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Surface Modification, Characterization and Physicochemical Study of Amphiphilic Silica Nanoparticles

Master of Science Thesis in the Master Degree Programme Materials and Nanotechnology

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This work has been performed at Chalmers University of Technology in cooperation with Eka Chemicals

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ABSTRACT

The term silica sol refers to a stable system of amorphous silica particles, finely dispersed in a surrounding liquid. The silica particles are covered by silanols groups (Si-OH), providing a clear hydrophilic character. The reactivity and the stability of silica sol are depending on various parameters such as pH and salt concentration.

In this work, the aim is to provide an amphiphilic character to the particles by surface modifications. The particles are modified hydrophilically by silane-containing poly (ethyleneglycol) methylether (MPEG-3GTO) and hydrophobically by isobutyl (trimethoxy) silane (iBu) and may, in addition to acting as stabilizers, also act as emulsifying agents in Pickering emulsions.

Since MPEG shows affinity to the silanol groups of the silica surface, the modifications are carried out under alkaline conditions, allowing the alkoxysilanes of the modifiers to be covalently attached to the silica surface. However, physisorption of already covalently attached PEG chains at the silica particles may lead to increased surface activity by increased particle-particle interactions. The evaluations are therefore carried out at pH 2, 4, 7 and 10 in order to study pH-related effects.

For the evaluation of the MPEG-3GTO grafting, a combination of thermogravimetric analysis (TGA) and nuclear magnetic resonance (NMR) diffusometry is used, indicating that 6% of the added MPEG-3GTO is covalently attached to the silica particles. This corresponds to 0.06 μmol MPEG-3GTO/m^2 silica surface.

Additionally, dynamic light scattering shows an increase in particle size from about 30 nm for unmodified particles, to about 50 nm for the totally modified. The latter value is also confirmed by the diffusion coefficient obtained from the NMR diffusometry measurement.

Measuring of surface tension shows that the most surface active sol is the one modified both by MPEG-3GTO and iBu at pH 4. This confirms that the amphiphilic silica nanoparticles have the highest surface activity achieved in the present work. In addition, the modified sol is shown to have a significant surface activity also in two different oil-water systems.

Finally, emulsification tests show that the toluene/water system emulsified with modified sol at pH 4 gives the best emulsion. However, this emulsion resembles much a Winsor III system, implying that attempts with more particles could be a good idea for future studies.

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Contents

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Introduction

In this study, silica sol, consisting of silica particles finely dispersed in a surrounding aqueous liquid, is investigated as an emulsifying agent and, at the same time, stabilizer in a Pickering emulsion. Since silica particles are not surface active and thus do not adsorb at the liquid-liquid interfaces, they have to undergo surface modifications with hydrophilic and hydrophobic modifiers to become amphiphilic. Furthermore, at low pH the affinity between the particles, and also the modifiers, increases, which leads to bridge flocculation and agglomeration. If the forces between the particles and the modifiers are of the right order of magnitude, these agglomerations may increase the surface activity of the modified sol. However, if the agglomeration is too severe, the sol may be deteriorated because of sedimentation.

1.1   Aim of the Project

In this Master Thesis, the possibility to use amphiphilic-modified silica nano particles as both emulsifiers and stabilizers is investigated.

The goal of the project is to modify silica particles with isobutyl (trimethoxy) silane (iBu) as a hydrophobic group and with silane-containing poly (ethyleneglycol) methylether (MPEG-3GTO) as a hydrophilic group. Furthermore, after purification of the sols, several techniques are used to characterize the modified silica sols and to determine how successful the modification is.

1.2   Limitations

When the sols are modified, the silica concentration is set to 5 weight-%, meaning that the optimal concentration for covalent attachment of alkoxysilane groups is not investigated. Furthermore, the molecular weight of the

MPEG used is 2000 g/mol, and whether a longer or shorter PEG chain would change the results is not investigated.

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Theory

Here, the concept and historical development of silica sol are explained. Further on, the paths of synthesis in this study will be presented as well as the theory behind Pickering emulsions. Finally, the methods used for characterization in the current work will be introduced.

2.1 Silica Sols

The term "silica sol" refers to a stable system of silica particles, finely dispersed in a liquid. The particles have an amorphous structure with the general formula SiO_2. Silica sols are used in numerous industrial applications (e.g. concrete additive, paint component and chromatographic materials).

2.1.1 The Historical Development

During the 20th century, it was discovered that silica sol could be stabilized by alkali addition. This was a big breakthrough, leading to stable silica sols able for commercial shipping. Previously, concentrations above 10 weight-% led to instant gelling, which occurs when the silanol groups of the silica surface form interparticle siloxane bonds [1].

2.1.2 The Silica Surface

The silica surface consists of about 8 μmol silanol groups per square meter [2]. With an isoelectric point at pH 2, the surface is negatively charged at alkaline pH. The electrostatic forces created between like-charged surfaces (as between two silica particles) arise from the overlap of electrical double layers. The magnitude of this repulsion is proportional to each surface's potential.
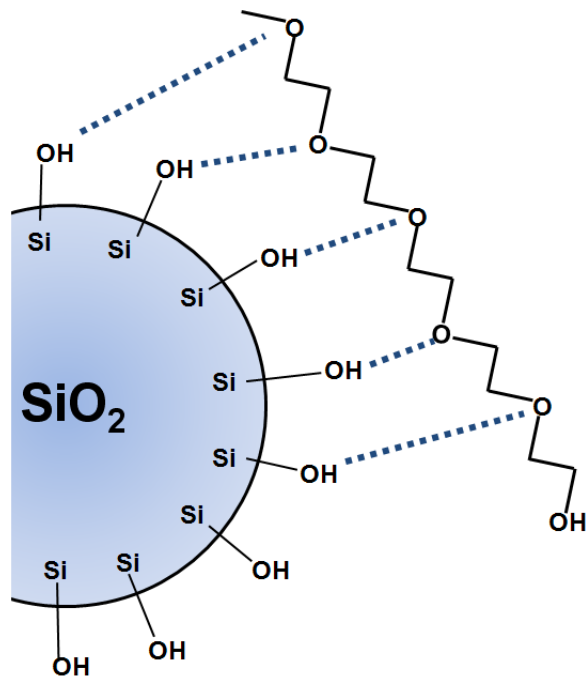
Figure 2.1: At low pH, the silica surface is uncharged, resulting in hydrogen bonds between the silanol groups of the silica surface and the oxygen atoms of the PEG chain.

Furthermore, attractive van der Waals interactions for silica spheres in the 10 to 100 nm size range vary as the inverse of the particle-particle distance. These interactions are always directly proportional to the particle size [3].

The interplay between repelling electrostatic forces and attractive van der Waals forces determines whether the silica sol will be stable or gel. Furthermore, because of the interparticle bonds formed when gelling, this state can not be reversed.

Another possibility, except addition of base, to avoid gelling in silica sol is therefore to screen the attractive van der Waals forces by covering the particles with an inert monolayer coating [1].

2.1.3 The Silica Surface Affinity to PEG

The affinity between poly ethylene glycol (PEG) and silica is due to hydrogen bonds formed between the silanol groups of the silica surface and the oxygen atoms of the PEG, see Figure 2.1. This affinity contributes to physisorption of the PEG chains at the silica particles. However, since the silanol groups are deprotonated at elevated pH, this affinity decreases as a function of pH [4].
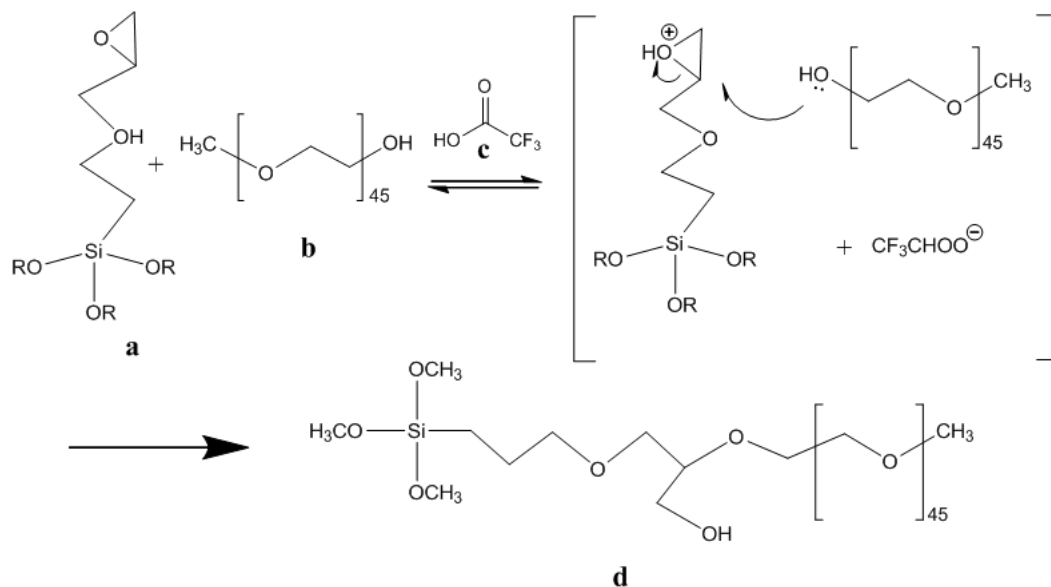
Figure 2.2: The epoxide ring-opening reaction via acidic catalysis. The mixture of 3GTO (a) and the catalyst (TFA) (c) results in an equilibrium where MPEG (b) makes a nucleophilic attack at the protonated 3GTO. The result (d) is the hydrophilic modifier MPEG-3GTO.

