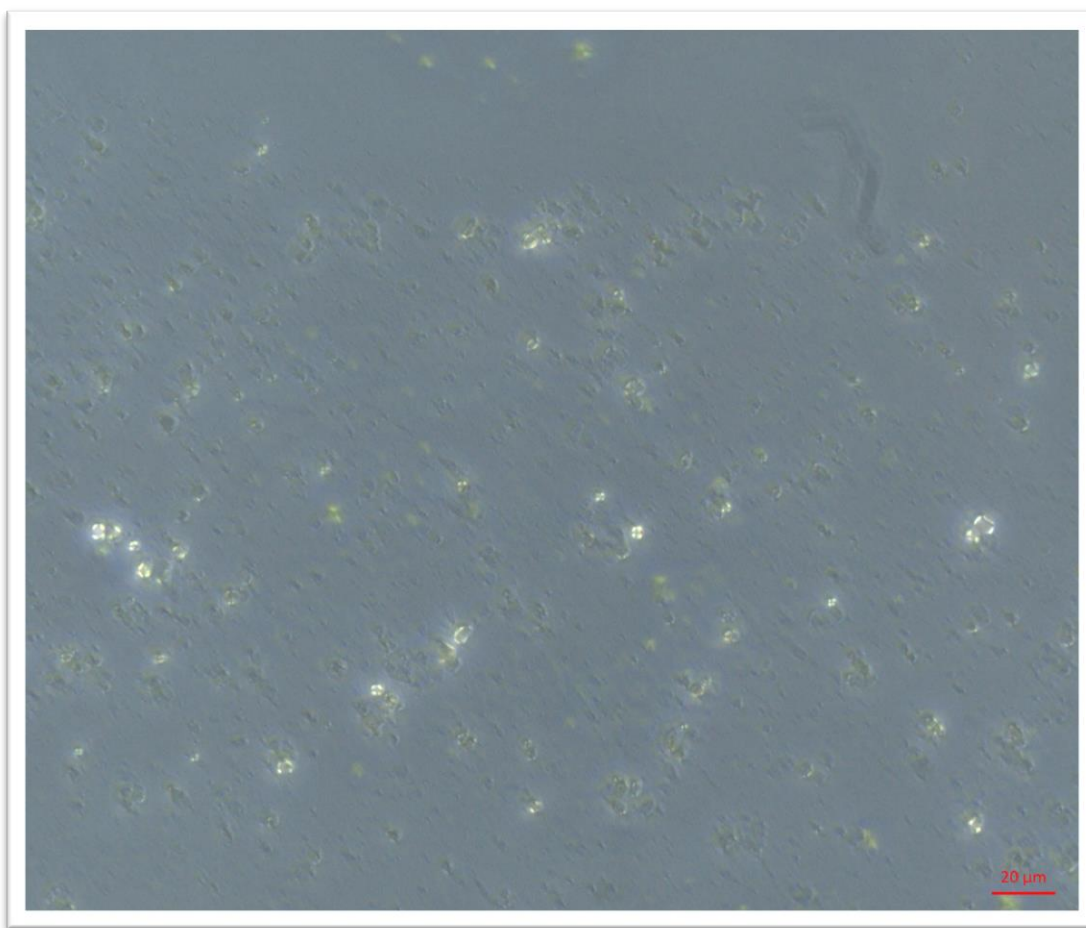
The reference system was studied in order to get a better understanding of the more traditional Pickering emulsions and gain a proper system to compare the results from the systems with surface modified silica.

#### 5.1.1 Surface charge of the silica flocs

The surface charge of the silica aggregates, aggregates in presence of the ferric salt and aggregates in presence of a chromium salt was determined by titration with a charged polymer, polybrene, using a particle charge detector. Since this method is based on the adsorption of, in this case, the cationic polymer, i.e. polybrene, the result is an indication of the available negative charges on the silica particles. In the buffer solution at  $\text{pH} \approx 4.5$  the silica aggregates were negatively charged and in presence of the ferric salt added prior to the flocculation, the relative charge was reduced with approximately 60%. The experiment with added chromium prior to flocculation showed that the solution was positively charged before the titration begun. This shows the importance of how the electrostatic stabilization can be influenced by the metal salts in the system emulsions made with unmodified silica. Data and calculations are shown in Appendix A.

#### 5.1.2 Aggregate size

The colloidal silica forms large aggregates in presence of the ferric salt. When only the condensation oligomer was used to aggregate the colloidal silica aggregates were around 2 microns, measured in a Zetasizer from Malvern. When both the condensation oligomer and ferric salt were added the colloidal silica floc size were about 7 microns. The total aggregation time was 90 minutes. The aggregates were studied by microscope and a typical image can be seen below in Figure 4. In figure 4 the image shows the aggregation after 30 minutes. See Appendix B for more details.

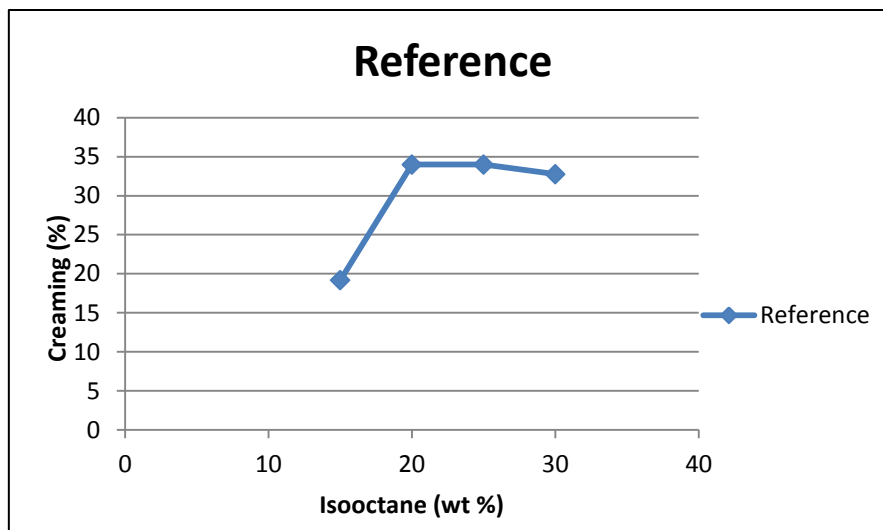


**Figure 4** Image of the silica aggregates with condensation oligomer and ferric salt. The magnification is 40 times and the red bar is equal to 20  $\mu\text{m}$ . The aggregation time is 30 minutes.

The sizes of the silica aggregates are larger than expected and it is not likely that aggregates with an average size of 7 microns are situated at the surface of droplets with sizes in the area of 20 microns. The combined shearing and adsorption at oil interface will probably reduce the aggregate size.

### 5.1.3 Oil phase interactions

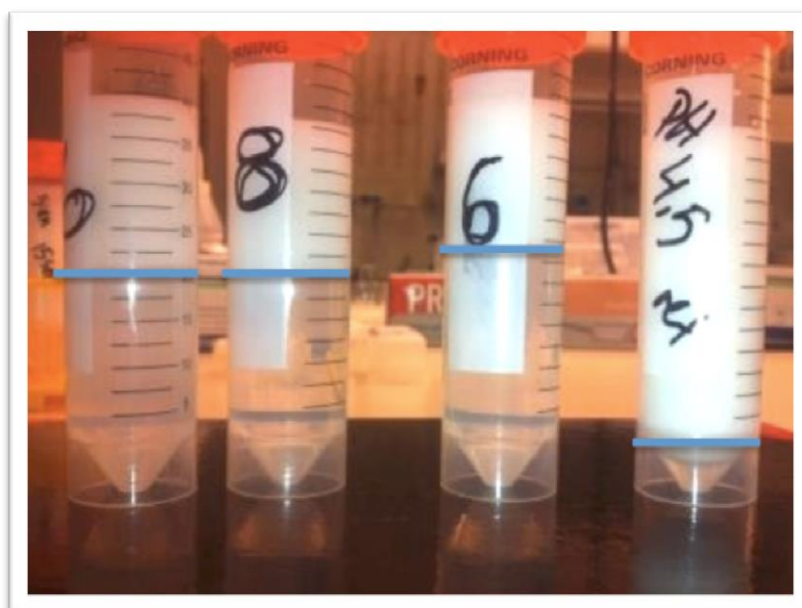
The reference system tested with the standard amount of silica added (0.038g silica/ml oil phase) showed differences in particle size and stability with different hydrophobicity in the oil phase. The initial mixture with 85 % MMA and 15 % isooctane resulted in an emulsion with small droplets and creaming of 19 % after 24 hours, see Figure 5. The other three oil phases, with 20-30 % isooctane, resulted in much more creaming, less stable emulsion and bigger droplets. It is clear that the reference system is greatly dependent on the oil phase composition. The degree of creaming is depending of the difference in density between the continuous phase and the dispersed phase. If larger amounts of isooctane are added to the oil phase, it will increase the differences in density between the continuous and dispersed phase, and thereby enhance creaming. According to stokes law (Equation 3) the size of the dispersed particles have the greatest impact on the increasing the velocity of a dispersed sphere, and hence the creaming. More creaming is therefore an indication of larger droplets especially when emulsifying solvents with decreased density.



