

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Functionalization and characterization of aqueous silica sols
and their application in Pickering emulsions

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CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover: Microscope image of emulsified oil (Exxsol D60) using surface functionalized colloidal silica as emulsifier. The silica particles were functionalized using two types of silanes, one with hydrophilic polyethylene glycol groups and one with hydrophobic propyl groups. The oil was mixed with fluorescent dye prior to emulsification. Björn Elgh is kindly acknowledged for taking the image.

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ABSTRACT

The main objective of this thesis is to create an understanding of how surface functionalized colloidal silica can be utilized in emulsions stabilized solely by particles, so called Pickering emulsions. To achieve this, water-based silica sols have been functionalized with hydrophilic and hydrophobic groups. The amounts of attached surface functional groups on the particles have been characterized using NMR spectroscopy, including NMR diffusometry. To further explore the attained properties of the modified particles, they have been studied using zeta potential and surface charge measurements as well as studies of how pH affects the flocculation of the functionalized silica sols. The emulsification abilities of the modified particles were evaluated by preparing Pickering emulsions using particles with varying degrees and combinations of hydrophilic and hydrophobic groups. In emulsion systems the wettability of the particles and the interfacial tension at the oil/water interface are relevant parameters, why surface and interfacial tension at the silica suspension/air and silica suspension/oil interfaces have been analyzed.

Hydrophilic functionalization of the silica sols was achieved by attaching methyl poly(ethylene glycol) silane (mPEG silane) to the silica particle surface. This way provides an efficient reduction of surface charge density, a pH dependent and controllable flocculation behavior is achieved and surface activity of the particles is reached. These properties are all beneficial for emulsion formulation. The hydrophobic functionalization of the silica sols was accomplished by attaching organosilanes containing propyl, methyl and octyl groups. It was found that colloidal silica functionalized with hydrophobic groups produced emulsions with smaller emulsion droplets compared to using *i.e.* unmodified silica. The emulsification performance was however further improved by attachment of both mPEG silane and propyl silane, preferably in combination with one more organosilane. The balance between hydrophilic and hydrophobic groups is of high importance, where a high degree of mPEG silane renders particles too hydrophilic to be efficient as emulsifiers. When studying the effect of silica particle size, it was found that smaller particles reduce the emulsion droplet size distribution due to the larger surface area available for stabilization. Also the pH and the salt concentration are important for efficient emulsion droplet formation. A pH below 6 to 4, depending on the particle used, is beneficial and in some cases required for emulsion formation. The low pH provides bridge-flocculated particles owing to the mPEG silane functionalization. The Pickering emulsions obtained display a high stability towards coalescence over a long period of time (from five weeks to 1.5 years).

Keywords: functionalized colloidal silica, Pickering emulsions, NMR spectroscopy, surface activity

List of publications:

- I. Surface activity and flocculation behavior of polyethylene glycol-functionalized silica nanoparticles
Sanna Björkegren, Lars Nordstierna, Anders Törnrona, Michael Persson and Anders Palmqvist
Journal of Colloid and Interface Science, 2015. 452(0): p. 215-223
- II. Hydrophilic and hydrophobic modifications of silica particles for Pickering emulsions
Sanna Björkegren, Lars Nordstierna, Anders Törnrona and Anders Palmqvist
Submitted for publication

Contribution report to the listed publications:

- I. Responsible for all experimental work, except for the NMR measurements, which were performed and analyzed together with Lars Nordstierna. Responsible for writing the manuscript.
- II. Responsible for all experimental work. Responsible for writing the manuscript.

Other publications not included in this thesis:

- i. A new emulsion liquid membrane based on a palm oil for the extraction of heavy metals
Sanna Björkegren*, Rose Fassihi Karimi*, Anna Martinelli, Natesan Jayakumar and Mohammad Ali Hashim
Membranes, 2015. 5(2): p. 168-179

*Contributed equally in performing the experimental work

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INTRODUCTION



Figure 1. An emulsion (milk) in a silica container (glass).

Most of us are subjected both to emulsions and to silica (SiO_2) every day. Drinking homogenized milk from a drinking glass is one example; milk is butterfat globules dispersed in a water-based media, thus an emulsion, and the glass is composed of mainly silica.

There are various examples of everyday life emulsion systems, including personal care products such as skin lotions, hairstyling products and cosmetics, pharmaceutical products such as topological creams with controlled release, paints and coatings, and other food products such as mayonnaise. Taking mayonnaise as an example, it consists of rapeseed oil, (or

some other oil, forming the discontinuous phase) dispersed in vinegar or lemon juice (the continuous phase) and some added egg yolk. This is what an emulsion is: a mixture of two or more normally immiscible liquids, where one liquid is dispersed in the other as droplets or globules. Egg yolk proteins and lecithin, which is a group of fatty substances occurring in egg, and act as the emulsifier and emulsion stabilizer. Without these proteins and lecithin the two normally immiscible phases (oil and water-based vinegar/lemon juice) would quickly separate.

Silicon dioxide is an oxide of silicon with the empirical chemical formula SiO_2 . Silicon originates from exploding stars, is present in for example sand and clays and is the 7th most abundant element on Earth. Silicon dioxide, or silica, is the major component of the Earth's crust [2]. Silica exists in at least 12 different forms, of which all but one have tetrahedral crystal structures where each silicon atom is bound to four oxygen atoms [3]. This thesis is dedicated not to the material of the drinking glass mentioned above, but to silica nanoparticles suspended in water, also known as silica sols. These are already utilized in numerous industrial processes and commercial products, such as retention aid in paper making, as additives in paints, as binder in foundry applications, for beverage clarification, and in polishing products [4].

INTRODUCTION

The work presented in this thesis explores the use of silica nanoparticles for the formulation of emulsions, where they act as emulsifiers and emulsion stabilizers. Emulsions stabilized by particles (Pickering emulsions) instead of surfactants (traditional emulsions) are distinguished by an ability to disperse high volume fractions of discontinuous phase and a high stability towards coalescence [5, 6]. Traditional emulsions can in many applications be replaced by particle-stabilized ones, and when using silica particles an environmentally benign system can be accomplished. The silica particles are inherently hydrophilic, and in order to promote adsorption at the interfaces of the emulsion droplets, the silica surface is functionalized. A typical functionalization reduces the concentration of the surface silanol groups, decreases the surface energy and surface charge density of the particles and makes the surface more hydrophobic [7]. The silica particles are characterized in various ways, in order to gain control of the functionalization process and to be able to elucidate the types and amounts of surface species required for obtaining functioning emulsifying agents.

Objectives

The aim of this work was to create an understanding of how surface modified colloidal silica behaves and how they can be utilized in emulsion systems. To achieve this, the work has been focused on the following tasks:

- To functionalize silica sols with hydrophilic and hydrophobic groups
- To evaluate the stability and determine the amount of surface functionalization on the silica particles
- To identify suitable characterization methods that can be used for the study of surface modified silica particles
- To explore the behavior of the surface modified particles in colloidal and surface chemical contexts

Two papers are included in this thesis. In Paper I silica particles were functionalized with a poly(ethylene glycol) silane (mPEG silane), to investigate the functionalization procedure, characterization methods and the altered surface chemical properties obtained such as surface activity. Silica surfaces grafted with poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG) have been and are still frequently studied [8-11]. PEGylated particles often have uses in biomedical applications [12-15], but also in other applications such as coatings [16]. PEGylation of the particles yields a reduction of the surface charge density, and can induce steric stabilization thus allowing applications in a broader pH range. Partial coverage of the silica surface allows studies of how the pH influences particle-PEG interactions.

Silica particles with either chemisorbed or grafted hydrophobic organosilanes can be employed to study and control the wettability of the particles [17, 18]. This produces homogeneously functionalized particles. In Paper II however, the silica particles were functionalized with both hydrophilic and hydrophobic species, to obtain heterogeneous particles. The mPEG silane constituted the hydrophilic part of the modification. The hydrophobic functionalization was accomplished by using various degrees of organosilanes containing propyl, methyl or octyl groups.

CHAPTER ONE

1 Emulsions

Emulsions are mixtures of two or several normally immiscible liquids, in most cases oil and water, where either oil droplets are dispersed in water, producing an oil-in-water (o/w) emulsion, or water is dispersed in oil, generating a water-in-oil (w/o) emulsion. By the addition of surface active agents such as surfactants, which reduce the interfacial tension between the two liquid phases, and in combination with energy input, emulsions can be formed. In similarity to surfactants, colloidal particles can adsorb at the interface of the liquids and can thereby also stabilize emulsions, producing so called Pickering emulsions [5, 19, 20]. For this to occur the particles should be wetted by both phases, thus be partly hydrophilic and partly hydrophobic. The liquid of higher wetting capacity will generally constitute the continuous phase of the emulsion. The size of the particles will influence the system, and for efficient stabilization the particles should preferably be more than one magnitude smaller than the emulsion droplets [21]. It means that nanoparticles are required in order to produce emulsions with droplets of sub-micron size.

1.1 Surface activity and interfacial tension

Surface tension is what holds a drop of liquid together and is correlated to the cohesive energy in the liquid. Water for example has a high cohesive energy density and therefore also a high surface tension. At the surface of a liquid an asymmetry of cohesive forces exist and this gives rise to a certain surface tension [1]. In similarity, at the interface of two liquid media, *e.g.* oil and water, a certain interfacial tension exists. The origin of interfacial tension is exemplified in Figure 1-1: a molecule in the bulk liquid senses identical intermolecular forces in all directions, while a molecule

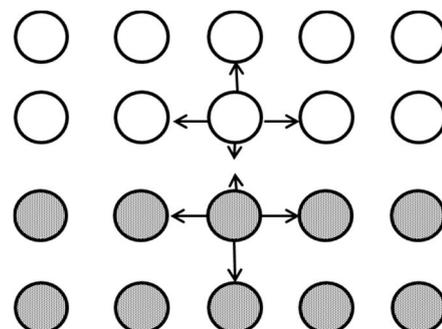


Figure 1-1. The imbalance of attractive forces at an interface causes the interfacial tension. Redrawn from [1].

at the interface lacks this attraction in one direction [1]. This leads to a minimization of the contact area between the oil and the water phases. This is the reason to why it is beneficial to reduce the interfacial tension between the phases, achieved through addition of surface active species like surfactants, in order to create an emulsion where the surface area between oil and water increases enormously. Surfactants possess a driving-force to assemble at interfaces, due to their amphiphilic nature. Particles can also be surface active, in the sense that they as well assemble at interfaces [5].