2.1.4 Surface Modifications

During surface modifications of silica, an alkoxysilane group of the modifier reacts with a silanol group of the silica surface. A model for this reaction has been developed by Görl and Hunsche [5] who suggest that the reaction consists of two steps: first the alkoxy groups of the silica surface are hydrolysed to produce silanol groups and then the condensation reaction can occur.

2.1.5 Synthesis of the Hydrophilic Moiety

The hydrophilic moiety is in this study synthesised by an acid-catalysed epoxide ring opening of (3-glycidyloxypropyl) trimethoxysilane (3GTO) which undergoes a nucleophilic attack by poly (ethyleneglycol) methylether (MPEG) [6]. The mechanism for this reaction is shown in Figure 2.2. The use of end-capped PEG allows only one side of polymer to react, resulting in the requested product.

2.2 Pickering Emulsions

The fact that finely divided, insoluble solid particles may stabilize an emulsion was first discovered by Pickering [7], hence the term Pickering emulsion. He discovered that colloidal particles that are wetted more by water than by oil can both stabilize an oil-in-water emulsion and, at the same time, act as emulsifying agents.

2.2.1 Effect of Particle Concentration

In a study performed by Gelot et al. [8], the effect of the silica particle concentration in the range 0-2% on emulsion stability was analysed, showing a number of interesting results. First, the emulsion stability increases with an increase in the particle concentration. Second, a minimum particle concentration is required to form any kind of stable emulsion. This implies that the emulsion droplets need a sufficiently dense layer of stabilizing particles around them. A third observation from the study is that the average droplet size is decreased with an increasing particle concentration. These smaller droplets have a larger interfacial area that enables more particles to reach them. However, this trend is not permanent; the relationship between emulsion stability and particle concentration is not linear and there exists an upper limit concentration where the stability ceases to increase.

2.2.2 Effect of Particle Size

The particle size is one of the more important factors when stabilizing an emulsion, since the emulsion stability is increased with a decreasing particle size. However, this effect is only valid down to a minimum size, where the effect of Brownian motion becomes significant and the particles no longer stay at the interface [9].

2.3 Methods of Characterization

Here follows a brief introduction and theoretical background to the methods used for the characterizations in the current work.
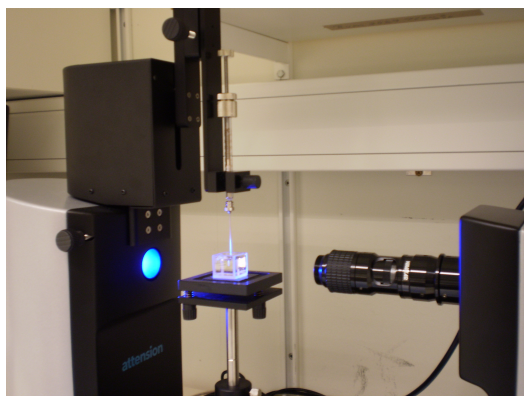
Figure 2.3: The pendant drop measurement equipment used in this study. The cuvette contains the surrounding media, and the liquid to be evaluated is in the syringe.

2.3.1 Physicochemical Properties

2.3.1.1 Interfacial Activity Measurements

In this study, the surface tension is measured by the Du Noüy ring method. Furthermore, interfacial tension measurements at the oil-water interface are performed with the pendant drop method. The latter experiment is completed with an oscillating drop technique to evaluate the dynamic interfacial tension.

Du Noüy Ring The Du Noüy ring method of measuring surface tension is one of the most traditional. During the measurement, a platinum ring is submerged in the liquid. The force required to pull the ring through the surface is measured [10].

Pendant Drop The pendant drop technique is an optical method of measuring the surface or interfacial tension. Here, a drop of the liquid is formed and a camera records an image. The surface tension is then calculated from the drop shape. In addition, the interfacial tension between a surrounding media, for instance an organic solvent, and the liquid can be measured, see Figure 2.3.

When the drop is formed, an oscillating device can be switched on, allowing the drop to oscillate at a certain frequency and with a certain amplitude. Surface active particles may, in this way, get the extra energy they might need to migrate to the interface. However, if the interfacial tension is not affected by oscillation, this indicates that the particles reach their state of equilibrium without addition of energy to the system, i.e. spontaneously.

2.3.1.2 Dynamic Light Scattering

The dynamic light scattering (DLS) technique is frequently used for particle sizing. The method is based on measurements of the diffusion of a colloid, which is correlated to the particle size. This technique is nondestructive, measures particle size in the range from nm to μm, and is widely used for small-scale applications. However, the solution to be measured must be highly diluted to prevent strong multiple scattering and/or backscattering, therefore the method is often considered too complicated for industrial applications.

When the light from a laser beam hits the particles of the suspension, it scatters in all directions. In case of unwanted backscattering of too turbid solutions, the light hits more particles before reaching the sensor [15].

2.3.2 Characterization of the Surface Modification

2.3.2.1 NMR Diffusometry

Nuclear magnetic resonance (NMR) diffusometry is a non-invasive technique by which information about molecular translational motion can be obtained [11, 12]. NMR spectroscopy deals with the interaction between radiofrequency magnetic radiation and atomic nuclei in a static magnetic field. The working principle of NMR diffusometry is to measure the displacement of the observed spins during the measuring time, which is used to deduce a value of the self-diffusion coefficient of the probe species.

The intensity observed in the NMR measurment for a monodispersed diffusant can be related to the diffusivity via the Stejskal-Tanner equation [13]:

$$I = \exp\left(-4\pi^2 q^2 \Delta D\right) \tag{2.1}$$

where I is the signal intensity, the product $q^2\Delta$ is denoted the squared gradient and D is the self-diffusivity of the particle. The latter is related to the particle size via the Stokes-Einstein relation [14]:

$$D = \frac{k_B T}{3\pi\mu d_p} \tag{2.2}$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, μ is the dynamic viscosity of the solvent and d_p is the particle diameter.
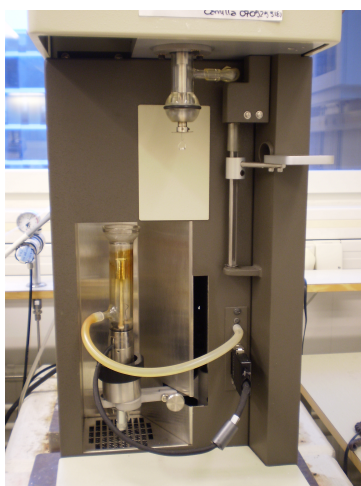
Figure 2.4: The thermogravimetric analyser used in this study.

2.3.2.2 Thermal Gravimetric Analysis

A thermogravimetric analyzer (TGA) determines changes in weight of a sample as a function of temperature. In a small aluminium cup, 5-10 mg dry sample is added. Then the equipment, see Figure 2.4, encapsulates the sample and starts a predetermined program. The program consists of a combination of isotherms and temperature ramps, depending on the parameter investigated.

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Materials and Methods
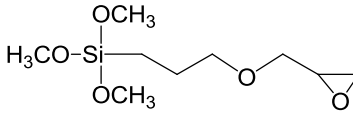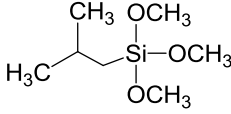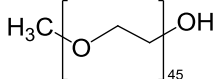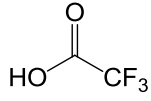
3.1 Experimental Procedures

3.1.1 Surface Modifications of Silica Nanoparticles

In this study, silica nanoparticles are modified to become surface active, i.e. to adsorb spontaneously at the interface. In order to achieve this goal, hydrophilic and hydrophobic moieties are attached to the silica surface. The silica sol is manufactured by Eka Chemicals under the name Bindzil 40/130. These numbers refer to that the silica content of the sol is about 40 weight-% and that each gram of silica particles has 130 m^2 surface.

