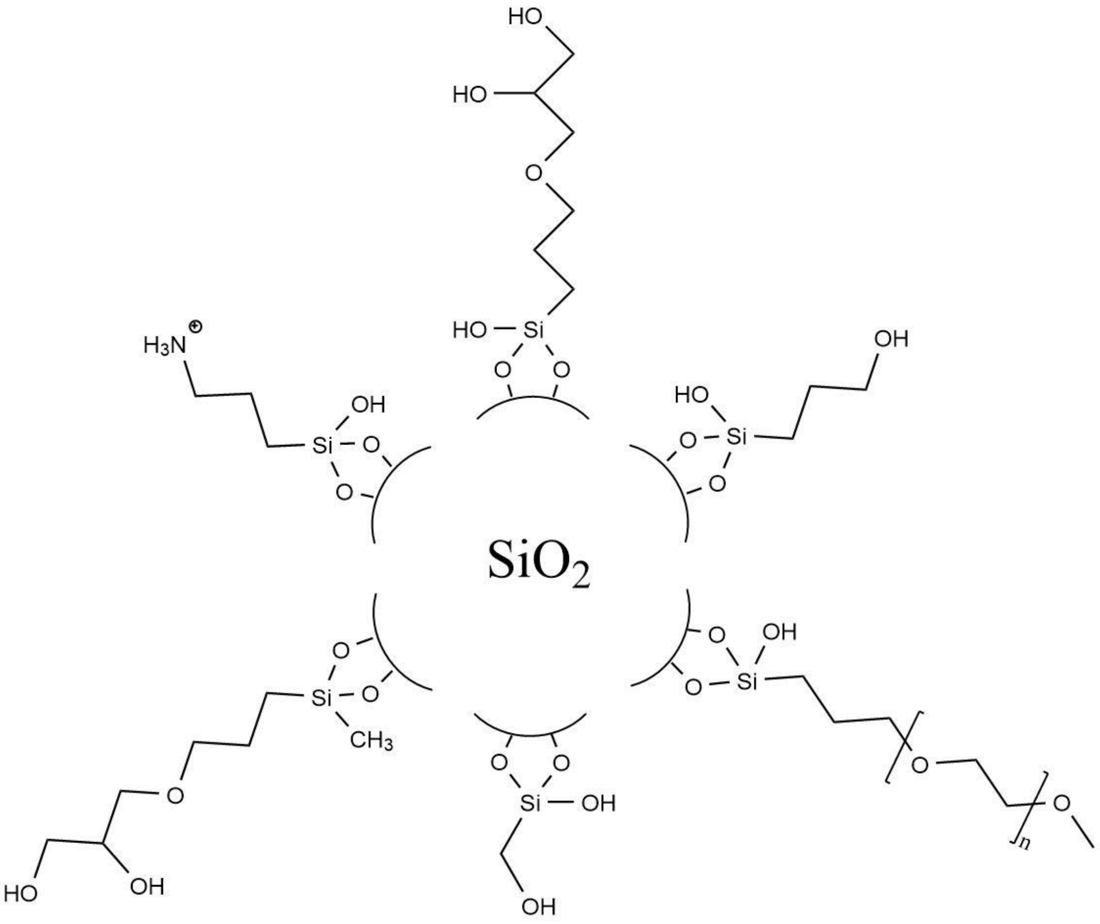

Stability of Silane Functionalized Colloidal Silica

Improvement and understanding of stability towards aggregation in presence of electrolytes at high pH

Master's Thesis in Materials Chemistry

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Department of Chemistry and Chemical Engineering
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This thesis has been performed in cooperation with AkzoNobel Pulp and Performance Chemicals AB.

Cover: Illustration of six different silane modifications done on colloidal silica particles during the project (Frida Bilén)

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Abstract

Silica, (SiO_2), is the most common compound in the earth's crust and is useful in many applications. One form of silica that is commonly used for many different applications is aqueous colloidal silica. For some of these, e.g. in coatings, it is important that the particles are separated in the dispersion and do not aggregate, and therefore the stability of the colloidal silica is central for these applications. To prevent aggregation of colloidal silica particles, the repulsion between the particles is very important, and two fundamental mechanisms that affect the stability of colloidal silica are defined: electrostatic repulsion and steric repulsion.

In this report, grafting of silanes onto silica particles was used to provide steric repulsion and thereby decrease aggregation. This was done to gain understanding of the stability of colloidal silica, with and without silane modifications, in order to create a system as stable as possible at high electrolyte concentrations and high pH. Several features of the silane such as length and charge were investigated as well as the surface coverage of silanes on the particle in order to evaluate the effect of structural differences of the silanes.

The stability of the modified silica sols was determined by measuring the turbidity of 1 % silica dispersions in the presence of electrolytes, and is was seen that the surface coverage and length of the silane had a great influence on the stability. A maximal grafting was also observed and excess silane seemed to influence the stability positively. A reason for this could be that the modification reaction needs an excess of silane in order to get a higher surface coverage or that the free silane in the solution buffers the system dilution. It was also seen in this study that approaches with reduced surface charge and shorter silanes were not very promising for the stability. However, a longer silane length and higher surface coverage were concluded to be excellent approaches for increased stability.

Keywords: Silane, Functionalized colloidal silica, Electrolytes, pH, Steric stabilization

Table of Contents

1 Introduction

Silica, or silicon dioxide (SiO_2), is a common compound that is useful in many different industries and can be present in many forms (1). One of these forms is as a dispersion, also called sol, of nanometer sized silica particles in a liquid medium (2). Silica sols are useful in various applications such as for clarification of beverages, as retention aid in papermaking and for chemical mechanical polishing (3) (4), and for some applications it is important that the sol is stable (5), which means the particles remain dispersed and do not aggregate. Above pH 7, the silica particles are highly negatively charged, and this provides an electrostatic stabilization that keeps the particles from aggregating (6). However, if the salt concentration in the sol is too high, the electrostatic repulsion will be reduced and the system becomes unstable (6). Divalent cations such as Ca^{2+} make the sol especially unstable, in particular at high pH (7) and elevated temperatures speeds up the aggregation. For applications with these tough conditions it is therefore important to provide other sources of stabilization, such as steric stabilization.

One way to provide steric stabilization to a sol is to modify the particles with silanes, and organofunctional alkoxy silanes are one preferred type for modifications of aqueous silica sols (5). Organofunctional alkoxy silanes consist of hydrolyzable groups and an organofunctional group connected by a silicon atom (8). The hydrolyzable groups can react with water to form silanols (Si-OH) that can attach to the silica particle surface (8), and suitable organofunctional groups can then provide steric stabilization for the system (7) (5). One type of silane that has been used with promising results in previous studies is 3-glycidoxypropyl-trialkoxy silanes (7) (5) (9). It has proven useful for stabilizing silica sols in moderate salt concentrations in pH 8-9 (7). However, more work is needed to determine if stability in even higher electrolyte concentrations at higher pH can be achieved.

In this project, hypotheses about the effect of structural differences of a few different silanes will be tested in terms of the colloidal stability. Three strategies for an increased stability are evaluated: Increasing the surface coverage of silane, modifying the surface charge of the particles and changing the length of the silane.

1.1 Aim

The aim of this work was to gain understanding of the stability of colloidal silica, with and without silane modifications, in order to create a system as stable as possible in presence of high electrolyte concentrations at high pH. This was done by investigating how the stability towards aggregation was affected by surface coverage with silane, silane length and charge. A number of different silanes were used for functionalization, see Appendix A, in order to evaluate the effect of different structural differences of the silanes.

1.2 Limitations

This work will deal with no other form of silica than aqueous colloidal amorphous silica. The only type of stabilizing modifications to be done is functionalization with silanes. Additionally, no other colloidal silica than one certain AkzoNobel product will be studied, meaning the production method and particle size distribution will be limited to one.

To minimize the number of test parameters, pH, silanes, silica concentrations, salt types, surface coverages and temperatures will be limited to a few. Furthermore, the pH interval for the stability evaluations will be limited to the upper pH region, pH 8-10. How the aging of the modified sols affects the stability will not be evaluated in this study.

2 Theory

2.1 What is silica?

Silica, or silicon dioxide (SiO_2), is the most common compound in the earth's crust and occurs in two forms: amorphous and crystalline silica (1) (10). In this report, silica will refer to the amorphous form of silicon dioxide. Silica is an attractive material because it is mechanically stable, has a well-defined solid-liquid interphase and its surface can be modified easily (11). Silica is commonly used in the industry e.g. in cement industry, production of glass and pigment stabilization (10) (12).

The silica surface is mainly built up by siloxane groups (Si-O-Si) and silanol groups (SiOH) (13). There is an equilibrium between the silanols and siloxanes through a hydrolysis reaction where the siloxanes at the surface can react with water to form silanols, and a condensation reaction where two silanols form a siloxane bond and water, see Figure 1. This equilibrium depends to a large extent on temperature, pH and humidity (13). For completely hydroxylated surfaces, such as in aqueous colloids, there is a maximum amount of silanol groups which corresponds to a surface coverage of about 7.6 µmol/m^2 (5). When dispersed in water, the water molecules are physically adsorbed to the silanol groups through hydrogen bonding, and thus they make up a hydrate cover around the silica (14).

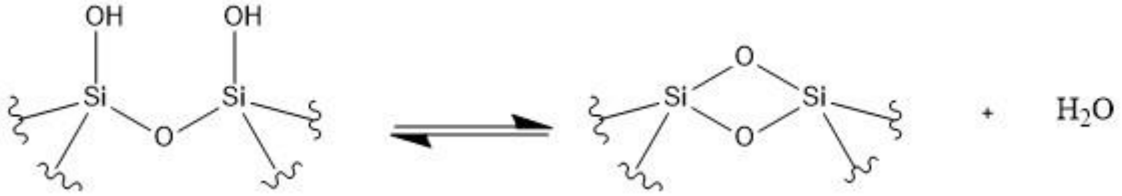

Figure 1. Illustration of the equilibrium between silanol and siloxane bonds on the silica surface.

The silanol groups give many properties to the silica and affect for example stability and surface charge (6). The isoelectric point of silica is around pH 2, so at higher pH the surface has a net negative ionic charge since some silanols are deprotonated. Below pH 2 it can have a net positive charge since some silanols are protonated (6), see Figure 2.

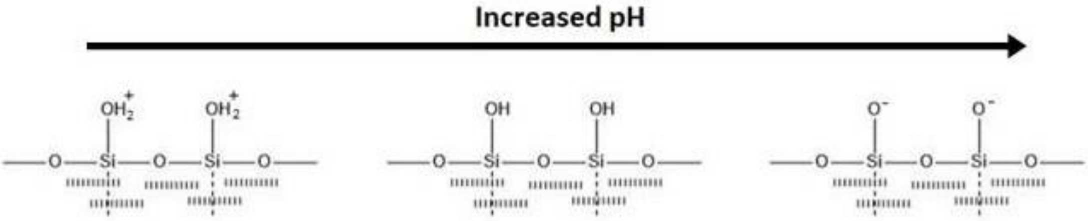

Figure 2. Illustration of the effect of pH on the surface charges of colloidal silica.