**Figure 5** The effect of creaming in the reference system after 24 hours for different mixtures of oil phases.

#### 5.1.4 pH dependence

The reference system was observed at different pHs. When using the regular buffer solution the pH of the emulsion is 4.5. The pH of the emulsions were also changed to pH 6, 8 and 10 and the emulsions were observed in a microscope. Interestingly the samples with pH 4.5 and 10 showed characteristics of fairly stable emulsions whereas the samples 6 and 8 showed poor stability and large emulsion droplets that were in process of coalescence. The interesting result here is the fairly stable emulsion at pH 10, this emulsion showed better stability than the samples close to neutral pH. The tendency towards creaming was remarkably lower in the sample at pH 4.5 but the sample at pH 10 showed less creaming than at pH 6 and 8. The strong effect of pH is very interesting since the tested surface modified silica showed much less influence of emulsion properties when pH was varied. It is clear that this system relies heavily on electrostatic stabilization.



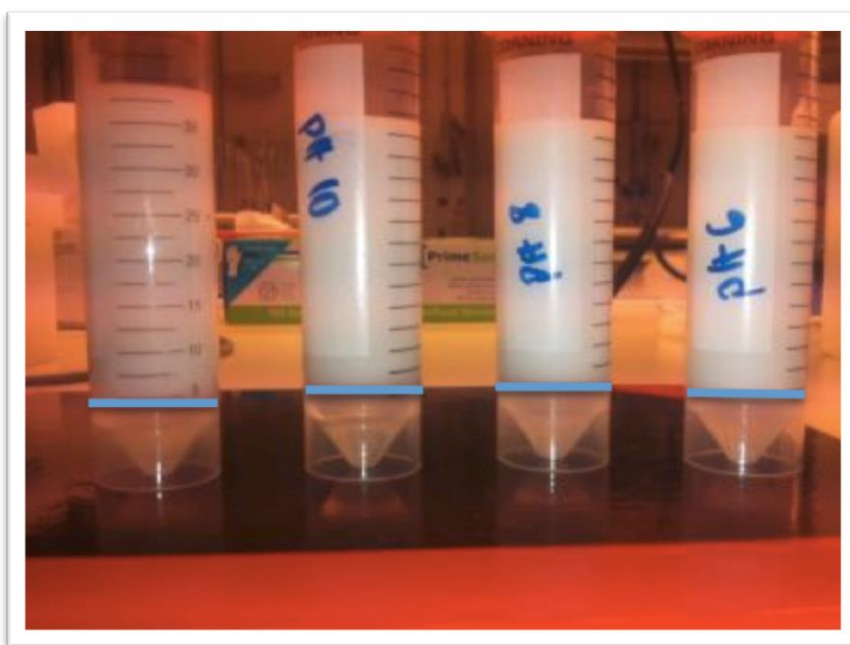
**Figure 6** Photograph of four reference system solutions with different pH in the water phase. The pH values 10, 8 and 6 from left to right shows very high degree of creaming whereas pH 4.5 shows very low creaming.

## 5.2 Results for the novel system

The results from the experiments with the novel system will be presented in this part.

### 5.2.1 pH dependence

The emulsion system with modified colloidal silica showed a high degree of emulsion stability independent of pH, in contrast to the previous described system with pre-aggregated silica. All emulsions with pH from 4 to 10 showed a good stability. The four samples with pH 4.5, 6, 8 and 10 showed all the same degree of creaming after 24 hours. The absence of pH dependence leads us to believe that electrostatic stabilization is less important and the system with modified silica are stabilized mainly by steric hindrance. The silica used is CS 2 with 0.043 g/ml oil phase.



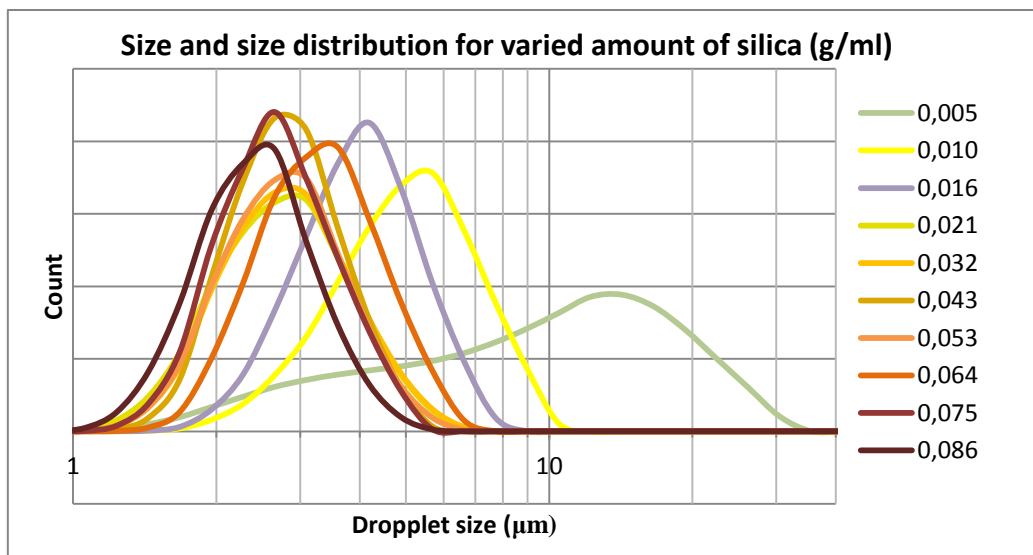
**Figure 7** Photograph of four emulsion systems with modified silica at different pH's. The pH values are 4.5, 10, 8 and 6 from left to right and all samples shows low creaming.

### 5.2.2 Thermal stability

The experiment with thermal stability showed no changes in the emulsion characteristic when exposed to an elevated temperature (80°C) for three hours. The emulsions remained the same and no further creaming was observed.

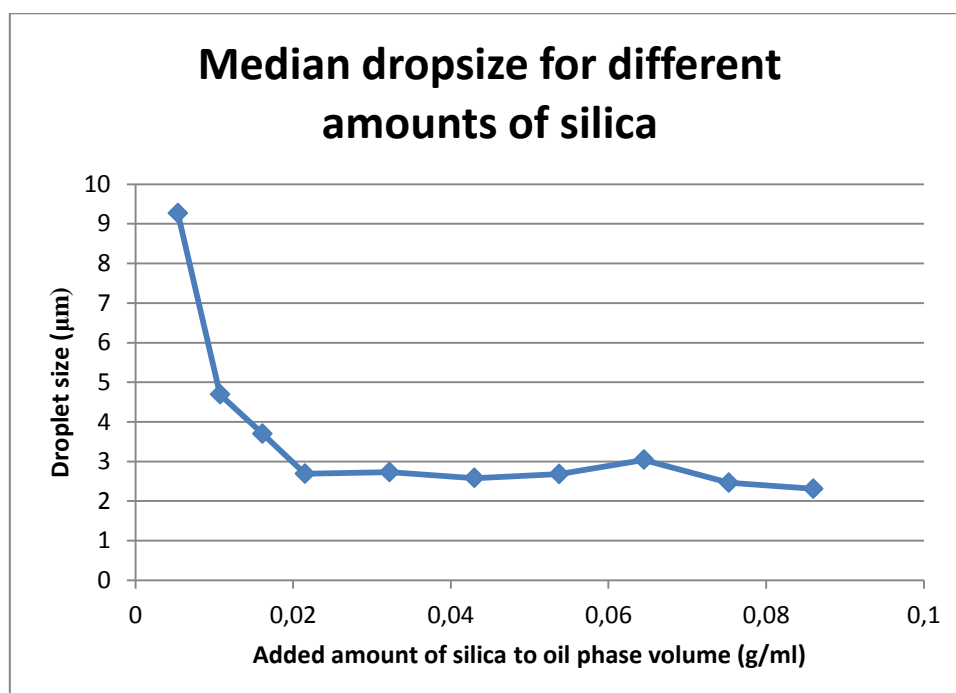
### 5.2.3 Impact on added amount of silica

When varying the amount of silica to stabilize an emulsion system with fixed amount of water and oil, large differences in the droplet size were shown. At high amounts of silica, the emulsion droplets are small with a narrow size distribution. When the amount of silica is decreased the droplets grow slightly in size and the size distribution widens. At very low amounts of silica the emulsion droplets increase considerably in size with a broader size distribution and finally the emulsions become unstable, see Figure 8.