The hydrophobic moiety used is isobutyl (trimethoxy) silane (iBu) and the hydrophilic moiety poly (ethyleneglycol) methylether (MPEG). However, since the reaction between a molecule and the silica surface occurs when an hydroxylgroup at the surface is replaced by an siloxane group, each molecule attached to the surface must contain a siloxane group at one end. This is already the case for iBu, but for MPEG to be able to covalently bind to the surface it must be modified by a coupling agent. The coupling agent used for this purpose is (3-glycidyloxypropyl)-trimethoxysilane (3GTO), see Table 3.1.

Since MPEG consists of a long polymer chain it might cause steric hindrance at the silica surface. The hydrophobic iBu is therefore reacted first with the silica particles. In this way, the risk that iBu might have difficulties to reach the silica surface is eliminated. Then prior to the MPEG-3GTO grafting, the sol is purified by ultrafiltration.

Abbreviation	IUPAC Name	Structure
3GTO	(3-Glycidyloxypropyl) trimethoxysilane	
iBu	Isobutyl(trimethoxy) silane	
MPEG	Poly(ethyleneglycol) methylether	
TFA	Trifluoroacetic acid	

Table 3.1: Chemicals used in this study. All are manufactured by Aldrich.

3.1.1.1 Synthesis of the Hydrophilic Modifier

3GTO and MPEG in 1:1 mole equivalents are dissolved in toluene. The mixture is heated up to 60°C in an oil bath. At this temperature, two mole equivalents of TFA are added. After five hours of reaction time, the TFA and the toluene are removed by evaporation under reduced pressure at 60°C.

To make sure that all TFA is removed, the sample is redissolved in toluene which is once again removed. This procedure is repeated twice.

3.1.1.2 Grafting of the Modifiers at the Silica Surface

To ensure that the added hydrophilic or hydrophobic modifier is given maximum possibility to evenly reach the silica surface, the substances are added during two hours. Then the reaction is carried on for another two hours. To avoid the difficulties of adding a small amount evenly during two hours, an automatic syringe is used. However, a drawback using this syringe is that it contains a dead volume of about 1 ml in the tube between the syringe and the reactor. In addition, a plug is installed at end of the syringe, preventing the engine to continue pressing the piston until the device breaks, but also contributing to that about 1 ml always is left in the syringe. This is taken
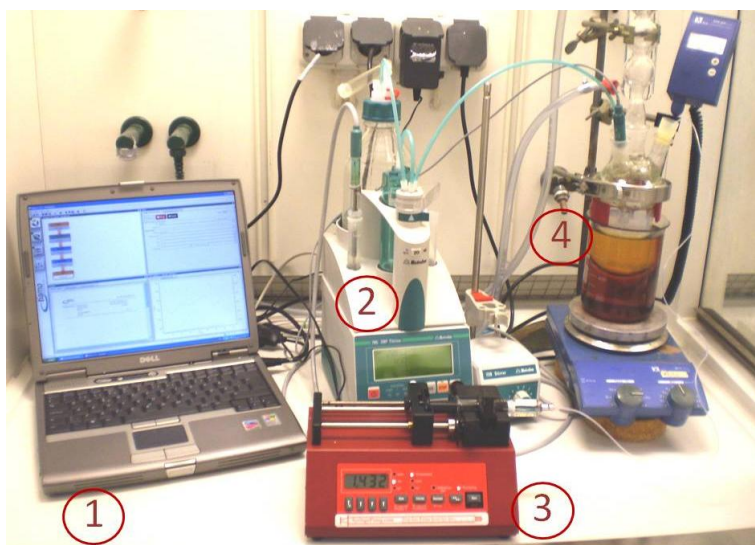
Figure 3.1: The experimental setup where the laptop (1) controls the pH detector (2) and the syringe pump (3), which in turn determines the outcome in the reactor (4) that is held at a temperature of 90°C with an oil bath.

into account when the amount to be added is calculated. Furthermore, although the exact mass that is about to be added is hard to predict it is easy to measure afterwards how much that actually was added.

During the reaction, the silica sol is diluted to 5 weight-% to increase the chances of a homogeneous grafting. The pH is adjusted to 10 by addition of NaOH and the silica is thereafter heated up to 90°C in an oil bath. The addition time of the modifiers is 2 hours, then the reaction is continued for another 2 hours. To avoid physisorption of the PEG chain at the silica surface, the pH is maintained at 10 during the whole reaction, decreasing MPEG affinity to silica.

As the desired pH of 10 might change during the addition and reaction, the pH is controlled using an automatic titrator that is set at pH 10 and that adds NaOH if the pH drops. Both the syringe and the automatic titrator are controlled by a laptop computer, see Figure 3.1.

Purification by Ultrafiltration After each step of grafting, the sol is washed in a Millipore Corporation Ultrafiltration Cell to remove any unreacted reactants. The filter used is made of regenerated cellulose and two pore sizes are used: 5000 and 30 000 nominal molecular weight limit (NMWL) [16]. In contrast to ordinary filtration, ultrafiltration does not create any filter cake and the colloidal silica remains dispersed while water and small molecules are

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filtered off [1]. During the purification, half of the ultrafiltration cell is filled with sample and the other half with milli-Q water of which the pH is adjusted to 10 with NaOH. This procedure is repeated five times.

3.2 Evaluation of the Properties of the Modified Silica Sol

As it has been mentioned, the silica sol is modified at pH 10. However, during the evaluations of its properties, the sol is evaluated at four different pH: 2, 4, 7 and 10, adjusted by addition of a few drops of HCl or NaOH. Since the modified sol concentration is set to 5 weight-% before the pH is changed, the sol concentration is slightly altered. Any effects of these small changes of concentration are however neglected in this work.

3.2.1 Thermal Gravimetric Analysis

Determination of the amount of MPEG-3GTO grafted at the silica surface is performed with an Perkin-Elmer TGA 7 Thermogravimetric Analyzer (TGA). The program applied is:

1. Hold for 2 min at 30°C

2. Heat from 30°C to 600°C at 10°C/min

3. Hold for 40 min at 600°C

The reason for analysing the modified silica using TGA is that the MPEG-3GTO is incinerated whereas the silica is intact. The TGA contains a very sensitive scale and the result of the method can be viewed as a weight-versus-time (or temperature) plot.

Before the TGA measurements, the samples are dried using a SPD Speed-Vac manufactured by Thermo Electron Corporation, operating at 75°C and vacuum down to 0.1 torr.

3.2.2 NMR Diffusometry

Five different samples are evaluated by 1H nuclear magnetic resonance (NMR) diffusometry. Free MPEG in water as well as free MPEG with SiO_2 are used as references. The samples of the modified silica sols analysed are of three different degrees of ultrafiltration: the first one is not filtrated at all, whereas one was ultrafiltrated with filters with 5000 NMWL pore size and the last

one was ultrafiltrated with 30 000 NMWL pore size. All samples have a concentration of about 5 to 8 weight-% and are at pH 10.

The measurements are done on a Bruker DRX600 spectrometer, equipped with a Bruker diffusion probe with a maximum gradient strength of 1200 G/cm. All diffusion experiments are performed with $\Delta = 50$ ms diffusion time, $\delta = 1$ ms gradient pulse length, and the gradient strength linearly ramped from 15 to 1000 G/cm in the conventional stimulated-echo sequence.

3.2.3 Dynamic Light Scattering

Dynamic light scattering (DLS) is applied to measure the particle size, with the purpose to compare the silica particles containing hydroxyl groups, iBu and MPEG. The background electrolyte used in all measurements is a 25 mM NaCl solution at pH 7. At this pH, the MPEG chains should be fully extended. Furthermore, the concentration of silica particles is 1 weight-% for unmodified silica sol as well as the sol modified only with iBu and 0.1 weight-% for the MPEG modified silica sol. The used equipment is a ZetaPALS Zeta Potential Analyzer, manufactured by Brookhaven Instruments Corporation.

3.2.4 Interfacial Activity Measurements

3.2.4.1 At the Air-Water Interface

The surface tension is assessed by the Du Noüy ring method. The instrument used in this study is a Sigma 70 from KSV. Both modified silica sol, silica sol modified with iBu and MPEG-3GTO separately, as well as pure milli-Q water and unmodified silica sol are evaluated at the four different pH.