2.2 Colloidal silica

Amorphous silica can be present in colloidal form, which is a microscopically heterogeneous system, where the particle size is in the nanometer range (15) (2). A two-phase colloidal dispersion is a system where one phase is dispersed as particles in a continuous phase, which can be gaseous, liquid or solid. The type of dispersion where solid particles are dispersed in a liquid continuous phase is called a suspension or a sol (2). Colloidal silica occurs in both organic and aqueous systems. However, due to environmental and cost requirements, the aqueous system is the most common one in the industry (3). Colloidal silica has been used for many different applications in industry as e.g. retention aid in papermaking, for clarification of beverages, to provide certain properties to paints and coatings or for polishing of electronic materials (4). For some applications, e.g. in coatings, it is important that the particles are separated in the dispersion and do not aggregate (5). Therefore, the stability of the colloidal silica is central for these applications.

2.3 Colloidal stabilization

Colloidal particles tend to aggregate and form larger particles due to van der Waals forces, high surface energy, and the large surface area to particle size ratio (6) (10). Eventually, all colloidal dispersions will phase-separate due to that they are thermodynamically unstable (16), but there are ways to stabilize the system sufficiently to consider it stable. Repulsion between the particles is very important in colloidal systems to induce stability. There are two fundamental mechanisms that affect the stability of colloidal silica: electrostatic repulsion and steric repulsion (2) (3).

2.3.1 Electrostatic stabilization

The surface of a charged colloidal particle is covered by a layer of mobile electrolyte ions, and due to the Coulomb interaction between the particle charges and the electrolytes, the concentration of counter ions will be much higher than that of coions in the layer close to the surface. This ion layer together with the surface charges on the particle form an electrical double layer that affects the electrostatic interaction between the dispersed species, see Figure 3 for an illustration of the double layers (17). When a particle gets close to another particle, the balance of attractive van der Waals interactions and the repulsive forces from the double layers controls if the dispersion is stable or not (2). If the repulsive force is sufficient to balance the attractive forces, the system will be stable and the particles remain separated. Oppositely, if there is no barrier between the interacting particles they will start to aggregate, either as a reversible or irreversible process. Electrostatic interactions are therefore very important in stabilization of colloidal systems (2).

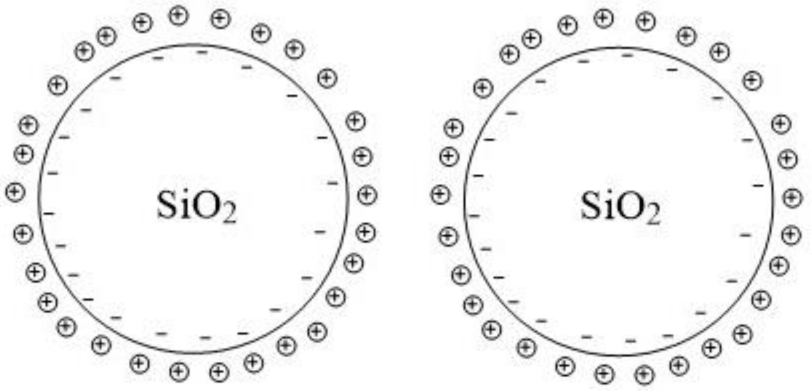

Figure 3. An illustration of the double layers on charged colloidal silica particles.

To understand the stability of colloids, the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory can be used since the theory explains the interplay between the double-layer repulsive forces and the van der Waals attractive forces (16). From this theory, it is possible to determine whether the colloid is stable or whether aggregation will occur. This is done by studying the potential energy as a function of the distance between particle surfaces (2), where the potential energy is the sum of both the van der Waals energy and the potential from electrostatic repulsion of the electrical double-layers.

The repulsive forces from the double-layer interaction are highly affected by charges and the electrolyte concentration in the continuous phase (16). When the charged particles come very close together, the electron clouds will overlap resulting in a strong repulsion. When salt is present, it shields the charges on the particles and will have a major influence on the system's stability. Above the so called Critical Coagulation Concentration (CCC), the salt concentration is high enough to make the aggregation very rapid (7). In applications where the electrolyte concentration exceeds the CCC, or in unstable pH ranges, the electrostatic stabilization is insufficient to prevent aggregation, and steric stabilization is needed.

For colloidal silica, the surface charge is highly dependent on the pH, and therefore, so is the electrostatic stability of the sol (6). At low pH, around 2-3, the system is metastable due to several different mechanism that will not be discussed in this report, however in the pH range 3-7 colloidal silica easily aggregates. Above about pH 7, the silica surface has enough anionic charges to cause repulsion between two particles and hence the stability increases with pH when salt is absent (6).

2.3.2 Steric stabilization

Steric stabilization uses molecules that are adsorbed or chemically grafted to the particle surface (18) (16), see Figure 4. When two particles get close together and the chains start to entangle, there will be a decrease in entropy that causes a repulsive force which gives the steric stabilization (16). Polymers can be used as a modification on the silica surface to increase the steric repulsion and thereby increase the stability (3), and this is common in e.g. food processing and production of paints, coatings and pharmaceuticals (3). To get a good steric stabilization it is important to use attached molecules that are sufficiently soluble in the solvent (7) (16). For larger nanoparticles, with a diameter greater than 100 nm, it is usually necessary to use oligomers or polymers to stabilize a colloid in a high electrolyte concentration solution (7). For smaller particles however, it may be sufficient with shorter molecules (7). For silica nanoparticles, the silanol groups on the surface can act as reactive groups and enable grafting for steric stabilization (5).

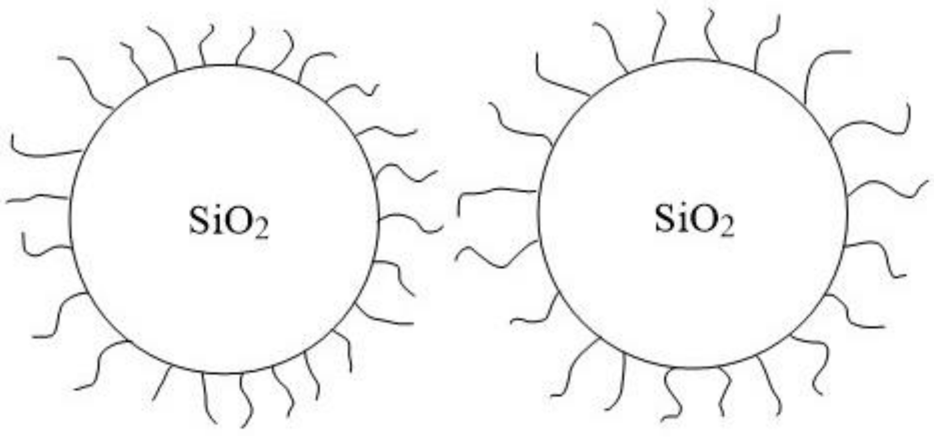

Figure 4. Illustration of chemically grafted or adsorbed molecules to silica particle surfaces for steric stabilization.

It is however important to remember that even if the particles are sterically stabilized, addition of salt may still influence the stability. For example in the case where divalent counter ions are added, such as Ca^{2+} for anionically charged particles, the salt ions may act as a bridge between charges on the particles and cause destabilization even though some steric stabilization has been made (6) (7). An illustration of this bridging interaction can be seen in Figure 5. The type, charge and length etc. of the sterically stabilizing molecule may affect how well the colloid can withstand destabilization by addition of salt (7).

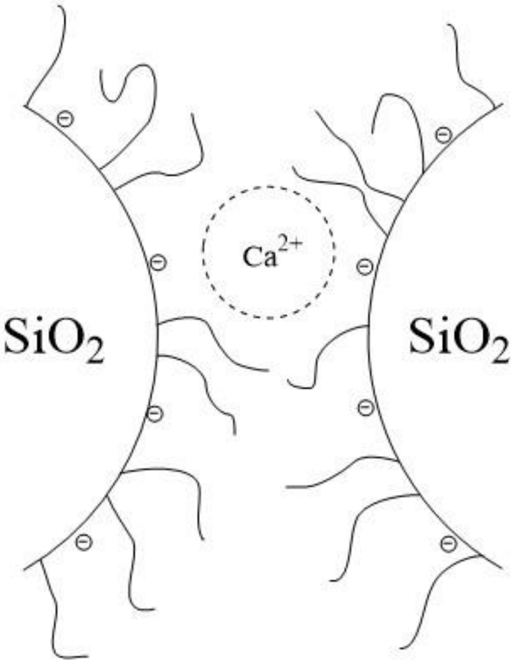

Figure 5. Illustration of the bridging interaction between a divalent calcium ion and negatively charged silica particles with some steric stabilization.

2.3.2.1 Silane modifications of silica

One common modification that can be used to gain stability is grafting of organofunctional silanes, hereafter referred to only as silanes. A silane has a characteristic Si-C bond and is a coupling agent which may create an organofunctional modification of a mineral substrate surface (8). The structure of a silane consists of a silicon atom that acts as a stable link between an organofunctional group R and hydrolyzable groups X, which results in the general formula X_3SiR (8). The hydrolyzable groups are intermediates in the formation of silanol groups for bonding to the silica surface (8). The most common type of silane is the trialkoxy silane, $(OR')_3SiR$, where the hydrolyzable parts are alkoxy groups (5).

The attachment of trialkoxy silanes to a silica surface is a two-step process (8). Firstly, there is a hydrolysis reaction where the hydrolyzable groups react with water to form $(OH)_3SiR$ (8), which makes the silanes more hydrophilic, and then a condensation reaction where the hydroxyl groups at the silane reacts with the deprotonated silanol groups on silica surface to form Si-O-Si bonds (8). The grafting to the surface results in an increase in pH since hydroxyl ions are created in the reaction (4). An unwanted self-condensation reaction where the silanes polymerize occurs parallel to the grafting to the surface (8). Therefore, the hydrolyzed silane mixture should be added slowly to the sol during a modification reaction to favor the wanted reaction (8). These three reactions are presented in Figure 6.