1.1.1 Amphiphilic particles

In theory, the best stabilizing effects of particles for Pickering emulsions are achieved when the particles are symmetrically positioned between the two liquid phases [22]. This implies that the particles resemble Janus particles, having two distinct areas differing from each other in terms of surface chemistry or polarity. The name comes from the two-faced Roman god Janus, since the particles are said to have two faces or regions; one region being polar and one region being non-polar, providing a true amphiphilic character of the particle. Originally the Janus term

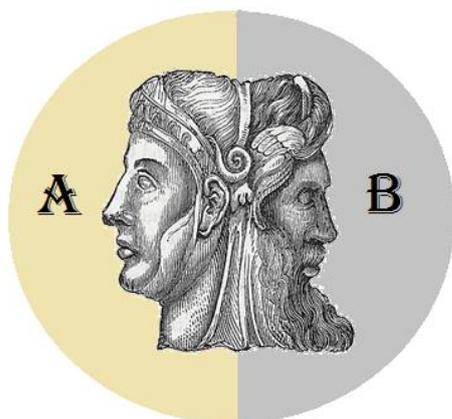


Figure 1-2. A Janus particle has two faces or regions A and B with *e.g.* differing surface chemistry.

referred to particles with two equal areas of polar/non-polar regions (see Figure 1-2), however the ratio between the regions may also be varied [22, 23]. It has been theoretically predicted that a 3-fold increase in adsorption energy can be achieved, if the ratio of the polar to non-polar region is 50:50, compared to a homogeneous particle [22]. This has also been studied experimentally, where increased adsorption energy was achieved [24, 25]. In practice Janus particles are often tedious to produce and therefore not yet suitable for industrial applications. Some of the particles discussed in this work have been surface modified with both hydrophobic and hydrophilic groups, providing a heterogeneous surface modification, but have not been proven to have a true Janus character.

1.2 Pickering emulsions

As mentioned in the Introduction, Pickering emulsions can be used in many applications as an alternative to traditional emulsions, or when surfactant-free systems are needed. The surfactant-free character of the Pickering emulsions can be a desired property in for example cosmetics and pharmaceutical applications in which the surfactants can cause skin irritation [26].

Another desired feature of the Pickering emulsions is the high stability of the system. The adsorbed particles will efficiently hinder droplet coalescence, since they can act as a mechanical barrier between the phases [27, 28]. In addition, the particles adsorb in principle irreversibly at the interface of the emulsion droplet, if the three phase contact angle θ is close to 90° (see Figure 1-3) [21]. The large adsorption energy for particles at the oil/water interface results in a high energy barrier for spontaneous desorption. Eq. 1.1 is valid for spherical particles with smooth, uniform surface structures, and shows that the desorption energy, ΔG_d , depends on the mentioned contact angle θ , the particle radius r , and the interfacial tension between the oil phase and the water phase γ_{ow} [21].

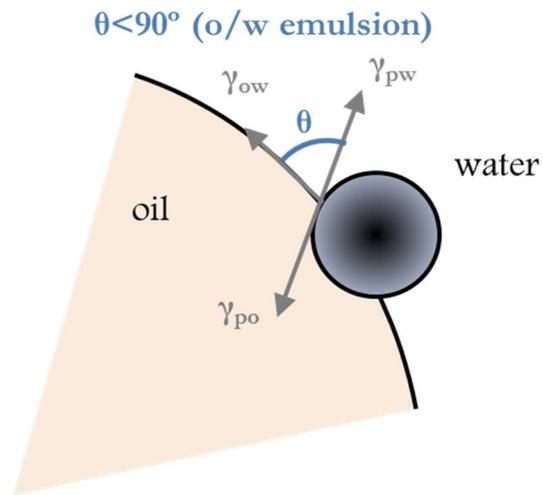


Figure 1-3. Simplified illustration of a solid particle at the interface of an oil droplet dispersed in water, positioned in equilibrium at the oil-water interface with the contact angle θ .

$$\Delta G_d = \pi r^2 \gamma_{ow} (1 - \cos \theta)^2 \quad \text{Eq. 1.1}$$

$$\cos \theta = \frac{\gamma_{po} - \gamma_{pw}}{\gamma_{ow}} \quad \text{Eq. 1.2}$$

The contact angle and is dependent on the particle-oil, particle-water and oil-water interfacial tensions γ_{po} , γ_{pw} and γ_{ow} according to Young's equation (Eq. 1.2) and it describes the wettability of the particles [29]. A particle with $\theta = 90^\circ$ is equally wet by both liquid phases and is strongly held at the interface. For such particles, also for small ones with radii of 5-10 nm, $\Delta G_d \gg 10k_B T$ [21, 30]. A rapid decrease in desorption energy is noted at either side of 90° , and when θ approaches 0° (hydrophilic particles) or 180° (hydrophobic particles) $\Delta G_d < 10 k_B T$ [5].

Often the particle needs to be modified, for example by hydrophobizing the particle surface, in order for the particles to be suited for Pickering emulsion applications. This can be achieved through physical adsorption or by covalent attachment of surface species.

1.2.1 Destabilization mechanisms

Depending on the application of the emulsion, different degrees of instability may be tolerated. As an example, creaming or sedimentation of the emulsion may not be tolerated for food applications or facial creams, while in other applications such as enhanced oil recovery this type of separation is allowed. Through a gentle shake of a creamed or sedimented emulsion the original appearance of the emulsion is regained, since this separation is simply due to gravitational forces. More severe destabilization mechanisms of the emulsions are due to coagulation and coalescence [26]. Bridge flocculation can also occur, when the emulsion droplets are partially covered and particles are shared between pairs of adjacent droplets [21]. At low concentrations of emulsifying agent the initial droplets will coalesce until the oil/water

interface of each droplet is covered with a sufficiently large amount of particles to stabilize the droplets [21, 31]. Saleh *et al.* [32] have suggested that small droplets play a key role in emulsion stability and that there has to be enough particles to cover the droplets, else large droplets are formed in an unstable emulsion. The driving force for increased droplet size is described by Laplace pressure difference ΔP (Eq. 1.3), where r is the droplet radius. When the droplets are completely covered they are sterically hindered from coalescence.

$$\Delta P = 2\gamma_{ow}/r \quad \text{Eq. 1.3}$$

Other results have shown that stable emulsions can also be obtained when the emulsion droplets are not fully covered with particles [33]. The mechanisms behind remain to be explored for a full understanding, but one explanation could be stabilization through bridging monolayers with emulsion droplets sharing particles [27].

1.3 Emulsification process

A common way to obtain an emulsion is through homogenization using an Ultra Turrax, a Silent Crusher or similar device, for example a kitchen hand blender which can be used for preparation of home-made mayonnaise. For the creation of Pickering emulsions a relatively high energy input is required to achieve small emulsion droplets. This often induces foaming, making it difficult to evaluate the emulsification ability of the particles, since some of the particles would be trapped in the foam. Emulsification can also be performed using a Magic Lab device (see Figure 1-4), which recirculates the product. The recirculation provides efficient shearing thus a high input energy but still gives low generation of foam.



Figure 1-4. Magic Lab used for emulsification. The recirculation provides a high input energy but still give a low foam generation.

CHAPTER TWO

2 Colloidal silica and surface functionalization

Colloidal silicas are dispersions, often concentrated, of discrete amorphous silica particles in a liquid. The colloidal state comprises particles in the size range of 1 nm to 1 μm . These are particles small enough not to settle through gravitational forces, their movement due to Brownian motion dominates over the gravitational one, but large enough to have properties distinct from of a true solution [4]. Colloidal particles in dispersion do not decrease the freezing point of the liquid, since the particles are not solved, but they do scatter incoming light. The particles are made up of colonies of approximately 10^3 to 10^6 atoms [4]. If the liquid in which the silica particles are maintained is organic, the suspension is referred to as an *organosol* and when the liquid is water it is called an *aquasol* or *hydrosol* [4]. The colloidal systems used in this work are all water-based and will be referred to simply as *silica sols*.

2.1 Surface chemistry and stability of colloidal silica

The nature of the colloidal silica surface depends on the status of its hydrate and hydroxylic cover, which in its turn is affected by for example heat treatment of the silica [34]. The functional groups that exist and constitute the hydroxylic cover are silanol groups (hydroxyls) and surface siloxanes (siloxane bridges). Single (isolated), vicinal and geminal (silanediol) silanol groups are found (Figure 2-1), and physically adsorbed water molecules are hydrogen-bonded to all types of silanol groups building up the hydrate cover [4]. The silanol number, α_{OH} , of fully hydroxylated amorphous silica lie within the range 4.2-5.7 OH groups nm^{-2} [35]. According to Zhuravlev, the average value $\alpha_{\text{OH}} = 4.9$ OH groups nm^{-2} is considered a physiochemical constant, since it is independent of origin and surface characteristics such as specific surface area [35]. The value corresponds to 8 μmol of silanol groups m^{-2} surface. These can in water be ionized bearing a charge density that increases with pH; pK_a of the SiOH is around 9.2 [2]. At the isoelectric point, reported to be found around pH 2, a silica sol is metastable, and above pH 7 the concentration of surface charge is sufficient to cause mutual repulsion between the particles, which provides stability towards gelling of the sol, see Figure 2-1 [2, 4]. When the sol displays colloidal stability, the particles do not settle nor aggregate at a significant rate [4]. 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 [2]. During flocculation, the particles are linked by bridges induced by a flocculating agent long enough to allow the aggregated structure to remain open and voluminous [2]. Coagulation leads to the formation of compact aggregates that are macroscopically separated and in which the silica concentration increases [2].

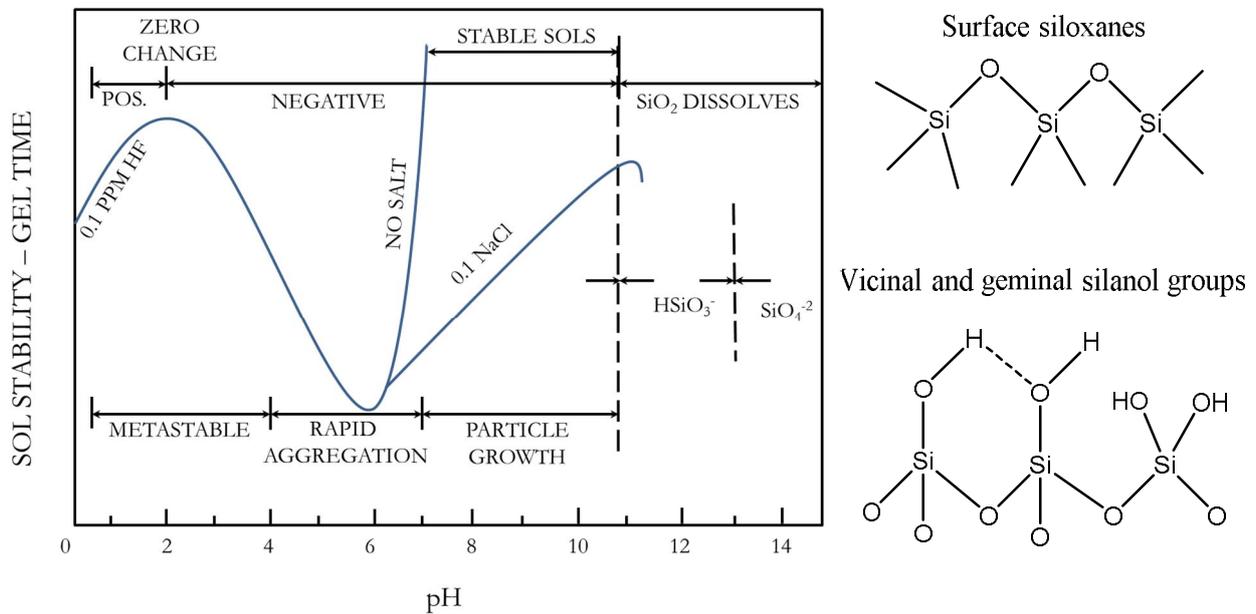


Figure 2-1. Left: Influence of pH on sol stability or gel time of the water-colloidal silica systems. Reproduced from [2]. Right: Some of the groups involving Si-O bonds identified on the surface of amorphous silica.