3.2.4.2 At the Oil-Water Interface

The interfacial tension is evaluated by the pendant drop technique. The instrument used in this study is a Theta from Attension. As in the surface tension measurements, both modified silica sol, silica sol modified with iBu and MPEG separately, as well as pure milli-Q water and unmodified silica sol are evaluated at the four different pH. Furthermore, since each modified sol containing MPEG also have some MPEG free in the solution, a sample containing only free MPEG is also measured. The amount of MPEG in this sample corresponds to the amount of free MPEG in the silica sol modified with both iBu and MPEG-3GTO.

The interfacial tension is evaluated between the aqueous samples and toluene as well as between the aqueous samples and dodecane. However,

to remove unwanted oxidation products of dodecane, it is first purified by filtration through alumina.

The interfacial tension between dodecane and the samples is also evaluated with the oscillating pendant drop technique.

3.2.5   Emulsification Tests

The modified silica sols at pH 4 and 10 are used as emulsifiers for the system water/oil. The oils used in this experiment are toluene and dodecane. The latter is purified by filtration through alumina. The amount of silica is 0.5 weight-% of the oil and the emulsions are prepared by a Heidolph DIAX mixer, operating at 20 000 rpm for five minutes. The result of each sample is evaluated at three different points in time: directly after emulsification, after five minutes and after ten minutes.

4

Results and Discussion

4.1 Synthesis of the Hydrophilic Modifier

The liquid chromatography performed at Eka Chemicals shows that the synthesised MPEG-3GTO contains 6.7 weight-% unreacted 3GTO of which 1.2% are epoxides. Since MPEG has a molecular weight of about 2000 g/mol and 3GTO only 236 g/mol, this means that 63% of the 3GTO molecules are unreacted after the reaction. Hence, this reaction yield is 37%.

The appearance of the synthesised MPEG-3GTO is much like a very firm wax, that appears more solid every time is it redissolved in toluene and evaporated.

4.2 Modifications of the Silica Particles

The silica sol is modified by iBu and MPEG-3GTO at pH 10, then the surface activity properties of the sol are evaluated at four different pH. As the pH is lowered by HCl, it is observed that if the pH is decreased fast, the system turns white and phase separates quickly. Furthermore, if the pH is decreased at a slower rate, with proper stirring in between the drops of HCl, the system still becomes white, but separates only after a couple of days. In Figure 4.1, both samples have the same pH of 2 but the one to the right is more stable due to a slow pH decrease.

The reason why some silica sols become white and phase separate is that the silica particles form interparticle bonds, agglomerate and sediment. Figure 4.2 shows silica sol modified by both iBu and MPEG at pH 2, 4, 7 and 10. The pH is slowly adjusted for the sample with pH 2 and 4. The sample at pH 2 seems stable at first but phase separates after a couple of days. However, the sample at pH 4 remains stable.
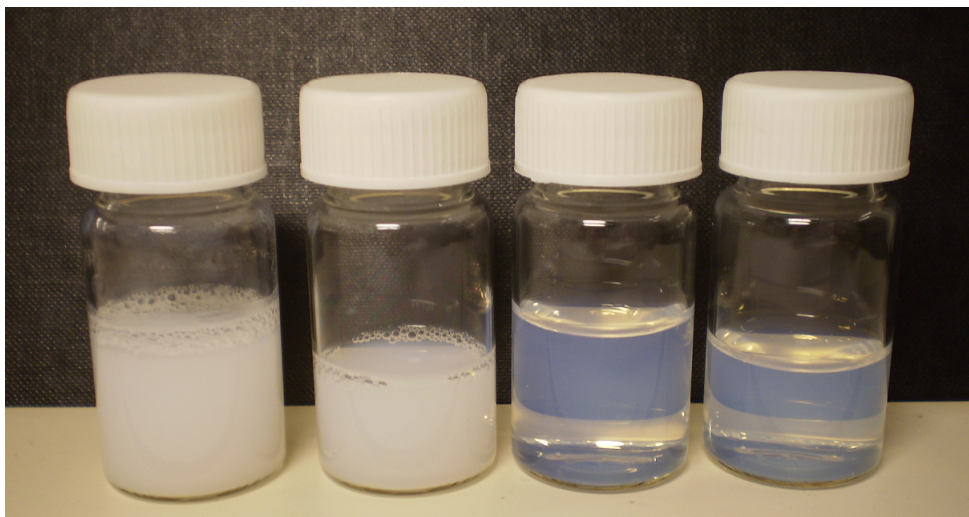
Figure 4.1: Silica sol with a concentration of 5 weight-% modified by iBu and MPEG-3GTO at pH 2. The sample to the left is exposed to a fast decrease of pH from 10 to 2, whereas the sample to the right experiences a slow decrease.

Figure 4.3 shows pure silica sol at 5 weight-%, also with the same set of pH. No visual differences can be noticed. However, as shown in Figure 4.4, silica sol modified with iBu experiences a small change in color and becomes slightly whiter as the pH decreases. This is due to interparticle interactions that make the particles of the sol agglomerate to some extent but not severely enough for the silica to sediment.

On the contrary, the silica sol modified only by MPEG-3GTO, see Figure 4.5, becomes white and phase separates both at pH 2 and 4. The agglomeration that occurs when the sol becomes white and phase separates is due the increased affinity of the PEG chain towards the silica surface. In addition to the particle that the PEG chain is covalently attached to, it also shows affinity towards other particles, resulting in a bridge flocculation between particles, as discussed in Section 2.1.3. Furthermore, the fact that silica sol modified only with MPEG-3GTO shows less stability towards agglomeration than the sol modified with both MPEG-3GTO and iBu, indicates that iBu somewhat helps the silica particles to remain stable.

During the reaction where iBu is attached to silica particles, 0.2217 g iBu is added. As the molecular weight of iBu is 178.3 g/mol, this corresponds to 1243.6 μmol. The amount of silica in the batch is 11.3547 g, resulting in 1476.1 m^2 silica surface and 0.84 μmol iBu/m^2.

After grafting of iBu, 3.0340 g of MPEG-3GTO is added to the silica sol. Since the molecular weight of MPEG-3GTO is 2211.3 g/mol, this corresponds to 1372.0 μmol and 0.93 μmol MPEG-3GTO/m^2.