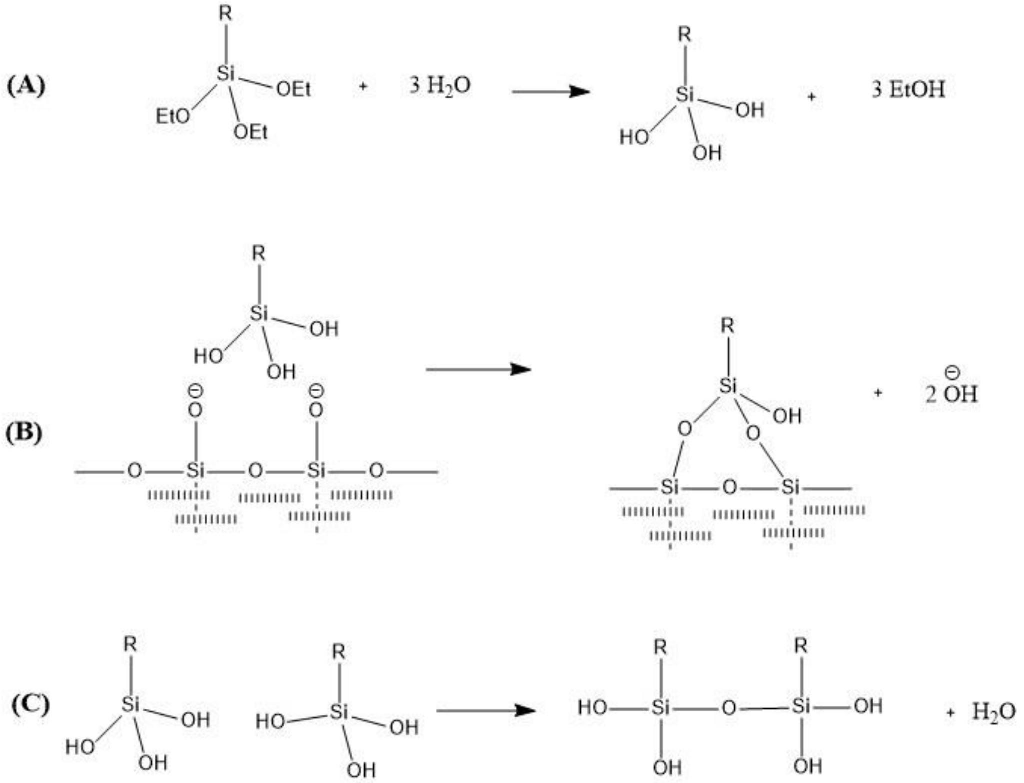

Figure 6. The hydrolysis and condensation reactions during the attachment of a silane to a silica surface. a) Hydrolysis reaction where the hydrolysable groups are ethoxides b) the condensation reaction where the silane attaches to the silica surface c) the condensation side reaction where the silanes polymerize.

It is not likely that all three of the silane hydroxyl groups react with the surface due to steric reasons, see Figure 7 for the alternatives (5). At high pH, the hydroxyl groups that are not bound to the surface may be deprotonated and have a negative charge (19).

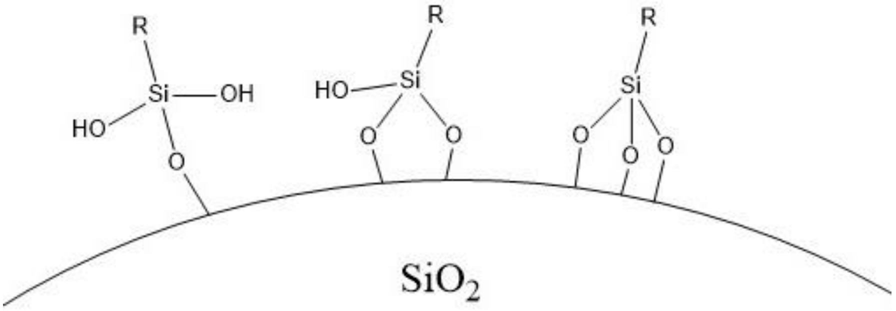

Figure 7. Illustration of silanes bound to a silica surface with one, two or three siloxane bonds.

The silane should be soluble enough in the solvent for the hydrolysis to take place (5) and good solvation is also needed for the steric stabilization to dominate over the van der Waals forces (7). Therefore, the organofunctional group cannot be too hydrophobic. The hydrolyzed silane should also be stable enough not to self-condensate (5). The hydrolysis can be done in a separate step, a pre-hydrolysis, by choosing an appropriate pH interval where the hydrolysis is fast but the condensation reaction is slow to avoid polymerization (5). In theory it should be possible to react roughly half of the surface silanols with silanes, depending on the silane size (4). This means that the maximum surface coverage of silanes on the colloidal silica should be just below 4 µmol/m^2.

2.3.2.2 Potential silanes for stabilization at high salt concentrations

One type of silane that has been used with promising results in previous studies to stabilize colloidal silica is 3-glycidoxypropyl-trialkoxy silanes (7) (5) (9). It has proven useful for stabilizing silica sols in moderate salt concentrations at pH 8-9 (7). However more work is needed to determine if stability in even higher electrolyte concentrations at higher pH can be achieved. Three potential strategies for an increased stability are to increase the surface coverage of silane on the silica particles, either with a 3-glycidoxypropyl-trialkoxy silane or another one, to use other silanes that can modify the surface charge of the particles or to use silanes with a longer organofunctional group.

One way to evaluate if an increased surface coverage can contribute to a higher stability is to use larger amounts of a 3-glycidoxypropyl-trialkoxy silane, e.g. 3-glycidoxypropyl-triethoxy silane (GPTE), during the modification to try to achieve a better surface coverage and see how this affects the stability. Another way to evaluate the effect of the surface coverage is to use shorter silanes. The length of the silane's organofunctional group may affect the grafting ability so that a shorter silane can be more easily grafted to the surface and thereby give a higher surface coverage per amount added silane. A shorter silane may also be grafted in between GPTE silanes to cover up unused space, and this could potentially result in an increased stabilization. Three short silanes that could be used for this evaluation are 3-methacryloxypropyl-trimethoxy silane (MPTM), 3-chloropropyl-triethoxy silane (CPTE) and chloromethyl-triethoxy silane (CMTE). The end groups of these three silanes can be hydrolyzed to form hydroxyl groups.

All three hydrolyzable groups on the GPTE silane are usually not grafted onto the silica surface due to steric reasons (5), and the remaining hydrolyzable groups can be deprotonated at high pH which means they contribute to the negative charge of the particles. If divalent cations are present, this could in theory cause more bridging between the particles and lead to destabilization. Therefore, one way to reduce the surface charge is to modify the sol with a silane with fewer hydrolyzable groups than three so that this charge contribution is minimized. 3-glycidoxypropylmethyl-diethoxy silane (GPMDE) is such a silane which has the same organofunctional group as GPTE, but has a methyl group and only two hydrolyzable groups. Another way to prevent bridging with divalent cations might be to modify the sol with cationically charged silanes. One such cationic silane is the 3-aminopropyl-triethoxy silane (APTE).

One hypothesis about steric stabilization is that a longer organofunctional group would provide a better steric stabilization. In previous studies, poly(ethylene glycol) (PEG) silanes have been used for surface modifications of silica and for increasing stabilization, and these silanes can be much longer than the GPTE silane (20). One example of a poly(ethylene glycol) silane is the methyl-poly(ethylene glycol)-trimethoxy silane (MPEGTE) which has a molecular weight of 678 g/mol. At low pH, PEG silanes interact with silica surfaces and cause aggregation. However, this interaction is pH dependent and decreases with an increase in pH (20). Another property of PEG molecules is a clouding behavior that results in a phase separation at high temperatures (16). The clouding behavior arises because the PEG-chain takes on a more hydrophobic conformation at higher temperatures which causes a phase separation and a cloudy appearance. The temperature at which this behavior starts depends to a large extent on the PEG chain length and the electrolytes in the solution. Some electrolytes, such as Cl^-, cause a lowered clouding temperature while others increase the temperature limit for clouding (16).

2.4 Characterization methods

In the following sections, the theory behind some of the analysis methods used in the project are described.

2.4.1 Sears titration method

Sears titration method is a rapid method which determines the specific surface area of colloidal silica particles, developed 1956 by George W. Sears Jr (21). Sears method measures the amount of base required to raise the pH of the solution from 4 to 9. This is then used to determine the specific surface area through equation (1), where S is the specific area in square meter per gram and V is the volume 0.1 M NaOH required for a 1.5 g sample of silica in milliliters (21).

$$S = 32V - 25 \tag{1}$$

The titration is carried out in a saturated sodium chloride solution to eliminate any effect of unintentional small amounts of electrolytes in the sample and to increase the amount of adsorbed base (22). This method has the advantages that it is rapid, applicable for particles in colloidal solution as well as for powders and it is accurate for particles with a very high surface area (21).

When using the Sears titration method on silane modified silica particles, the measured value is not the true surface area of the particles. Attachment of silanes will modify the silica surface and influence the pKa of the silanols on the surface, and this may decrease the amount of base needed for the titration. Therefore, a decrease in measured surface area is an indication of a modification on the surface and not necessarily of a smaller surface area in this case.

2.4.2 Dynamic light scattering

Dynamic light scattering (DLS) is a method that can be used to determine the size of colloidal particles. In this technique, the sample is irradiated with light which is scattered by the particles in the sample. Since the particles are moving constantly in the solvent due to the Brownian motion, which means motion due to collisions with surrounding molecules, the intensity of the scattered light will fluctuate (23) (24). The rate of the fluctuations will depend on the speed of the Brownian motion since a faster motion makes the intensity of the scattered light fluctuate faster. This can be used to determine the size of the particles, because small particles move faster than larger ones (24).

The size determined by the DLS measurement is the hydrodynamic size of the particles. The hydrodynamic radius includes not only the radius of the particle, but also the size of the layer of molecules that interacts closely to the particle and moves and scatters light together with it (23). This means that for e.g. a sterically stabilized colloidal particle, the hydrodynamic radius would include the steric shell and its hydration layer as well as the particle itself, and the result from DLS measurements may therefore differ from particle sizes determined by other techniques that do not take the steric shell into consideration (23).

2.4.3 Turbidity measurements

Turbidimetry is another light-scattering method that can be used for evaluation of colloidal systems. Turbidity can be described as a measure of the lack of transparency or the amount of cloudiness of a liquid (25), and for suspensions of particles smaller than the wavelength of light there is an increase in turbidity for increased particle or aggregate size (26). This means turbidity measurements can show the amount and rate of aggregation of dispersed particles in a liquid by monitoring the loss of intensity of the light beam passing through the sample (27).

Turbidity is usually measured with a turbidimeter (27), and the method is fast, precise, reproducible and no calibration is necessary (28).

2.4.4 Particle charge titration

The apparent surface charge density can be estimated with particle charge density measurement by using a streaming current detector for colloidal charge measurement in aqueous solutions. The particle charge measurement detects the streaming potential between two electrodes and by titration with a polyelectrolyte titrant or an acid/base to the point of zero charge (PZC) (20). The equivalent charge per mass can thereafter be calculated from equation (2) and equation (3) (20), where N is the equivalent concentration, V is the volume, MW is the molecular weight and C is the concentration.

$$\boldsymbol{N_{polybrene} = \frac{C_{polybrene}}{MW_{polybrene}} * 2\frac{eq}{mol}} \tag{2}$$

$$\boldsymbol{\frac{eq}{g} = \frac{V_{\ polybrene} * N_{polybrene}}{V_{\ silica\ suspension} * C_{silica}}} \tag{3}$$

2.4.5 Ultrafiltration

Ultrafiltration (UF) can be used for separation of particles with different sizes, analyze the size distribution of particles by using filter membrane with different known pore diameters, or to separate colloidal particles from the suspending medium e.g. water, small ions and solutes (29) (30) (6). In contrast to normal filtration, ultrafiltration retains colloidal particles as a concentrated sol (6). On small laboratory ultrafilters with a horizontal membrane, high turbulence is important to maintain high flux and is done by a mechanical stirrer located very close to the membrane. UF is a technique which is used for purifying and concentrating colloids with a minimum consumption of energy (6).