2.2 Functionalization of colloidal silica

The use of silica materials, *e.g.* glass-fibers, functionalized with silane derivatives has been on the market since the 1950's [36, 37]. The work presented in this thesis comprised functionalization of colloidal silica by silylation of the surface shown in Figure 2-2.

The types of silica sols used are seen in Table 2-1. Silanes with organofunctional and hydrolysable groups were used for the functionalization, seen in Table 2-2. The results presented in Paper I concerns silica particles functionalized only with methyl polyethylene glycol silane (mPEG silane). Silica particles functionalized with different combinations of the silanes in Table 2-2, including mPEG, are presented in Paper II. The functionalizations were prepared via a direct, water-based route and at relatively high silica concentrations (20-40 wt% SiO₂).

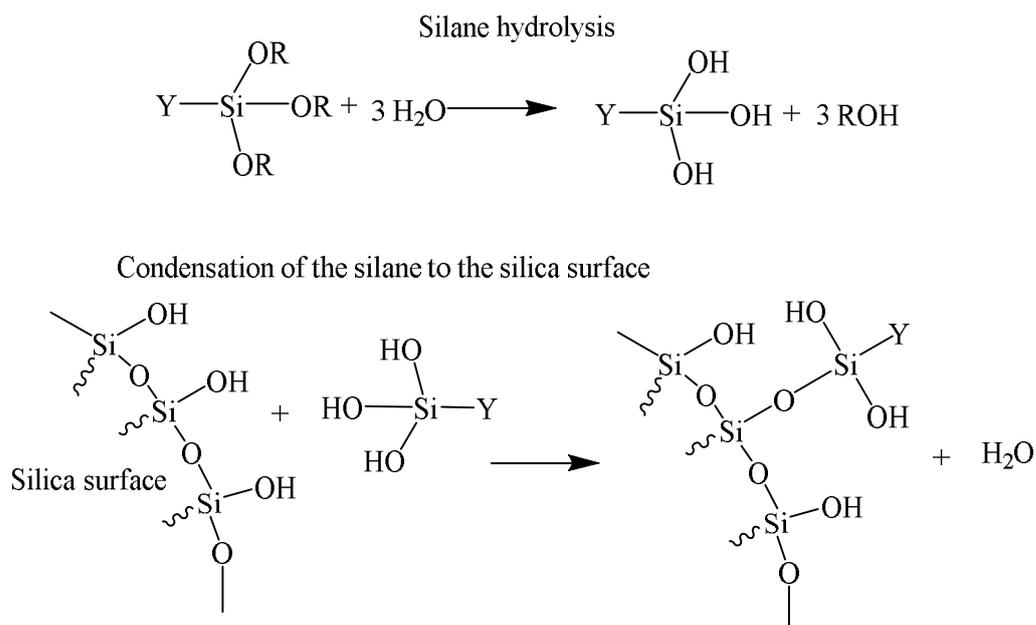


Figure 2-2. Silylation of the silica surface.

Table 2-1. Colloidal particles used, all provided by AkzoNobel Pulp and Performance Chemicals (PPC) AB.

Commercial name	Specific surface area (m ² /g)	Average particle diameter (nm)*	Native pH	Native conc. (wt% SiO ₂)	Abbreviation
Bindzil 30/360	360	8	9.1	31	Bz360
Bindzil 40/130	130	21	10.1	40	Bz130
Bindzil 2034DI	200	14	2.8	34	Bz200

* The average particle diameter was calculated from the specific surface area [2], which was measured by Sears titration [38].

Table 2-2. Silanes used for the functionalization of silica presented in this thesis.

Product name	Manufacturer	Chemical structure	Character	Abbreviation
Silquest A-1230 Silane	Momentive	(H ₃ CO) ₃ Si(CH ₂) ₃ (OCH ₂ CH ₂) ₁₁ OCH ₃	Hydrophilic	mPEG
Ethoxy trimethylsilane	Sigma-Aldrich	H ₅ C ₂ OSi(CH ₃) ₃	Hydrophobic	TMEO
Dimethoxy dimethylsilane	Sigma-Aldrich	(H ₃ CO) ₂ Si(CH ₃) ₂	Hydrophobic	DMDMO
Dynasylan PTEO	Evonik	(H ₅ C ₂ O) ₃ Si(CH ₂) ₂ CH ₃	Hydrophobic	PTEO
Trimethoxy (propyl) silane	Sigma-Aldrich	(H ₃ CO) ₃ Si(CH ₂) ₂ CH ₃	Hydrophobic	PTMO
Silquest A-137 Silane	Momentive	(H ₅ C ₂ O) ₃ Si(CH ₂) ₇ CH ₃	Hydrophobic	OTEO

CHAPTER THREE

3 Analytical techniques

3.1 NMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was used in the work presented in both Papers I and II for determination of the amounts of bound surface species on the silica particles. In Paper I NMR diffusometry and analysis of the relaxation behavior of the species was employed, and in Paper II NMR spectroscopy was used to determine the concentrations of the silanes in the samples.

NMR spectroscopy utilizes the ability of atoms, or more precisely the nuclei of atoms, to absorb and reemit electromagnetic radiation due to the change of the nuclei spin states. This is achieved through the application of a directed magnetic field. The NMR spectrum is a plot of the intensity of absorption on the vertical axis against frequency on the horizontal axis and

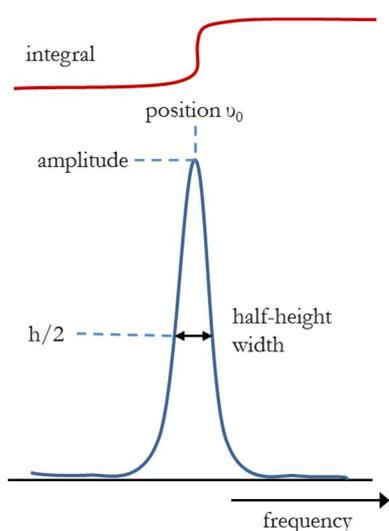


Figure 3-1. An absorption mode lineshape.

provides information about the chemical and physical properties of the atoms or molecules in the sample. In order for a nucleus to be detected with NMR it must possess a nuclear spin, which is associated with a magnetic moment. Nuclei with odd mass and/or odd atomic number, such as ^1H , ^{13}C and ^{29}Si , which are relevant for this work, possess a nuclear spin, although the natural abundance of both ^{13}C and ^{29}Si is low (1.08 % and 4.67 %, respectively) [39].

Figure 3-1 shows the typical Lorentzian lineshape of an NMR signal, where the peak is centered at position ν_0 in Hz and has amplitude of height h . The width is measured at half of the peak height, $h/2$. The separation between two peaks relative to their linewidth, and also their lineshape, will determine whether the peaks are resolved or not [40]. The position of the peak is usually given as the chemical shift in ppm, as this scale is independent of the magnetic

field strength. In the chemical shift scale the position of the peak is given relative to the position of a reference peak from a reference compound. The chemical shift of the nuclei in the sample is dependent on its specific chemical environment, wherefore different nuclei in a molecule give rise to different chemical shifts [40].

The size of the integral of the peak gives the intensity of the signal, which is directly proportional to the amount of nuclei that give rise to the signal. NMR can thus be used quantitatively, as the integral intensity is directly proportional to the concentration of the molecules (nuclei) in the sample.

3.1.1 T_1 and T_2 relaxation

NMR spin relaxation is the phenomenon that describes how the bulk magnetization from the spins in a sample, after magnetic perturbation, returns to its thermal equilibrium value. The rate of relaxation is sensitive to the physical environment of the nuclei and the nature of motion that the molecule is undergoing. When an external magnetic field (B_0) is permanently applied to a sample, the magnetic moments of the spins in the sample interact with the field and align along a given z-axis. Using the descriptive vector model, the bulk z-magnetization (M_z) is the sum of the z-components of the magnetic moment of each spin. The x- and y-components are distributed randomly at equilibrium, resulting in no net transverse magnetization. To record a spectrum, a short radio-frequency (RF) pulse is applied, which generates an oscillating second magnetic field B_1 perpendicular to the static field B_0 . The length of the RF-pulse can be tuned to transfer the magnetization of the nuclear spins into the xy-plane, where experimental detection can be carried out. Such RF-pulse is denoted as a 90° -pulse and all magnetic z-components are rotated onto the same axis in the xy-plane. This effect is called phase coherence where all magnetic moments are aligned in the same direction, and subsequently to the end of the RF-pulse the magnetic moments start to precess about the z-axis. At this situation the spins are not at equilibrium. Also, the energy of the spins is increased because alignment of the spins with the z-axis is the low energy arrangement. The spins therefore need to lose energy in order to come back to equilibrium.

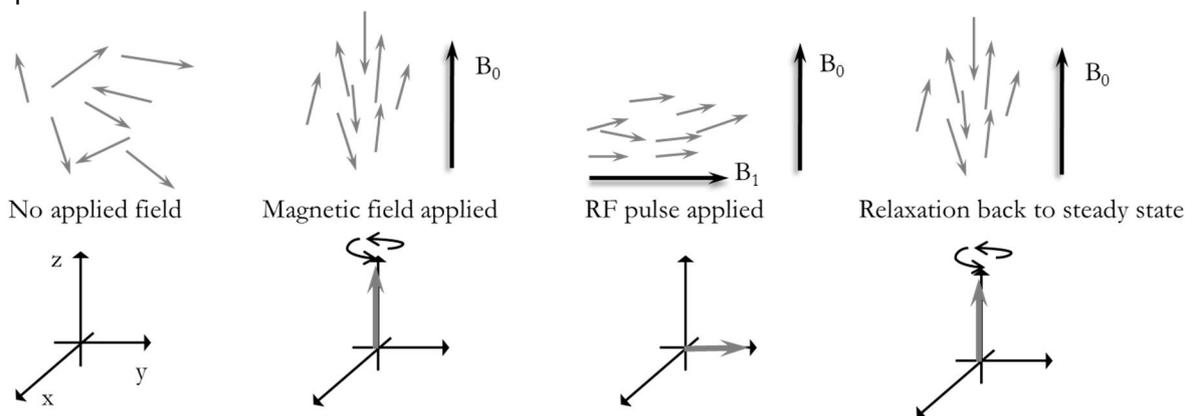


Figure 3-2. Using the vector model, showing how the magnetic moments from individual spins are first randomly distributed when no magnetic field is applied and then aligns with the applied magnetic field B_0 and precess about the z-axis. When an RF pulse is applied, the magnetic moments align in the xy-plane, and still precess about the z-axis, and finally back to equilibrium due to relaxation.