Figure 4.2: Silica sol with a concentration of 5 weight-% modified by iBu and MPEG-3GTO and, from the left to the right, pH 2, 4, 7 and 10.
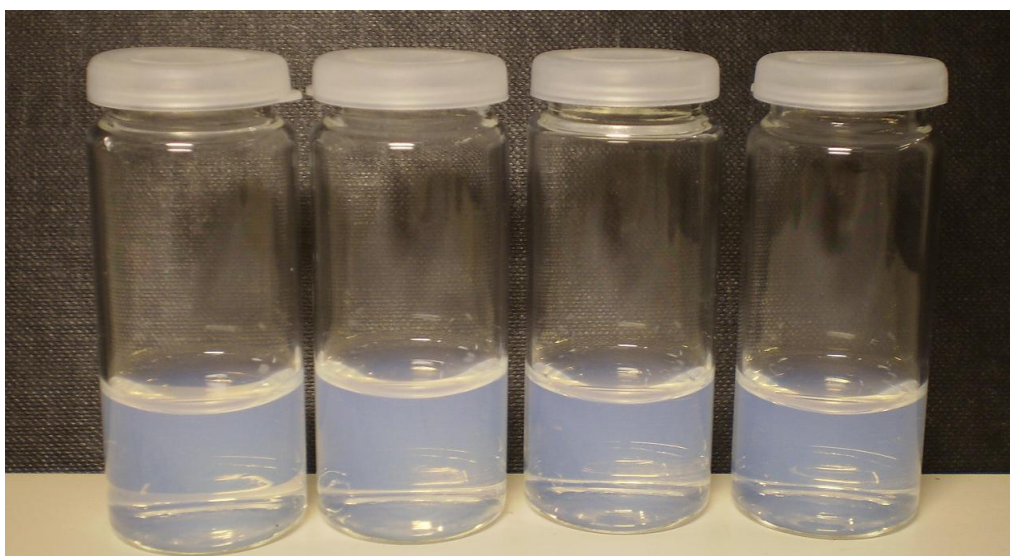
Figure 4.3: Unmodified silica sol with a concentration of 5 weight-% and, from the left to the right, pH 2, 4, 7 and 10.
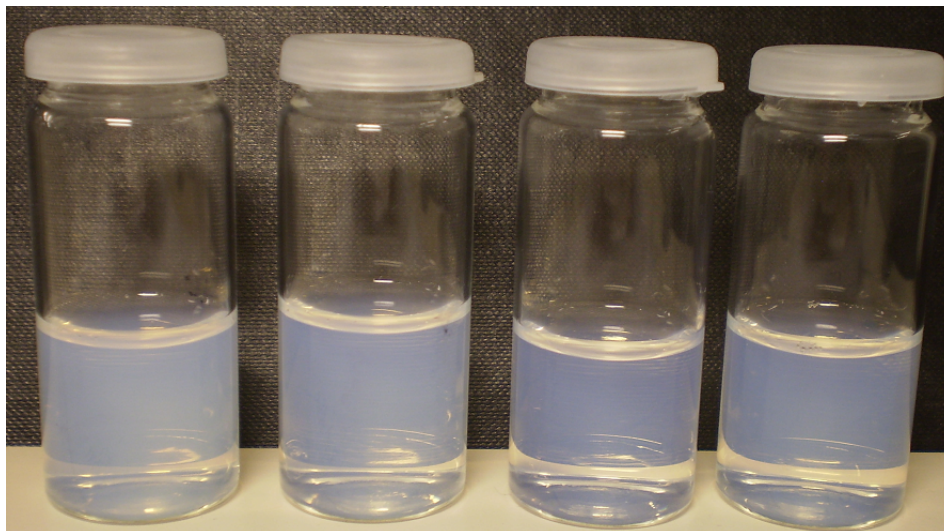
Figure 4.4: Silica sol with a concentration of 5 weight-% modified by iBu and, from the left to the right, pH 2, 4, 7 and 10.
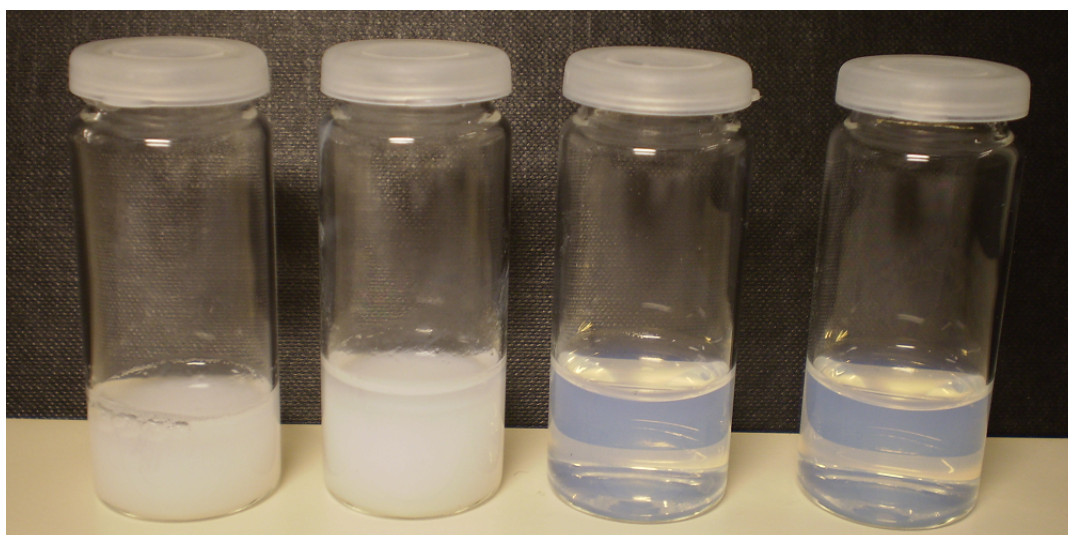
Figure 4.5: Silica sol with a concentration of 5 weight-% modified by MPEG-3GTO and, from the left to the right, pH 2, 4, 7 and 10.

4.3 Evaluation of the Grafting Efficiency

4.3.1 NMR Diffusometry

The NMR diffusometry results can be seen in Figure 4.6. The ratio between grafted MPEG and MPEG free in the solution is calculated from the ratio between the slope of the curve at low x-values and at higher x-values. As shown, for both of the reference samples, the pure MPEG sample and the MPEG and silica sample, the magnitude of the slope remains unchanged. This indicates that 0% of the MPEG is grafted. This is anticipated at pH 10 since MPEG has low affinity towards the silica surface. Furthermore, the lines do not match entirely because one of the samples contains silica, in addition to MPEG, which has a small effect on the diffusion of MPEG in that sample.

The graph also shows that in the unfiltrated modified silica sol, 6% of the MPEG-3GTO is attached. This is also the result for the sample that is ultrafiltrated with the 5000 NMWL filter. The sample ultrafiltrated with the 30 000 NMWL filter contains 84% attached MPEG-3GTO. These results indicate that during ultrafiltration, the pore size of the filter should not be as small as 5000 NMWL, even though this pore size in theory is large enough for the MPEG-3GTO molecules to cross. A possible explanation for this is that MPEG-3GTO molecules form oligomers like O-Si(R)-O-Si(R)-O with a molecular weight higher than 5000 g/mol. However, the fact that 16% of the MPEG-3GTO in the sample are still free corresponds well to the amount of dilution during ultrafiltration.

The diffusion coefficient of the MPEG-3GTO and iBu-modified silica particles is determined to be $8.4 \cdot 10^{-12}$ m^2/s, corresponding to a particle size of 52.1 nm.

4.3.2 Thermal Gravimetric Analysis

In order to ensure the accuracy of this method in the case of incinerating organic-containing modifiers, five samples with known contents are evaluated. As Figure 4.7 shows, the differences between expected and experimental values are very small (at most 1.6%). However, since this method does not differentiate between modifiers covalently attached to the silica surface and modifiers in solution, it must be combined with another analysis technique to verify that all the weight loss during the combustion is due to covalently attached modifiers. A technique suitable for this is NMR diffusometry.

