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.

Keyword: Pickering emulsions, PIT method, functionalized colloidal silica, emulsion stability

1. Introduction

Emulsions are a class of disperse systems consisting of two immiscible liquids, where one liquid is dispersed in another in the form of droplets [1]. Typically, one phase is organic (the oil phase) and the other is an aqueous phase [2]. 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 [1]. 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 [3].

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 [4]. 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 [5,6]. The high resistance to coalescence is a major benefit of the stabilization by solid particles [5]. The surfactant-free character of Pickering emulsions makes them suitable for various applications [7]. 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 [2].The stability towards coalescence depends on the hydrophobicity of the particles [8]. 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 [9].

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 $\theta = 90^{\circ}$ [6,8].



Fig.1.

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 [10].

In this thesis, silica nanoparticles modified with hydrophobic and hydrophilic groups are used as emulsifiers to stabilize o/w Pickering emulsions. One advantage is when using colloidal silica particles an environmentally benign system can be accomplished since they rank as one of the most environmentallyfriendly, industrial chemical products [11].

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. Silica surface was functionalized with hydrophilic and hydrophobic groups. The silica particles used are modified with the hydrophilic methyl poly(ethylene glycol) silane (mPEG) and hydrophobic propyl silane. The purpose of functionalization was to find a surface chemistry of the particles suitable for emulsion applications.

In this work, the Phase Inversion Temperature (PIT) method was used in order make stable emulsions [2]. 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 [2]. 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. Experimental section

2.1. Materials

Colloidal Silica Particles with the trade name Levasil SP2138 were provided by Akzo Nobel Pulp and Performance Chemicals (PPC), listed in Table 1. These particles have a surface area of 130 m²/g, as measured by Sears titration. The particle diameter is given as measured with DLS at alkaline conditions at 1 wt% at S_1O_2 .

The oil 1-butanol (Merck, 99.5%) with density 0.81 g/ml of density was used for the emulsification process. Calcium Chloride (Merck, 99%), Hydrochloric acid (Sigma-Aldrich, 37% conc) Sodium Hydroxide (Sigma-Aldrich, 98%) were used for salt and pH adjustments.

2.2 Methods

2.2.1 Purification by UF

The silica sol was purified before usage through UF from PALL in order to remove unreacted silence species and to reduce the salt content. UF removed 70—80 % of unbound silanes and the membrane has 76mm of pore size, 41.8 cm² of effective filtration area. 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.

2.2.2 Emulsions to achieve 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).

Preparation of Aqueous phase: The aqueous phase was

Table 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 (μ mol sinlane /m ² S ₁ O ₂) ^[1]	SSA (m ² /g) [2]	Reduction of SSA (%) $^{[3]}$	DLS particle diameter (d _{v,} nm) ^[4]
Levasil SP2138 with propyl+mPEG	1 propyl 0.5 mPEG	130	39	26.7
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.

^[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.

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

prepared by mixing the modified silica particles, desired amount of calcium chloride and distilled water in a round M). The electrical conductivity of the aqueous phase was measured in order to compare with the conductivity of the emulsion obtained.

<u>PIT method:</u> The aqueous phase was mixed with the oil phase (1-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 room temperature 21±3 °C.

<u>Characterization of emulsions</u>: 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).

2.2.3 Emulsification process for emulsion diagrams

The aqueous phase was prepared in the same way as in the PIT method.

<u>Preparation of emulsions:</u> A 10 ml mixture of oil, water, silica and /or without salt was emulsified in a 25 ml round glass vessel. The emulsifications were conducted using an Ultra Turrax operating at the speed 12000 rpm at constant temperature. The temperature was controlled through oil bath with silicone oil. The emulsification time was 10 min. After emulsification the emulsions were cooled in ice until room temperature.

The emulsions were characterized in the same way described above.

2.2.4 Microscopy

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 and characterize them. In addition, a fluorescence lamp was used.

3. Results and Discussion

3.1 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

glass beaker. Following, the pH was adjusted with hydrochloric acid (0.5 M) and sodium hydroxide (0.1 functionalized with mPEG and propyl groups (Table 1). The pH of the aqueous phase was adjusted to pH 4.

During emulsification with particles modified with only mPEG silane an emulsion was formed, but immediately after sheering the emulsion completely phase separated. Fig.2, (emulsion A) clearly shows the two phases formed immediately after homogenization process with particles only modified with mPEG groups.



Fig.2

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 adde



Fig.3

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, PIT at 85 ° C emulsion A; mPEG and propyl groups (blue•) as emulsifiers, PIT at 57 ° C emulsion B; with propyl groups (red•) as emulsifiers, no PIT observed, emulsion C.

This result show that these particles are too hydrophilic and, therefore, not suitable as emulsifiers. Fig.2, also shows that emulsion C, with only propyl groups as emulsifier, starts to cream. 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. Fig.3 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 [12], 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 PIT was observed at 85 ° C for emulsion A and at 57 ° C for emulsion C. Fig. 3 also shows that PIT only occurs when particles modified with mPEG groups are used as emulsifiers. This shows that PIT is directly related to the cloud point that strongly depends on conformational changes of the mPEG chain due to the temperature [13,14].

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.

