

Thermo-responsive Pickering emulsions stabilized by surface functionalized silica

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ABSTRACT

The main objective of this thesis was to study the behaviour of surface-modified silica particles as emulsifiers and emulsion stabilizers in oil-in-water emulsions. The silica particles were functionalized with mPEG (methyl polyethylene glycol) and propyl groups and in order to understand their emulsification abilities, different conditions were explored, such as temperature, pH of the aqueous phase, salt concentration and oil/water ratio. The phase inversion conditions were investigated, which can be used to make monodisperse emulsions with small droplets. Emulsion diagrams were made in order to understand the behaviour of the particle at different o/w ratios.

It was found that the presence of mPEG groups is required to achieve the phase inversion temperature (PIT) at which the emulsions inverted from o/w to w/o. The PIT is affected by changes in salt concentration and pH of the aqueous phase. It was found that Pickering emulsions are reversible, like surfactants systems, but need energy input from the homogenization process in order to invert from w/o to o/w. A significant temperature hysteresis of the PIT was found between the increasing and decreasing temperature. In order to make emulsions stable over time, silica particles functionalized with both mPEG and propyl groups should be use as emulsifiers and there is need to find a balance in the system in salt concentration, since higher salt concentration with the propyl functionalization can induce higher flocculation. The presence of salt gives stability over time. Emulsions with 0.1 M of CaCl₂ were stable for more than 3 months.

Key words: Pickering emulsions, PIT method, functionalized colloidal silica, emulsion stability.

RESUMO

O objetivo deste trabalho foi estudar o comportamento de partículas de sílica modificadas com grupos superficiais hidrófilicos (grupos de propil) e hidrofóbicos (metil polietileno glicol, denominado mPEG) como emulsificantes e estabilizadores de emulsões de óleo em água. Foram estudadas diferentes condições como temperatura, pH da fase aquosa, concentração de sal e rácio óleo/água. As condições de inversão se fases foram investigadas pois podem ser utilizadas para a preparação de emulsões com pequenas gotículas e monodispersas. Para entender o comportamento das partículas em emulsões com diferentes rácios óleo/água foram feitos diagramas de emulsão.

Verificou-se que a presença de grupos mPEG é necessária para atingir a temperatura de inversão de fases (PIT) na qual as emulsões invertem de o/a para a/o. Os resultados indicam que a PIT é afetada por alterações na concentração de sal e pH da fase aquosa. As emulsões de Pickering são reversíveis, como as emulsões tradicionais, mas precisam de energia proveniente do processo de homogeneização para inverter de a/o para o/w.

Para fazer emulsões estáveis ao longo do tempo, partículas de sílica modificadas com mPEG e grupos de propil devem ser usadas como emulsionantes mas há necessidade de encontrar um equilíbrio no sistema relativamente á concentração de sal adicionada, uma vez que elevadas concentrações em conjunto com os grupos de propil pode induzir floculação em excesso. Verificou-se também que presença de sal dá estabilidade ao longo do tempo. Emulsões com 0,1 M de CaCl₂ permaneceram estáveis durante 3 meses.

Palavras-chave: Emulsões de *Pickering*, PIT método, sílica coloidal modificada, estabilidade de emulsão.

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LIST OF ABBREVIATIONS

CP	Cloud Point
DLS	Dynamic Light Scattering
mPEG	methyl poly(ethylene glycol)
NMR	Nuclear Magnetic Resonance
o/w	Oil in Water
PIT	Phase Inversion Temperature
RT	Room Temperature
SSA	Specific Surface Area
SEM	Scanning Electron Microscopy
ТЕМ	Transmission Electron Microscopy
UF	UltraFiltration
w/o	Water in Oil

PARAMETERS

θ	Contact angle
Ε	Desorption energy
r	Particle radius
γ_{ow} .	oil/water interfacial tension
γ_{po}	Particle-oil interfacial tension
γ_{pw} ,	Particle-water interfacial tension

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1 INTRODUCTION

The pioneering work in the area of particle-stabilized foams and emulsions was conducted by Ramsden and Pickering in the 20th century and has grown in the recent years [1]. S.U Pickering gave name to the phenomenon of emulsions stabilized by solid particles, so called Pickering emulsions, which differ from traditional emulsions that are stabilized by surfactants [2,3].

Emulsions are a class of disperse systems consisting of two immiscible liquids, where one liquid is dispersed in another in the form of droplets [4]. Typically, one phase is organic (the oil phase) and the other is an aqueous phase [5]. To disperse two immiscible liquids, one needs a third agent, namely the emulsifier. The choice of the emulsifier is crucial in the formation of the emulsion and its long-term stability [4]. In this thesis, silica nanoparticles modified with hydrophobic and hydrophilic groups are used as emulsifiers to stabilize o/w Pickering emulsions.

Silica or silicone dioxide (SiO₂) is the 7th most abundant element of the earth and it has played an important role for the development for many plants and animals. In present technology, the great variety of application areas ranges from catalyst in oil refinery to microcircuits and fibber optics [6]. Silica exist at least in 12 different forms and in this work, silica nanoparticles suspended in water, also referred to as silica sols, is used [7]. There are already utilized in numerous industrial process and commercial products such as retention in paper makings as additives in paints, as binder in foundry applications, for beverage clarification, and polishing application [8].

There are several emulsion systems present in everyday life. Personal care, hairstyling products and cosmetics, pharmaceutical products, paints and coatings and food products are examples of the wide range of emulsion applications [9]. The surfactant-free character of Pickering emulsions makes them suitable for various applications [10]. For example, in cosmetics and pharmaceutical formulations, where surfactants often display adverse effects in skin irritation, food industry to stabilize products, like ice crystals in ice cream and fat particles in whipped cream [5]. Another advantage is when using colloidal silica particles an environmentally benign system can be accomplished since they rank as one of the most environmentally-friendly, industrial chemical products [11].

In this work, the Phase Inversion Temperature (PIT) method was used in order make stable emulsions [5]. In PIT method, phase inversion is driven by a temperature change without varying system composition where hydrophobic interactions are the driving forces of the phenomena [5]. Phase inversion is a commonly used method for surfactant systems and it is characterized by low energy requirements. For systems stabilized by colloidal particles, PIT is a new field to explore.

The behaviour of the surface modified particles was studied at different conditions such as temperature, salt concentration, pH of aqueous phase and oil/water ratio. The main objective of this work is to understand the system itself, which can open up for interesting applications in the future,

since PIT method applied to Pickering emulsions is to the best of our knowledge an unexplored research field.

2 AIM OF THE PROJECT

The aim of this work was to achieve thermo-responsive Pickering emulsions, stabilized with silica particles functionalized with hydrophobic and hydrophilic groups. To achieve this the work was focused on:

- Study how the emulsification abilities could be altered if changes in temperature, combined with emulsification at different conditions (pH of aqueous phase, salt concentration, oil/water ratio) are introduced.
- Apply Phase Inversion Temperature (PIT) method in order to obtain monodisperse emulsions with high stability and small droplets.

3 THEORETICAL BACKGROUND

3.1 EMULSIONS

An emulsion is a colloidal dispersion of two or more immiscible liquids where one liquid is dispersed in another in the form of droplets. Emulsions often consist of water as one phase (called aqueous phase), an organic liquid as the other phase (called oil phase) and a third agent, namely emulsifier or emulsion stabilizer. There are two main types of emulsions, i.e. oil-in-water (o/w) emulsions, when oil droplets are dispersed in water, which means that oil is the dispersed phase and the water the continuous phase, and water-in-oil (w/o) emulsions, when water is dispersed in oil, and the oil constitutes the continuous phase [3,4].



Figure 3.1 Illustration of o/w and w/o emulsion. A: oil droplets (grey) dispersed in water continuous phase (blue). Right: Water droplets (blue) dispersed in oil continuous phase (grey).

Emulsions have a large range of applications in industry and o/w emulsions are by far the most important. Common applications are food, pharmaceuticals, paint, glues, and agrochemical formulations [12,13].Spreads (margarines) it is a well know example of w/o emulsion in food industry. Emulsions are also used in cosmetic products, detergents and for liquid extraction and oil recovery [14,15]. There also exist the so called multiple emulsions which may be w/o/w or o/w/o emulsions. These systems are of interest in for example drug delivery [13].

Colloidal dispersions tend to aggregate and coalesce to decrease surface energy. In emulsions, the interfacial tension is high and therefore, the tendency to reduce the interfacial area leads to the coalescence of the dispersed droplets and separation into two phases. The choice of the emulsifier is crucial in the formation of the emulsion and its long-term stability, since it will lower the interfacial tension, reducing the importance of surface energy [4]. There are three general classes of materials that can, under proper circumstances, act as emulsifiers and/or emulsion stabilizers, being this colloidal particles, polymers and surfactants [4,16].