3 Materials and methods

The experimental procedures of the projects as well as the chemicals used are described in the following sections.

3.1 Materials

Colloidal silica particles were provided by AkzoNobel Pulp and Performance Chemicals. The particles were anionically charged and sodium stabilized and had a surface area of 349 m^2/g, as measured by Sears titration method. The concentration of the sol was 30.99 wt% and the pH 10.25. The silanes chloromethyl-triethoxy silane (CMTE) and 3-chloropropyl-triethoxy silane (CPTE) were purchased from Gelest, and the silanes 3-glycidoxypropylmethyl-diethoxy silane (GPMDE), 3-methacryloxypropyl-trimethoxy silane (MPTM), methyl-poly(ethylene glycol)-trimethoxy silane (MPEGTM), 3-aminopropyl-triethoxy silane (APTE) and 3-glycidoxypropyl-triethoxy silane (GPTE) were purchased from Momentive. Additional information about the silanes and the colloidal silica sol can be seen in Appendix A. The cationic polyamine Floquat FL 2250 was provided from SNF. The salts used in the stability evaluations were calcium chloride hydrate ($CaCl_2{\cdot}H_2O$) and sodium chloride (NaCl). Reagent grade sodium hydroxide and hydrochloric acid, 1 M or 0.1 M were used to adjust pH. Deionized water was used for all experiments.

3.2 Modification method

For the silanes that were not already water soluble, the hydrolysis reaction was preferably done in a separate step, a pre-hydrolysis, to get a more hydrophilic and reactive silane and prevent a two phase system upon addition to the sol. Some of these silanes did not however seem to hydrolyze during the pre-hydrolysis, and then this step was excluded. The pre-hydrolysis and the modification steps are described in the sections below.

3.2.1 Pre-hydrolysis

The pre-hydrolysis was performed by adding 1 M HCl dropwise to water, until pH ~2.5 was reached. The acidic water was thereafter added in excess to the silane. The mixture was stirred vigorously in room temperature until the solution was transparent. The acidic conditions of the pre-hydrolysis favor the hydrolysis of alkoxy groups over the unwanted self-condensation.

3.2.2 Silane modifications of silica

The silica sol was heated and kept under controlled temperature within an interval of 50-100 °C while stirring. When the desired temperature was reached, the pre-hydrolyzed or pure silane was added dropwise at a dosage rate of 0.5-2 µmol silane per m^2 silica surface area per hour, using a dispensing unit. No adjustment of the pH was done, since the naturally high pH of the sol results in a rapid condensation reaction of the silanes to the silica surface. The base-catalyzed epoxide ring-opening reaction for GPTE and GPMDE is also favored at these conditions. Some modification products contained a combination of GPTE and another silane, and this functionalization was done by modification of the already GPTE-modified sol with the second silane.

3.3 Characterization of modified sols

The modified sols were characterized in several ways, including determination of specific surface area from Sears titration, particle size from dynamic light scattering, apparent particle charge from particle charge titration and by calculating a yield from ultrafiltration. These methods are described in the sections below. Additionally, the sols were characterized by measuring pH, conductivity, density and concentration. All sols were not possible to characterize by all methods.

3.3.1 Sears titration method

Sears titration method was used to determine the specific surface area for all sols, using a 888 Titrando, from Metrohm. A sample containing 1.5 g SiO_2 and approximately 100 ml water was acidified with 1 M hydrochloric acid to adjust the pH to ~2.85. Thereafter, approximately 30 g sodium chloride was added and the volume was adjusted to approximately 150 ml with water and the mixture was stirred until the salt had dissolved. The titration was thereafter carried out with 0.1 M sodium hydroxide and titrated from pH 4 to 9. The pH was being checked by a calibrated electrode during the titration.

3.3.2 Dynamic light scattering

Dynamic light scattering (DLS) was used to measure the size of the silica particles, using a Zetasizer Nano-ZS from Malvern instrument. About 0.5 wt% SiO_2 was added to 20 mM NaCl solution in a cuvette, to achieve an attenuator value of 6-8. All measurements were made in five replicates for each sample and were performed at 25 °C. The Z-average, which is an intensity mean, and standard deviation of the five runs were recorded by the instrument.

3.3.3 Particle charge titration

The apparent surface charge density of the colloidal silica particles was measured by a Mütek Particle Charge Detector (PCD), using the cationic polyamine FL2250 with a molecular weight of 7500 g/mol, see Figure 8. The silica sol was diluted with water to a concentration of 0.1 wt% or 0.5 wt% silica and was adjusted to pH 10. Approximately 10 g diluted sol was used for each titration and the cationic polyamine FL2250 was used in a concentration of 0.2 g/ml or 1 g/ml as a titrant. The titration was performed with a Mettler-Toledo Autotitrator which titrated until the point of zero charge (PZC) was reached. The charge per mass was thereafter calculated from the titrated volume required to reach the PZC, see Appendix B. All measurements were made in triplicate and an average charge per mass value was obtained. For additional information, see Appendix C.

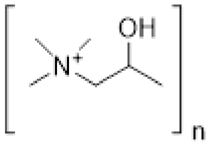

Figure 8. Structure of the cationic polyamine FL2250.

3.3.4 Yield measurement

Ultrafiltration was used to determine the yield of the syntheses. This was done by using a lab-scale stirred ultrafiltration unit from Micon with 30 kDa cutoff filters since the 100 kDa filter had too large pores to retain the silica particles, and the 5 kDa filters turned out later in this study to have too small pores and did not let all free silane through, see discussion in Appendix D. Approximately 150 ml silica sol, diluted or undiluted, was added to the filtration unit. About 1.5 bar nitrogen gas was used and the sample was stirred during the filtration. Approximately 15-20 ml filtrate was collected and sent for analysis with total carbon (TC) analysis, and ethanol or methanol content was determined by HPLC. The yield was thereafter calculated by equation (4) from these results, see Appendix E.

$$\mathbf{Yield} = \mathbf{1} - \frac{\textbf{total carbon in filtrate} - \textbf{carbon from ethanol/methanol}}{\textbf{carbon added from hydrolyzed silane}} \quad (4)$$

3.4 Stability evaluations

All samples were prepared by adding firstly water and thereafter salt solution, NaCl or $CaCl_2$, to the silica sol and the mixture was stirred. Samples with the highest salt concentrations were prepared from 2 M $CaCl_2$ or 4 M NaCl, and adding a small amount of silica sol to obtain a SiO_2 concentration of 1 %. HCl or NaOH were used to adjust pH. The samples were poured into three vials and were left in room temperature, 50 °C or 80 °C. After 1 h, the turbidity was measured or observed. The turbidity measurements are described more in detail below.

3.4.1 Turbidity measurements

The turbidity was measured to evaluate the stability of the silica sols, using a 2100P Turbidimeter from HACH. Approximately 20 ml of sample from the stability test was added to a vial and the turbidity was measured. Samples with turbidities above 150 NTU were deemed too turbid and were considered aggregated. Examples of different turbidities measured in NTU are shown in Figure 9.

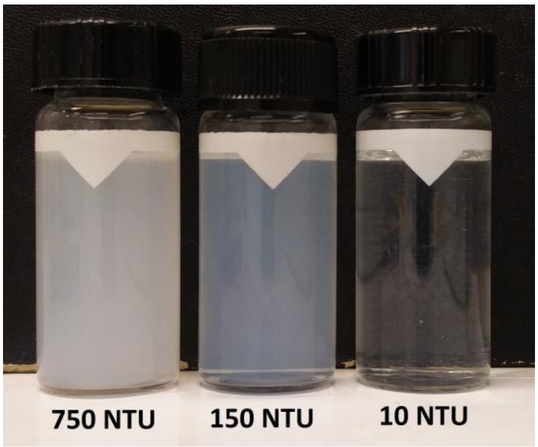

Figure 9. Comparison between three dispersions with different turbidities.

4 Results and Discussion

The results from this study include characterizations of the modified sols done with several different silanes, and also results from stability evaluations with NaCl or $CaCl_2$. The results are presented based on the three topics of this report: how the stability is affected by surface coverage (sections 4.1 and 4.2), surface charge (sections 4.3. and 4.4) and silane length (section 4.5). Several different modifications have been done and in this report the names of the modifications are denoted "silane abbreviation"-"added amount of silane", e.g. GPTE-4 for a modification with 3-glycidoxypropyl-triethoxy silane with 4 µmol/m^2 added silane. When two silanes are combined, the name denotes "the first modification" + "the second modification", e.g. GPTE-2+APTE-4 for a combination of 2 µmol/m^2 added GPTE silane and 4 µmol/m^2 added APTE silane. A list of all attempted modifications from the project is presented in Appendix F.

4.1 Stability effects from higher surface coverage by addition of more silane

To evaluate if a larger amount of added silane during the modification would result in a higher surface coverage and thereby an increased stability, functionalization with the silane GPTE was done, see Figure 10 for the hydrolyzed silane structure. The results from the evaluation of whether a higher surface coverage could be achieved are presented in section 4.1.1 and the stability evaluations for the modifications are presented in section 4.1.2.

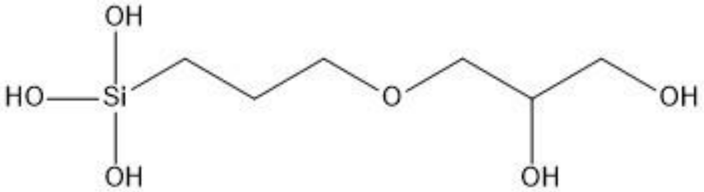

Figure 10. The structure of the hydrolyzed GPTE silane.

4.1.1 Modifications with GPTE silane

Several characterization results, see Table 1, indicate that the condensation reaction, i.e. the attachment of the silane to the particle, occurred during the modification. The pH increases after the modification reaction, which indicates that the silanes attach to the particle. The conductivity decreases with increased amount of silane added.

Table 1. Results from characterization of modifications with GPTE silane.