NMR diffusometry shows that both the modified but unpurified silica sol and the sol purified with the 5000 NMWL filter have the same ratio between
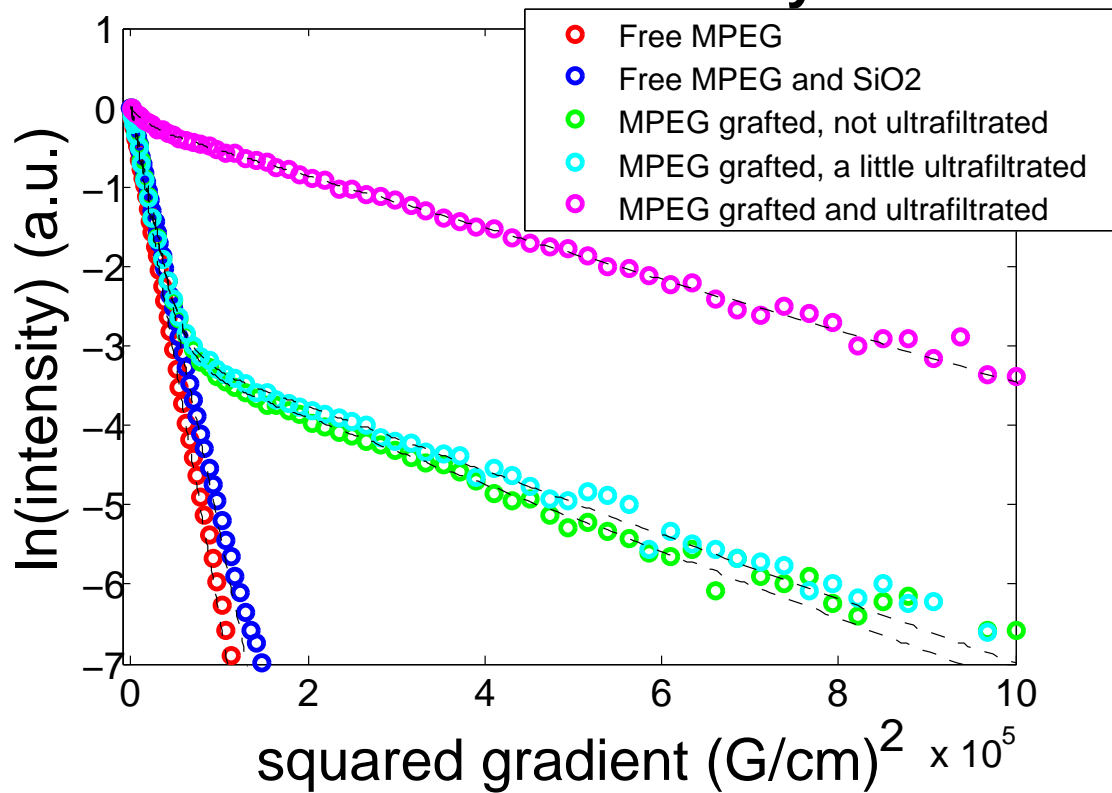
Figure 4.6: Results from the NMR diffusiometry. Free MPEG and MPEG + SiO2 are reference samples. The sample named a little ultrafiltrated is purified with the 5000 NMWL filter and the ultrafiltrated sample is purified with the 30 000 NMWL filter.
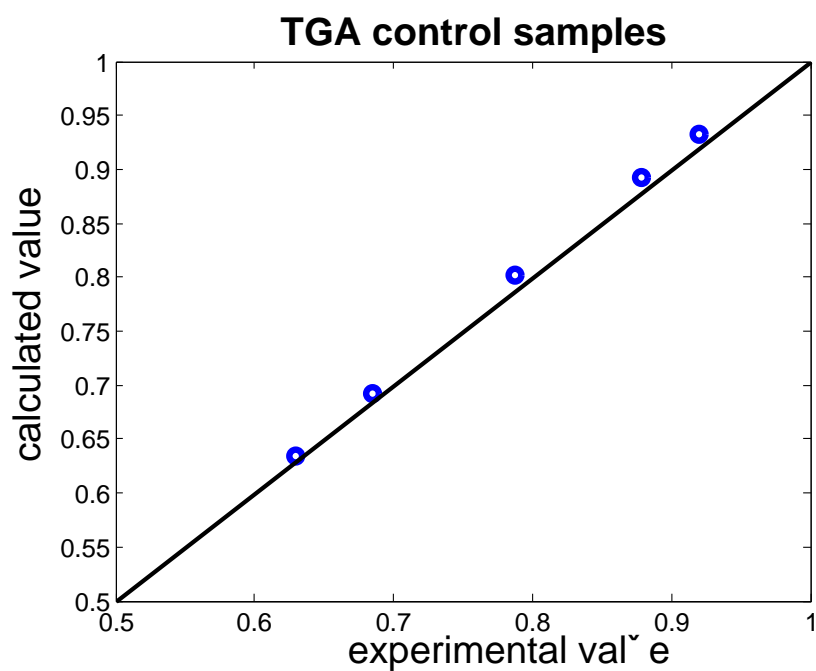
Figure 4.7: TGA where samples with known contents (y-axis) are compared with their experimental value (x-axis).
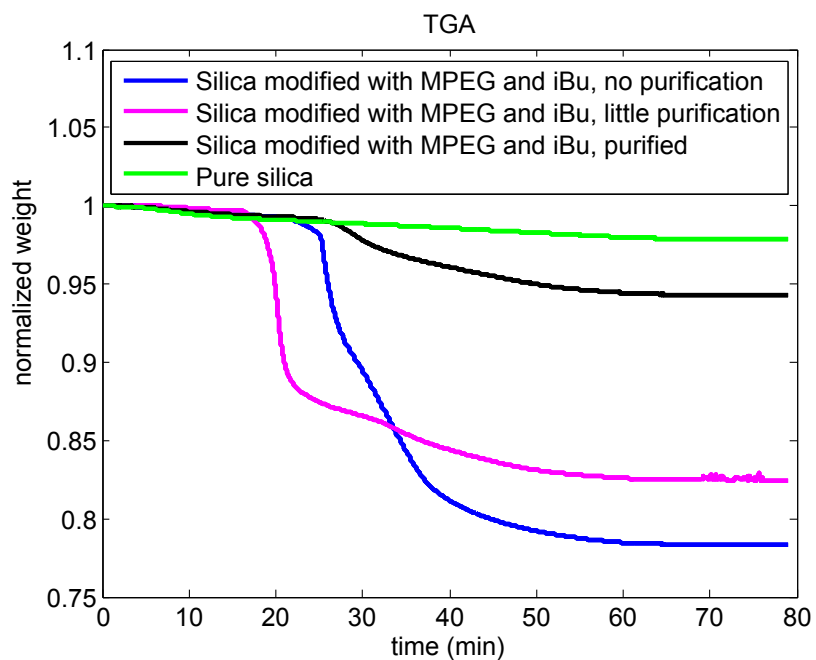
Figure 4.8: TGA of modified- as well as unmodified silica. The normalised weight is plotted as a function of time. Maximum temperature is 600°C.

MPEG that is covalently attached at the silica particles and MPEG that is free in the solution. However, the TGA results show different content of organic material between these samples. The probable reason for this is that, during ultrafiltration with the 5000 NMWL filters, unreacted 3GTO, which is a much smaller molecule than MPEG, is filtered off.

Figure 4.8 shows the results from the TGA of modified silica sol as well as pure silica. The latter shows a weight loss of 2.17%. Modified silica sol with no filtration shows a weight loss of 21.71%. After little ultrafiltration this number is reduced to 17.57%. After total ultrafiltration the weight loss is only 5.76%. However, since the unmodified silica sample contains 2.17 % water, it is reasonable to believe this is the case for the other samples as well, hence this weight is subtracted from the modified samples. As a result, the modified but unpurified silica contains 19.55% MPEG-3GTO, the modified silica with little purification contains 15.41% MPEG-3GTO and the totally purified contains 3.59% MPEG-3GTO.

Since TGA results shows that 3.59 weight-% of the modified and totally ultrafiltated silica particles contain MPEG-3GTO but the NMR results shows that 16% of the MPEG is still free in the solution, this results in that 3.02 weight-% of the silica particle weight is MPEG. If all the added MPEG-3GTO had attached to the silica, this would correspond to 21.09% of the total weight and a surface coverage of 0.93 μmol MPEG-3GTO/m^2. The corresponding surface coverage obtained in the current work is therefore 0.14 μmol MPEG-3GTO/m^2.

On the contrary, calculations straight from the NMR diffusometry results, which show that 6% of the MPEG in the unpurified sample is covalently attached at the silica surface, show that 0.06 μmol MPEG-GTO/m^2 silica surface is covalently attached. The latter calculation is probably more correct than the one based on TGA. The reason for this is that MPEG might bind more water than silica, resulting in that the assumption that all dried sols would contain the same amout of water is wrong.

4.3.3 Dynamic Light Scattering

The volumetric particle size is determined to be 33.0 nm for the unmodified silica sol, with a polydispersity of 0.01. After attachment of iBu, the particle size is measured to be 32.1 nm with a polydispersity of 0.12. The differences between these values can be seen as negligible for the purpose of the current work, and the increased polydispersity from the iBu-grafted silica sol indicates that the iBu might be a bit inhomogeneously grafted among the silica particles.

Furthermore, the volumetric particle size measurement of the silica sol

with both iBu and MPEG-3GTO grafted on shows a diameter increase to 52.1 nm with a polydispersity of 0.16. This diameter increase corresponds to a 10 nm long PEG chain at both ends of the spherical silica particle. According to Chern et al. [17], a fully extended PEG chain has an estimated length of 8.9 to 16.9 nm, indicating that the measured silica particle diameter increase of 20 nm is a reasonable value if two MPEG chains are attached on both sides of the particle. The sol in this measurement is at pH 7, resulting in little affinity of the PEG chains towards the silica surface, hence the chains should be almost fully extended.

4.4   Interfacial Activity

### 4.4.1   At the Air-Water Interface

The results of the surface tensions measured by the Du Noüy ring technique for sols at a concentration of 5 weight-% can be seen in Figure 4.9.

As expected, pure silica sol shows almost no surface activity and does not depend on the pH. Furthermore, the iBu-modified silica sol is even less surface active than the unmodified sol. This is because of the hydrophobic character of iBu. However, the value for iBu-modified silica sol at pH 2 is significantly lower than the rest. This indicates that, at pH 2, interactions between the silica particles make them agglomerate at the surface, leading to increased surface activity.

The lowest surface tension (48.2 mN/m) is achieved by the modified silica sol containing both iBu and MPEG-3GTO at pH 4, followed by the same sample at pH 6 and pH 10. The reason why the pH 2 shows a higher value (64.4 mN/m) is probably due to that the system is phase separated.

The silica sol modified with MPEG-3GTO only shows a similar trend in surface activity when compared to the silica sol modified with both iBu and MPEG-3GTO. However, the surface tension is, at all pH, higher for the sol modified with MPEG-3GTO only. This shows that iBu contributes to increased surface activity, hence the particles should be modified with both modifiers for optimal surface activity.

The slight decrease of the surface tension of the milli-Q water should be disregarded.