Surfactants (surface active agents) are usually added in order to decrease the interfacial tension and in part added stability to the system. Polymers and small colloidal particles are added primarily as stabilizers, rather than emulsifiers [4].

Traditional emulsions are stabilized by surfactants, which has a driving force to assemble at the interface, due to their amphiphilic nature [3].

3.1.1 EMULSION STABILITY

Due to oil/water immiscibility, emulsions tend to be phase separated at thermodynamic equilibrium; hence emulsion stability is one of the main problems in several industrial applications. Controlling emulsion stability during storage and use is therefore a major challenge [1,9].

The stability of emulsions is a kinetic and relative concept. An emulsion is considered stable if it is resistant to physical changes over a practical length of time, depending on the application [13,16]. However, it is important to remember that there is no such thing as a truly stable emulsion. All emulsions are thermodynamically unstable [16]. Regarding emulsion destabilization, emulsions have three common breakdown mechanisms: flocculation, creaming or sedimentation and Ostwald ripening, see Figure 3.2. 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 [1,13,17].



Figure 3.2 The different processes involved in the breakdown of an unstable emulsion. Picture taken from [1] .

Flocculation shown in Figure 3.2 (b) refers to the mutual attachment of individual emulsion drops into flocs. Creaming and sedimentation, shown by Figure 3.2 (c) are processes caused by gravity, where a concentration gradient due to the density differences between the two liquids is formed. When the oil phase has a lower density than the aqueous phase, o/w emulsion tends to cream, and w/o emulsions to sediment. Ostwald ripening shown in Figure 3.2 (d) occurs when the dispersed phase has a limited

solubility in the continuous phase so that large drops grow as smaller drops decrease in size due to the transport of soluble liquid from the small droplet through the continuous phase [1,13,16,18].

Coalescence shown in Figure 3.2 (e) refers to the joining of two (or more) drops to form a single drop of greater volume, resulting in a decreased interfacial area. Although it results in significant microscopic changes in the condition of dispersed phase, for example changes in average droplet size and distribution, but it may not immediately result in a macroscopically apparent alteration of the system. The breaking of an emulsion shown by Figure 3.2 (f) refers to a process in which a gross separation of the two phases occurs. In such an event, the identity of the individual drops is lost, along with the physical and chemical properties of the emulsion. However, obviously represents a true loss in stability of the emulsion. Another process by which an emulsion is transformed is phase inversion, where the dispersed phase becomes the continuous phase and *vice versa* [16].

Depending on the application of the emulsion, the level of emulsion break down has varying importance. For example, for many food emulsions, cream is unacceptable and an emulsion that does so would be considered broken [1, 13,16,17].

3.1.2 PICKERING EMULSIONS

Pickering emulsions are emulsions stabilized by solid particles in place of surfactants [2]. The high resistance to coalescence is a major benefit of the stabilization by solid particles [2]. The stability towards coalescence depends on the hydrophobicity of the particles [19]. Particles adsorb strongly to liquid-liquid interfaces, and the energy of attachment depends on the contact angle, θ_{ow} , that the particles make with the oil-water interface [20].



Figure 3.3 Illustration of a solid particle at an oil-water interface, positioned in equilibrium, creating the three phase contact angle θ , which on depends on the three interfacial tensions, particle-oil, γ_{po} , particle-water, γ_{pw} , oil-water γ_{ow} . The particle has θ <90°, is an o/w emulsion stabilizer [8].

Hydrophilic particles exhibit low θ_{ow} (measured into the aqueous phase) and preferentially stabilize o/w emulsions. More hydrophobic particles with substantially higher θ_{ow} stabilize w/o emulsions and the changeover in this particles occurs at $\theta = 90^{\circ}$ [3,19].

The energy required to remove the particle from the interface in given by Equation 1.1. in which the sign inside of the bracket is negative for removal into the water phase, and positive for removal into the air or oil phase. Then, according to Equation 1.1. the higher adsorption energy for particles at the oil/water interface results in a high energy input required for desorption [10,19,21]. When θ = 90° the particle is equally wet by both liquid phases and the energy of attachment of a particle to a oil-water interface is maximum [3,19]. Which means that the particles, in this conditions are strongly held at the interface and links directly to the stability of both types of emulsions [19].

$$E = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2$$
 Equation 1.1

One consequence of the very high energy of attachment of particles at the interface, relative to the thermal energy kT, is that particles once at interfaces can be thought of as effectively irreversible at interfaces. This is in sharp contrast to surfactant molecules, which adsorb and desorb on relatively fast timescale, since it is a more dynamic system. [2,3,8,22]

Equation 1.1 is valid for spherical particles with smooth, uniform surface structures, and shows that the desorption energy, depends on the contact angle, the particle radius, *r*, and the oil/water interfacial tension, γ_{ow} . Since the energy of attachment depends on the square of the particle radius, it decreases significantly for smaller particles [10,19,21].

According to the Young's Equation, Equation 1.2, the contact angle, θ , depends on the three interfacial tensions: particle-oil, γ_{po} , particle-water, γ_{pw} , oil-water γ_{ow} as can be see in Equation 1.3. [19].

$$\gamma_{po} - \gamma_{pw} = \gamma_{ow} \cos \theta_{ow}$$
 Equation 1.2
 $\cos \theta = \frac{\gamma_{po} - \gamma_{pw}}{\gamma_{ow}}$ Equation 1.3

Pickering emulsions can be substituted for classical emulsion in most applications. The surfactant-free character has attracted particular attention in cosmetics and pharmaceutical applications, in which the surfactant can cause skin irritation. Hemolytic behaviour, air entrapment and foaming are examples of other applications [2,5,7,23].

3.1.3 EMULSIFICATION PROCESS

There are several tools to make an emulsion and one thing that distinguishes them is the energy input, since they have the same principle. Higher the energy, the smaller the emulsion droplets, which

increase the stability [7]. A common way to produce an emulsion, and also present in our day life, is a kitchen hand blender which can be used to produce home-made mayonnaise for example.

In this work, Pickering emulsions were produced through homogenization using an Ultra Turrax (Figure 3.4). It generates much higher shear forces than a regular blender thanks to the two blades that move very close to each other to produce fine emulsions.



Figure 3.4 Ultra Turrax used for emulsification.

3.2 STABILITY OF COLLOIDAL SILICA

The stability, type (o/w or w/o), morphology and characters of Pickering emulsions are highly dependent on the properties of solid particles. Colloidal Silica is one of the most extensively studied particles as Pickering emulsifiers because are easily obtained and modified [2].

Colloidal silica is a concentrated dispersion of a discrete amorphous silica particles in a liquid with the general molecular formula SiO_2 [24]. If the liquid is organic the suspension is called *organosol* and when the liquid is water, most commonly, it is referred as *aquasol* or *hydrosol* [24]. The particle size is small enough to be unaffected by gravitational forces yet large enough to disassociate from a true solution. This gives a span of a particle diameter between 1 a 1000 nm but a characteristic range of commercial silica sols is between 5 to 100 nm [24]. In this work the colloidal systems are all water-based and will be referred to simply as *silica sols*.

The surface of silica particles has been studied for a long time. The nature of the colloidal silica depends on the status of its hydrate or hydroxylic cover. The bulk structure terminates at the surface at two different ways: oxygen on the surface through siloxane bridges (\equiv Si-O-Si \equiv) or silanol groups (\equiv Si-OH) [24,25]. The structure of the surface is important for the properties of the colloidal silica particle and can be modified to tune the silica performed [6].

Bare silica particles are inherently hydrophilic due to the OH groups thus generally unable to stabilize Pickering emulsions made with common oils because of the total wetting of the silica by the water. However, stable o/w Pickering emulsions stabilized by bare silica can be prepared with polar oils [2]. Surface modification of the solid particles can make it more hydrophobic in order to meet conditions of partial wetting by water and oil. In this work, the silica surface was functionalized with hydrophilic and hydrophobic groups. The silica particles used are modified with the hydrophilic methyl poly(ethylene glycol) silane, called (mPEG) and hydrophobic propyl silane, (Figure 3.5). The purpose of functionalization was to find a surface chemistry of the particles suitable for emulsion applications. The functionalized particle where characterized in two ways, quantitative information (degree of functionalization and surface activity) and qualitative evaluation (flocculation behaviour and emulsification abilities) [7].





Functionalization with mPEG silane efficiently reduces the surface charge of the silica surface and generates surface-active particles. These properties in combination with the alkyl groups that increase the hydrophobicity of the particles would render a material suitable as both an emulsifier and an emulsion stabilizer [7,26].