This process, when the z-magnetization is returned to its equilibrium value, is called *longitudinal relaxation* or *spin-lattice relaxation*. The longitudinal relaxation involves the flow of energy between spins due to molecular motion. The random thermal motion of the molecules drives the z-magnetization back to its equilibrium value.

Transverse relaxation is the process by which transverse magnetization decays to its decoherence equilibrium value of zero net magnetization in the *xy*-plane.

The longitudinal and transverse relaxations can be expressed as first order equations with rate constants R_1 and R_2 , where R_1 is the longitudinal relaxation rate and R_2 is the transverse relaxation rate. The inverse of the relaxation rates gives the relaxation times T_1 and T_2 .

$$\frac{dM_z}{dt} = -(M_z - M_0)R_1 ; T_1 = 1/R_1 \quad \text{Eq. 3.1}$$

$$\frac{dM_{xy}}{dt} = -M_{xy}R_2 ; T_2 = 1/R_2 \quad \text{Eq. 3.2}$$

3.1.2 NMR diffusometry

With NMR diffusometry the loss of intensity during a magnetic field gradient pulse is followed. The intensity decrease provides information on the physical movement of the molecules in the sample during a certain time, and thereby the self-diffusion coefficient can be obtained. The pulsed gradient stimulated spin-echo (PGSTE) method [41] was employed in this work. Eq. 3.3 below describes the decayed intensity I compared to equilibrium intensity I_0 , where Δ is the diffusion time, δ is the gradient pulse length, τ_r is the gradient ringing delay, T_1 and T_2 are the longitudinal and transverse relaxation times, respectively, D is the diffusion coefficient, γ is the ^1H gyromagnetic ratio and G is the gradient field strength. The equation can be simplified into Eq. 3.4.

$$I = \frac{1}{2}I_0 \exp\left\{-\frac{\Delta - \tau_r}{T_1}\right\} \exp\left\{-\frac{2\delta - \tau_r}{T_2}\right\} \exp\{-D(\gamma\delta G)^2(\Delta - \delta/3)\} \quad \text{Eq. 3.3}$$

$$I = C \exp\{-Dk\} \quad \text{Eq. 3.4}$$

If the observed diffusion, D_{obs} , is a population average, representing for example one fraction, p , of species bound to particles in a suspension and one fraction, $1-p$, of species free in the surrounding liquid (see Eq. 3.5) then the intensity follows Eq. 3.6, where C_f and C_b are functions of the relaxation times of free and bound species, respectively. By fitting the equations in MatLab or similar D_{free} , D_{bound} and p can be extracted.

$$D_{obs} = pD_{free} + (1 - p)D_{bound} \quad \text{Eq. 3.5}$$

$$I(k) = pC_f \exp\{-kD_{free}\} + (1 - p)C_b \exp\{-kD_{bound}\} \quad \text{Eq. 3.6}$$

The NMR diffusometry measurements were conducted on a Bruker Avance 600 spectrometer, equipped with Diff30 diffusion probe. Other NMR measurements were performed on a Varian 400 MHz spectrometer and a Bruker 800 MHz spectrometer.

3.2 Light scattering techniques

3.2.1 Dynamic light scattering

The size and the zeta potential of the silica particles were measured using dynamic light scattering (DLS) with a Zetasizer Nano-ZS from Malvern Instruments. DLS is a widely used technique for determining particle size distributions, generally within the range of a few nm up to around 1 μm . The method employs determination of the Brownian motion of the particles in the system, referred to as the translational diffusion coefficient. The diffusion coefficient, D , is related to the size, or more specifically the hydrodynamic radius, R_H , of the particles in a fluid of dynamic viscosity η via the Stokes-Einstein equation (Eq. 3.7), where k_B is the Boltzmann's constant and T is the absolute temperature.

$$D = \frac{k_B T}{6\pi\eta R_H} \quad \text{Eq. 3.7}$$

The size obtained is the radius of a sphere having the same translational diffusion coefficient as the particle. A particle in motion scatters light that is frequency shifted, referred to as the Doppler shift. The frequency spectrum is Fourier transformed by a so called correlator, from which a correlation curve and correlation function is obtained. The correlation function is analyzed using cumulant analysis [42].

3.2.2 Zeta potential and surface charge

Silica particles in water with a pH above 2 have a negative charge that increases with pH. By functionalizing the silica surface, a reduction in surface charge should be observed. In addition, less sensitivity towards changes in pH and salt concentration could be achieved, since the attachment of functional groups can induce steric stabilization of the silica particles. This was assessed in both Papers I and II by analyzing the zeta potential, and, in Paper I, also by measuring the apparent surface charge through polyelectrolyte titration. The zeta potential, ζ , of colloidal particles in liquids often determines the stability of the system, where a low absolute value leads to aggregation. As a rule of thumb, the zeta potential of an electrostatically stabilized system should be $\geq \pm 30$ mV. The absolute value of zeta potential is normally discussed, *i.e.* the zeta potential is said to decrease if it becomes less negative. Determination of the zeta potential can be achieved by applying an electric field on the sample in a capillary cell, making the particles undergo electrophoresis. The zeta potential is calculated from the velocity of the particles in the electric field.

The polyelectrolyte titration was conducted on a Mutek Particle Charge Detector (PCD). The measured value depends on the polyelectrolyte used, in this case polybrene ($\text{C}_{13}\text{H}_{30}\text{Br}_2\text{N}_2$), which is cationic and has two equivalent charges per mole. The titration is terminated once the point of zero charge of the suspension has been reached. The required volume of added polybrene

depends on the amount of available groups on the silica surface and the value enables calculation of the equivalent charge per mass (eq/g).

3.2.3 Laser diffraction

Laser diffraction, conducted on a Malvern Mastersizer Micro Plus, was used for determination of the emulsion droplet size distributions. This technique is used for sizing from the submicron range up to several millimeters, and is therefore suitable for analyzing the sizes of the emulsion droplets obtained in this work. The emulsion droplets are dispersed in a liquid media (water for o/w emulsions) and laser is passed through the sample. The laser is diffracted by the particles, and the diffraction pattern is characteristic of the particle size. Mie theory is used to transform the measured data to a particle size distribution [43].

3.3 Surface activity techniques

The surface activity of the particles was assessed using the DuNoüy ring method, conducted on a Sigma 70 Tensiometer. For measurements of both surface and interfacial tension, a platinum ring is hung on a balance and submerged below the interface being tested. The interface is either the surface of a liquid (measuring surface tension) or the interface between *e.g.* oil and water (measuring interfacial tension), as seen in Figure 3-3. The ring will carry a meniscus of the liquid upwards. The meniscus will eventually tear from the ring, however prior to this event it will carry a maximum volume, thus a maximum force F_{max} is detected. The ring is returned to its original position just before the meniscus tears and the process can be repeated until the values of surface or interfacial tension levels out. The surface or interfacial tension, γ , is calculated from the maximum force experienced by the balance as the ring is raised according to Eq. 3.8, where d is the diameter of the ring and f is a correction factor accounting for an additional volume of liquid being raised due to the proximity of one side of the ring to the other [44].

$$\gamma = f \frac{F_{max}}{2\pi d} \quad \text{Eq. 3.8}$$

In Paper I, the measured surface tensions of diluted suspensions of mPEG functionalized silica particles are discussed. The interfacial tensions of oil and functionalized silica sols are assessed in Paper II.

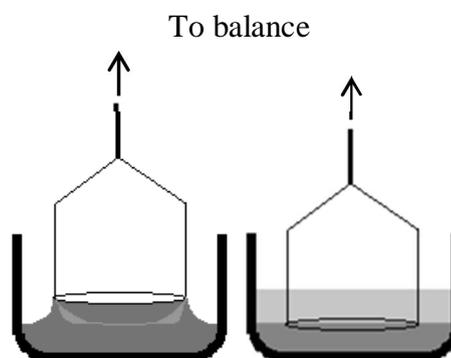


Figure 3-3. The DuNoüy ring method, for assessment of surface tension/interfacial tension. A platinum ring is submerged into the liquid with highest density and the tension at the interface is measured.

3.4 Other analytical techniques

3.4.1 Turbidity measurements

When light is passed through a suspension, the light is scattered due to interactions with the particles. The turbidity of a suspension of particles increases with the particle size. In order to qualitatively study the aggregation behavior of a suspension, a UV/Vis spectrophotometer can be used, which operates at the UV and visible spectra (light of wavelength 200-400 nm). If the absorbance of the suspension is recorded where the molecular absorbance of the system is low, an increase in absorbance, *i.e.* increased scattering of light is therefore due to an increase in turbidity.

3.4.2 Elemental analysis

Elemental analysis was performed using an Elemantar Vario MICRO cube for determination of the carbon content in functionalized silica nanoparticles. The dried suspensions are, with this method, incinerated at 1100 °C in a tin vial and the carbon content is determined from the amount of CO₂ gas developed.

CHAPTER FOUR

4 Results and discussion

In this work colloidal silica has been functionalized with hydrophilic and hydrophobic groups, by silylation of the silica particle surface. The purpose has been to gain an understanding of what new properties that can be obtained by functionalizing the silica particles, and to assess these in an appropriate way, for example by finding a surface chemistry of the particles suitable for emulsion applications. The functionalized particles were characterized providing both quantitative information, in terms of *e.g.* the degree of functionalization and the surface activity, and qualitative evaluation concerning the flocculation behavior, emulsification abilities and other surface chemical properties.

The three types of functionalizations mainly used are shown in Figure 4-1. Paper I deals only with PEGylated particles, while we in Paper II explore particles modified with different combinations of surface species.