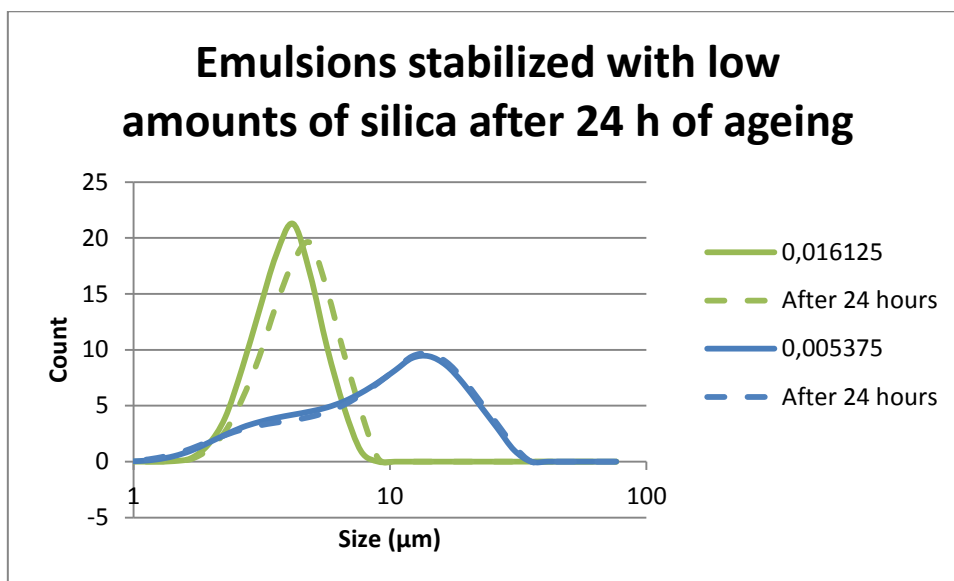
**Figure 8.** The graphs show size distributions of emulsion droplets stabilized by varying amounts of the same type of surface modified colloidal silica (CS 2). The added amount of silica (to the right) is expressed in grams per milliliter of the oil phase.

At high amounts of silica the emulsions become more monodispersed with smaller droplets. The high amount appears to be sufficient to get full coverage of all the droplets with the smallest possible size, 7 nm, of the modified silica. Lower amounts of silica results in insufficient coverage which increases the polydispersity and the size of the emulsion droplets. There is only enough silica to stabilize few of the very smallest droplets. At very low amounts of silica the particles increases in size drastically and the emulsion is very polydispersed and unstable. This phenomenon can easily be observed in Figure 9 where the median droplet size is plotted against added amount of silica.



**Figure 9.** The mean droplet size from the graphs in figure 8 as a function of added amount of silica (CS 2) per milliliter of oil phase.

All emulsions, regardless of amount of silica added showed good stability over 24 hours. This was tested with two of the lowest amount of silica and can be seen in Figure 10.

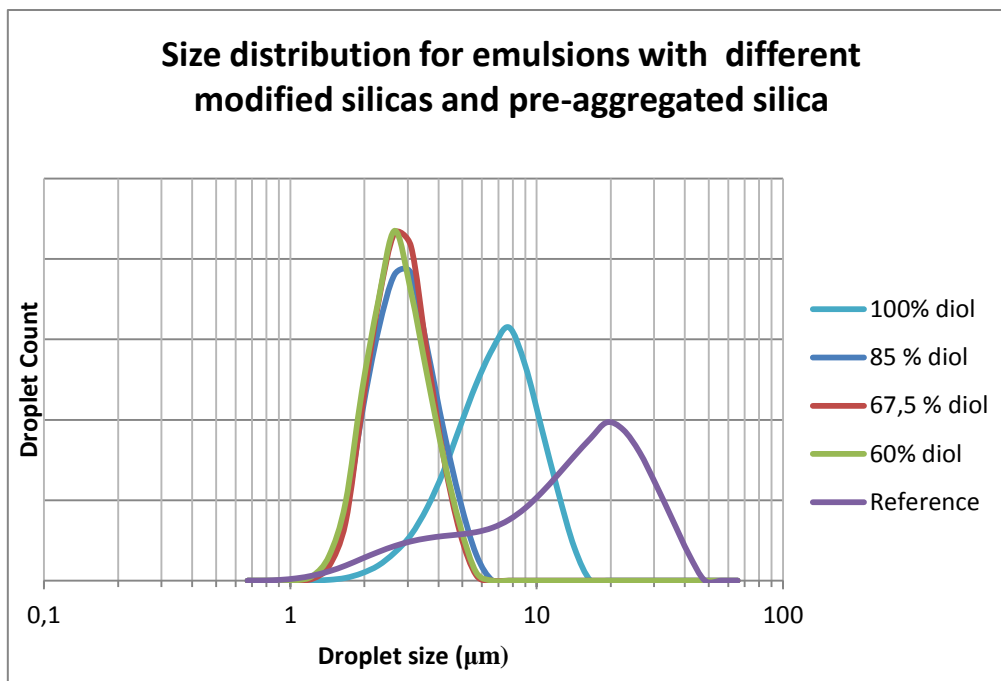


**Figure 10.** *The stability of emulsions with very low amount of silica particles (CS 2.).*

The emulsion stability when adding high amounts of silica at different surface modifications is presented later in this chapter. The result shown in Figures 8,9 and 10 were conducted with 67.5:32:5 surface modification on 7 nm silica particles.

#### 5.2.4 Impact of surface hydrophobicity

The impact of the surface modification was tested by having constant added amount of silica and particle size. The results show that the emulsion stabilized by pre-aggregated non-surface modified silica has a much larger droplet size and broader size distribution. A silica with only hydrophilic surface modification were tested as well which resulted in droplet sizes between the system with pre-aggregated silica and the emulsion stabilized with both types of surface modifications. Regarding the type of surface modification the results appears to be similar when changing the hydrophilic/hydrophobic balance, see Figure 11.