Name	Functionalization [µmol silane/m^2 SiO_2]		Yield [%]	Surface area [m^2/g, ± 5]	Apparent surface charge [meq/g, ± 0.037]	Conductivity [mS/cm]	pH	Diameter [nm, ± 0.5]
	Added amount	Amount bound						
Bare sol	-	-	-	350	0.68	5.46	10.25	11
GPTE-1	1.0	0.99	99	265	0.41	4.60	10.69	17
GPTE-2	2.0	1.92	96	215	0.38	4.13	11.60	15
GPTE-3	3.0	2.97	99	195	0.36	3.92	11.05	18
GPTE-4	4.0	3.48	87	180	0.33	3.62	11.25	18
GPTE-5	5.0	3.90	78	170	0.36	3.35	11.22	18
GPTE-6	6.0	3.66	61	165	0.35	3.07	11.09	18
GPTE-8	8.0	3.68	46	145	0.32	2.79	11.12	18

The functionalized sols show a decrease in measured surface area from Sears titration when the amount of added silane increases. This decrease in measured surface area indicates that less silanol groups on the silica particles are available for interaction with OH^-, meaning more silane has attached to the silica surface. The results from DLS measurements also show that the hydrodynamic diameter increases with the amount of added silane to a certain level, which strengthen the hypothesis that more silane attaches when the added amount is increased. The yield calculated from the ultrafiltration results indicated that almost all silanes attached to the surface when adding 3 µmol/m^2 or less. When adding more however, the yield seemed to be lower and the amount bound leveled out just below 4 µmol/m^2, and more added silane does not seem to give a higher surface coverage for the GPTE silane above this level. The accuracy and precision of the method for determining the yield are however not very high and it is therefore difficult to determine precise yields.

The results from the particle charge titration measurements in pH 10 shows that the apparent surface charge is significantly decreased by silane modification compared to bare silica sol, also indicating some attachment of the silane to the silica particle. The particle charge titration with a polymer titrant is highly dependent on the polymer type and size, since it can only measure the accessible silanol groups on the silica surface. According to these results, the effect of silane modification leveled out after 2 µmol/m^2 of added silane, but increase in bound silane is seen from the yield calculations. The decrease in effect with higher amount of silane from the particle charge titration is probably because a low amount of attached silane to the particle is enough to make the surface inaccessible for the polymer.

4.1.2 Stability of GPTE modified sols

Stability evaluations of GPTE functionalized silica were performed with two different salts: NaCl and $CaCl_2$.

4.1.2.1 Stability of GPTE modified sols in NaCl

The results from the stability evaluations with NaCl for the GPTE-modified silica sols are presented in Table 2 for pH 9 and in Table 3 for pH 10.

Table 2. The turbidities of 1 % SiO_2 dispersions (pH 9) with different NaCl concentrations after 1 h in 80 °C.

	Turbidity [NTU] - pH 9					
	NaCl concentration					
Name	100 [mM]	500 [mM]	1000 [mM]	2000 [mM]	3000 [mM]	3900[a] [mM]
Bare sol	6.28	157	X	X	X	X
GPTE-2	---	---	7.35	8.48	11.2	26.0
GPTE-4	---	---	---	8.06	8.17	---
GPTE-5	---	---	8.20	8.75	---	---
GPTE-6	---	---	---	---	---	7.16
GPTE-8	---	---	---	---	---	7.58

X = not analyzed, but results at lower salt concentrations indicate a turbidity above 150 NTU.
--- = not analyzed, but results from other measurements indicate a transparent dispersion.
[a] Approximate concentration.
Results predicted to be above 150 NTU are marked gray.
Not all modifications were evaluated in NaCl.

Table 3. The turbidities of 1 % SiO_2 dispersions (pH 10) with different NaCl concentrations after 1 h in 80 °C.

	Turbidity [NTU] – pH 10					
	NaCl concentration					
Name	100 [mM]	500 [mM]	1000 [mM]	2000 [mM]	3000 [mM]	3900[a] [mM]
Bare sol	6.33	197	X	X	X	X
GPTE-2	---	---	7.37	8.83	10.6	25.7
GPTE-4	---	---	---	8.74	---	---
GPTE-5	---	---	8.40	8.40	---	6.93
GPTE-6	---	---	---	---	---	7.05
GPTE-8	---	---	---	---	---	6.92

X = not analyzed, but results at lower salt concentrations indicate a turbidity above 150 NTU.
--- = not analyzed, but results from other measurements indicate a transparent dispersion.
[a] Approximate concentration.
Results predicted to be above 150 NTU are marked gray.
Not all modifications were evaluated in NaCl.

As can be seen from the results, to achieve stability for 1 h in 80 °C in 3900 mM NaCl, about 2 µmol/m^2 added amount GPTE silane was sufficient for both the pH 9 and pH 10 systems. This means stability is relatively easy to obtain for the sols in NaCl with only a low surface coverage with the commonly used GPTE silane, independent of pH. Therefore, the focus of this project was on stability in $CaCl_2$ where the conditions are much tougher, and modifications with the other silanes were only evaluated in $CaCl_2$ solutions.

4.1.2.2 Stability of GPTE-modified sols in $CaCl_2$

In the tables below, the results from the stability evaluations of GPTE-modified silica sols of different surface coverages are presented. Table 4 shows the results for 1 % silica dispersions with pH 9 after 1 h in 80 °C, and Table 5 shows the same but at pH 10.

Table 4. The turbidities of 1 % SiO_2 dispersions (pH 9) with different $CaCl_2$ concentrations after 1 h in 80 °C.

	Turbidity [NTU] - pH 9					
	$CaCl_2$ concentration					
Name	10 [mM]	100 [mM]	500 [mM]	750 [mM]	1000 [mM]	1900[a] [mM]
Bare sol	> 1000	X	X	X	X	X
GPTE-1	413	> 1000	X	X	X	X
GPTE-2	12.4	671	693	X	X	X
GPTE-3	---	17.2	133	X	X	X
GPTE-4	---	---	9.42	8.90	8.60	7.10
GPTE-5	---	---	10.0	9.00	8.40	---
GPTE-6	---	---	---	---	8.35	---
GPTE-8	< 10[b]	< 10[b]	< 10[b]	< 10[b]	8.19	6.17

X = not analyzed, but results at lower salt concentrations indicate a turbidity above 150 NTU.
--- = not analyzed, but results from other measurements indicate a transparent dispersion.
[a] Approximate concentration.
[b] No exact value of the turbidity was measured, but the dispersion was completely transparent.
Results predicted to be above 150 NTU are marked gray.

Table 5. The turbidities of 1 % SiO_2 dispersions (pH 10) with different $CaCl_2$ concentrations after 1 h in 80 °C.

	Turbidity [NTU] – pH 10					
	$CaCl_2$ concentration					
Name	10 [mM]	100 [mM]	500 [mM]	750 [mM]	1000 [mM]	1900[a] [mM]
Bare sol	> 1000	X	X	X	X	X
GPTE-1	n.a.	X	X	X	X	X
GPTE-2	n.a.	> 1000	X	X	X	X
GPTE-3	n.a.	841	698	X	X	X
GPTE-4	n.a.	146	548	X	X	X
GPTE-5	---	11.5	53.2	n.a.	177	X
GPTE-6	---	---	---	---	28.0	21.5
GPTE-8	---	< 10[b]	< 10[b]	---	9.72	7.69

X = not analyzed, but results at lower salt concentrations indicate a turbidity above 150 NTU.
--- = not analyzed, but results from other measurements indicate a transparent dispersion.
n.a. = not analyzed.
[a] Approximate concentration.
[b] No exact value of the turbidity was measured, but the dispersion was completely transparent.
Results predicted to be above 150 NTU are marked gray.

At both pH 9 and 10, the stability towards aggregation in $CaCl_2$ solution increased with a larger amount of added silane. At pH 9, GPTE-4 seems to be enough to stabilize the system in 80 °C since the 1900 mM $CaCl_2$ solution had a turbidity below 10 NTU after 1 h, and a visual observation showed that it was still completely transparent after 80 days at 80 °C. In pH 10 however, both GPTE-4 and GPTE-5 turned out to aggregate with the highest salt concentration, while GPTE-6 and GPTE-8 showed excellent stability and were almost transparent after 80 days at 80 °C, which was observed visually. Stability evaluations were also done on GPTE-6 and GPTE-8 at 120 °C for pH 9 with 1900 mM $CaCl_2$, and no difference in stability was observed between the two modifications since both had some aggregation (100-150 NTU) after three days. Since no apparent improvement was observed with 8 µmol/m^2 added silane compared to 6 µmol/m^2, and they both seemed very stable towards high electrolyte concentrations, it was deemed unnecessary to continue with even higher surface coverages.

The reason for the improvement in stability with larger amount of added silane is not completely understood. The Sears titration indicates a small increase in surface coverage when more silane is added during the modification, and this could explain the increase in stability. According to literature and the ultrafiltrations with 30 kDa filters however, the maximum graftable amount should be just below 4 µmol/m2 (4) and that would not explain the increase in stability above GPTE-4 where the difference in actual surface coverage is low between the different modifications. That could mean the free silane in solution is causing the increased stability for these modifications. If that is the case, a high excess of free silane in solution might be needed to shift the equilibrium towards the higher surface coverage during the modification, or to prevent silanes from leaving the particles when diluting the sol. That could mean that an amount of the silanes leave the particle if the sol is diluted, and an equilibrium would result in less silanes leaving when more silanes are free in solution. It might also be the case that the small increases in surface coverage close to a complete monolayer still have a large effect on stability. Ultrafiltration with a 5 kDa filter resulted in very high yields, see Appendix D, which could mean the free silane in solution polymerize and create too large clusters to pass through the filter. These polymers do not seem to have a negative effect on the stability however, since the stability is high even with large amounts of free silane. Hypotheses of how the reason for the improved stability can be evaluated further are discussed in section 6 Future work.

4.2 Stability effects from surface coverage by shorter silanes

One hypothesis was that a silane with a shorter organofunctional group may be more easily grafted to the surface and thereby give a higher possible surface coverage. To investigate this theory and if it could contribute to a better stability, two shorter silanes were used for functionalization of the sol, see Figure 11 for molecular structure of the two hydrolyzed silanes. It was also tested whether the shorter silanes could be grafted in between the GPTE silanes to fill unused space where the GPTE silane was too large to be grafted, and thereby increase the surface coverage to a larger extent than with the GPTE silane alone. The results from the modifications are presented in section 4.2.1 and the results from the stability evaluations are presented in section 4.2.2.

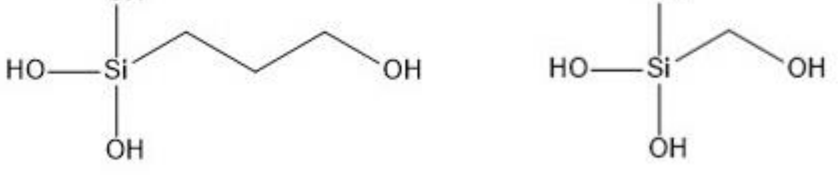

Figure 11. The structure of CPTE and CMTE silanes, where the chlorines and the ethoxy groups have been hydrolysed.

4.2.1 Modification with shorter silanes

The attempts to modify the sol with only the CPTE silane resulted in gels even after optimizing the reaction conditions, which indicated that the organofunctional group is too hydrophobic.

Either the hydrophobicity was caused by the propanol group of the silane, or because the hydrophobic chlorine end group was not hydrolyzed. A second silane, with a methacrylic end group, which would after hydrolysis result in the same molecule with a propanol group, was evaluated as well but it also resulted in gels and this supports the theory that the resulting molecule is the problem and not the chlorine end group.