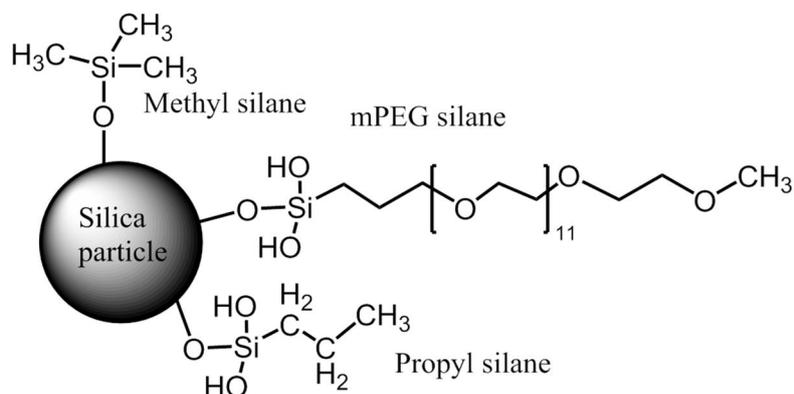


Figure 4-1. Schematic drawing of the three types of functionalizations mainly used: methyl, propyl and mPEG groups.

4.1 Determination of amount of surface functionalization on the colloidal silica

The systems discussed in Paper I are silica particle suspensions functionalized with only mPEG silane. The mPEG group is hydrophilic and has a relatively long (poly)ethylene oxide chain that, in alkaline conditions, extends out from the particles resulting in a T_2 long enough to

be detected with NMR spectroscopy. These properties make NMR diffusometry a potential tool for determining the functionalization yield (the amount of bound silane compared to the total amount of added silane). By determining the fractions of fast- and slow-moving species in the samples, or the free and bound mPEG silanes, respectively, the yield of functionalization can be calculated. Indeed, a strict two-component attenuation of the logarithmic NMR signal intensity versus $k = (\gamma G \delta)^2 (\Delta - \delta / 3)$ was obtained for all samples. Figure 4-2 shows the stimulated spin echo profile from particles grafted with $0.155 \mu\text{mol mPEG silane m}^{-2}$.

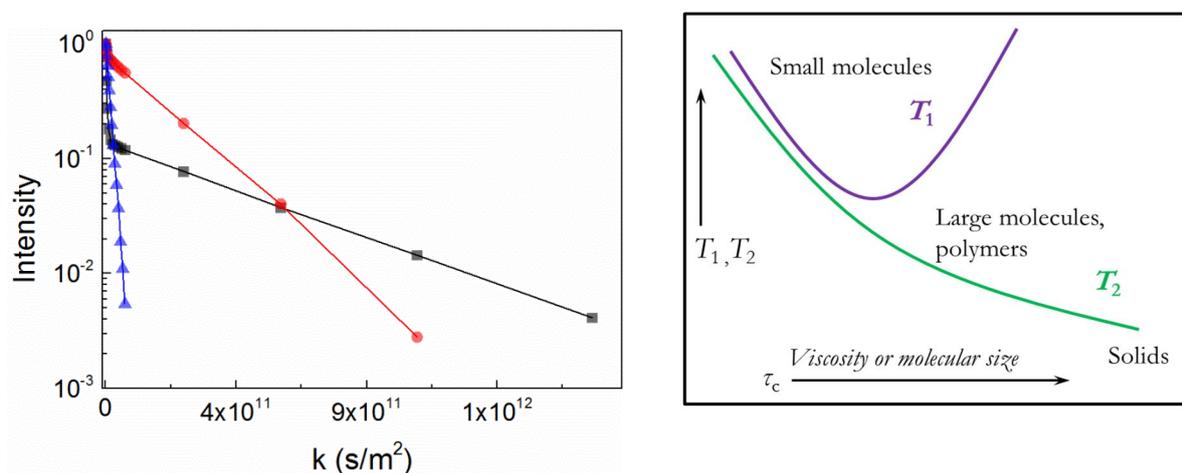


Figure 4-2. Left: Stimulated spin echo profile from NMR diffusometry measurements of silica particles grafted with $0.155 \mu\text{mol mPEG silane/m}^2$ and of free aqueous mPEG silane (blue \blacktriangle). Before purification by ultrafiltration (black \blacksquare), 17% of the silanes are attached to the particles, and after purification 75% of the silanes are attached to the particles (red \bullet). The steeper slope of the filtered suspension is due to a more diluted sample. Right: Typical variations in the transverse and longitudinal relaxation times, T_1 and T_2 , respectively, with the rotational correlation time τ_c .

The relaxation times T_1 and T_2 for both free and bound species are required for fitting the data by standard non-linear regression (see Eq. 3.6). These values were obtained by standard inversion recovery and CPMG pulse sequences, and strict bi-exponential behavior was noted. The longitudinal relaxation time T_1 was measured to be 336 ms for free silane and 1.96 s for bound silane. The measured transverse relaxation time T_2 is 259 ms for free silane in suspension and 16 ms for bound silane. The significantly decreased value of T_2 and the increased value of T_1 indicate reduced mobility of the species (see Figure 4-2), which means that the bound species is associated to the silica surface. Experiments with varying diffusion times were performed to substantiate covalent linkage. Identical results were obtained and it can therefore be concluded that the residence time of the species was more than several hundreds of milliseconds, discarding the possibility of non-covalent adsorption since it would most likely result in shorter residence times. The self-diffusion coefficients obtained are in the order of $3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for free silane, and $5 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ for bound silane, with variations due to differences in concentrations *i.e.* viscosity and obstruction. This higher relative difference of the self-diffusion coefficients, compared to the relaxation times, provides superior sensitivity of diffusometry for quantification of the functionalization yield, although the relaxation times also provide information on the local

molecular mobility [45]. Table 4-1 provides an overview of the results collected for the samples functionalized with only mPEG silane.

Table 4-1. Functionalized silica sols studied in Paper I, showing the amounts of Silquest A-1230 Silane (mPEG silane) added and bound, respectively. The particle diameter, volume average, is given as measured with DLS at alkaline conditions. The bound amount was calculated from the NMR diffusion data together with the relaxation times, from which the surface coverage, and subsequently the amount of free silane, is obtained. The synthesis temperature was 70 °C for all samples except 0.21mPEG, for which the synthesis was conducted at room temperature.

Sample name	Functionalization ($\mu\text{mol silane m}^{-2} \text{SiO}_2$)		DLS particle diameter (d_v , nm)
	Added amount	Amount bound	
<i>Unmodified</i>	-	-	30.8
0.07mPEG	0.27	0.068	29.7
0.15mPEG	0.9	0.155	31.0
0.16mPEG	0.9	0.162	31.2
0.21mPEG	1.0	0.215	-
0.31mPEG	1.8	0.315	31.7

NMR diffusion measurements were not suitable for the particles having mixed modifications, such as the ones discussed in Paper II. Silanes with short and hydrophobic groups, such as propyl and methyl groups, and are immobilized when bound to a particle surface. This leads to very short T_2 and in turn a non-detectable NMR signal. The particles were instead analyzed indirectly, through measuring the amounts of free silane in supernatants from centrifuged samples. Two methods were used; *method a)* and *method b)*. In *method a)* the ratio between the different types of free silanes in the supernatants was obtained by NMR and was recalculated into carbon weight ratios. Elemental analysis of dried, purified particles provided the carbon contents arising from bound silanes in the samples. This allowed calculation of the amounts of each type of free silanes in the samples and thereby also the amounts of each type of bound silanes, from which the yields are obtained. NMR spectroscopy was employed also in *method b)*, but with the purpose to obtain the concentrations of free silanes in the supernatants. This was done by preparing calibration curves of hydrolyzed silanes (propyl silane, mPEG silane and trimethyl silane). The yield of the functionalization was simply obtained by comparing the concentration of free silane in the supernatants to the total amount added during the functionalization. The results from *method a)* and *method b)* deviate, as can be seen in Table 4-2.

Table 4-2. Comparisons of the yields obtained using the two different methods for the three main types of functionalizations.

Yields	<i>Method a)</i>	<i>Method b)</i>
mPEG silane	30-56 %	60-70 %
Propyl silane	99-84 %, one sample with 32 %	99-96 %
Methyl silanes	Four samples with 85-93 %, one sample with 20 and 49 %	40-60 %, one sample with 97 %

Considering the mPEG silane, a contributing factor could be that the purification procedure applied for *method a)* was not satisfactory. Also, the NMR peaks arising from ethanol and methanol are overlapping the peaks from the mPEG silane making it difficult to determine the concentrations even though the integral values were compensated for this. Both ethanol and methanol are present in the samples as rest-products from the functionalization and are important for the colloidal stability of the functionalized particles.

A difference in yield between *method a)* and *method b)* is observed also for the hydrophobic silanes. However, the results, using both methods, indicate a high yield when it comes to attaching the propyl silane. Considering the methyl silane, the results are less straight forward and deviate more between the methods. One reason is the low solubility of the methyl silane in water, which leads to the need of increased ethanol content when making the calibration curves. The solvent influences the NMR signal and this makes it difficult to directly use the calibration curves. The NMR signals from these silanes were barely detectable in the particle suspensions of the functionalized colloidal silica studied, which indicates that most of the added silane is attached to the particles, but it may also have precipitated or aggregated during the functionalization.

Table 4-3 provides an overview of the results collected for the samples functionalized with mPEG silane and the different types of hydrophobic groups, as well as combinations thereof. The bound amounts given in the table are average values obtained from the two methods (*method a)* and *method b)*) used.

Table 4-3. Functionalized silica sols studied in Paper II, showing the amounts of Silquest A-1230 Silane (mPEG), Ethoxy trimethylsilane (TMEO), Dimethoxy dimethylsilane (DMDMO), Triethoxy (propyl) silane (PTEO), Trimethoxy (propyl) silane (PTMO) and Triethoxy (octyl) silane (OTEO) added and bound, respectively. Particle diameter and zeta potential are averages from three replicated measurements conducted using DLS, at alkaline conditions (pH 9-10). The given particle diameter is the volume average.