The functionalized silica particle was previously analysed using Nuclear Magnetic Resonance (NMR) spectroscopy to determine the amount of bound surface species on the silica particles. The size and the zeta potential of the particles were measured using Dynamic Light Scattering (DLS), which is a widely used technique for determining particle distribution, generally within a range of a few nm up to 1 μ m. The Laser diffraction was used for determination of the emulsion droplet size distributions [7].

One big advantage of colloidal silica is that they ranked as one of the most environmentally friendly products in industrial chemistry [24]. Colloidal silica has a wide range of applications, being these adhesives, beverage clarification, cleaning products, electronics, paper and packing, textile, water treatment in others [7,26].

3.2.1 STABILITY OF SILICA SOLS

The repulsive forces between two colloidal particles in a colloidal suspension need to be larger than the attractive forces to keep the particles from aggregation [27]. A silica sol is said to be stable if the particles do not settle or aggregate at a significant rate. Gelation, coagulation and flocculation are different forms of aggregation [24].

Above pH 2 the silica surface will be negatively charged due to the deprotonation of the silanol groups with cations acting as counterions. Due to the increased surface charge of the silica particles at increased pH the silica sol has a high stability towards gelling due to the mutual repulsion between the particles. At the isoelectric point, around pH 2, the silica sol is metastable. The silica sol also has a high stability at towards gelling at low pH due to the large possibilities to form hydrogen bounds between the silanol groups and the water, which is possible since very few or no protons are exchanged for cations. The formation of hydrogen bonds between the water and the silica surface reduce the flocculation rate since a layer of water is physically adsorbed to the silica surface. When the sol displays colloidal stability, the particles do not settle or aggregate at significant rate [7,6,28,29].

Gelling occurs when the particles are linked in branched chains, filling the volume of the sol and resulting in viscosity increase, which eventually solidifies the sol into a gel. The stability of silica sol is decreased by the addition of salt since stability is further decreased when the charge is increase. During flocculation, the particles are linked by bridges induced by a flocculation agent long enough to allow the aggregate structure to remain open and voluminous. Coagulation leads to the formation of compacts aggregates that are macroscopically separated and in which the silica concentration increases [6,7].

Stability can also be enhanced with surface modification, an example is surface modification with silanes, which reduces the surface charge of the particles and the steric stabilization phenomenon allows these sols to be stable from pH 2-11 [7].

3.3 CLOUD POINT AND PIT

Cloud point is the temperature at which a solution becomes cloudy due to an onset of phase separation caused by conformational changes of the polyoxyethylene chain, where a polar conformation is dominating at low temperatures and non-polar conformation at higher temperatures [30]. This results in an increase of hydrophobicity [13]. The clouding point depends strongly on the polyoxyethylene chain length and less influenced by the hydrophobic part.

Clouding is also strongly dependent on co-solutes such as electrolytes by salting in and salting out. The decrease of the cloud point (CP) by decreasing the solubility of non-ionic surfactant, becoming less soluble, at high salt concentrations, is called salting out, while the opposite effect is called salting in. However, the effect of addition of electrolytes is not absolute and may change with concentration [13,30].

A solution of a non-ionic surfactant containing polyoxyethylene is known to have cloud points in a well defined temperature [31]. In this work, since mPEG chains are attached to the silica particles used as emulsifiers, cloud points may well exist in this systems. Unpublished preliminary studies indicate that exists a CP for silica particles functionalized with mPEG. In similar so surfactants systems, when the salt concentration increases, the cloud point decrease.

The CP can be used as a guideline to study phase inversion conditions since clouding occurs below, but close to PIT [4,30]. The PIT is the temperature at which an emulsion invert from o/w to w/o and first introduced in 1969. It has received more attention in the past few years due to its advantages such as low cost over other high energy methods [32]. In PIT, phase inversion is given by a temperature change without varying system compositions [5].

Hydrophobic interactions are the driving force of the phenomena and are important for the phenomena description [5]. In the same way as CP, PIT works on the basis of the changes in the affinity of a polyoxyethylene-type non-ionic surfactant with temperature [32]. In this silica particles functionalized with mPEG and propyl groups, is strongly affected by the mPEG functionalization.

The PIT can be determined by measuring the electrical conductivity of an emulsion system with increasing the temperature, since the electrical conductivity of w/o emulsions comparing with o/w ones differs by several orders in magnitude. The conductivity can also be used to determine the type of emulsion [5,33,34].

The PIT measurements can be used for a guide for preparation of stable emulsions since emulsions with very small droplet sizes can be produced when the emulsification process is carried out near the PIT temperature, however, they are very unstable towards coalescence at that temperature, due to the low surface tension (see Figure 3.6) [4,5,35]. Thus, a rapid cooling process and with a storage temperature far away from the PIT temperature are needed to produce fine and stable o/w emulsions.



Figure 3.6 Variation of interfacial tension with temperature of an w/o emulsion [4].

It is important to take into account that the PIT varies for every given system depending on the components. The PIT is a low energy route to make stable emulsions [5].

3.4 FACTORS THAT AFFECT EMULSIFICATION ABILITIES

The temperature, the pH of aqueous phase and the addition of an electrolyte are important parameters in emulsification abilities in Pickering emulsions in general. Since the silica particles were functionalized with mPEG and propyl groups, it is important to understand how this variables act in terms of silica—silica and silica—PEG interactions and consequently how they influence the emulsion stability in these project.

3.4.1 TEMPERATURE

Changes in temperature will influence the polarity of the mPEG chains since the polar conformation will dominate at lower temperatures and the non polar at higher temperature. Also when the temperature increases the interaction with mPEG and water is affected. The solubility of the mPEG will decrease leading to a less favourably interaction with water [7,8,13]. This intramolecular conformational change of mPEG chains leads to an inversion of the emulsions and the PIT can be observed.

3.4.2 PH OF AQUEOUS PHASE

The aqueous phase of the emulsions is constituted by water, silica particles and salt (when added).

The pH is an important parameter in disperse systems. The surface charge of the silica particles is affected by the pH of the aqueous phase. An increase in pH also increases the surface charge of the silica particle due to deprotonation of the silanol groups. A decrease in pH will decrease the surface charge (due to protonation), facilitating the adsorption of the particles at the oil-water interfaces [8, 36,37].

pH changes will also influence the interactions between mPEG and silica sols since they are temperature and pH dependent [38]. The physical adsorption of mPEG to silica surface is caused by hydrogen bonding between the silanol groups of the silica surface and the ether oxygen of the mPEG chain. As pH increased the deprotonation of silanol groups is increased thus decreasing the possibilities of hydrogen bonding between mPEG and silica surface. So at lower pH, the mPEG—silica interactions increase and weak bridge flocculation can occur (see Figure 3.7) [38]. Contrary at higher pH, the mPEG—silica interaction decrease, and the mPEG would point out from the particle surface.



Figure 3.7 Hypothesis of flocculation behaviour of silica particles in function of pH.

The adsorption of mPEG to the silica surface is decreased as the pH is increased. At lower pH weak flocculation is achieved. Previous studies show that flocculation, together with reduced surface charge density at acidic conditions clearly facilitated the emulsion formation [7,30,34].

3.4.3 ELECTROLYTE

When salt is added to the silica suspension, the charges are screening. Then the Van der Walls attraction become dominant and can therefore induce flocculation [10,36].

The addition of salt also decrease the solubility of the mPEG in water, called salting out effect of the particle [13,39]. The salt will facilitate the adsorption at the oil interface by altering the hydrophobicity of the particles, making the particles more hydrophobic. These phenomena also make the particles become close to each other and weak flocculated. Flocculation clearly facilitates the emulsion droplet formation [26]. Weakly flocculated particles have been shown to be beneficial for good emulsification abilities, since non-flocculated samples produced emulsions with larger emulsions droplets [7,10,26,37]. At higher salt concentration the flocs size and extent may be larger and the adsorption is reduced, which show that strongly flocculated particles are poor emulsifiers [10,37].

4 MATERIALS AND METHODS

This section characterises the materials used in the present research, such as chemical's company and purity. Also, the method followed in all experiments is presented in the current section. The set up used is also shown for a better understanding of the laboratory techniques used in the master's thesis work.

The experiments for the development of the thesis were carried out in the laboratory of Chalmers University of Technology, in Gothenburg, and in Akzo Nobel Pulp and Performance AB, in Bohus.