To prevent the problem with a too hydrophobic silane, two approaches were suggested: use an even shorter chain, e.g. CMTE, to get a more hydrophilic silane, or add CPTE onto an already GPTE silane modified sol. Both approaches resulted in a low viscous dispersion, yet with a thin gel film for CMTE and increased turbidity for the case of the combination of GPTE with CPTE, and the results from the characterizations can be seen in Table 6. Another reason for combining the CPTE with GPTE was to investigate if the shorter silanes could be used for covering unused space between the GPTE silanes, and therefore the CMTE was combined with GPTE as well.

Table 6. Results from characterization of modifications with CMTE and combinations of GPTE with CMTE or CPTE.

Name	Added amount [µmol silane/m^2 SiO_2]	Surface area [m^2/g, ± 5]	pH	Conductivity [mS/cm]	Diameter [nm, ± 0.5]
Bare sol	-	350	10.25	5.46	11
CMTE-2	2	300	9.92	8.38	25
GPTE-2+ CMTE-2	2+2	180	10.21	7.55	25
GPTE-2+ CPTE-2	2+2	n.a.	10.19	11.62	68

n.a. = not analyzed.

The modification characterization trends are mostly the same as for the modifications with the GPTE silane, however the conductivity increased remarkably instead of decreasing and the pH decreased instead of increasing, which probably was due to release of chloride ions from the silane. That would also strengthen the hypothesis that the resulting molecule with a three carbon long chain with a hydroxyl group at the end was too hydrophobic, instead of that the hydrophobicity was caused by the chlorine still being attached to the silane. The hydrodynamic diameter from DLS measurement for GPTE-2+CPTE-2 was also remarkably high and the dispersion was turbid, which probably was due to some silica aggregates. The yield measurements for sols modified with CMTE did not give any reliable results since the carbon content from the hydrolyzed silanes was very small and this resulted in a too low accuracy, and the yield from GPTE-2+CPTE-2 could not be determined due to aggregates in the sol.

4.2.2 Stability of CPTE and CMTE modified sols

The stability of the sols modified with CMTE silane and combinations of GPTE with CPTE or CMTE are presented in Table 7, where the results from turbidity measurements after 1 h in 80 °C for 1 % SiO_2 dispersions in pH 9 are presented.

Table 7. The turbidity of 1 % SiO_2 dispersions (pH 9) with different $CaCl_2$ concentrations after 1 h in 80 °C.

	Turbidity [NTU] – pH 9					
	$CaCl_2$ concentration					
Name	10 [mM]	100 [mM]	500 [mM]	750 [mM]	1000 [mM]	1900[a] [mM]
Bare sol	> 1000	X	X	X	X	X
CMTE-2	239	> 1000	X	X	X	X
GPTE-2+ CMTE-2	8.03	383	X	X	X	X
GPTE-2+ CPTE-2	26.8	911	> 1000	X	X	X

X = not analyzed, but results at lower salt concentration indicate a turbidity above 150 NTU.

[a] Approximate concentration.

Results predicted to be above 150 NTU are marked gray.

The stability of the sol modified with CMTE shows only a small improvement compared to the unmodified sol, and the combinations of GPTE with CPTE or CMTE did not show any particular improvements compared to the GPTE-2 they originated from. These shorter silanes should in theory be able to give a higher surface coverage compared to the GPTE silane, but since the stability was not improved significantly it could mean that the steric stabilization from a longer chain is much more important for the stability than the surface coverage itself. The length of CMTE is about 3.5 Å and CPTE is about 6.1 Å long, compared to 9.4 Å for GPTE, calculated from Chem3D, and the lengths of the shorter silanes might not be enough to stabilize the system from bridging with Ca^{2+} ions, since a hydrated calcium ion have a diameter of 4.6-5.0 Å (7). For the CPTE silane, another reason for the lack of stability could be that the silane is too hydrophobic and instead of stabilizing the system contributes to a destabilization since there is an attraction between the hydrophobic groups on the particles.

Since the surface coverage with GPTE silane reaches a maximum just below 4 µmol/m^2, it would be interesting to investigate CMTE with a larger amount added silane to see if its non-bulky shape can lead to even higher surface coverages than 4 µmol/m^2 and provide a better stability. Since the GPTE-modified sols have a considerable increase in stability even with only a small increase in surface coverage, this could mean that if a higher maximum surface coverage could be achieved with a short silane such as CMTE, it might be useful even though the stabilities at low surface coverages were not very promising for this silane. An investigation of a higher surface coverage with CMTE was however not prioritized in this study due to that the functionalizations with CMTE did not show any significant improvements for the stability.

4.3 Stability effects from reduction of charges by fewer alkoxide groups

To evaluate if a silane with fewer hydrolysable groups, which may become negatively charged in high pH, would result in increased stability, the silane GPMDE which is illustrated in Figure 12, was grafted to the particle. GPMDE consists of one methyl group and two hydrolysable groups instead of three hydrolysable groups. The results from the modifications of the more hydrophobic silane are presented in section 4.3.1, and the results from the evaluation of whether a reduced surface charge of the particle can increase stability by preventing bridges with Ca^{2+} are presented in section 4.3.2.

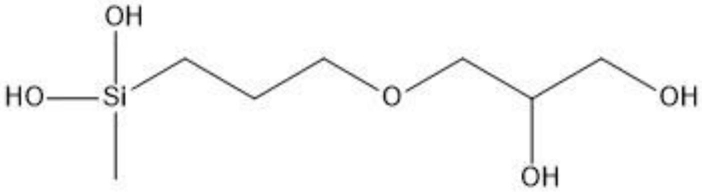

Figure 12. The structure of the hydrolyzed GPMDE silane.

4.3.1 Modifications with GPMDE silane

Since the stability results for the GPTE silane seemed promising with 4 µmol/m^2 added silane in pH 9, the same amount of silane was chosen to be evaluated for the GPMDE silane in order to compare the results. One modification with even higher silane amount, 8 µmol/m^2, was done in addition so that the stability per surface coverage could be evaluated for this silane as well.

The characterization results for the GPMDE silane modifications can be seen in Table 8. The trend for pH, conductivity and hydrodynamic diameter was the same as for the modification with GPTE silane, and therefore the same conclusion can be drawn: that the condensation reaction has occurred and the silane has attached to the silica surface. The surface area from Sears titration also shows the same trend as for the GPTE silane, which indicates more attachment of the silane to the particle with larger amount added silane.

Table 8. Results from characterization of modifications with GPMDE silane.

Name	Added amount [µmol silane/m^2 SiO_2]	Surface area [m^2/g,± 5]	Apparent surface charge [meq/g, ± 0.037]	pH	Conductivity [mS/cm]	Diameter [nm, ± 0.5]
Bare sol	-	350	0.67	10.25	5.46	11
GPMDE-4	4.0	160	0.33	11.54	3.99	26
GPMDE-8	8.0	135	0.33	11.55	2.68	19

The apparent surface charge determined by particle charge titration shows that no considerable difference in apparent surface charge can be seen for GPMDE silanes compared to the GPTE silanes with corresponding surface coverage. This does not necessarily mean that the charge has not been reduced for GPMDE compared to GPTE, since the GPTE results indicate that the surface was not considerably available for the titrant polymer.

4.3.2 Stability of GPMDE-modifications

Stability evaluations were done for the GPMDE-modifications in 1 % silica dispersions in pH 9 with different salt concentrations. The turbidities of the dispersions after 1 h in 80 °C are presented in Table 9.

Table 9. The turbidities of 1 % SiO_2 dispersions (pH 9) with different $CaCl_2$ concentrations after 1 h in 80 °C.

	Turbidity [NTU] – pH 9					
	$CaCl_2$ concentration					
Name	10 [mM]	100 [mM]	500 [mM]	750 [mM]	1000 [mM]	1900[a] [mM]
Bare sol	> 1000	X	X	X	X	X
GPMDE-4	---	22.1	> 1000	X	X	X
GPMDE-8	17.1	60.6	95.1	X	X	X

X = not analyzed, but results at lower salt concentration indicate a turbidity above 150 NTU.
--- = not analyzed, but results from other measurements indicate a transparent dispersion.
[a] Approximate concentration.
Results predicted to be above 150 NTU are marked gray.

The stability increased with GPMDE modification compared to unmodified sol, but compared to the GPTE silane, the stability was not remarkable since GPTE-4 was stable up to the maximum salt concentration in pH 9 whereas GPMDE was not completely transparent in 500 mM $CaCl_2$ with either surface coverage. The methyl group on the silane was expected to lower the surface charge of the particle compared to with GPTE and thereby reduce the bridging with $CaCl_2$, but since GPMDE provided less stability than GPTE, this theory was not supported. The methyl group might still contribute to a lower surface charge, but is not likely due to results from Sears titration and particle charge titration. Additionally, the lack of stability could also indicate that the hydrophobic part of the silane contributes to a destabilization. The GPMDE silane was not evaluated any further in this study since the stability did not live up to the expectations.

4.4 Stability effects from introduction of cationic charges

In order to evaluate whether a silane with a cationic end group would result in a better stabilization due to repulsion of the bridging Ca^{2+} ions, functionalization with the silane APTE was done, see Figure 13. The results from the evaluations of the modifications are presented in section 4.4.1 and the results from the stability evaluations for the functionalized sols are presented in section 4.4.2.

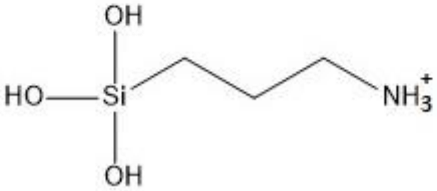

Figure 13. The structure of the hydrolyzed APTE silane.

4.4.1 Modification with APTE silane

A gel was formed during the modification with the cationic silane. The NH_3^+ group on the APTE silane has a pKa of around 10.6 (31) which means that during the modification, where the pH is about 10.25, the silane is partly positively charged. The negative charges on the silica surface might have attracted the positively charged silane, which is illustrated in Figure 14, and formed a network resulting in gelling.

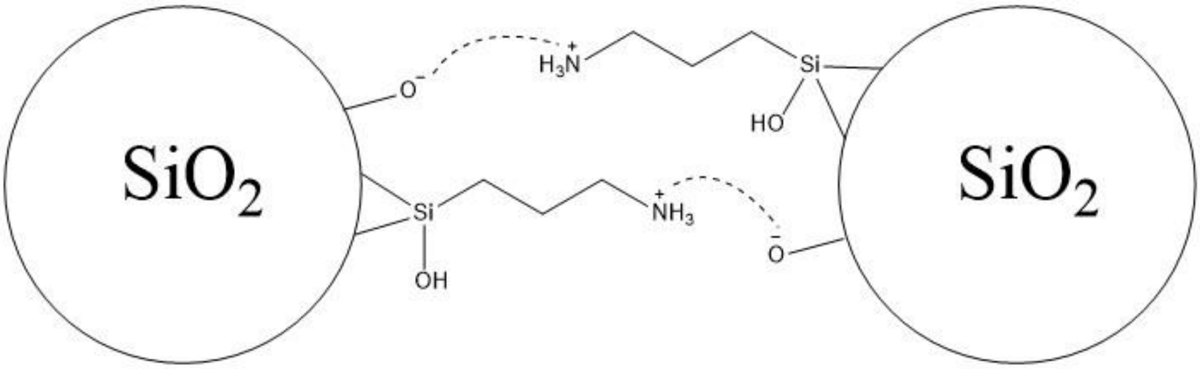

Figure 14 APTE silane bridging to silica particle.