3.2 Effect of salt concentration and pH on PIT

A set of factors that could affect the PIT were investigated. 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.



Fig.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.

PIT is influenced by both the pH and salt concentration, as can be seen in Fig. 4. In relation to the salt concentration, it is possible to see that the PIT increase when the salt concentration decrease [10,13,15]. 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. In combination with the screening charge effect, will facilitate the adsorption at the oil interface and consequently reduce the PIT increasing the salt concentration [16]. Fig. 4 also 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. 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.

Emulsification abilities - Effect of pH

The pH can influence the PIT but also the emulsification abilities, since at higher the pH, higher the charge of the silica particles [15,17]. When the silica particles are charged are more difficult to stabilize an w/o the emulsion, due to the formation of SiO⁻ groups on the silica surface, which make the particles more hydrophilic [18]. Interactions between mPEG and silica sols are temperature and pH dependent [19] since the adsorption of mPEG to the silica surface is decreased as the pH is increased. To increase the understanding of the system, 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 $^{\circ}$ C.

The results show that emulsions at pH 4, with and without salt, start to cream. In the presence of salt, the emulsion 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 55 °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 these emulsion. The emulsion at pH 7 and without the presence of salt completely phase separated in less than one week due to the high surface charge of the silica particles. Comparing to the naked eye, the presence of salt makes an important difference on emulsion aspect [7,17]. In the presence of salt the emulsion was stable towards coalescence and with small and close-packed droplets. At pH 9 the emulsions start to cream without salt and gel with salt. At this pH the particles are too charge, which make them too hydrophilic that prefer to stay at the aqueous phase.

It was also observed that the emulsion produced 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 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 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. These results show that at pH 4 and pH7 the emulsions were both stable but when the emulsion are cooled, emulsions at pH 4 are more stable and with small droplets size.

3.2 Emulsification abilities – 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 first thing that can be observed from the obtained emulsions is that the creamed phase decreases with the salt concentration. The emulsions were compared three months after and the cream phase had not increased, which is a good stability signal. The creaming rate is directly proportional to the droplets diameter, and can be estimated from Stokes' equation, Eq. (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 [20].

$$v = \frac{2r^2(\rho - \rho_0)g}{9\eta} \tag{1}$$

According to Eq. (1), creaming is reduced by small droplet radius and consequently, from Fig.5 by low salt concentration. Microscopy images show that when the salt concentration decreases the droplet size decreases. In emulsions with no added salt the droplets were smaller, but in the presence of salt more mono dispersed emulsions were obtained, see Fig.5. A possible explanation for the aspect seen in Fig.5 in emulsions E 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 reduction of the net charge [10, 21, 22]. It is possible to conclude that 0.5 M is a higher salt concentration and therefore not a suitable to stabilize these emulsions.

It was observed that the emulsion D (0.1 M CaCl2) is stable after three months, unlike emulsion F (no added salt). This can be explained by the presence of salt [9,10,15]. 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 [10,15] but in excess can initiate a more-extensive flocculation,



Fig.5

Microscopy images of emulsified butanol in water using silica particles with mPEG and propyl groups as emulsifiers with 0.5 M of $CaCl_2$ added to the aqueous phase (emulsion C), 0.1 M of $CaCl_2$ (emulsion D), 0.1 mM (emulsion E) of $CaCl_2$ added to the aqueous-phase and no added salt (emulsion F). 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.

which had a destabilizing effect on the emulsions [18, 21].. This high aggregation of the particles it is probably due to the propyl group's functionalization 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 [10,15], but in excess can initiate a more-extensive flocculation, which had a destabilizing effect on the emulsions [18,21]. 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 have smaller droplets, an increase in the to homogenization time or in the speed should be take into account [15].

3.3 Emulsions reversibility

The way as a colloidal particle adsorbed to a fluidfluid 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 [6]. In principle, Pickering emulsions could switch back like surfactant systems. However, the desorption energy to move from the interface is much higher.





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

In order to investigate if Pickering emulsions switch back, in this case, from w/o to o/w, 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.

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



Fig. 7

Conductivity as function of temperature during emulsification of butanol in water with silica particles functionalized with mPEG and propyl groups as emulsifiers. The (•) represent the heating process where the PIT is visible and the (×) represent the cooling process, where the switch back temperature is visible. a) Emulsification with 0.1 m M of CaCl₂ added to the aqueous-phase at pH 4, cooling process with water bath; b) Emulsification with 0.1 m M of CaCl₂ added to the aqueous-phase at pH 4, cooling process with oil bath. c) Emulsification with 0.1 M of CaCl₂ added to the aqueous-phase at pH 4. The PIT is 75.5 °C

of aqueous emulsions with different pH, salt concentration and rate of heating/cooling were studied. Fig. 7 a) and b) show that the switch back temperature c) 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. Fig.7 c) 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 CaCl₂ added to the aqueous phase. The results in Fig.7 d) 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 Dower PIT, which will induce to lower hysteresis.

3.4 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. 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.

Fig.8 summarise the results of all emulsions diagrams performed for the different temperatures in the presence of salt and without. Fig.8 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 [12]. 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 silicato-oil ratio. In this case, it should be calculated silica-towater, 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.



d)

Fia.8

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.

4. 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).

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