4.1 MATERIALS

The chemicals used in this research are listed in Table 4.1. Butanol was chosen as oil phase in all carried experiments since these had been successfully emulsified used unmodified silica particles by Frelichowaska and with modified silica particles by Sanna Björkegren [7,40].

hemical Company and Purity			
1-butanol	Merck, Germany, 99.5%		
Calcium Chloride (CaCl ₂)	Merck, Germany, 99%		
Hydrochloric acid (HCI)	Sigma-Aldrich, Sweden, 37% conc.		
1-octanol	Aldrich, Sweden, 99%		
Silicone Oil	VWR, BDH Chemicals		
Levasil SP2138 (Silica sol)	AkzoNobel Pulp and Performance Chemicals, 40 wt\% SiO_2 , sodium stabilized.		
Sodium Hydroxide (NaOH)	Sigma-Aldrich, Sweden, 98%		
Sudan I	Sigma-Aldrich, Sweden, 95%		

Table 4.1 Chemicals used in the experiments

4.2 METHODS

4.2.1 PURIFICATION BY ULTRAFILTRATION (UF)

The silica sol was purified before usage through UF in order to remove unreacted silence species and to reduce the salt content. Known from previous studies [8], UF removed 70—80 % of unbound silanes and the membrane specifications are listed on Table 4.2. In contrast to ordinary filtration, UF

does not create any filter cake and the colloidal silica remains dispersed while water and small molecules are filtered off. The ultrafiltration cell is filled with around 60 grams of the non-purified sample and approximately 250 ml with water. The UF cell was washed with water and NaOH (0.1 M) before each UF.

Brand	PALL
Material of constructions	Filter Media: Omega [™] membrane
Pore size	76mm
Effective filtration Area	41.8 cm ²
pH Range	1-14
Operating Temperature Range	0-40°C

Table 4.2 Specifications of Ultrafiltration membrane disc filters

4.2.2 Phase Inversion Temperature (PIT) Method

In the same way as non-ionic surfactants, silica particles functionalized with mPEG and propyl groups in solution are sensitive to changes in temperature, due to the mPEG functionalization. The Phase Temperature (PIT) is the temperature at which the emulsion inverts from o/w to w/o. This temperature can be found by heating the emulsion in an oil-bath while homogenizing the mixture using an Ultra Turrax and measuring the conductivity through a digital conductivity meter. If the conductivity is high, it means that the system is still o/w, since the aqueous phase is the continuous phase, and the conductivity drops to a value much lower than the initial conductivity of the aqueous phase, it means that the emulsion has inverted to w/o and the oil is the continuous phase, since the conductivity of pure oil is almost zero μ S/cm. A clear difference is expected in conductivity when the emulsion inverts [31,41].

4.2.3 MICROSCOPY

In this work, emulsions were observed with microscopy using a Carl Zeiss Fluo microscope equipped with an Olympus digital camera. The emulsions were observed concentrated or diluted in its continuous phase. The optical microscopy was used to distinguish between o/w emulsions and w/o and to analyse them. In addition, a fluorescence lamp was used.

4.3 EXPERIMENTAL PROCEDURE

The experimental work consisted of two main parts: the PIT method and emulsification process for making emulsion diagrams.

4.3.1 PIT METHOD

In PIT experiments, the following variables were kept constant: emulsion volume (80 ml), 50/50 % oil/water volume ratio, which gives a 40,5 wt% of oil, silica-to-oil ratio of 0.075 g SiO₂/g oil, which gives a silica concentration of 6.1wt% in the aqueous phase, homogenization rate (12000 rpm).

4.3.1.1 SILICA CONCENTRATION

The silica concentration was calculated based on silica-to-oil ratio knowing from previous studies [7] that it would influence the emulsification abilities, since the available surface area of silica particles restricts the possible size of emulsion droplets. In order to ensure the presence of enough silica particles to stabilize the emulsions, the ratio 0.075 g SiO₂/g oil was kept constant in all emulsions during this work. From previous experiences, this silica-to-oil ratio would provide a surface area large enough to stabilize smaller emulsion droplets. Below, there is an example of silica concentration in 50/50 % (v/v) emulsion.

Calculation of concentration of silica (wt%) in 50/50 volume ratio emulsion in a total volume of 80 ml.

Oil phase: 40 ml of butanol ρ (butanol)=0.81 g/ml m butanol = 0.81×40 = 32,4 g of butanol Desired 0.075 g SiO₂/g oil

 $m Silica = 0.075 \times 32.4 = 2.43 g of Silica$

The mass concentration of silica in 50/50 emulsion is

 $\frac{\text{total of silica}}{\text{aquous phase}} \times 100 = \frac{2.43}{40} \times 100 = 6.1 \text{ wt\%}$

4.3.1.2 HOMOGENIZATION RATE

The homogenization rate of 12000 rpm was chosen according previous experiments that show that the energy input given during the emulsification is an important parameter, and an increase in the shear rate decrease the emulsions droplet size [7].

 Preparation of Aqueous phase: The aqueous phase was prepared by mixing the modified silica particles, desired amount of calcium chloride and distilled water in a round glass beaker. Following, the pH was adjusted with hydrochloric acid (0.5 M) and sodium hydroxide (0.1 M). The electrical conductivity of the aqueous phase was measured in order to compare with the conductivity of the emulsion obtained.

- 2. PIT method: The aqueous phase was mixed with the oil phase (butanol) and emulsified using an Ultra Turrax homogenizer operating at 12000 rpm. The emulsification started at 25°C to around ten degrees after observed PIT. Conductivity was measured continuously. In some emulsions after homogenization, half of the emulsion was immediately cooled to room temperature and the other half kept at PIT. Other emulsions were continuously stirred during the cooling process to study the reversibility. The cooled emulsions where stored at 20±1 °C.
- **3.** Characterization of emulsions: The emulsion type was identified trough conductivity measurements. Low conductivity values indicate oil continuous emulsions (w/o) whereas relatively high conductivity values are associated with water continuous emulsions (w/o). The emulsions stability were analysed by visual aspect, towards cream and sedimentation and by microscopy. Emulsions were stored at room temperature (21 ± 3 °C).



Figure 4.1 Experimental set-up used for PIT method.

4.3.2 EMULSIFICATION PROCESS FOR MAKING EMULSION DIAGRAMS

In emulsions for emulsion diagrams, the following variables were kept constant: emulsion volume (10 ml), pH of aqueous phase (3.8—4.2), homogenization rate (12000 rpm), silica-to-oil ratio of 0.075 g SiO_2/g oil, which gives a silica concentration of 6.1wt% in the aqueous phase.

- Preparation of Aqueous phase: The aqueous phase was prepared by mixing the modified silica particles, desired amount of calcium chloride and distilled water in a round glass beaker. Following, the pH was adjusted with hydrochloric acid (0.5 M) and sodium hydroxide (0.1 M) to 4 ± 0,2.The electrical conductivity of the aqueous phase was measured in order to compare with the conductivity of the emulsion obtained.
- 2. Preparation of emulsions: A 10 ml mixture of oil, water, silica and /or without salt was emulsified in a 25 ml round glass vessel with an Ultra Turrax homogenizer operating at 12000 rpm for 10 min at a constant temperature. After emulsification the emulsions were cooled in ice until room temperature.
- 3. Characterization of emulsions: Conductivity measurements were made immediately after emulsification and at room temperature, after quickly cooling in ice. Emulsions were stored at room temperature (21 ± 3 °C). The emulsions where characterized using microscopic and by visual aspect.



Figure 4.2 Experimental set up used for emulsification process for emulsion diagrams.

The same protocol was followed during the all the work, aiming to keep the same timeframes in order to minimize the experimental errors. Table 4.3 presents the list of equipment used in the experiments carried out during the master's thesis.

Equipments	Brand	
Heating plate	IKA	
pH meater	Metrohm	
Conductivity meater	Meater Taledo	
Ultra Turrax	IKA	
UF	Amicom	

Table 4.3 Equipments and respective brand used in all carried experiences.

5 RESULTS AND DISCUSSION

In the first part of this section, the results of PIT experiments with different types of functionalized silica particles are presented. In the second part, the effect of salt concentration and pH on the PIT is discussed. Also, the results from the emulsification ability of functionalized silica particles with mPEG and propyl groups, as function of salt concentration and pH, are evaluated. In the third and final part of the section, the emulsion diagrams are presented and discussed.

5.1 PHASE INVERSION TEMPERATURE

The main purpose of this work was to investigate phase inversion conditions, which can be used to control the emulsion stability. The PIT were studied by preparing Pickering emulsions with 40.5 wt% of oil, which gives 50/50 volume ratio and 6.1 wt% of silica particles in the water phase, which gives 0,075 g/g silica-to-oil ratio.