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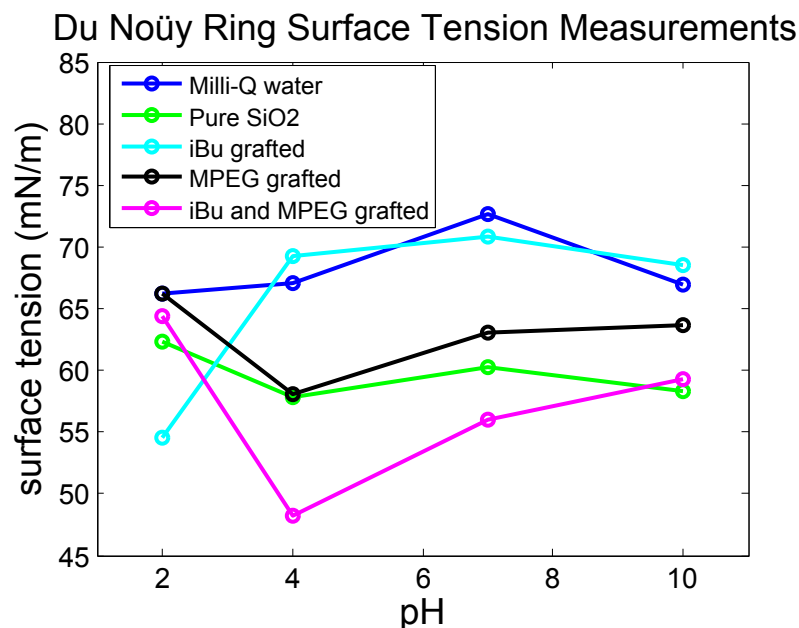
Figure 4.9: Surface tension as a function of pH. The lines are only added to guide the eye.

4.4.2 At the Oil-Water Interface

4.4.2.1 The Dodecane-Water Interface

The graph in Figure 4.10 represents the result from the interfacial tension measurements between the sols at 5 weight-% and dodecane. The interfacial tension between water at pH 7 and dodecane is measured to 49.94 mN/m, to be compared to the value 52.87 mN/m obtained by Zeppieri et al. [18] using an emergent drop technique. Since these values agree within a few percent, the trends reported in the current work are considered reliable.

The sol containing pure silica shows a small decrease in interfacial tension. Furthermore, the trend regarding iBu-modified silica is the same as in the case of the air-water interface: silica sol modified with iBu shows less surface activity compared to the pure silica. This is due to the hydrophobic character of the former.

As expected, the lowest interfacial tension values are observed for the silica sol modified by iBu and MPEG-3GTO. However, it is surprising that the sol modified only by MPEG shows the same surface activity. This effect might be a result of bridge flocculations at the interface, as a result of the PEG chains interactions. Nevertheless, since this affinity should be somewhat pH-dependent, the interfacial tension would, in that case, decrease with
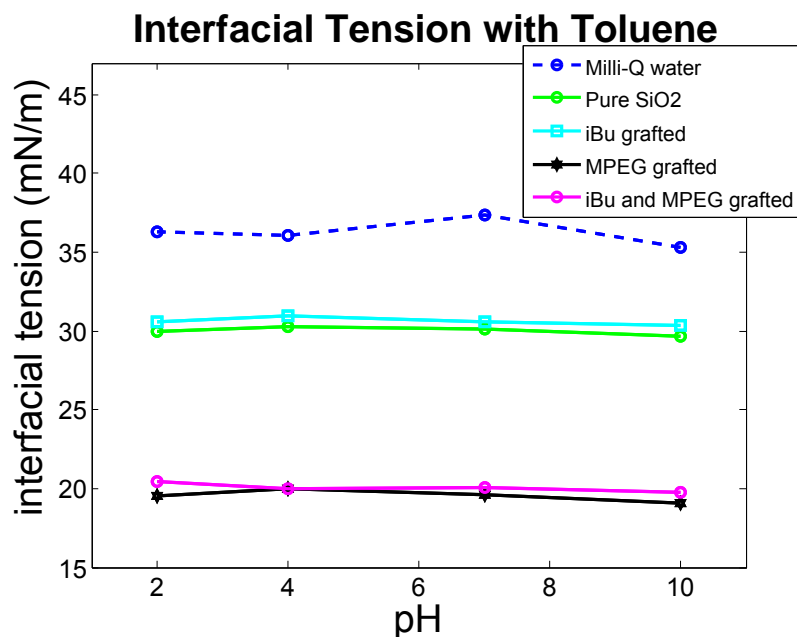
Interfacial Tension with Dodecane
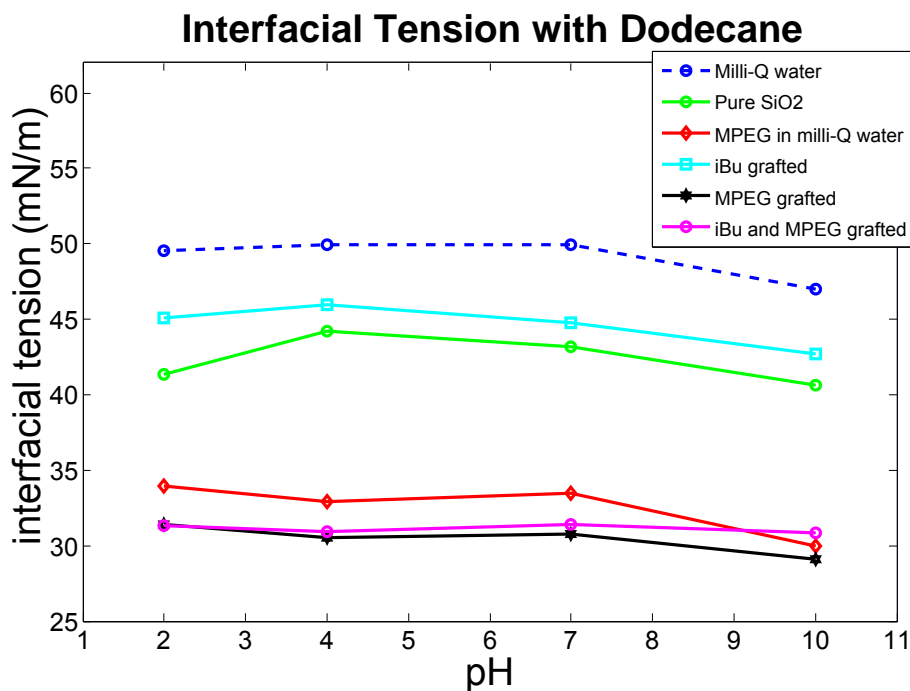
Figure 4.10: Interfacial tension between the samples and dodecane, as a function of pH. The lines are only added to guide the eye.

decreasing pH. As such a trend can not be observed, this is probably not the only explanation for the similar behaviour of MPEG-3GTO and iBu-modified sol and MPEG-3GTO-only modified sol.

It is possible that the degree of solubility of PEG in the oil phase could be important to explain the interfacial activity enhancement. But, since PEG is soluble in toluene but not in dodecane, and the surface activity trend is similar in both oils (as will be seen in the next section), this can most probably be excluded as an explanation.

However, since the pure silica sol shows similar interfacial activity as the sol modified with iBu only, it is reasonable that addition of covalently attached MPEG-3GTO provides a similar increase in interfacial activity.

Furthermore, the sample containing only MPEG in milli-Q also shows a low interfacial tension. This observation indicates that PEG chains alone contribute to reduced interfacial tension which might be an effect of bridge flocculations. However, pure MPEG lacks the ability of stabilizing an emulsion and is therefore not further investigated as an emulsifying agent/stabilizer.

Figure 4.11: Interfacial tension between the samples and toluene, as a function of pH. The lines are only added to guide the eye.

4.4.2.2 The Toluene-Water Interface

The interfacial tension between the sols at 5 weight-% and toluene is shown in Figure 4.11. The interfacial tension between water at pH 7 and toluene is measured to 37.38 mN/m. This value compares well to the value 35.0 mN/m obtained by Alpbaz et al. [19], using the drop weight method. Since these values agree within a few percent, the trends reported in the current work are considered reliable.

The trend regarding the toluene-silica sol interfacial tension resembles much the trend of the dodecane-silica sol: The sol containing pure silica as well as the iBu-modified silica sol show a small decrease in interfacial tension compared with pure water.