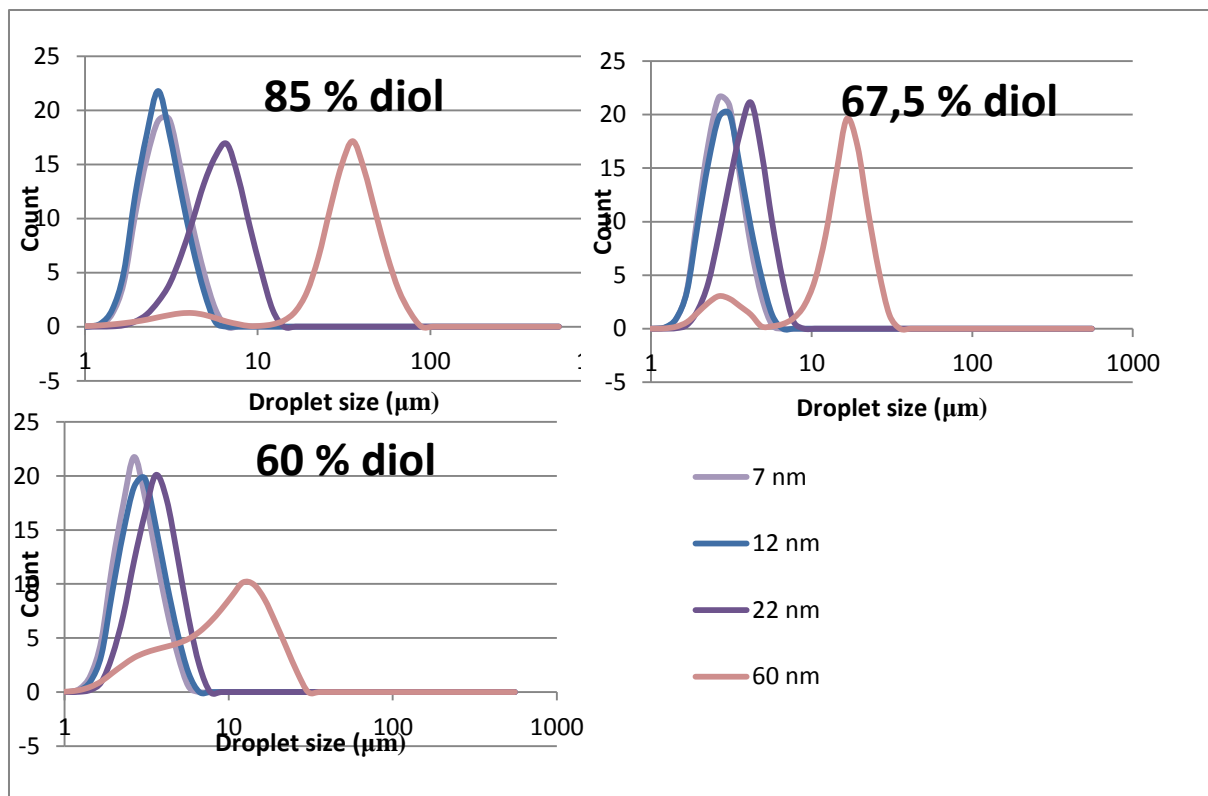


**Figure 11** Droplet size distribution of emulsions stabilized by different types of surface modified colloidal silica. The silica used was, in order of figure legend (from top); CS13, CS1, CS2, CS3 and REF.

The droplet size distributions of emulsions with pre-aggregated silica is quite similar to the result when very low amount of silica is added, i.e. with a secondary peak at small droplet sizes. The particle size is 7 nm and added amount is 0.043 g/ml for all surface modified silica, in the case of pre-aggregated silica 0.038 g/ml was added of silica with 12 nm silica in primary particle size.

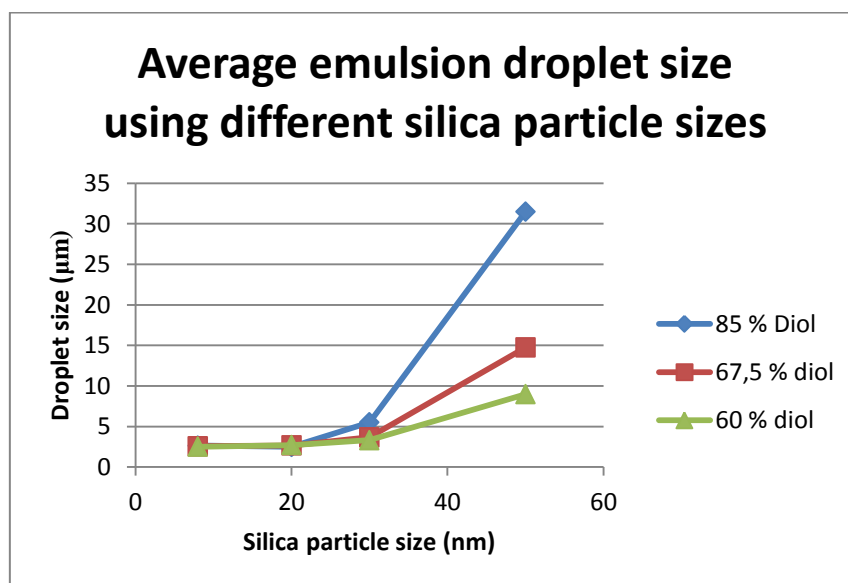
### 5.2.5 Impact of silica size

The different surface functionalities show different results with different particle size, which was not observed when altering only the surface functionality keeping the silica particle constant. The more hydrophilic surface functionality (85 % diol) shows greater difference between the particle sizes. The two smaller particle sizes stabilize emulsion droplets quite similar in size but the two larger silica particles increases the droplet size quite drastically. The other two silica functionalities (less hydrophilic-more hydrophobic) result in similar emulsion droplets both regarding mean size and size distribution for the three smaller silica particles. The difference between the surface functionality is more evident with the largest silica particle, see Figure 12.



**Figure 12.** The figure shows the emulsion droplet size distributions of all different silica particle sizes with the three types of surface modification with both hydrophilic and hydrophobic functionality. The silica amount is 0.043 g/ml oil phase.

Emulsions stabilized with 60 nm silica particles all give signals around 5 microns, these might be silica aggregates. The results from the graphs in figure 12 have been summarized in Figure 13, showing the median droplet size of emulsions stabilized by the different silica particle sizes.

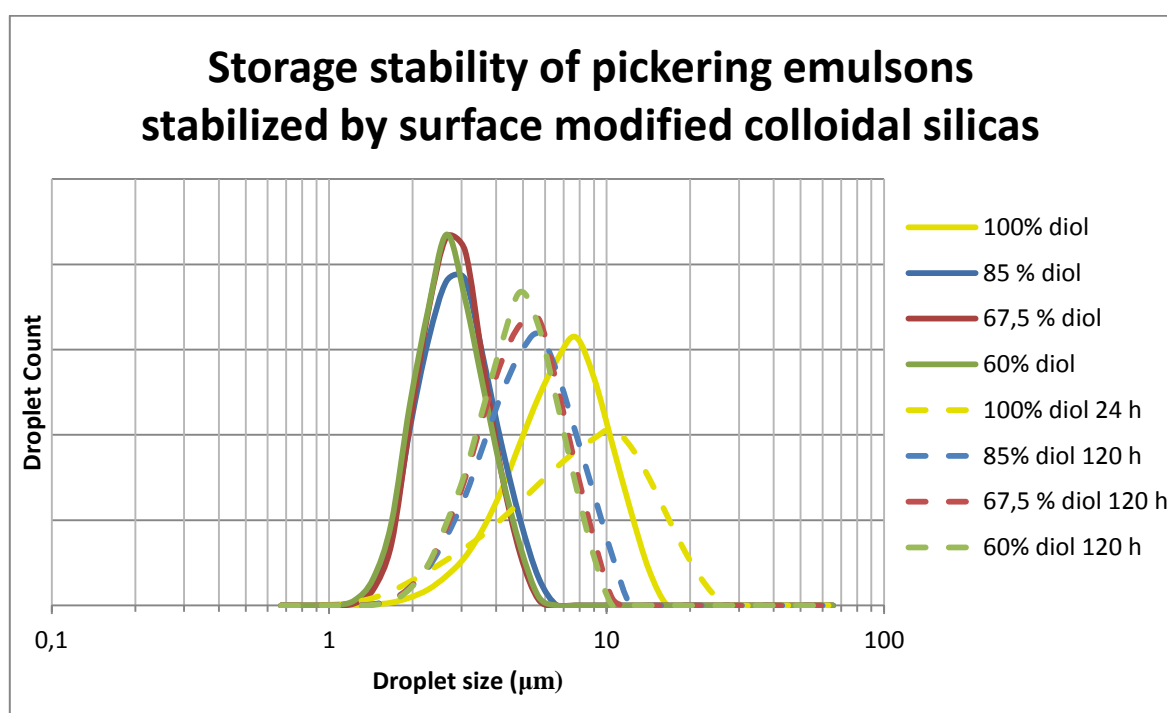


**Figure 13** Size distributions of emulsions stabilized by colloidal silica of different particle sizes.

The larger secondary peaks at around 5 microns for 67.5 % and 60 % diol functionality results in a smaller median droplet size but it's obvious that the other surface modification stabilizes larger emulsion droplets with the larger silica particles.