5.1.1 PIT METHOD WITH DIFFERENT TYPES OF FUNCTIONALIZED SILICA PARTICLES

Different types of functionalized silica particles were studied as emulsifiers through their hydrophobicity, hydrophilicity and a combination of hydrophobicity and hydrophilicity. In this study, emulsions consisting of water, butanol as oil phase and calcium chloride (0.5 M) as electrolyte, were stabilized by silica particles functionalized with hydrophobic propyl silane groups, hydrophilic mPEG silane groups and with silica particles functionalized with mPEG and propyl groups. Table 5.1 presents the specifications of the particles used. The pH of the aqueous phase was adjusted to pH 4 \pm 0.3 using HCI (aq.).

Table 5.1 Specification of the functionalized silica sols used in this study. Amounts of added mPEG silane and propyl groups, specific surface area before functionalization, reduction of SSA after functionalization and particle diameter are presented. Relatively large amount of the mPEG groups (around 50-80%) remain unreacted. SSA measurements and the surface functionalization were made by Sanna Björkegren.

Original silica sol	Functionalization (μmol sinlane /m ² S _i O ₂) ^[1]	SSA (m²/g) ^[2]	Reduction of SSA (%) ^[3]	DLS particle diameter (d _{v,} nm) ^[4]	
Levasil SP2138 with	1 propyl	130	39	26.7	
propyl+mPEG	0.5 mPEG			20	
Levasil SP2138 with propyl	1 propyl	130	19	30.1	
Levasil SP2138 with mPEG	2 mPEG	130	63	28.2	

^[1] Modification (added amounts) of propyl and mPEG groups in mol of added silane per area of silica particle.

^[2] Specific surface average value of colloidal silica particle, measured by Sears Titration [42].

^[3] Reduction of SSA after functionalization in %.

^[4] Particle diameter, volume average, is given as measured with DLS at alkaline conditions at 1wt% of SiO₂ measured by Sanna Björkegren.

During emulsification with particles modified with only mPEG silane an emulsion was formed, but immediately after sheering the emulsion completely phase separated. It was evident that the emulsion was unstable and it only formed because of the energy input given during the emulsification process. These results are in agreement with previous studies [7,8] showing that emulsions undergo complete phase separation within twenty four hours when only mPEG functionalized particles are used as emulsion stabilizers.



Figure 5.1 Pictures of emulsions obtained. Emulsion A: Picture captured immediately after homogenization process. The emulsion is stabilized by silica particles modified with mPEG groups. Emulsion B: Picture captured one week after homogenization process, the emulsion is stabilized by silica particles modified with mPEG and propyl groups. Emulsion C: Picture captured one week after homogenization process. The emulsions is stabilized by silica particles modified with only propyl groups. The pH of aqueous phase was adjusted to pH4 and 0.5 M of CaCl₂ was added to the aqueous phase.

Figure 5.1, (emulsion A) clearly shows the two phases formed immediately after homogenization process with particles only modified with mPEG groups. This result show that these particles are too hydrophilic and, therefore, not suitable as emulsifiers. Figure 5.1, also shows that emulsion C, with only propyl groups as emulsifier, starts to cream, as pointed by the blue line. This was visible within less than twenty four hours. The emulsion B, stabilized by silica particles modified with both groups, looks stable, after one week. It is possible to conclude that particles only modified with propyl groups are enough to produce an emulsion due to the hydrophobic character, but those are not stable as emulsions stabilized by particles functionalized with both groups.

To investigate a possible presence of PIT, emulsification was performed during an increase of temperature. The PIT could be identified from the electrical conductivity versus temperature plots where the conductivity drops significantly, down to a value much lower than the initial conductivity of the aqueous phases, when the emulsion inverts from o/w to w/o [33,34,43].



Figure 5.2 Conductivity as function of temperature during emulsification of butanol in water (0.5 M of CaCl₂ and pH 4) using particles modified with mPEG groups (green=) as emulsifiers, emulsion A; mPEG and propyl groups (blue[•]) as emulsifiers, emulsion B; with propyl groups (red[•]) as emulsifiers, emulsion C.

Figure 5.2 shows that, in the emulsion with silica particles functionalized with only propyl groups, the conductivity increases with temperature until around 100 °C, when the experiment was stopped because the emulsion started to boil at this temperature. An increase in solution's temperature leads to an increase in its conductivity [44], which explains the result observed. In emulsions with silica functionalized with both mPEG and propyl groups or only mPEG groups, there is an initial steady increase in conductivity with temperature and then a sharp decrease above a specific temperature. This behaviour of a sudden drop in conductivity is indicative of phase inversion, and in this specific case from o/w emulsion with a water continuous phase (high conductivity) to w/o emulsion with an oil continuous phase (low conductivity). The phase inversion conditions are presented in Table 5.2.

Table 5.2 Values of conductivity of aqueous phase, phase inversion temperature and conductivity at phase inversion of emulsions stabilized by silica particles modified with only mPEG groups (emulsion A) and by silica particles modified with propyl and mPEG groups (emulsion B) and. The emulsions contain 0.5 M of CaCl₂ added to the aqueous phase, pH 4 of aqueous phase, 50/50 %(v/v) and the ratio silca-to-oil is 0.075 g/g.

Emulsion	Cond. _{aq. phase} (mS/cm)	PIT(°C)	Cond. _{phase invertion} (µS/cm)
A	58.75	85 ° C	1660
В	39.04	57 ° C	586.2

Figure 5.2 shows that PIT only occurs when particles modified with mPEG groups are used as emulsifiers. It shows that PIT is directly related to the cloud point that strongly depends on conformational changes of the mPEG chain due to the temperature [13,31], as explained before in section Theoretical Background.

It is possible to conclude that particles functionalized with both groups are more suitable as emulsifiers and emulsion stabilizers. With these particles, the PIT was achieved and the emulsions were stable towards coalescence and creaming for at least one month. As a consequence, in all coming results, these particles were used, in order to achieve the PIT and study the emulsification abilities.

The PIT experiment with silica particles functionalized with mPEG and propyl groups with 0.5 M of CaCl₂ in the water phase, and at pH 4, was repeated twice with more data points, and the results are shown in Figure 5.3. The same batch of particles was investigated during ageing and three different results of PIT were obtained. This change in PIT can be due to a destabilization of the particles over ecrease on the PIT shows that they become more sensitive towards aggregation in time. The d the presence of higher salt concentrations. Comparing to non-salt samples, Figure 5.3 b) the PIT values are in the same range. No ageing affect is visible for emulsions with no added salt. This behaviour may be indicative of the limit of the concentration of salt that the particle can hold. Previous studies [7] show that the stability of the particles only functionalized with mPEG groups don not change over time. Also, the cloud point study with particles only modified with mPEG groups indicate that the cloud point does not change due to the ageing of he particles. This increased sensitivity towards salt of particles functionalized with propyl and mPEG groups may be explained by the introduction of the propyl groups. With propyl groups functionalization the flocculation is more pronounced and in addition with higher concentration, that also induced flocculation can be one explanation for this sensitive destabilization.

Given the three different results, the weighted average of 51 °C is the value presented for the PIT of emulsions with silica particles functionalized with mPEG and propyl groups, 0.5 M of $CaCl_2$ in the aqueous phase, at pH 4.



Figure 5.3 Conductivity as function of temperature during emulsification of butanol in water using particles modified with mPEG and propyl groups as emulsifier at pH 4. a): Emulsions with 0.5 M of CaCl₂ added to aqueous phase. PIT value of 53 °C obtained for the second experiment (blue ◆) made three months after functionalization of the silica particles, and 43°C obtained for the third experiment (orange ■) made one month after the second experiment. b): Emulsion with no added salt, PIT value of 74 °C obtained for the first experiment (yellow ▲) made three months after functionalization of the second experiment (green ●) made one month after the first experiment (green ●) made one month after the first experiment (green ●) made one month after the first experiment (green ●) made one month after the first experiment (green ●) made one month after the first experiment (green ●) made one month after the first experiment (green ●) made one month after the first experiment.

5.1.2 EFFECT OF SALT CONCENTRATION AND PH ON PIT

A set of factors that could affect the PIT were investigated. In order to understand if PIT is affected by the pH of aqueous phase and salt concentration, experiments with different pH of aqueous phase (pH 2, pH 4, pH 7, pH 9) and different salt concentrations (no salt, 0.1 M, 0.5 M) were performed.



Figure 5.4. PIT as function of salt concentration for different pH of aqueous phase for emulsions stabilized by silica particles functionalized with mPEG and propyl groups.

The data from Figure 5.4 shows that PIT is influenced by the pH and salt concentration. In relation to the salt concentration, it is possible to see that the PIT increase when the salt concentration decrease [7,8,13]. The presence of salt with increasing temperature decrease the solubility of the mPEG due to the salting out effect, increasing the hydrophobicity of the particles. This will facilitate the adsorption at the oil interface and consequently reduce the PIT increasing the salt concentration, as Figure 5.4 shows [45].