To prevent gelling, the cationic silane was added to an already modified GPTE-2 sol to provide some steric stabilization and enable the modification. The characterizations of the sols modified with a combination of GPTE silane with APTE silane can be seen in Table 10.

Table 10. Results from characterization of modifications with combinations of GPTE with APTE.

Name	Added amount [µmol silane/m^2 SiO$_2$]	pH	Conductivity [mS/cm]	Diameter [nm, ± 0.5]
Bare sol	-	10.25	5.46	11
GPTE-2+APTE-2	2	11.76	4.67	24
GPTE-2+APTE-4	4	12.01	3.87	27

The modification with the cationic silane onto an already GPTE-modified sol resulted in a low viscous dispersion and not a gel, in contrast to the modification with only APTE. This confirms the theory that the GPTE silane can provide sufficient steric stabilization to make the APTE modification. The results in pH, conductivity and hydrodynamic diameter show the same trend as for the modifications with the GPTE silane, and therefore is it likely that the APTE silane to some extent has attached to the silica particle. The surface area could not be measured by Sears titration because the cationic charges from the silane disturb the measurement.

To investigate if the modifications had resulted in the desired properties, which were cationic particles, surface charge titration was performed. The result for GPTE-2+APTE-2 showed a very low apparent surface charge in pH 10 and was therefore difficult to analyze. GPTE-2-APTE-4 was cationic at pH 10.

4.4.2 Stability of APTE modified sols

The sols modified with a combination of GPTE with APTE silane did not show significant improvements compared to the unmodified sol, see Table 11. The reason for the lack of stability might be due to that the cationic charges on the ends of the APTE silanes interact with the negatively charged surface of the particle, and provide a destabilizing bridging interaction in the same way as proposed in Figure 14. To avoid this, it might be possible to use even higher surface coverages to block all the anionic charges of the particles, but this is left for future studies due to lack of time in this project.

Table 11. The turbidity of 1 % SiO_2 dispersions with different $CaCl_2$ concentrations after 1 h in 80 °C.

	Name	**Turbidity [NTU] – pH 8 & 9**					
		$CaCl_2$ concentration					
		10 [mM]	100 [mM]	500 [mM]	750 [mM]	1000 [mM]	1900^a [mM]
pH 8	Bare sol	303	X	X	X	X	X
	GPTE-2+ APTE-2	n.a.	> 1000	X	X	X	X
	GPTE-2+ APTE-4	138	X	X	X	X	X
pH 9	Bare sol	> 1000	X	X	X	X	X
	GPTE-2+ APTE-2	> 1000	> 1000	X	X	X	X
	GPTE-2+ APTE-4	607	X	X	X	X	X

X = not analyzed, but results at lower salt concentration indicate a turbidity above 150 NTU.
n.a. = not analyzed.
^{a} Approximate concentration.
Results predicted to be above 150 NTU are marked gray.

4.5 Stability effects from increasing the length of the silane

To evaluate if a longer silane would result in a better steric stabilization, functionalization with the silane MPEGTM was done, see Figure 15. Since the MPEGTM silane was bulkier than the other silanes it could in theory be more difficult to graft to the silica surface due to steric reasons. Therefore, the modified silica sols were characterized to evaluate this, and the results from the evaluation are presented in section 4.5.1. The results from the stability evaluations for the modified sols are presented in section 4.5.2.

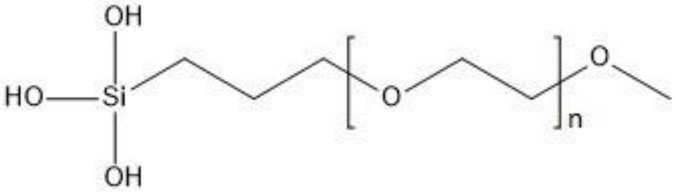

Figure 15. The structure of the hydrolyzed MPEGTM silane.

4.5.1 Modification with MPEGTM silane

Since the MPEGTM silane is considerably bigger and bulkier than the GPTE silane, the expected amount silane likely to bind to the silica surface was much smaller. Therefore, a lower surface coverage was chosen to start with, because a too high dosage was thought to end up as free silane in the modification step instead of binding in to the silica surface. It has however been observed in previous studies (20) that an excess of MPEGTM silane is needed for the modification, and therefore a sol with higher amount added silane during the modification was also done.

The characterization for the modification with MPEGTM silane can be seen in Table 12. The result in pH, conductivity, hydrodynamic diameter and surface area show the same trend as for the modifications with GPTE, and therefore it is likely that the MPEGTM silane has attached on the silica particle as well.

Table 12. Results from characterization of modifications with MPEGTM and a combination of GPTE with MPEGTM.

Name	Functionalization [µmol silane/m^2 SiO$_2$] Added amount	Functionalization [µmol silane/m^2 SiO$_2$] Amount bound	Yield [%]	Surface area [m^2/g,± 5]	Apparent surface charge [meq/g, ± 0.037]	pH	Conductivity [mS/cm]	Diameter [nm, ± 0.5]
Bare sol	-	-	-	350	0.68	10.25	5.46	11
MPEGTM-0.5	0.5	n.a.	n.a.	280	n.a.	10.78	4.30	18
MPEGTM-1	1.0	n.a.	n.a.	245	n.a.	10.95	3.73	18
MPEGTM-2	2.0	n.a.	n.a.	200	0.31	11.61	3.03	19
MPEGTM-4	4.0	1.68	42	160	0.33	11.19	1.56	21
GPTE-2+ MPEGTM-2	2+2	1.92+ 0.75	37[c]	170	n.a.	11.11	2.43	20

n.a. = not analyzed.

[c] Yield for the second modification of the sol.

Modification of the silica sol with MPEGTM silane resulted in a homogenous slightly yellow low viscous dispersion and no gel or gel film was formed. The yield from 30 kDa ultrafiltration was lower for MPEGTM silane than for GPTE silane, which was determined by comparing the yield results of MPEGTM-4, which was 42 %, with the yield result of GPTE-4, which was 89 %. A reason for this could be the more bulky geometry of the MPEGTM silane which makes it more difficult to graft onto the silica particle, and an excess of silane might then be needed in the modification in order to obtain a higher surface coverage. This has also been observed in previous studies (20), which strengthens the hypothesis.

The apparent surface charge measured for modification with MPEGTM silanes decreases compared to bare sol. This indicates that the MPEGTM silane has attached to silica particle to some extent, but no considerable difference between the modifications was seen.

4.5.2 Stability of MPEGTM modifications

The results from the stability evaluations for the modifications with the MPEGTM silane are presented in Table 13.

Table 13. The turbidity of 1 % SiO_2 dispersions with different $CaCl_2$ concentrations after 1 h in 80 °C.

		Turbidity [NTU]					
		$CaCl_2$ concentration					
	Name	10 [mM]	100 [mM]	500 [mM]	750 [mM]	1000 [mM]	1900[a] [mM]
pH 9	Bare sol	> 1000	X	X	X	X	X
	MPEGTM-0.5	> 1000	X	X	X	X	X
	MPEGTM-1	381	> 1000	X	X	X	X
	MPEGTM-2	10.7	530	X	X	X	X
	MPEGTM-4	12.0	13.1	11.3	n.a.	C	C
	GPTE-2+ MPEGTM-2	---	9.51	9.10	< 10[b]	< 10[b]	< 10[b]
pH 10	Bare sol	> 1000	X	X	X	X	X
	MPEGTM-0.5	n.a.	> 1000	X	X	X	X
	MPEGTM-1	n.a.	> 1000	X	X	X	X
	MPEGTM-2	n.a.	> 1000	X	X	X	X
	MPEGTM-4	---	13.3	20.20	n.a.	n.a.	n.a.
	GPTE-2+ MPEGTM-2	---	9.51	307	X	X	X

X = not analyzed, but results at lower salt concentration indicate a turbidity above 150 NTU.
--- = not analyzed, but results from other measurements indicate a transparent dispersion.
n.a. = not analyzed.
[a] Approximate concentration.
[b] No exact value of the turbidity was measured, but the dispersion was completely transparent.
C = not aggregated, but reversible clouding behavior was observed.
Results predicted to be above 150 NTU are marked gray.

The modification with 0.5 µmol/m^2 MPEGTM silane gave no improvement compared to the unmodified sol, but the other surface coverages show improvements in stability and a trend of increased stability with increased surface coverage. MPEGTM-4 shows an impressive stability towards aggregation and was non-aggregated at the highest $CaCl_2$ concentration. However, a reversible clouding behavior was observed in 80 °C at the highest $CaCl_2$ concentrations, which was most likely due to a hydrophobic conformation of the silane and not because of aggregation since the dispersion turned transparent again after cooling. Except for the clouding behavior at high salt concentrations, MPEGTM-4 was better than GPTE-4 since it was not aggregated in 500 mM $CaCl_2$ at pH 10. When comparing MPEGTM-4 with GPTE-2, which has approximately the same amount silane bound, calculated from the yield, the stability was remarkably better for the MPEGTM silane since GPTE-2 was aggregated in 100 mM $CaCl_2$ in pH 9. The combination of GPTE with MPEGTM seemed to be promising as well, since it was better than GPTE-4 in the same conditions. The combination also showed clouding behavior at 120 °C for the dispersions with the highest $CaCl_2$ concentration, so the lower limit for the clouding behavior seemed to increase when MPEGTM was combined with GPTE. These results show that a longer hydrophilic silane could provide a better stabilization.

5 Conclusions

The main conclusions from this project were that the GPTE silane contributed to a good steric stabilization of the silica particles and that an increased amount of added GPTE probably resulted in higher surface coverage until a maximal coverage was reached just below 4 µmol/m^2. A higher stability could however be obtained by addition of even more silane after this, which indicates that free silane in solution affects the stability positively, or that small increases in surface coverage is achieved even when getting close to the maximum due to a high excess in silane. The most stable modifications with GPTE silane also showed a stable dispersion after 80 days in 80 °C at pH 10 with approximately 2 M $CaCl_2$, indicating that a very stable system was achieved.

Grafting of shorter silanes, CPTE and CMTE, to the silica particle was thought to fill the space between the GPTE silanes and thereby give a better stability, but the results showed a decrease in stability instead. This was probably due to insufficient length of the silanes and in the case of CPTE, the hydrophobic part was the main reason for the instability and resulted in gelling.