Sample name	Silica sol	Functionalization ($\mu\text{mol silane m}^{-2} \text{SiO}_2$)		Particle diameter (d_v , nm \pm 2)	Zeta potential (mV, \pm 7)
		Added amount, order of addition	Amount bound		
Ref 1	Bz130	-	-	28.5	-45
Ref 2	Bz360	-	-	13.1	-42
Ref 3	Bz200	-	-	22.8	-
A	Bz130	1.0 TMEO	0.3 TMEO	28.0	-50
B	Bz130	1.06 PTEO	1.0 PTEO	27.0	-43
C	Bz130	2.0 mPEG	0.9 mPEG*	32.0	-29
D	Bz130	1.2 TMEO 1.05 PTEO	1.1 TMEO 0.7 PTEO	27.3	-43
E	Bz130	0.53 TMEO 0.53 PTEO	0.3 TMEO 0.5 PTEO	27.5	-44
F	Bz130	1.0 TMEO 1.0 mPEG	0.7 TMEO 0.5 mPEG*	28.9	-34
G	Bz130	1.0 PTEO 0.5 mPEG	1.0 PTEO 0.3 mPEG	30.2	-40
H	Bz200	0.95 mPEG 1.94 PTMO	0.45 mPEG* 1.93 PTMO*	30.5	-32
I	Bz130	1.5 PTEO 1.0 mPEG	1.5 PTEO 0.5 mPEG	28.7	-28
J	Bz200	2 PTMO 0.5 mPEG	1.9 PTMO* 0.2 mPEG*	73.0	-47
K	Bz130	1.6 PTEO 0.5 mPEG	1.6 PTEO 0.3 mPEG	26.2	-34
L	Bz130	0.53 TMEO 0.53 PTEO 0.52 mPEG	0.4 TMEO 0.5 PTEO 0.3 mPEG	28.2	-39
M	Bz130	0.5 OTEO 0.5 PTEO 0.5 mPEG	0.5 OTEO* 0.5 PTEO* 0.2 mPEG*	29.6	-40
N	Bz200	1.0 PTMO 1.0 DMDMO 0.5 mPEG	1.0 PTMO 0.7 DMDMO 0.3 mPEG	52.8	-41
O	Bz200	1.0 PTMO 0.5 mPEG	0.9 PTMO* 0.2 mPEG*	31.0	-40
P	Bz360	1.0 PTEO 0.59 mPEG	1.0 PTEO 0.3 mPEG	13.0	-32
Q	Bz130	1.05 PTEO 1.0 mPEG	1.0 PTEO 0.6 mPEG	29.3	-32

* Results using only method a)

Direct quantification of the amount of functionalization attached to the silica particles surface becomes more challenging when different types of modifications are used. NMR diffusometry works very well for water soluble and longer surface species, while for the shorter, hydrophobic chains the characterization methods still need to be further developed when the surface compositions on the particles are heterogeneous. One alternative that is yet to evaluate is solid state NMR together with elemental analysis of purified samples.

4.2 Surface and interfacial properties

4.2.1 Surface charge and surface activity

The PEGylated particles studied in Paper I show a clear reduction in surface charge as well as in the (absolute value of) zeta potential despite a relatively small amount of covalently attached mPEG, see Figure 4-3. Figure 4-3 also shows that the functionalization with mPEG makes the particles less affected by changes in pH, when the surface coverage is $0.155 \mu\text{mol mPEG silane m}^{-2}$ and above. An increased salt concentration to $\geq 100 \text{ mM}$ leads to severe aggregation of the particles in all samples apart from the high coverage one ($0.315 \mu\text{mol mPEG silane m}^{-2}$). For the latter, only moderate aggregation was noted through an increase in average particle diameter from 31.7 nm at alkaline conditions to $\sim 40 \text{ nm}$ at 100 mM salt and $\sim 90 \text{ nm}$ at 200 mM salt.

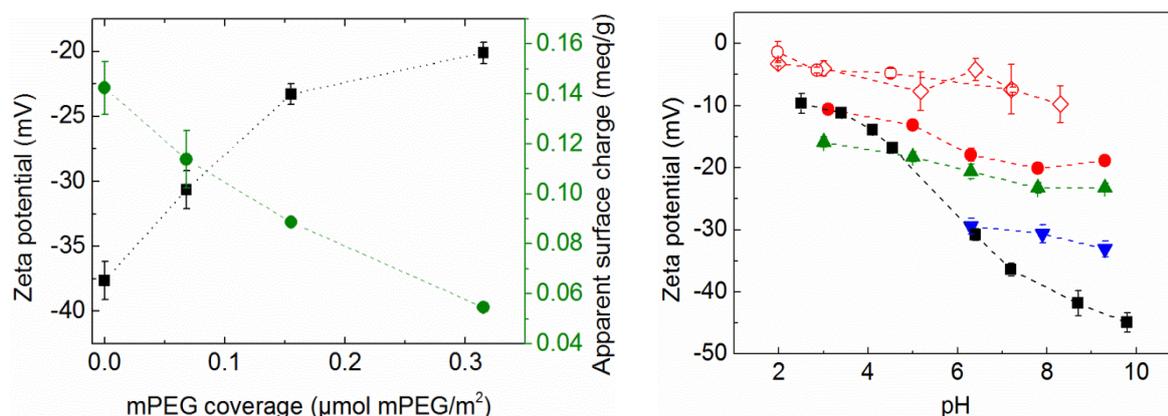


Figure 4-3. Left: Zeta potential in mV (black ■) and apparent surface charge in meq/g (green ●) as measured with PCD polyelectrolyte adsorption, as a function of the mPEG silane surface coverage in $\mu\text{mol mPEG m}^{-2}$ of the particles. Right: Zeta potential of dialyzed PEGylated samples as a function of pH, with varying salt concentrations and surface coverages: samples with 0.068 (blue ▼), 0.155 (green ▲) and 0.315 (red ●) $\mu\text{mol mPEG silane m}^{-2}$ are measured at 7 mM salt. Unmodified particles (black ■) are shown for comparison and have $\sim 10 \text{ mM}$ salt. For high surface coverage it was possible to measure at higher salt concentrations; 100 mM (red ○) and 200 mM (red ◇).

The zeta potential is the measured potential in the shear plane between the particle and the bulk solution that is created when the particle moves through an electric field [46]. When polymers are adsorbed to the particles and extend out into the diffuse layer, a movement of the shear plane further out from the particle surface occurs, which decreases the zeta potential [46]. Although the mPEG silane is relatively short ($\sim 4 \text{ nm}$) at the low salt concentrations in samples,

compared to the thickness of diffuse double layer, which should be > 90 nm, such an effect could be possible. However, since the apparent surface charge is significantly reduced, the main reason for the decreased zeta potential is presumably the reduced surface charge of the particles due to mPEG attachment.

Charged particles can only be depleted from a suspension, and thus adsorb at the interface, if the energy gain compensates for the energy barrier due to *e.g.* concentrating charged particles at the interface, and for the entropy loss [47]. A lower particle charge density will therefore lead to a higher surface activity, since a reduction of surface charge facilitates the adsorption at the air-water interface [47]. Figure 4-4 shows the effect of the PEGylated particles on surface tension, measured with the D nNouy ring method. The small reduction in surface tension caused by unmodified silica particles (~ 2 mN/m) is consistent with other findings [48, 49]. Slightly larger effects have been observed (~ 4 mN/m) for SiO_2 particles larger than the ones studied here [50].

The PEGylated particles have significant effect on the surface tension. These purified samples contain < 0.3 - 0.7 mM free mPEG silane, which renders a surface tension of ~ 60 - 62 mN/m. The surface tension observed for both high and medium surface coverage samples is well exceeding that caused by the free silane; ~ 56 mN/m for 0.15 mPEG and ~ 51 mN/m for 0.31 mPEG. This shows that the PEGylated particles are in fact surface active, and a higher degree of surface functionalization, which in turn leads to a larger reduction of surface charge density, was found to result in a more pronounced decrease of the surface tension.

Particles modified with only hydrophobic groups, such as sample B modified with propyl silane and samples D and E modified with both trimethyl and propyl silane, were found to reduce the surface tension with ~ 2 mN/m, in the same range as for unmodified particles. Interfacial tension measurements at the Exxsol D60-silica suspension interface revealed larger effects arising from the presence of the particles, both modified and unmodified ones. At Exxsol D60-distilled water interface the interfacial tension was measured to be 48 mN/m. The addition of unmodified particles reduced the interfacial tension to 37 - 39 mN/m. Heterogeneously modified particles, with both hydrophobic groups and the hydrophilic mPEG silane exposed slightly larger effects on the interfacial tension, a reduction to ~ 30 mN/m was noted, compared to the particles with only hydrophobic modifications and the effect increased with the amount of mPEG.

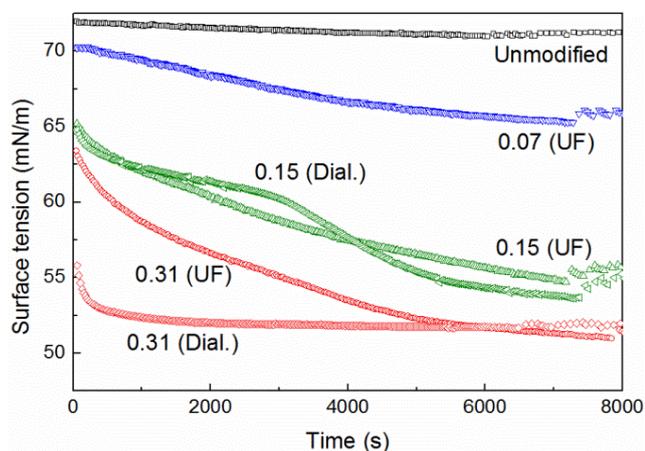


Figure 4-4. Surface tension as a function of time for mPEG functionalized silica particles at a concentration of 5 wt% SiO_2 and increasing surface coverage, from unmodified (black), 0.068 (**0.07**), 0.155 (**0.15**) and 0.315 (**0.31**) μmol mPEG silane m^{-2} . The samples are purified through ultrafiltration (UF) and dialysis (Dial.).

Figure 4-5 shows that modifying particles with only hydrophobic groups gives a very small effect on the zeta potential (samples B, E and D), providing one reason for the small effect on surface tension. Adding mPEG to the particles (samples 0.31mPEG, 0.15 mPEG, Q, I and K) gives a decrease in the absolute value of zeta potential, which in turn facilitates the adsorption at the interface, well in line with previous findings. In emulsion systems a reduction of surface charge is therefore beneficial, and functionalization with mPEG silane efficiently provides this feature.

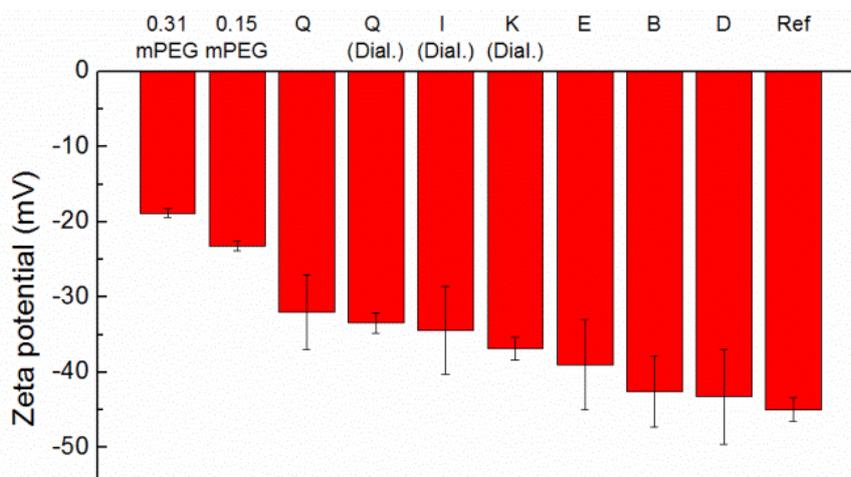


Figure 4-5. Zeta potential (in mV) at alkaline conditions, of mPEG modified particles (PEG 0.31 and PEG 0.15 have 0.31 and 0.15 μmol mPEG silane/ m^2 SiO_2 respectively), heterogeneously modified and dialyzed particles (Dial.) (Q, I, K) and hydrophobically modified particles (E, B, D). Bz 40/130 is shown as reference (Ref). See Table 4-3 for surface compositions of the silica particles.