Figure 5.4 shows that PIT increases with increasing pH. At higher pH higher the charge of the silica particles due to deprotonation of the silanol groups [7,26]. When the silica particles are charged is more difficult to stabilize the emulsion, due to the formation of SiO⁻ groups on the silica surface, which make the particles more hydrophilic [37]. The hydrophilicity of the particles increase and consequently the PIT also increase. Lower the pH, lower the surface charge of the silica particles, and thus more hydrophobic particles.

At lower pH the silica oil interactions increase. It is known that attractive forces between silica and poly (etylene oxide) exist and are pH and temperature dependent [38,46]. Silica modified particles with just mPEG display a pH flocculation behaviour. From Figure 5.4, with particles modified with both groups, it was also seen this dependence due to the presence of mPEG. Thus, at a lower pH it is possible to obtain bridges between the particles due to the PEG-silica interactions because of a medium/low

surface coverage of the silica particles. This will provide a weak flocculation that is beneficial for emulsification abilities. This can also contribute to decrease the cloud point and consequently the PIT.



Figure 5.5 Schematic draw of probable position of particles at a curved interface. For $\theta < 90^{\circ}$, solid stabilized o/w emulsions (left). With temperature effect, and facilitating by the presence of salt, the particles at the interface move deeper to the oil (right), and form w/o emulsions, where $\theta > 90^{\circ}$ [10].

The PIT was not achieved below 100 °C for emulsions at pH 9 with and without salt, which indicate that the PIT is probably higher than 100 °C. For the emulsion without salt, this result support the CP experiment, that the CP was also not achieved below 100 °C at the same conditions. For the emulsification with 0.5 M of CaCl₂ added to the aqueous phase, the emulsion completely gel and the PIT was not achieved, this may be explained by the higher salt concentration and higher pH.

5.2 EMULSIFICATION ABILITIES – PH, TEMPERATURE AND SALT CONCENTRATION

Emulsification abilities of silica particles functionalized with mPEG and propyl groups were studied as function of salt concentration and pH by varying these parameters in order to see the effect on emulsion stability. The emulsions were analysed visually to evaluate the stability towards creaming or sedimentation and by microscopy to determine the droplets size and the stability towards coalescence.

5.2.1 EFFECT OF PH

The pH is an important parameter for colloidal stability and also for emulsification abilities [7]. To increase the understanding of the system and the pH effect in the emulsification abilities emulsions were made at pH 4, pH 7 and pH 9 with and without salt (0.5 M of CaCl₂) during 10 min homogenization at 45 ° C.



Figure 5.6 Emulsions obtained for pH study. Emulsions obtained during 10 min emulsification at 45 °C, of butanol in water at different pH, stabilized by silica particles functionalized with mPEG and propyl groups. a): Picture captured two weeks after homogenization of emulsions at pH 4 with no added salt (emulsion D), with 0.5 M of CaCl₂ added to aqueous phase (emulsion E). b): Microscopy images of emulsification of emulsions at pH 7 with no added salt (emulsion F), with 0.5 M of CaCl₂ added to aqueous phase (cemulsion F), with 0.5 M of CaCl₂ added to aqueous phase (emulsion G) .d): Microscopy images of emulsion G captured the same day the emulsion was made. e): Pictures captured one week after of emulsions was made. e): Pictures captured one week after of emulsions at pH 9, emulsion with no added salt (emulsion H), emulsion with 0.5 M of CaCl₂ added to aqueous phase (emulsion I). f): Microscopy images of emulsion I captured the same day the emulsion was made, the emulsion droplets are coalescing.

Figure 5.6 a) shows that both emulsions at pH 4, with and without salt, start to cream. The microscopy image of the emulsion with 0.5 M of CaCl₂ added to the aqueous phase show different droplets sizes. This may be indicative of a border behaviour, since the emulsification was at 45 °C and the PIT for this emulsions was obtained between 43 °C and 57°C. This behavior can be similar to a bi continuous phase in surfactants system. It is known that emulsions are unstable at PIT due to the low surface tension [4], which can be explain the instability observed in the emulsion E.

The emulsion at pH 7 and without the presence of salt (emulsion F) completely phase separated in less than one week due to the high surface charge of the silica particles. Comparing with emulsion G, the presence of salt makes an important difference on emulsion aspect [10,26]. Emulsion G was stable towards coalescence and with small and close-packed droplets. After one week it started to cream. At pH 7 in the presence of salt the screening of charges and the repulsion of the particles make them stable against gel.

Figure 5.6 e) shows that at pH 9, without salt, the emulsion starts to cream within 12 hours. From the microscopy image, Figure 5.6 f), it is clear that the emulsion droplets undergo coalescence in the presence of salt. The picture was taken at the same day as the emulsion was made. At pH 9 the emulsions are too charged, the particles are too hydrophilic that the silica particles are in the aqueous phase.

It was also observed that the emulsion at pH 9 gel and the ones at pH 7 and pH4 did not gel, in the presence of salt This may be explained by the different behaviour of the surface groups due to the pH. At pH 7 the silica-mPEG interactions are enough to protect from aggregation, the m-PEG stays on the interface, even in the presence of salt. A possible behaviour of the mPEG groups is shown on Figure 5.7 (right), the mPEG stays on the surface of the functionalized particle, which makes it stable against gelling. At pH 9 the mPEG is sticking out from the particle surface due to the high surface charge facilitating the silica-silica interactions and allowing for irreversible aggregation of the silica particles. This behaviour is due to the functionalization of the silica particles.



Figure 5.7 Schematic drawing of the mPEG groups in the surface of the silica particle due to the different pH.

Previous studies [7] showed that the best performing pH of the emulsifiers is the lower range (pH<5), since it is favourable for emulsion stability and formation due to flocculation and reduced surface charge of the silica particles, since strongly flocculated particles are poor emulsifiers. Changes in pH of the system will alter the particle wettability and eventually destabilise the emulsions [37]. The particles should be wet by both liquid phases and should be weak flocculated to effectively stabilize emulsions and strongly flocculated particles are poor emulsifiers [37].

It was obtained stable emulsions at pH 4 and pH7 with low salt concentration. Figure 5.8 shows that in the emulsion K, at pH 4, the droplets are smaller then in the emulsion J, at pH 7. Knowing that an emulsions is more stable if has small and packed droplets the pH 4 is more suitable to stabilise these emulsions.



Figure 5.8 Pictures of emulsions captured at the same day, obtained after cooling during homogenization. The Emulsions were stabilized with silica particles functionalized with mPEG and propyl groups as emulsifiers, butanol, water, and 0.1 M of CaCl₂ added to the aqueous phase a): emulsion prepared at pH 7 of aqueous phase (emulsion J). b): emulsion prepared at pH4 of aqueous phase (emulsion K).

5.2.2 EFFECT OF SALT CONCENTRATION

The effect of the electrolyte on emulsification ability of silica functionalized particles with propyl and mPEG groups were studied to explore the optimum salt concentration. Emulsions with different salt concentrations were made and analysed in terms of stability towards creaming and coalescence. The droplet size was analysed by microscopy. The pH of aqueous phase was adjusted to pH 4 \pm 0.3 using HCI (aq). The salt concentration was varied from 0.5 M to no added salt. The list of emulsions made is presented in Table 5.3.

Table 5.3 List of emulsions prepared at pH4

Emulsion	Salt Concentration	PIT(° C)	
L	No salt	75 ^[1]	
М	0.1 mM	70 ^[2]	
Ν	0.1 mM	70 ^[2]	
0	0.1 M	60 ^[3]	
Р	0.5 M	51 ^[4]	

^[1] Weight average of two experiments.

^[2] Weight average of two experiments.

^[3] Weight average of three experiments.

^[4] Weight average of three experiments.

Figure Figure 5.9 clearly shows that the creamed phase increases with the salt concentration. The emulsion P with the higher salt concentration tested has the bigger creamed phase observed and also the emulsion L with so added salt presents the small creamed phase.



Figure 5.9 Pictures of emulsions obtained, showing the degree of creaming. The emulsions were stabilized with silica particles functionalized with mPEG and propyl groups as emulsifiers, butanol, water, and CaCl₂. The emulsions contain 50/50 % (v/v) and the ratio silica-to-oil is 0.075 g/g. - Salt concentration decreases from left to right. Picture captured after 3 months of emulsification Emulsions cooled during homogenization.

Figure 5.9 was captured three months after emulsions formation. In comparison with pictures taken one month after is possible to compare that the cream phase had not increased, which is a good stability signal. However, one month after the emulsions formation, an oil phase was not visible on the top of the emulsions and three months after it was, seen in Figure 5.9 (The emulsion M is the one with less oil phase.)