### 5.2.6 Storage stability

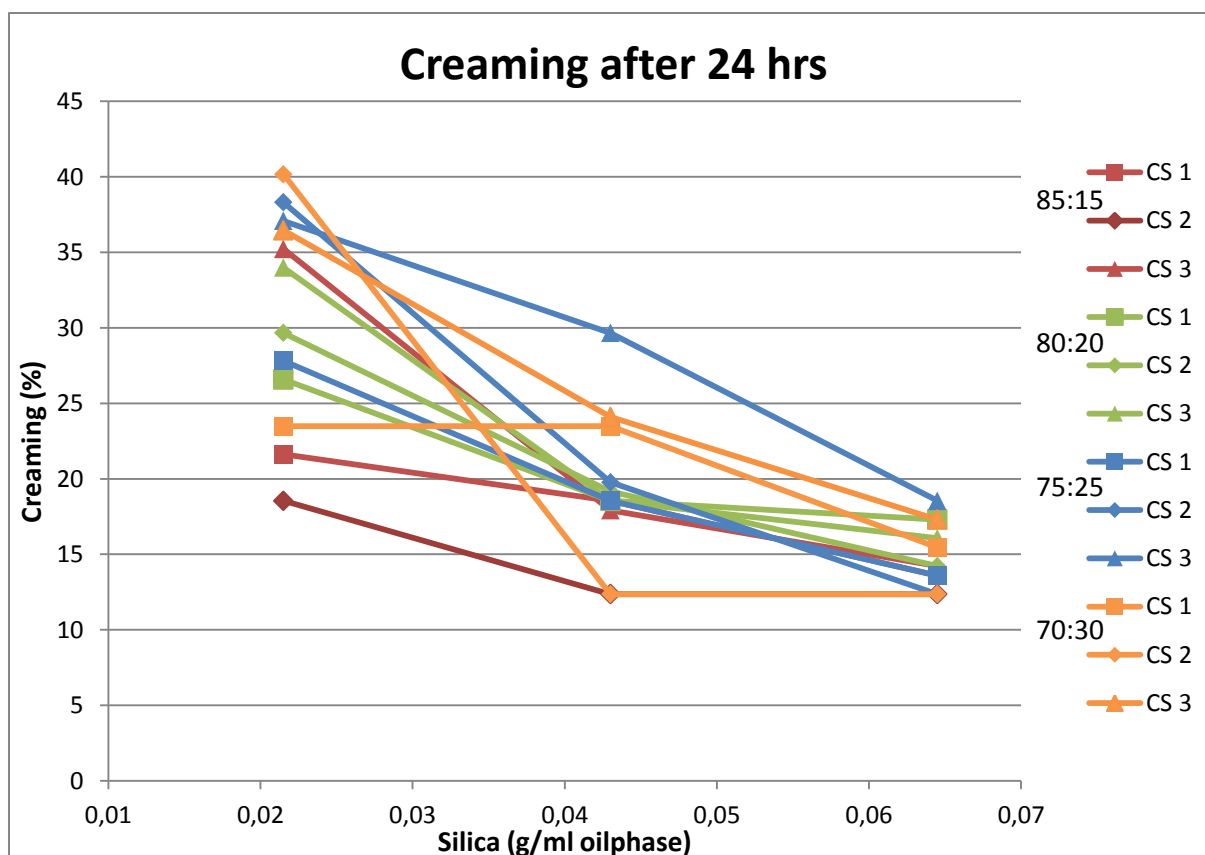
The effect of the different surface functionalities on storage stability was analysed with laser diffraction. All four emulsion samples contain 0.043 g/ml silica of the 7 nm size. The sample stabilized by silica modified with only a hydrophilic functionality showed a relatively large change in droplet size after 24 hours, no further measurements were done after 24 hours. The emulsions stabilized by silica modified with both hydrophilic and hydrophobic groups showed a similar behaviour regarding droplet size increase but less pronounced even after five days (120 hours) of storage, see Figure 14.



**Figure 14.** The diagram shows the size distribution of four emulsions stabilized by colloidal silica with four different types of surface modifications. The dashed lines show the same samples after ageing.

### 5.2.7 Creaming

Creaming of the emulsions stabilized by different types and amount of modified silica with different organic phases was evaluated after 24 hours. There is significantly little creaming in emulsions with silica modified with 85 % diol. The creaming is in general more pronounced with lower amounts of silica. Silica with 67.5 % diol modification shows the largest variations in creaming as a function added amounts of silica; the trend appears to change when the amount of isooctane gets too high 30 %, see Figure 15.

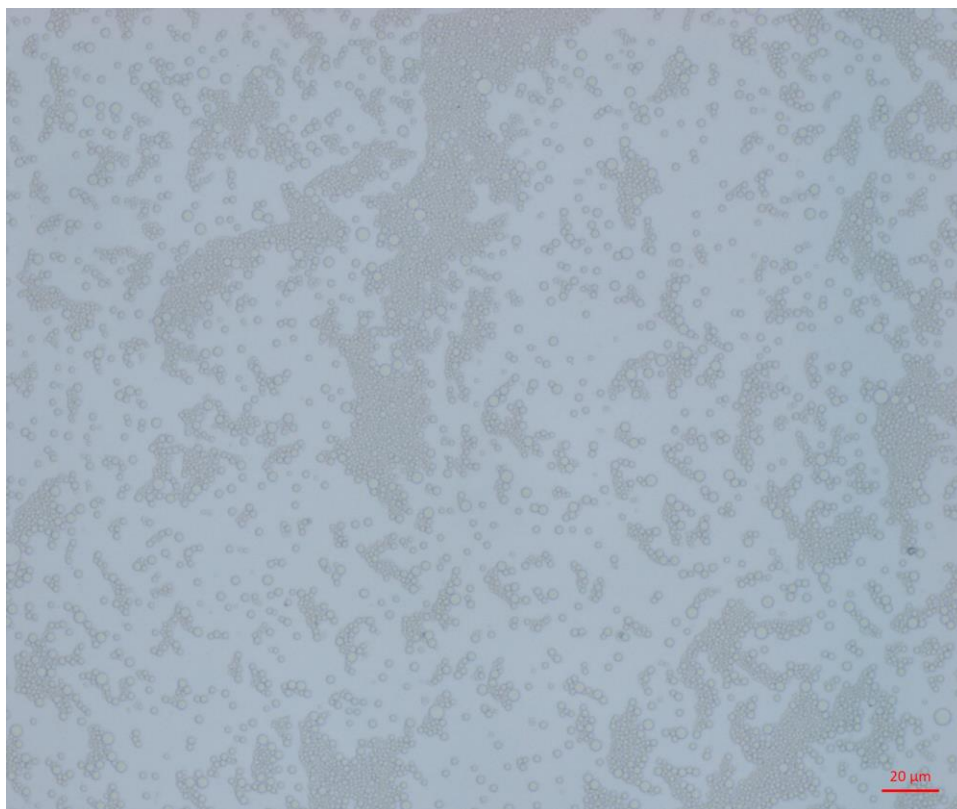


**Figure 15** Creaming experiments with silica particle stabilized emulsions with different oil phase compositions, s amounts of silica and silica surface functionality.