4.2.2 Flocculation behavior

Weakly flocculated particles have been shown to be beneficial for good emulsification abilities [51, 52]. Homogeneously modified colloidal silica, with medium and low amounts of mPEG silane (0.068, 0.155 and 0.215 μmol mPEG silane m^{-2} SiO_2 , respectively) display a pH dependent flocculation behavior; see Figure 4-6A and *Results* Paper I. The origin of the flocculation is presumably the pH- and temperature dependent attractive forces that exist between silica and poly(ethylene oxide) [53-55]. Also the heterogeneously modified particles, with both hydrophobic and hydrophilic surface species, provide the desired flocculation behavior due to the presence of mPEG (see Figure 4-6B). The flocculation is reversible: an increase in pH returns the sample to its original turbidity, but if the samples are left undisturbed at acidic conditions > 1-2 weeks and some water is allowed to evaporate, they settle and form a rigid gel.

Samples with higher degree of mPEG functionalization, 0.315 μmol mPEG silane m^{-2} SiO_2 , did not flocculate, which exposes the steric influence on stabilization. The particles modified with only hydrophobic modifications, such as samples B and E shown in Figure 4-6B, display very little or no flocculation upon a decrease in pH. These results show that, by grafting colloidal silica with mPEG silane, a stabilization of the particles is achieved in such a way that a controllable flocculation is obtained. It also shows the importance of pH, both for colloidal stability and for emulsification abilities.

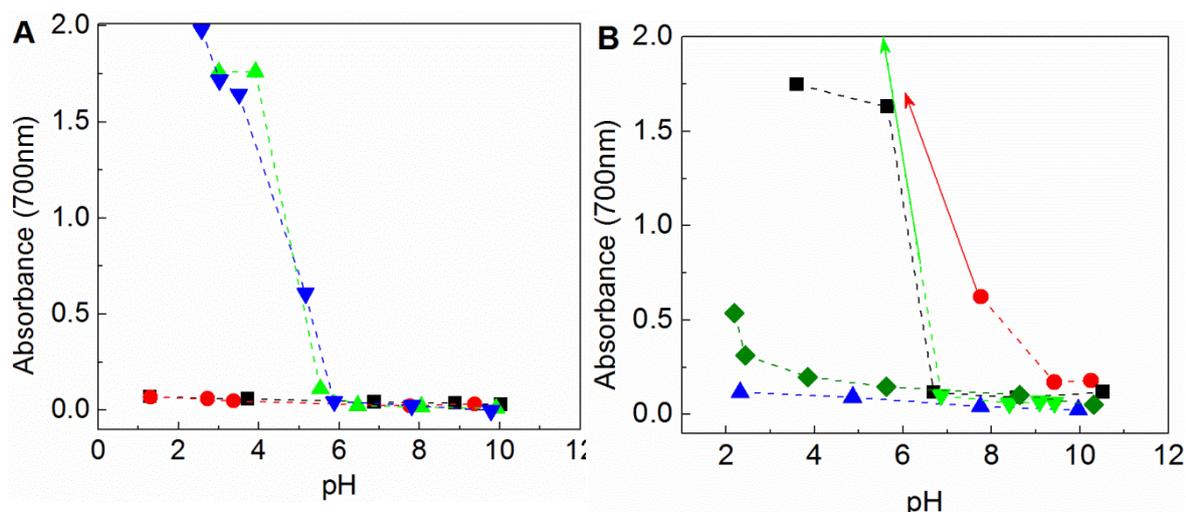


Figure 4-6. Absorbance at 700 nm measured with UV/Vis spectroscopy, showing the variations in turbidity as a function of pH: A) PEGylated particles with low (blue ∇), medium (green \blacktriangle) and high (red \bullet) degree of functionalization; 0.068, 0.155, and 0.315 μmol mPEG silane/ m^2 , respectively, and without functionalization (black \blacksquare). B) Samples N (red \bullet), K (green ∇), G (black \blacksquare), B (dark green \blacklozenge) and E (blue \blacktriangle). See Table 4-3 for surface compositions of the silica particles.

Figure 4-7 shows the ^1H MNR signal from the poly(ethylene oxide) units of the mPEG silane grafted on silica particles with (A) 0.155 and (B) 0.315 μmol mPEG silane/ m^2 SiO_2 , respectively, studied to obtain a further understanding of the flocculation behavior. The samples were ultrafiltrated, diluted in D_2O and ion-exchanged using a cation-exchange resin, and the ^1H spectra were collected as a function of pH.

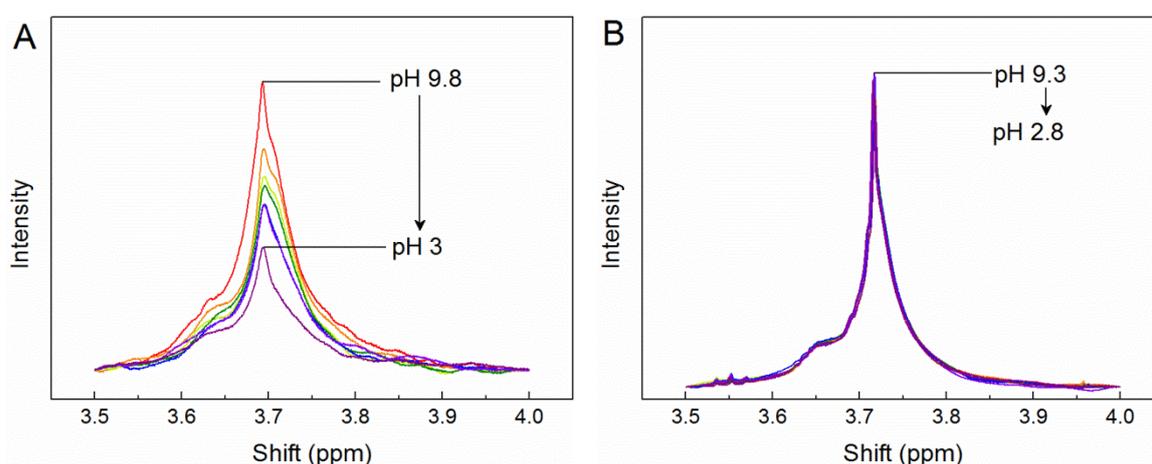


Figure 4-7. ^1H NMR spectra showing the peak arising from the poly(ethylene oxide) units of the mPEG silane grafted on silica particles with A: 0.155 μmol mPEG silane/ m^2 SiO_2 and B: 0.315 μmol mPEG silane/ m^2 SiO_2 , as the pH is decreased. The experiments were conducted on a Varian 400 MHz spectrometer.

The results show a decrease in intensity for (A), the sample with medium surface coverage of mPEG, most probably due to severe broadening of the peaks when mPEG silane adsorbs to the silica surface. Considering the turbidity increase observed for medium and low surface coverage

samples, and since the flocculation is reversible, an inter-particle bridge flocculation presumably occurs, causing the aggregation. For (B), no decrease in intensity is observed, in coherence with the turbidity results, but still surprising since the silica surface is not fully covered with mPEG silane. However, it demonstrates that even though the surface coverage of mPEG is relatively low, compared to the theoretical maximum amount, it has a large influence on the surface properties.

4.3 Evaluation of emulsification performance

4.3.1 Effect of the type of surface modification

The emulsification abilities of the surface modified colloidal silica were evaluated by preparing Pickering emulsions and comparing the emulsion droplet size distributions, where smaller emulsion droplets corresponds to a better performance.

Emulsification trials with PEGylated particles were performed to investigate if the particles, despite their hydrophilic character, could work as emulsifiers for polar oils. Butanol and ethyl acetate were chosen since these have been successfully emulsified using unmodified silica particles by Frelichowska *et al.* [56]. The trials were conducted using Silent Crusher M (Heidolph) equipped with a 50mm nozzle, working at the speed 10000 rpm – 17000 rpm. The emulsification time was kept at of 5 – 10 min. Emulsions formed only when the pH was decreased to below pH 4, but they were not stable towards coalescence for more than 5 days regardless of the amount of mPEG surface coverage. An example of emulsified ethyl acetate in shown in Figure 4-8, and the emulsion droplets started to coalesce immediately after emulsification. Emulsions of ethyl acetate were formed using unmodified particles, but also these readily coalesced and phase separation was observed after 3 days.

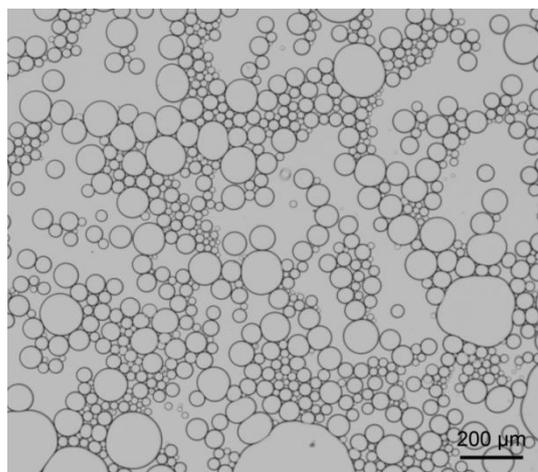


Figure 4-8. Microscope image of emulsified of ethyl acetate using PEGylated silica with $0.315 \mu\text{mol mPEG silane m}^{-2} \text{SiO}_2$ as emulsifier. The emulsion droplets are coalescing. The emulsion contains 20 wt% oil and 5 wt% silica particles in the water phase.

Particles modified with hydrophobic groups (propyl and methyl silanes) and mPEG silane were used to emulsify Exxsol D60, a non-polar mixture of hydrocarbons with chain lengths of 10-12 carbons that contains n-alkanes, isoalkanes, cyclics and a small fraction of aromatics (<2 %). The emulsifications were conducted using MagicLab device and the pH was adjusted to 3.9 ± 0.3 using HCl (aq). Figure 4-9 shows that unmodified particles could be used to emulsify Exxsol D60 when MagicLab was utilized, and there is little change in the emulsion droplet size over time (> 5 weeks). Particles modified with only mPEG silane on the other hand, produced

emulsions with larger droplets ($\sim 30 \mu\text{m}$ in median size) that underwent complete phase separation within 24 h.