The creaming rate is directly proportional to the droplets diameter, and can be estimated from Stokes' equation, Equation 5.1, where *r* is the droplet radius, ρ the density of the droplets, ρ_0 the density of the medium, *g* is the local acceleration due to gravity and η the viscosity of the continuous phase [18].

$$v = \frac{2r^2(\rho - \rho_0)g}{9\eta}$$
 Equation 5.1

According to Equation 5.1, creaming is reduced by small droplet radius and consequently. From Figure 5.10 when the salt concentration decrease the droplets size decrease. Microscopy images show that when the salt concentration decreases the droplet size decreases.



Figure 5.10 Microscopy images of emulsified butanol in water using silica particles with mPEG and propyl groups as emulsifiers with 0.5 M of CaCl₂ added to the aqueous phase (emulsion P), 0.1 M of CaCl₂ (emulsion O), 0.1 mM (emulsion M) of CaCl₂ added to the aqueous-phase and no added salt (emulsion L). The emulsions contain 50/50 % (v/v) and the ratio silica-to-oil is 0.075 g/g. Images captured at the same day as emulsion formation.

Figure 5.10 show that emulsions with no added salt (emulsion L) small droplets were obtained, but in the presence of salt there are more mono dispersed. A possible explanation for the aspect seen in emulsions P is the higher salt concentration, which can destabilize the emulsions due to higher flocculation of the particles and consequently break them, since the presence of salt induce flocculation of the silica particles due to the screening of the charges [8,47,48]. It is possible to conclude that 0.5 M is a higher salt concentration and therefore not a suitable to stabilize these emulsions.

Figure 5.11 show that emulsion O is stable after three months, unlike emulsion L. This can be explained by the presence of salt [7,8,20].



Figure 5.11 Microscopy images of emulsified butanol in water with silica particles with mPEG and propyl groups as emulsifiers with 0.1 M of $CaCl_2$ (emulsion O) and no added salt (emulsion L). Images captured three months after the emulsification process.

From the results it is possible to conclude that to make an emulsion stable over time (more than three months) there is the need to find a balance in the system. Salt is needed but in a small amount. The salt is needed because it is proved that it gives stability over time and that without salt it is created an oil phase on the top. Salt also provide the particle flocculation [7,8], but in excess can initiate a more-extensive flocculation, which had a destabilizing effect on the emulsions [37,47]. This high aggregation of the particles it is probably due to the propyl group's functionalization.

The higher salt concentration can also increase the droplet size. In order to have smaller droplets, an increase in the homogenization time or in the speed should be take into account [7].

5.3 EMULSIONS REVERSIBILITY

The way as a colloidal particle adsorbed to a fluid-fluid interface is different from a surfactant molecule. In surfactant system, they adsorb and desorb in a relatively fast timescale comparing with colloidal particles that are strongly held at the interface [3].

In principle, Pickering emulsions could switch back like surfactant systems. However, the desorption energy to move from the interface is much higher. In order to investigate this, the emulsions were cooled, according with the PIT method. Some were cooled in the ice, fast cooling and without energy input during cooling and others were cooled during homogenization, with energy input.

The results show that all emulsions cooled during homogenization switched back, the opposite was observed without homogenization, for emulsions cooled in ice. It is possible to conclude that energy input given by the homogenization process is needed in order to switch back emulsions stabilized by silica particles modified with mPEG and propyl groups.



Figure 5.12 Schematic draw of particles at the interface moving deeper to the water due to energy input.

5.3.1 HYSTERESIS – DIFFERENCE BETWEEN SWITCH BACK TEMPERATURE AND PIT

During the reversibility study of the emulsions was discovered a significant difference between the PIT and switch back temperature. To pinpoint important factors, such as the cooling/heating rate, salt concentration, pH of aqueous emulsions with different pH, salt concentration and rate of heating/cooling were studied. From literature, this hysteresis can be explained due to the rate of heating/cooling [49].

Table 5.4 Experimental results of PIT and switch back temperature for emulsions with butanol, in water (0.1 m M of $CaCl_2$ and pH 4) using particles modified with mPEG and propyl groups as emulsifier. Values of hysteresis, rate of cooling and time of cooling predictions.

Emulsion	PIT(° C)	Switch back T (° C)	Hysteresis	Rate of heating (° C/min)	Time of cooling
Q	69	42.4	27	2.4	~5 min
R	71	42	30	1.9	\sim More than 2 hours



Figure 5.13 Conductivity as function of temperature during emulsification of butanol in water (0.1 m M of CaCl₂ and pH 4) with silica particles functionalized with mPEG and propyl groups as emulsifiers. The (blue•) represent the heating process where the PIT is visible and the (blue×) represent the cooling process, where the switch back temperature is visible. a): cooling process with water bath, (emulsion Q). b): cooling process with oil bath (emulsion R.

Figure 5.13 show that the switch back temperature was the same no matter the cooling rate. It is possible to conclude that the switch back temperature is independent of the rate of cooling and consequently the hysteresis as well.

Different salt concentration and the pH have been studied to try to understand what hysteresis depends on.



Figure 5.14 Conductivity as function of temperature during emulsification of butanol in water with silica particles functionalized with mPEG and propyl groups as emulsifiers. a): Emulsification with 0.1 M of CaCl₂ added to the aqueous-phase at pH 2. The PIT is 48 ° C, seen in the heating process (blue •) and the switch back temperature is 42 ° C, seen in the cooling process (blue ×). b): Emulsification with no salt at pH 4. The PIT is 75.5 ° C, seen in the heating process (orange •) and the switch back temperature is 45 ° C, seen in the cooling process (orange ×).

Figure 5.14 a) shows that the emulsion invert from o/w to w/o at 48 ° C and switch back at 42 ° C. This emulsion was prepared at pH 2 and 0.1 M of $CaCl_2$ added to the aqueous phase. The results in Figure 5.14 b) show that the emulsion invert at 75.5 ° C and switch back at 45 ° C. This emulsion was made

at pH 4 and with no added salt. In this case, the PIT increased but the switch back temperature didn't, which caused a large increase in hysteresis.

The same switch back temperature range was observed for all emulsions, independent on the pH and salt concentration. Lower homogenization time was observed for emulsions with lower PIT, which will induce to lower hysteresis.

5.4 EMULSION DIAGRAMS

Emulsion diagrams were produced to obtain an overview on how the particle behaviour is altered by changes in temperature and salt concentration. Emulsions were made at pH 4 at a certain temperature and salt concentration in different oil/water ratios and characterized (type of emulsion, stability towards creaming, coalescence or sedimentation and analysed with microscopy). The temperatures were chosen taking into account the PIT results in order to make a diagram before and after the phase inversion conditions. One diagram was made for each temperature and salt concentration, find in Appendix A all the diagrams made. The higher salt concentration of 0.5 M was chosen to ensure that the PIT is reached and cleared observed. These experiments were done before the knowledge of the effect of the higher salt concentration in emulsifications abilities as explained before in salt concentration study.

The emulsions were homogenized during 10 min and conductivity was measured directly after homogenization and after cooling on ice and compared with the conductivity of the aqueous phase.

Parameters		
Temperatures	RT, 45 ° C, 55 ° C, 65 ° C, 85 ° C ^[1]	
Salt Concentration	No salt, 0.5 M	
o/w volume ratio	20/80, 50/50, 80/20	

Table 5.5 Emulsion diagrams chosen parameters

^[1]Temperature just for no added salt emulsions.

Figure 5.15 shows an example of an emulsion diagram for 0.5 M of $CaCl_2$ added to the aqueous phase at 55 ° C.



Figure 5.15 Emulsion diagram for 0.5 M of $CaCl_2$ at 55 °C, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.

By the conductivity values it is possible to see that the emulsions with 80/20 and 50/50 volume ratio are w/o emulsions, $(1^{st} \text{ and } 2^{nd} \text{ point of the diagram from the left})$ and the emulsion with 20/80 o/w volume ratio (3^{rd} point) , it is an o/w emulsion.

Table 5.6 Conductivity measurements of the aqueous phase, before homogenization, after 10 min homogenization and after cooling. Emulsions contained butanol in water (0.5M of $CaCl_2$ at pH 4) with silica functionalized with mPEG and propyl groups as emulsifiers.

o/w volume ratio	Cond. aq. phase	Conductivity directly	Conductivity
	(µS/cm)	after homogenization (μ S/cm) ^[1]	after cooling (μ S/cm)
20/80(S)	42580	38980	30440 µS/cm
50/50(T)	42750	436.4	779.6 µS/cm
80/20(U	39400	187.9	109.3 μS/cm

^[1]Conductivity measurement after 10 min homogenization.