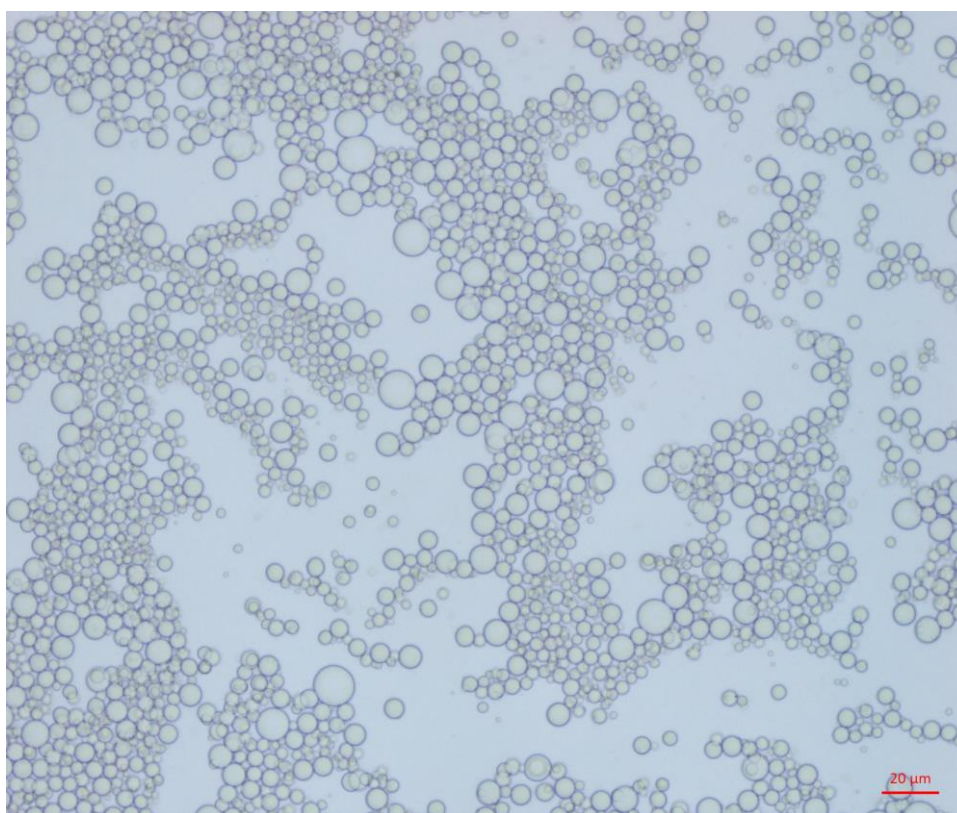
The creaming increases with larger differences in density and with more isooctane content the droplets become lighter and hence the creaming increases. This will result in increased creaming for the samples with oil phase containing more isooctane. However, according to Stokes law (equation 3) the radius of the droplets are more important than the density change and a stronger trend with increased creaming for larger droplets should be visible. In the plot above the only clear trend to recognize is the reduced creaming for high amounts of silica; this is easily understood since a larger amount of silica can cover a larger surface and therefor stabilize smaller droplets. It appears that the more hydrophilic silica can stabilize smaller droplets when the amount of silica reach critically low levels.

### 5.3 Microscopic imaging

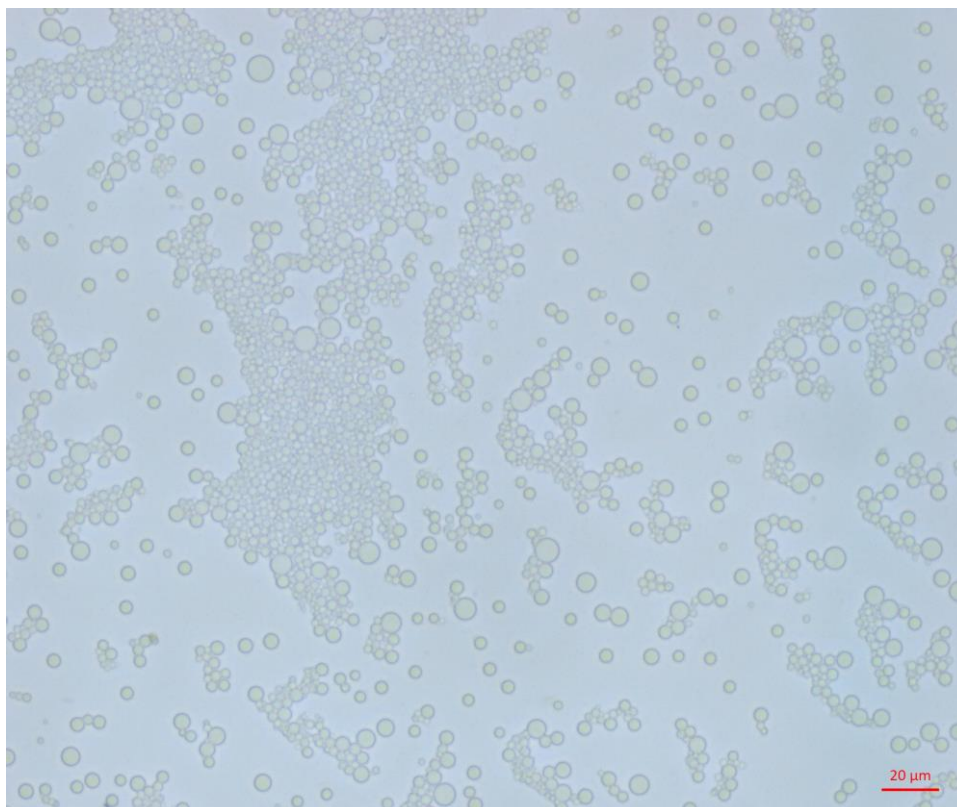
All emulsions stabilized by CS1, CS2 and CS3 have been analysed in light microscope. Below we see microscope figures that strengthen the results already described above. In Figure 16 and Figure 17 we can see an emulsion with CS2 silica in an 85:15 oil phase with magnifications of 20x and 40x. The emulsions contain small droplet in contrast to the emulsions with pre-aggregated silica in Figure 18 and Figure 19. By looking carefully the CS2 system it seems to have droplets that are less polydisperse. However, it can be difficult to determine how polydispersed the emulsion is, only by visually inspection, which makes it important to use other methods like DLS for verification.



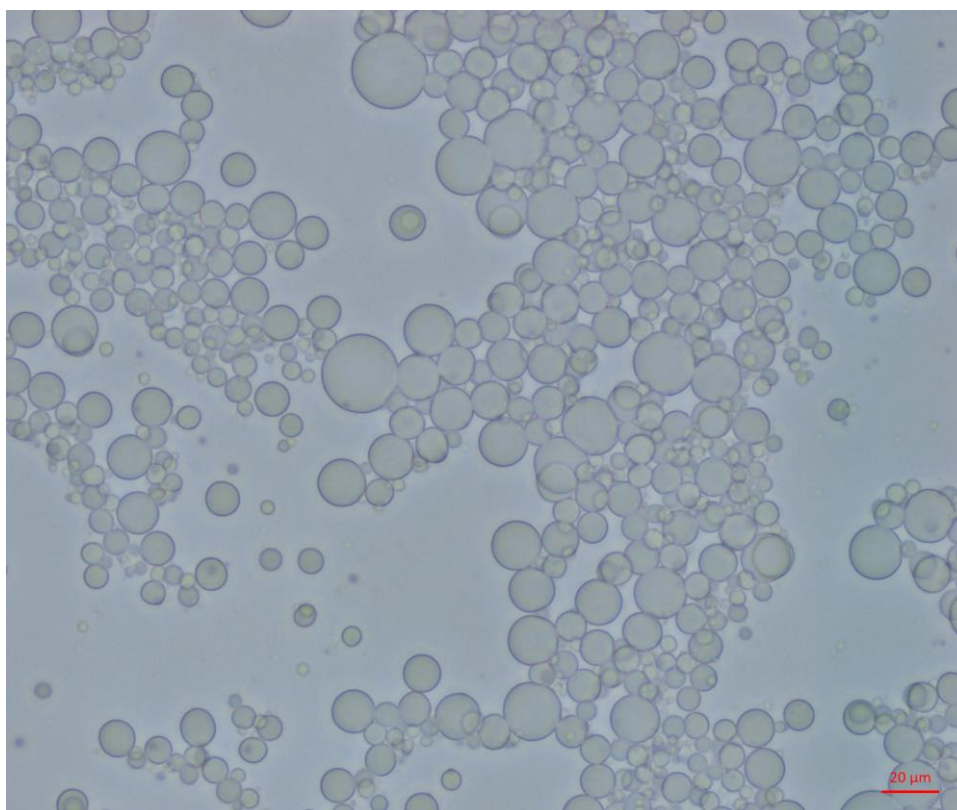
**Figure 16** CS2 0.0215g/ml oil phase, with an 85% oil phase and 20 x magnification.