The lowest interfacial tensions are achieved with the silica sols modified with MPEG-3GTO alone as well as the silica sol modified with MPEG-3GTO and iBu. The reasons for the similarity in interfacial activity between these two sols are discussed in the previous section.
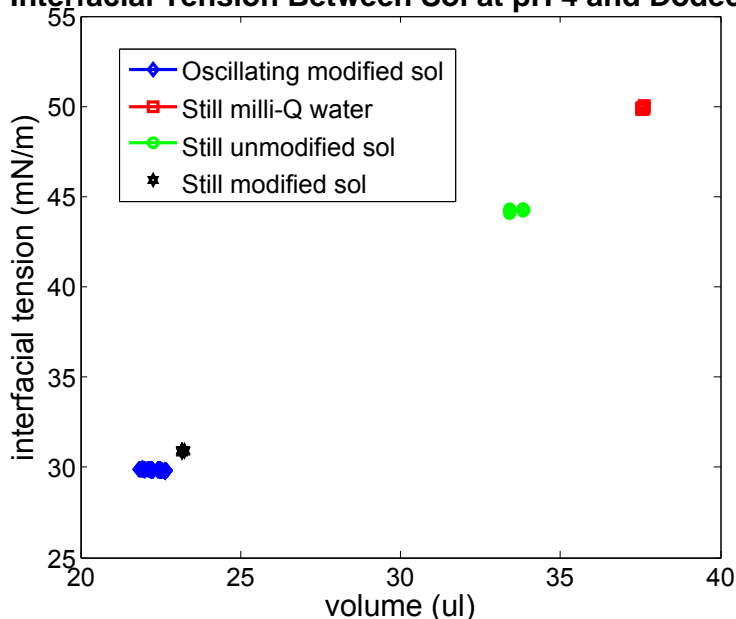
Figure 4.12: Interfacial tension between the sample oscillating with a frequency of 0.1 Hz and dodecane, as a function of the drop volume. The still modified sol, unmodified sol and the milli-Q water samples are added as references.

4.4.2.3 The Dodecane-Water Interface During Oscillation of the Water

The results of the experiments carried out with the oscillating pendant drop device are shown in Figure 4.12, where the interfacial tension is plotted as a function of the volume of the drop. The conclusion drawn from this study is that the modified silica particles go to the interface spontaneously.

4.5 Emulsification Tests

All emulsions between water and oil, with modified silica sol at pH 4 and 10 as emulsifiers, show clear similarities to a Winsor III system, with equal amounts of water and oil in excess right after the emulsification. However, most of the emulsions are not very stable from start and the stability decreases further after already 10 minutes for some of the emulsions.

The most stable emulsion is created by toluene as the oil phase and the modified silica sol at pH 4, see Figure 4.13. This emulsion still shows some stability after one week, but the drop sizes are quite large. This means that the modified silica particles can stabilize large interfaces. Furthermore, the

t = 0 min   t = 5 min   t = 10 min
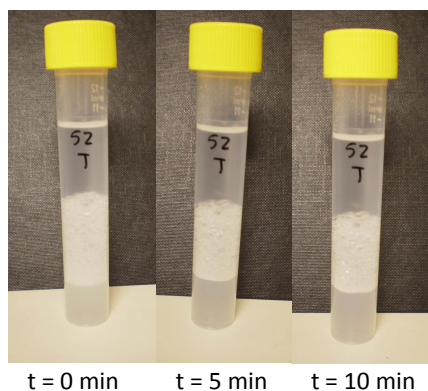
Figure 4.13: Modified silica sol at pH 4 as emulsifier between 30% water and 70% toluene. The amount of emulsifier is 0.5 weight-% silica particles of the oil mass.

t = 0 min   t = 5 min   t = 10 min
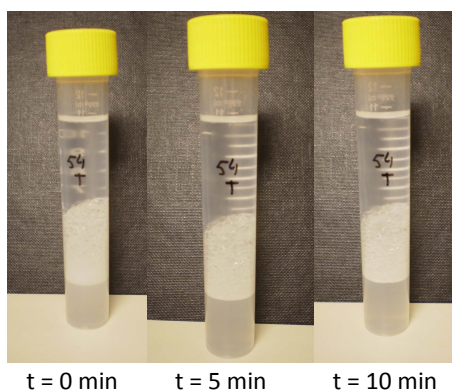
Figure 4.14: Modified silica sol at pH 10 as emulsifier between 30% water and 70% toluene. The amount of emulsifier is 0.5 weight-% silica particles of the oil mass.

emulsion between toluene and the modified silica sol at pH 10, see Figure 4.14, also resembles a quite stable Winsor III system.

Of the dodecane-containing emulsions, the system where modified silica sol is at pH 4, see Figure 4.15, shows better stability than the system containing modified silica sol at pH 10, see Figure 4.16.

In summary, in all emulsions there is a lack of particles, resulting in Winsor III systems after emulsification. The emulsions created in this study contain a mass of modified silica particles corresponding to 0.5 weight-% of the oil phase. Furthermore, the emulsions are likely to be oil in water.

t = 0 min   t = 5 min   t = 10 min

Figure 4.15: Modified silica sol at pH 4 as emulsifier between 30% water and 70% dodecane. The amount of emulsifier is 0.5 weight-% silica particles of the oil mass.
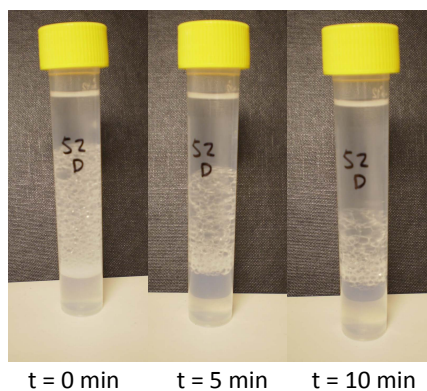

t = 0 min   t = 5 min   t = 10 min

Figure 4.16: Modified silica sol at pH 10 as emulsifier between 30% water and 70% dodecane. The amount of emulsifier is 0.5 weight-% silica particles of the oil mass.
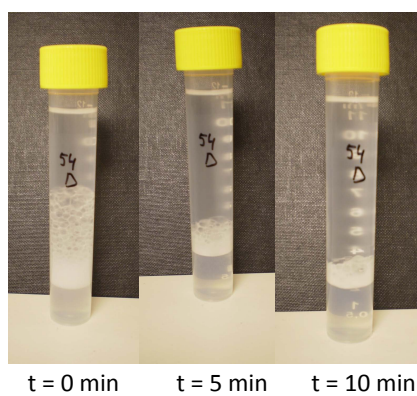
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Conclusions

In the current work, silica nanoparticles are modified by covalent attachment of a hydrophilic and a hydrophobic moiety, resulting in amphiphilic surfaces.

The hydrophilic moiety consists of poly (ethyleneglycol) methylether (MPEG) ($M_w = 2000$ g/mol) that is reacted with the coupling agent (3-glycidyloxypropyl) trimethoxysilane (3GTO) under acidic conditions. It is determined by liquid chromatography that the MPEG-3GTO reaction has a yield of 37%.

The hydrophobic modifier is isobutyl (trimethoxy) silane (iBu). This is the moiety that is first reacted with the silica surface, in order to avoid the steric hindrance that the PEG chains may cause if reacted first. The surface modifications are carried out in a 5 weight-% silica sol, and at pH 10 in order to avoid high affinity of the PEG chains towards the surface. Between each step of the grafting, the silica sol is purified with milli-Q water at pH 10 during ultrafiltration in order to remove unreacted reactants.

An estimation of the amount of MPEG-3GTO covalently bonded to the silica surface is obtained using nuclear magnetic resonance (NMR) diffusiometry. The surface coverage of MPEG-3GTO over the silica particles obtained in the current work is 0.06 μmol MPEG-3GTO/m^2.

Thermogravimetric analysis (TGA) shows, in combination with NMR, that the surface coverage of MPEG-3GTO over the silica particles is 0.14 μmol MPEG-3GTO/m^2. However, the result from NMR diffusometry only is probably more reliable due to increased water content in MPEG-3GTO-modified silica compared to pure silica.

The size of the particles of the sol are measured using dynamic light scattering. After grafting of MPEG-3GTO, the particle size radius increases approximately 10 nm to 52.1 nm, a reasonable size increase for PEG chains attached to the surface. The latter value is also confirmed by the diffusion coefficient obtained from the NMR diffusometry measurement.

Measurements of surface tension show that the most surface active sol

is the one modified both by MPEG-3GTO and iBu at pH 4. This confirms that the amphiphilic silica nanoparticles have the highest surface activity achieved in the present work. In addition, the modified sol is shown to have a significant surface activity also in two different oil-water systems.

Furthermore, emulsions are prepared using 70 weight-% oil, 30 weight-% water and 0.5% of the oil mass in modified silica particles. The result shows an oil in water emulsion with excess of both oil and water. This indicates that a larger amount of particles should be used in the future.

6

Future Studies

Future studies in this field could include determination of the optimum amount of modifiers to attach to the surface, and in addition the optimal conditions for the grafting reactions could be investigated. Furthermore, how the properties of the modified silica sol vary with the PEG chain length has not been investigated, this could be an interesting parameter.

Furthermore, the MPEG-3GTO synthesis in the current work showed that 63 % of the 3GTO molecules have not reacted with MPEG, hence this synthesis route needs further studies and improvements.

The emulsifications parameters such as water/oil ratio and amount of modified sol should also be investigated. The fact that all emulsions prepared inn the current work resemble Winsor III systems indicate that adding a larger amount of modified particles could be a good idea.

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