^[2]Conductivity measurement after fast cooling in ice.

Table 5.6 shows, by comparing the conductivity values after cooling with the values directly after homogenization, that emulsions after cooling with ice, didn't switch back. The same fact was verified for all emulsion diagrams. These results support the previous ones that that the energy input during the homogenization is required to switch back from w/o to o/w.

Regarding the first point of the diagram in Figure 5.15 (emulsion U), comparing the conductivity of the aqueous phase with final conductivity showed in Table 5.6, it is possible to see that the emulsion inverted at this conditions. The same occurred with the emulsion T. This result is in agreement with the PIT previous experiments, for emulsions with 50/50 % (v/v) o/w ratio, 0.5 M CaCl₂, which the PIT was obtained around 51 °C. Contrary the emulsion S did not invert at 55 °C.

Figure 5.16 shows pictures of the emulsions S,T and U with different oil/water ratios at 55 °C. It is possible to conclude from that between the three ratios used, the 50/50 is the best to study and stabilize these type of emulsions over time [23] since the emulsification failure at high and low oil content.



Figure 5.16 Pictures of emulsions obtained with different oil/water ratios. Emulsions prepared with silica particles functionalized with mPEG and propyl groups as emulsifier, butanol in water (0.5 M CaCl₂ at pH 4) after 10 min homogenization at 55°C. Emulsions cooled in ice. Pictures captured one week after homogenization. Emulsion U: 80/20 oil/water volume ratio, Emulsion T: 50/50, emulsion S: 20/80

Figure 5.16 (emulsion U) shows that the silica particles had sedimented with the water phase and all the oil came to the top and formed an oil phase, just with one week after the emulsion formed. It was observed that the emulsification failure at high oil content [23]. The emulsion T looked stable after one week, but the microscopy image, as it was mentioned before, showed a strange phase due to the excess of salt concentration used. From the emulsion S it is possible to conclude that the ratio 20/80 is not favourable since an emulsion was not formed. This behaviour may be explained by the poor coverage at the oil/water interface by silica [23] due to the calculations of the ratio silica-to-oil. In this case should be calculated to silica-to-water in order to have enough particles to stabilize the emulsions, once here the emulsion is formed by almost 80% of water (in volume).

Figure 5.17 summarise the results of all emulsions diagrams performed for the different temperatures in the presence of salt and without.

Figure 5.17 a) show that, in the presence of salt, the emulsions with low water content (80/20 oil/water volume ratio) all emulsions after 10 min homogenization displayed low conductivity (w/o emulsions), increasing with temperature [44]. This can be explained by the oil/water ratio, since 80% of the emulsion is constituted by oil which is easier to become the continuous phase. For the 50/50 oil/water volume ratio emulsions, they inverted according the PIT results, w/o emulsions was formed above 55 °C. Finally, for higher water ratio emulsions the conductivity increased with the temperature but o/w emulsions were obtained. These results can be explained by the calculations silica-to-oil ratio. In this case, it should be calculated silica-to-water, in order to ensure enough particles to stabilize the emulsion. In this case, the emulsions are constituted of 80% of water (in volume) and in order to invert from o/w to w/o is need to ensure that there is enough coverage at the interface oi/water, and for that is needed to calculate in order to the water, since is more water than oil and in a significant amount.



Figure 5.17 Conductivity values expressed as function of water ratio of emulsions at different Temperatures of butanol in water with silica functionalized with mPEG and propyl groups. A: Emulsions prepared with 0.5M CaCl2 added in the aqueous phase. B: Emulsions prepared with no added salt.

By comparison the graph A and B presented in Figure 5.17 b) it is possible to see that same conclusions can be taken with and without salt. The calculation of the water ratio is presented in Appendix B.

6 **CONCLUSIONS**

This project was focused on studying the behaviour of silica particles functionalized by mPEG and propyl groups in their use as emulsifiers and emulsion stabilizers through the PIT method. The studies of the emulsification abilities in different conditions such as temperature, pH of the aqueous phase and salt concentration have resulted in an improved understanding of this surface modified particle as emulsifier and emulsion stabilizer.

It has been shown that mPEG groups were required to achieve the PIT. This can be explained by the strong temperature dependence of the polyoxyethylene chain. Emulsions stabilized by silica particles functionalized with mPEG and propyl groups were more suitable as emulsifiers and emulsion stabilizers compared to particles functionalized with only mPEG or propyl groups. With these particles, the PIT was achieved and the emulsions were stable towards coalescence and creaming for at least one month.

The results presented also showed that the PIT is affected by changes in salt concentration and in pH of the aqueous phase. Increasing the salt concentration results in a decrease of the PIT due to the salting out effect on the mPEG. Lowering the pH causes a decrease of the PIT, since the particles are less charge thus more hydrophobic and also due to the silica-mPEG interactions that increase at lower pH inducing flocculation.

A different behaviour from bare silica was found in emulsions with silica particles functionalized with mPEG and propyl groups at pH 7. The functionalization of the particles makes them stable against gelling at pH 7 in the presence of salt. A possible explanation is the behaviour of the mPEG groups, which stays on the surface, protect against gelling. It was also found a sensitivity towards salt of the particles over time due to the propyl functionalization in combination with the higher salt concentration. This destabilization was not observed in emulsions prepared without salt content.

Overall, from this work it can be concluded that to achieve emulsions stable over time (more than three months), there is a need to find a balance in the system according the salt concentration, salt is needed but in a small amount in order to promote weak flocculation and stability over time (around 0.1 M).

7 FUTURE WORK

Oil phase

In this master thesis work, only butanol was used as oil phase. It would be interesting to study oils of different hydrophobicity. This could increase the stability of the emulsions and facilitate the use of Laser Diffraction, to measure the droplets size. Octanol and olive oil are examples of possible oils. A few studies with octanol were made and good emulsions were obtained.

Electrolytes

In order to develop a deeper understanding of the salt effect on PIT and on emulsification abilities, experiments with different electrolytes could be performed.

Fluorescence microscopy

Use microscope with fluorescence light in order to better understanding the type off emulsions before and after the PIT. For this study are needed time and microscopy lessons.

Homogenization

Increase the homogenization time, in order to decrease the emulsion droplet size [7]. The emulsions made for emulsion diagrams study were homogenized during 10 minutes. The time was chosen according with my deadline.

<u>SAXS</u>

Use small-angle X-ray scattering (SAXS) to study the aggregation of the silica particles, in order to better understand at which conditions they aggregate and further study the aggregation dependence on emulsification abilities.

TEM

Use transmission electron microscopy (TEM) to be able to see how the particles are at the interface.

SEM

Emulsion drop interfaced cannot be visualized using optical microscopy; the technique of freeze fracture scanning electron microscopy (SEM) has been applied to these systems by Binks *et all* [10] It is a good technique to understand the interfacial structure of the emulsion, the arrangement of the particles at the interface and the size of the droplets.

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9 APPENDICES

9.1 APPENDIX A – EMULSION DIAGRAMS

Emulsion diagrams were performed at RT, 45 ° C, 55 ° C, 65 ° C with 0.5 M of CaCl₂ and at RT, 45 ° C, 55 ° C, 65 ° C, 85 ° C with no added salt. The following diagrams present these results.



Figure 9.1 Emulsion diagram for 0.5 M of $CaCl_2$ at RT °C, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.2 Emulsion diagram for 0.5 M of CaCl₂ at 45 $^{\circ}$ C, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.3 Emulsion diagram for 0.5 M of $CaCl_2$ at 65 °C, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.4 Emulsion diagram at RT with no added salt, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.5 Emulsion diagram at 45 °C with no added salt, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.6 Emulsion diagram at 55 °C with no added salt, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.7 Emulsion diagram at 65 °C with no added salt, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.



Figure 9.8 Emulsion diagram at 80 °C with no added salt, showing conductivity values after 10 min homogenization for emulsions of butanol in water stabilized by silica particles functionalized with mPEG and propyl groups.

9.2 APPENDIX B – CALCULATION OF WATER RATIO

Calculation of the particle ratio for an emulsion ratio of 80/20 %(v/v)

 $Particle ratio = \frac{\frac{g_{silica \ particles \ presented \ in \ emulsion}}{P_{silica \ particles}}$ Equation 9.1

Water ratio = 0.2 - particle ratio

Table 9.1 Particle and water ratio results for emulsions for emulsion diagrams

Emulsions volume ratio (o/w)	Water	Particle
20/80	0,795	0,005
50/50	0,486	0,014
80/20	0,178	0,022

The calculations were made with 2.21 g/ml of density of the particles and a volume of 10 ml.