By modifying the silica particles with hydrophobic groups the median emulsion droplet size is significantly reduced, as can be seen in Figure 4-9 (samples A, B and D). The introduction of the hydrophilic mPEG group to the particles surface, such as for sample G, decreases the median emulsion droplet size even further. The emulsions produced using these heterogeneously surface modified particles showed a very low degree of droplet coalescence over time; almost no change in the emulsion droplet size distributions was observed over the course of five weeks.

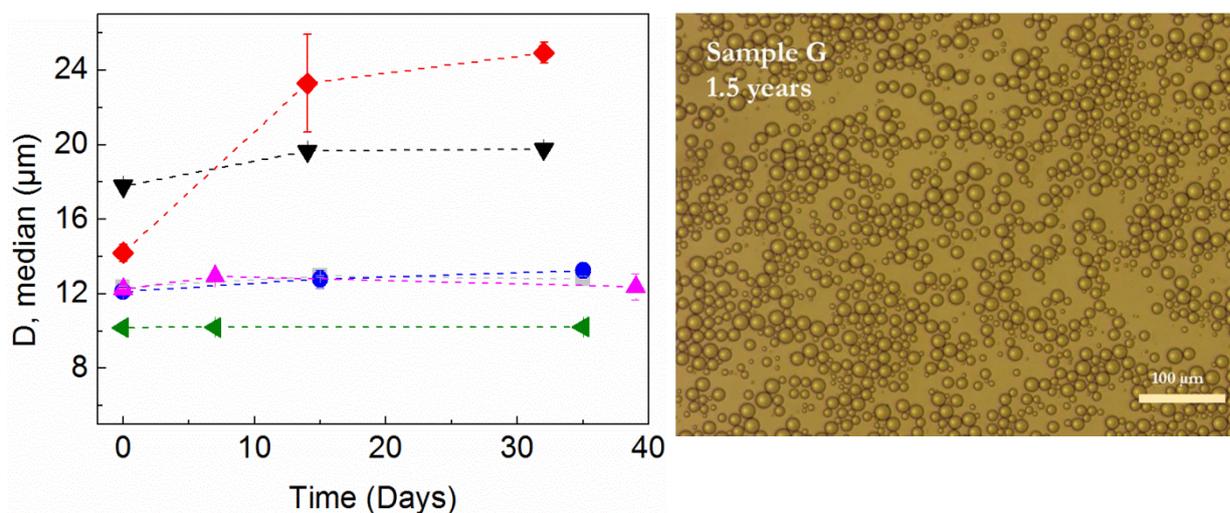


Figure 4-9. Left: Median emulsion droplet size as a function of time, of emulsified Exxsol D60 using Bz130 (black ▼) and Bz360 (red ◆) for reference, and samples A (grey ■), B (blue ●), D (pink ▲) and G (green ◀) as emulsifiers. The emulsions contain 40 wt% oil and 2.5 wt% silica particles in the water phase. The results shown are average from three replicated measurements. Right: Microscope image of emulsified Exxsol D60 using sample G as emulsifier, 1.5 years after emulsification. The scale-bar represents 100 μm . See Table 4-3 for surface compositions of the particles.

It is clear that a combination of hydrophobic groups and hydrophilic mPEG facilitates emulsification. The functionalization conditions however, are important. If the mPEG silane is added before addition of the hydrophobic group, as for sample H, emulsions with emulsion droplets of 22 μm in median size was observed. Also, adding $\sim 1 \mu\text{mol}$ mPEG silane $\text{m}^{-2} \text{SiO}_2$, compared to samples with $\sim 0.5 \mu\text{mol}$ mPEG silane added $\text{m}^{-2} \text{SiO}_2$, renders emulsions with emulsion droplets of 18-15 μm in median size, compared to $\sim 10 \mu\text{m}$ in median size. The mPEG silane obviously has a large influence on the emulsification abilities as well as the surface properties of the particles.

4.3.2 Effect of pH

As already mentioned, pH is an important parameter in disperse systems. Figure 4-10 shows how the median emulsion droplet size decrease as a function of pH. At the pH conditions where a turbidity increase is observed, around pH 6 for sample K and pH 8 for sample N (compare Figure 4-6A), a significant reduction in emulsion droplet size is seen. This demonstrates that

flocculation, together with the reduced surface charge density at acidic conditions, clearly facilitates the emulsion formation. Addition of electrolyte to the suspensions achieves a reduction of the surface charge density and flocculation, and thereby is also emulsification facilitated (see *Results*, Paper II).

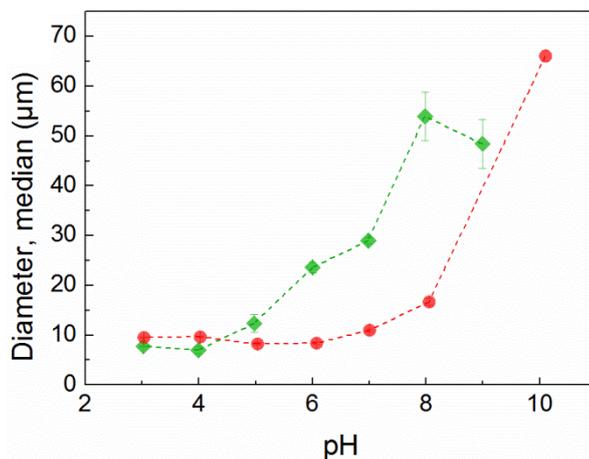


Figure 4-10. Median emulsion droplet size as a function of pH for emulsions obtained using samples N (red ●) and K (green ◆) as emulsifiers. The oil content in these emulsions is 19 wt% and the silica-to-oil ratio is 0.065. See Table 4-3 for surface compositions of the particles.

4.3.3 Other factors influencing emulsification abilities

The silica-to-oil ratio will influence the emulsification abilities, since the available surface area of the silica particles restricts the possible size of the emulsion droplets. The particle size influences the emulsion droplet size in a similar way, since a smaller particle has a larger specific surface area. This is seen in Figure 4-11, where the smaller particle (sample P) already at low silica contents has a surface area large enough to stabilize smaller emulsion droplets.

Another relevant parameter is the energy input during the emulsification; an increase in shear rate from 10000 rpm to 20000 rpm reduces the median emulsion droplet size from 10.2 μm to 3.6 μm, using sample G as emulsifier, and the droplet size was unchanged for at least five weeks.

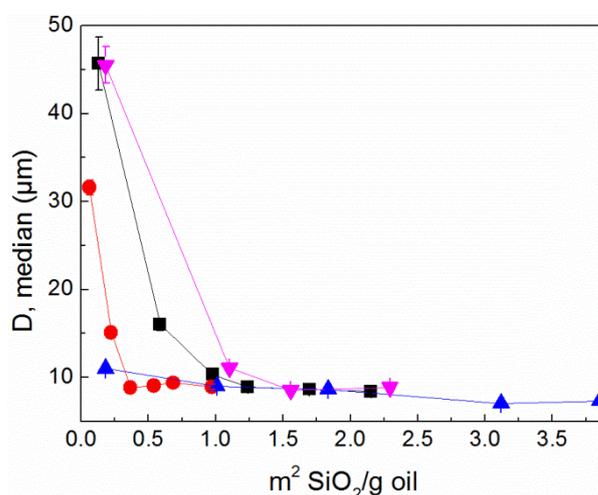


Figure 4-11. Emulsion droplet size as a function of surface area silica-to-oil content. The emulsions contain 19 wt% oil and were prepared using the following particles as emulsifiers: Samples G (black ■), P (blue ▲), N (red ●) and M (pink ▼). See Table 4-3 for surface compositions of the silica particles.

CHAPTER FIVE

5 Concluding remarks

Through a direct and water-based route, colloidal silica functionalized with mPEG silane, methyl silane, propyl silane and octyl silane, as well as various combinations of the surface functionalities have been prepared. For particles functionalized with only mPEG silane, NMR diffusometry proved to be an excellent method for quantification of the amount of mPEG attached, and the measurements also confirmed covalent binding to the silica surface. Both the apparent surface charge density and the zeta potential are significantly affected by the presence of bound mPEG, even though the maximum surface coverage obtained ($0.315 \mu\text{mol mPEG silane m}^{-2} \text{SiO}_2$) is relatively low compared to the theoretical amount of available OH-groups ($8 \mu\text{mol m}^{-2} \text{SiO}_2$). Surface active particles were obtained when the surface coverage was $0.15 \mu\text{mol mPEG silane m}^{-2} \text{SiO}_2$ and above. At medium surface coverage ($0.215 \mu\text{mol mPEG m}^{-2}$), and below, a pH dependent aggregation behavior was observed. It was concluded that this reversible phenomenon originates from the attractive PEG-silica interaction and the aggregation is caused by inter-particle bridge flocculation. The higher surface coverage sample showed steric stabilization towards flocculation.

In summary, functionalization of colloidal silica with mPEG silane provides *i)* a controllable and pH dependent flocculation behavior, *ii)* a significant reduction of surface charge density and *iii)* surface active particles. These properties are crucial for emulsification abilities. PEGylated particles, however, are hydrophilic in character and in order to produce particles that efficiently can emulsify non-polar oils, hydrophobic surface functionalization is required. Homogeneously modified particles with hydrophobic surface species have an improved emulsification capability, compared to unmodified ones. It was found that a combination of hydrophilic mPEG and the hydrophobic propyl silane, preferably in combination with another hydrophobic group such as methyl groups, renders particles with superior emulsification abilities. These heterogeneously modified particles are surface active, display pH-dependent flocculation behavior and have a reduced surface charge density. All these properties facilitate adsorption at an oil-water interface and emulsion droplet formation. Furthermore, the addition order of the silanes during the

functionalization, the salt concentration of the silica suspension, the pH and the surface area SiO_2 -to-oil ratio were identified as important variables that influence the emulsion formation and the emulsification performance of the particles.

The characterization of heterogeneously modified particles, with mixtures of surface species attached, is challenging and needs further studies, in particular concerning the quantification of the amounts attached. The methods used in Paper II provide an indication of the yields of the functionalization, which makes it possible to compare the different samples, but more quantitative methods need to be developed.

6 Abbreviations

Bz130	Bindzil 40/130
Bz200	Bindzil 2034DI
Bz360	Bindzil 30/360
DLS	Dynamic Light Scattering
FID	Free Induction Decay
mPEG	methyl poly(ethylene glycol)
DMDMO	Dimethoxy dimethylsilane
TMEO	Ethoxy trimethylsilane
NMR	Nuclear Magnetic Resonance
OTEO	Octyl triethoxy silane
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PPC	Pulp and Performance Chemicals
PTEO	Triethoxy (propyl) silane
PTMO	Trimethoxy (propyl) silane
SLS	Static Light Scattering
UV/Vis	Ultraviolet-visible

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