**Figure 17** Reference system, with an 85% oil phase and 20x magnification.



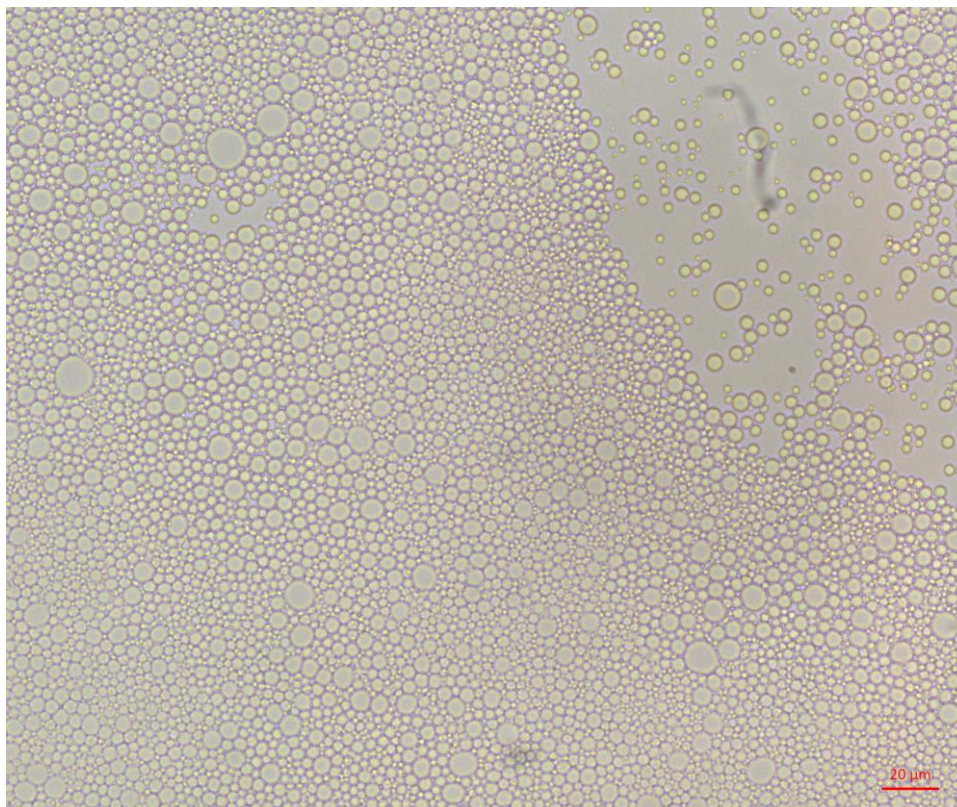
**Figure 18** CS2 0.0215g/ml oil phase, with an 85% oil phase and 40x magnification.



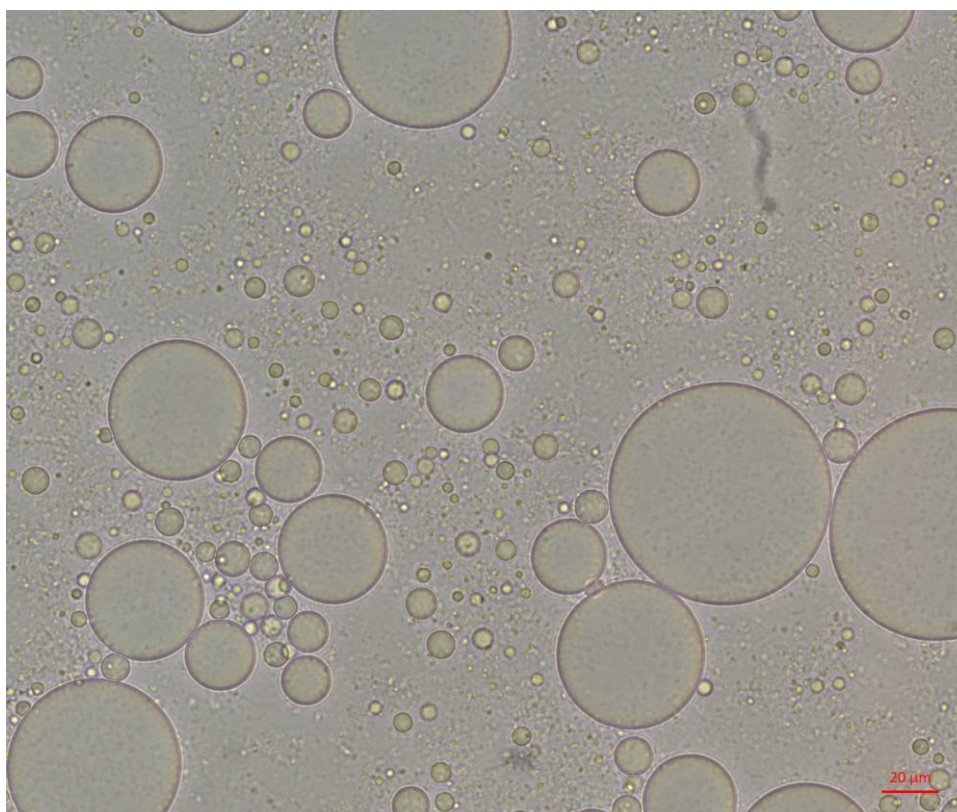
**Figure 19** Reference system, with an 85% oil phase and 40x magnification.

Figure 20 and Figure 21 shows that although the oil phase composition changes the modified silica particles are able to create good emulsion with small droplets. This distinguishes the system with

modified silica from the system with pre-aggregated silica significantly as the latter system has major problems with for example polydispersity and large droplets when changes in the oil phase are made.



**Figure 20** *CS1 with a 70% oil phase and 40x magnification.*



**Figure 21** *Reference system with a 70% oil phase and 40x magnification.*

## 6. Discussion

### 6.1 The influence of pH

The two systems show different properties when altering the pH of the emulsions. System with pre-aggregated silica is highly influenced by pH changes in the water phase due to its electrostatic stabilization mechanism. The system with modified particles is independent of the pH in the system, since it is mainly stabilized sterically. Systems that have a high tolerance towards acidity and alkali is advantageous due to its robustness. This indicates that the stabilization with particles can be used for different systems independent of the pH without risk of coalescence. The system with modified particles can therefore be a better concept for emulsification. On the other hand if coalescence is desired the system with pre-aggregated silica has potential when an emulsion is needed initially, e.g. during synthesis, and then triggered to coalesce addition of alkali (or acid).

### 6.2 Pre-aggregation of silica

The flocculation of silica for stabilization of emulsions is well known, but has not been the main focus in this thesis. However, the free silica aggregates appears to be very large with respect to the emulsion droplets they stabilize. This leads us to believe that the aggregates are sheared apart during the homogenization. The silica aggregates are still larger than the original colloidal silica and will therefore diffuse slower in the continuous phase. The slower diffusion might give the emulsion droplets more time to grow before the silica completely covers the interface and thereby stabilizes it. This can be an interesting way to control the emulsion size by controlling aggregation speed and could be interesting for further studies. The two emulsions using iron and chromium during aggregation behaved differently. The chromium based emulsions have larger amounts of the ions and are introduced during the first 30 minutes of aggregation which results in a positive net charge of the aggregates. The other system with iron ions results in negative net charge of the aggregates. Although these two systems stabilize the emulsions with opposite net charges the results are fairly similar.

### 6.3 A toolbox with the modified silica

The main reason of this work was to investigate the properties of particle stabilized emulsions using surface modified silica. Below the different parameters possible to vary in order to control the droplet sizes and size distribution will be discussed. The size of the emulsion droplets is important for the emulsion properties and its possible applications. Smaller droplets have the advantage of high surface area which is advantageous in chemical reactions by increasing the exposed area between immiscible reactants. Larger droplets require less emulsifiers and can be used when the high surface area isn't of importance e.g. when the dispersed phase is emulsified only for encapsulation. The droplet size can also control the release rate of medicine and properties when manufacturing micro particles

#### 6.3.1 Particle size

The particle size of the colloidal silica is one of the most evident tools for size control of the emulsion droplets. Our results clearly indicate that smaller particles stabilize smaller droplets, and vice versa. However, emulsion droplet size as a function of added silica was not thoroughly evaluated for all the silica particle sizes used. The silica particles we obtained varied from 7 to 60 nm in particle size. It would be interesting also to see how medium sized particles (between 22 and 60 nm) would behave and the resulting emulsion droplet sizes. The larger silica particles have smaller secondary peaks in the laser diffraction data that might be aggregated silica. Chavalier et al (31) get a similar peak in their work and determine it to be an excess of silica. The fact that the more hydrophobic particles have a higher count in DLS on the possible aggregates further indicates that the silica particles attract each other in order to lower their energy. One explanation for the silica aggregates might be that the slow

diffusion hinder the particle from reaching an interface. More data need to be collected with a complete size span of particles to see the true impact of particle size. Also the larger particles will have higher attractive forces towards each other. It might be possible that particle size shows a synergy with the amount of silica or surface modification. Our experiments were limited to few particle sizes and we were not able to investigate possible synergies.

The possibilities of mixing particle sizes could increase the possibility of optimization even more. The voids in the interface structure made by large silica particles could possibly be filled by smaller silica particles. It might also be a good idea to use surfactants or polymers as emulsifiers when using silica particles with a larger particle size in order to make the emulsion droplets quickly and then use the particles as stabilizers.

### 6.3.2 Surface modification of silica

The results obtained so far showed minor differences between the different surface modifications of the silica particles when varying degrees of hydrophilic and hydrophobic functionalities. There is a clear difference between these three and plain silica and silica with only hydrophilic functionalities. Both functionalities seem important in several of the experiments conducted but the degree of functionality seems less important. In the experiments with varying particle sizes we can see that for the larger silica particles with higher hydrophilicity stabilizes emulsion droplets with a narrow size distribution and give less aggregation of excess silica, see Figure 12. This shows that the surface functionality does matter although not significantly for the smaller particles. In the creaming experiments it can be observed that for small amounts of added silica, the more hydrophobic surface functionality results in emulsions with larger droplets. This might be a way to control the droplet size when adding less amount of silica.

It is possible that the role of surface functionalities would play a greater role when combining the surface modified silica with co-emulsifiers like polymers and surfactants when stabilizing emulsions. The interactions between these molecules and the silica particle would largely be dependent on the functionalities on the surface and might play a great role in stabilizing emulsions with more complex component mixes.

It is hard to predict the outcome of using other surface functionalities but one might think that it will be crucial when investigating other types of oils/solvents. Modifying silica with larger molecular chains like polymers might further increase the sterical hindrance and add a dimension of control when varying pH and hydrophobicity of the oil phase.

It is apparent that the surface functionality will be of great importance when optimizing the emulsions of different oil and water phases, stabilized with only colloidal silica as well as in more complex systems.

### 6.3.3 Storage stability

Like a good cheese or a fine wine the emulsion droplets can utilize the aspect of time to alter its properties for the better, or worse. We can see that one way to produce larger droplets is by leaving the emulsions for ageing. The ageing time is an easy parameter to control and would be an easy tool to grow larger droplets. It is hard to say anything certain about how the emulsions will perform after ageing, from the experiments we have concluded. The aged emulsions stabilized by surface modified silica showed a slightly higher polydispersity, which isn't necessarily a negative result since polydispersed emulsion have many applications.

#### 6.3.4 Amount of silica

From the results obtained by varying the amount of silica it is evident that the amount is an important parameter in order to control the properties of the emulsions. A high amount of silica gives nice and narrow particle size distribution, and a low amount of silica gives a broad particle size distribution. In Figure 9 shows that there will be a minimal amount of silica required for a desired particle size and polydispersity. This is important when optimizing a process or system in order to minimize the raw material cost and waste.

If one decides to mix particle sizes of the modified colloidal silica, it is important to understand that the total amount of silica required will be larger the larger the particle size. A possible optimum amount of silica in order to achieve a close packed structure the number of silica particles is depending on the size ratio of the silica particles used. The number of silica particles for a given concentration is much higher for the sols with smaller particles size. Adding the same amount of two colloidal silica with different particle size, would result in the larger particles being under-represented in number.

#### 6.4 Data quality

The data we have collected are not backed up by statistical significance due to lack of time. However great care has been taken in order to make the data as reproducible as possible. All experimental steps of importance have been carried out by the same individual throughout the whole master thesis project. Also all instruments used were up to date in terms of calibration and service.

## 7. Conclusions

### 7.1 Pickering emulsions with pre-aggregated silica

- This system relies on electrostatic stabilization.
- The system shows poor pH stability and can only be used around pH 4.5.
- Generally, the system stabilizes larger droplets when using the same amount and size of silica particles than the system with modified silica. The size distribution is broader and some excess silica can be seen in the light scattering curves.
- Higher creaming is an indication of larger droplets in the system. With higher hydrophobicity of the dispersed phase, i.e. more isooctane, the creaming increased. This shows that the system with pre-aggregated silica, relying on electrostatic stability, is more sensitive towards the oil phase composition.

### 7.2 Pickering emulsions with surface modified silica

- Higher amounts of silica stabilize emulsions with smaller droplets in a narrow size distribution. When the emulsion is saturated with silica particles the droplets will reach a minimum.
- Smaller silica particles will result in an emulsion with smaller droplets which is a useful for size control in future emulsions.
- The surface functionality showed to be less important than expected, as long as the surface is modified with both hydrophobic and hydrophilic functionalities the particles stabilizes emulsion droplets well. The surface functionality might be of greater importance when varying oil phase or when using surfactants or polymers as co-stabilizers. When using only hydrophilic surface functionality the results are not as promising.
- It is possible to store the emulsions in order to grow the droplets. This is a possible way to control the particles size by simply leaving the emulsions to rest.
- The modified silica resulted in Pickering emulsions with great pH stability and seems possible to use in the pH range of 4-10.

## 8. Future work

An interesting area for future could be to look further at how a combinations of different modified silica particles sizes could affect the emulsions, through the particle size and particle size distribution. One possible hypothesis is that Pickering emulsions show equal behaviour as packed surfactants and hence can help to control the size of the emulsion droplets.

Another interesting work is to look deeper into how the oil phase interacts with the water phase, and what role the silica particles has in this system. Through the information it could be possible to better optimize the oil / water phase.

In this master thesis work, we have only investigated some few modifications of silica particles. It would be interesting to further look at different types of modifications of silica particles in order to draw new conclusions in the area of silica based Pickering emulsions and how the emulsion droplets interact.

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## 10. Appendix

### 10.1 Appendix A

Measurement of charge density on pre aggregated silica.

The four following water phases was prepared according to the recipe:

1. Buffer + LX
2. Buffer + LX + KO
3. Buffer + LX + KO + FEN
4. Buffer + Cr + LX + KO

The solutions 2-4 was stirred for 30 minutes before the net charge was determined with automatic titration of Polybrene to neutral solution while measuring mV.

The calculations are done with the formula:

$$\text{Relative charge} = \frac{X_{\text{Polybren}} \times V_{\text{Polybren}}}{m_{\text{sample}} \times C_{\text{sample}}}$$

Where

$$X_{\text{Polybren}} = \frac{C \times Z}{M} = 0,02 \left( \frac{\text{Charge}}{L} \right)$$

Where Z is the amount of charges per polybren molecule. The concentration of the sample was 0.2 g/L

The following volumes of a solution with 3.748 wt% polybrene was used on 10 g water phase:

1. Buffer + LX
  - a. No experiments done
2. Buffer + LX + KO
  - a.  $V_{\text{Polybren}} = 0.8457 \text{ ml} \rightarrow \text{Relative charge} = 0.008457$
  - b.  $V_{\text{Polybren}} = 0.8753 \text{ ml} \rightarrow \text{Relative charge} = 0.008753$

This gives a mean value of 0.008605 Charges/g

3. Buffer + LX + KO + FEN
  - a.  $V_{\text{Polybren}} = 0.7604 \text{ ml} \rightarrow \text{Relative charge} = 0.007604$
  - b.  $V_{\text{Polybren}} = 0.3555 \text{ ml} \rightarrow \text{Relative charge} = 0.003555$

The first run was faulty and the second value will be used for comparison.

4. Buffer + Cr + LX + KO
  - a. Positive from start

## 10.2 Appendix B

The same solutions were analysed with Malvern Zetasizer Nanoseries ZS after the samples were rested for about 90 minutes. The average diameter of the particles was:

1. Buffer - 29 nm
2. Buffer + LX + KO – 2136 nm
3. Buffer + LX + KO + FEN – 6278 nm
4. Buffer + Cr + LX + KO – No valid data