When trying to improve the stability by reducing the number of alkoxy groups on the silane, the methyl group of the GPMDE silane was thought to reduce the bridging with calcium ions compared to the silanes with more hydrolysable groups. The stability results however show less stability than for the GPTE silane, which might be because the hydrophobicity of the methyl group either contributes to destabilization or difficulties to graft the silane to the surface.

Modification with the cationic APTE silane also resulted in gelling, but this however was thought to be due to bridging between the negatively charged surface and the positively charged silane end group. A successful modification of APTE to an already modified GPTE-sol was made, but this did not show an improvement in stability.

The modification with the longer MPEGTM silane showed an excellent stability with only a small amount of attached silane compared to the promising GPTE-modified sol, which indicates that increased silane length would give a better stability. There was however a problem with a clouding behavior for the case of MPEGTM, and it was concluded that more work needs to be done here in order to get a more stable functionalized silica sol.

The final conclusion is that the best stability in presence of high electrolyte concentrations and pH can be achieved by using a high surface coverage of a silane with a long hydrophilic organofunctional group.

6 Future work

In this study, several silanes were investigated for their contribution to the stability in systems with high electrolyte content. Only one divalent cation was tested as a tougher condition however, and it would be interesting to investigate the influence of another divalent ion, e.g. Mg^{2+}.

Some approaches, i.e. surface coverage by shorter silanes with CMTE and introduction of cationic charges with APTE, were not sufficient to obtain stability. These two silanes would be interesting to investigate at higher surface coverages, e.g. GPTE-2+APTE-6 and CMTE-8 respectively, and see if stability can be achieved.

A promising approach that already showed excellent stability in this study was the longer silane MPEGTM, but a problem with clouding behavior at high salt concentration and temperatures was seen. Therefore, more work should be done in order to remedy the clouding behavior of MPEGTM or investigate if another long hydrophilic silane, which does not show clouding behavior, can be used instead.

It was also seen that the amount of free silane in solution might have an impact on the stability and it would be interesting to extend the understanding of the function of free silane. This could be tested by doing stability evaluations with dispersions of varied SiO_2 concentrations to see if sols with higher amounts of added silane still have considerably higher stability after more extensive dilution of the free silane.

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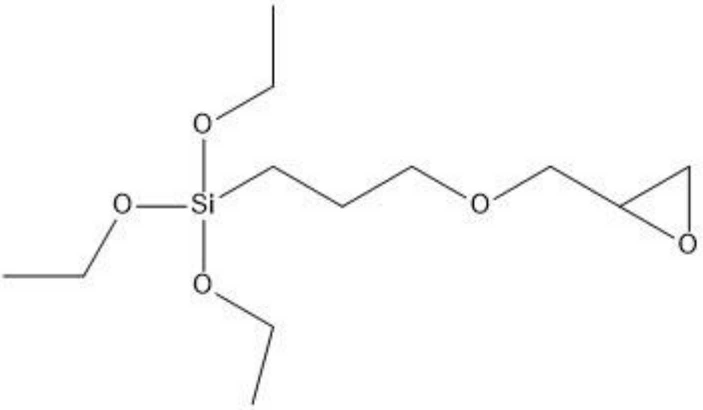
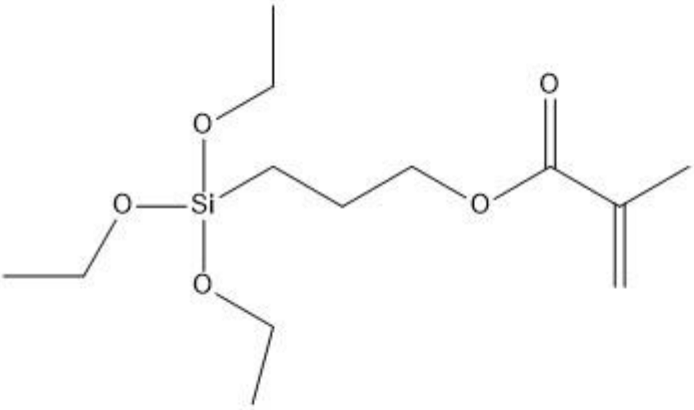
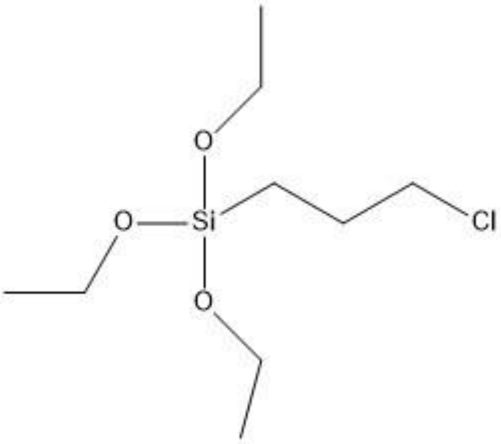
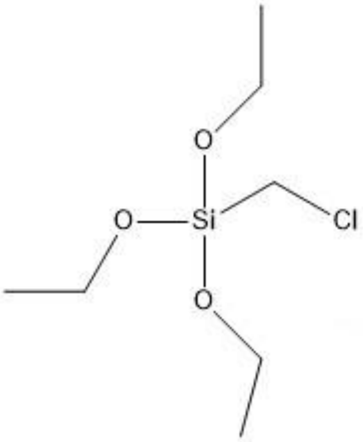
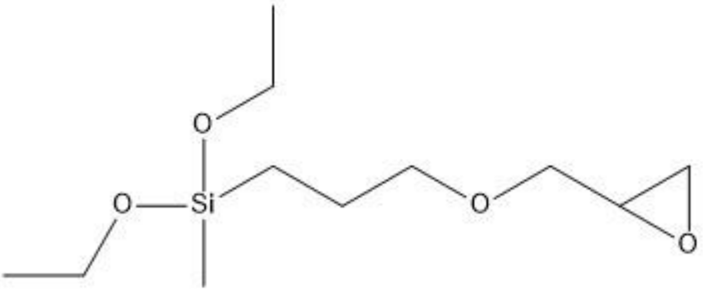
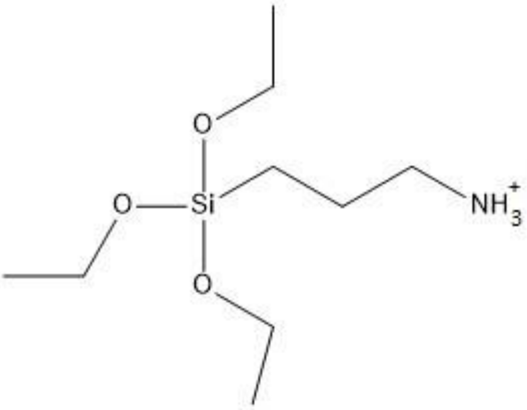
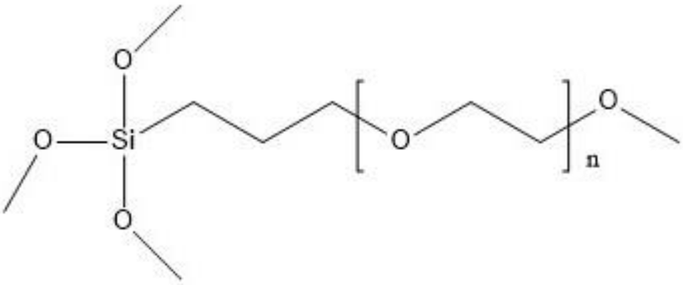
Appendix

A Structure and information of all silanes studied

Table A 1. List of structure and information of all silanes studied in the project.

3-glycidoxypropyl-triethoxy silane (GPTE) MW: 278.4 g/mol CAS: 2602-34-8	
3-methacryloxy-propyl-trimethoxy silane (MPTM) MW: 248.4 g/mol CAS: 2530-85-0	
3-chloropropyl-triethoxy silane (CPTE) MW: 240.8 g/mol CAS: 5089-70-3	

Chloromethyl-triethoxy silane (CMTE) MW: 128.7 g/mol CAS: 15267-95-5	
3-glycidoxypropyl-methyl-diethoxy silane (GPMDE) MW: 248.4 g/mol CAS: 2897-60-1	
3-aminopropyl-triethoxy silane (APTE) MW: 221.4 g/mol CAS: 919-30-2	
Methyl-poly(ethylene glycol)-trimethoxy silane (MPEGTM) MW: 678 g/mol Silquest A-1230 from Momentive	

B Calculations from the particle charge titration to charges in the sample

$$Charge_{titrand}\ [eq] = \frac{Mass_{titrand}[g]}{1000} * Concentration_{titrant}\left[\frac{g}{l}\right] * Charge_{titrant}\left[\frac{moleq}{g}\right] * torrhalt_{titrant}[\%]$$

$$Mass_{SiO_2}\ [g] = Mass_{sample}[g] * Concentration_{silica\ in\ sample}\ [\%]$$

$$Charges_{in\ sample}[\frac{eg}{g}] = \frac{Charge_{titrand}[eq]}{Mass_{SiO_2}}$$

C All measurements from particle charge titration

Table C 1. List of all measurements from particle charge titration.

Name	Silica concent-ration [%]	Weight of solution [g]	PCD start	PCD end	Volume [ml]	Concent-ration polyamine (g/ml)	Comments
Bare sol	0.1	10.02	-1700	220	9.01	0.2	
Bare sol	0.1	9.98	-1700	126	8.8004	0.2	
Bare sol	0.1	9.99	-1400	30	4.4467	0.2	
GPTE-1	0.5	10.00	-1230	150	5.3956	1.0	
GPTE-1	0.5	9.99	-1175	370	5.4560	1.0	
GPTE-1	0.5	10.01	-1218	230	5.3578	1.0	
GPTE-2	0.1	9.99	-1200	100	5.0187	0.2	
GPTE-2	0.1	9.98	-1600	120	4.9145	0.2	
GPTE-2	0.1	9.99	-1550	170	4.9315	0.2	
GPTE-3	0.5	10.00	-1110	180	4.8025	1.0	
GPTE-3	0.5	10.02	-1023	225	4.7373	1.0	
GPTE-3	0.5	9.99	-1023	0.33	4.6380	1.0	
GPTE-4	0.1	10.00	-1400	320	4.3510	0.2	
GPTE-4	0.1	10.01	-1500	400	4.7476	0.2	
GPTE-4	0.1	10.01	-1400	290	3.8249	0.2	
GPTE-5	0.5	9.99	-1030	0.99	4.7383	1.0	
GPTE-5	0.5	10.01	-1009	192	4.7461	1.0	
GPTE-5	0.5	10.01	-889	122	4.6967	1.0	
GPTE-6	0.1	9.99	-1300	180	4.7176	0.2	
GPTE-6	0.1	10.05	-1260	190	4.6694	0.2	
GPTE-6	0.1	10.00	-1220	180	4.5332	0.2	
GPTE-8	0.1	10.01	-1250	250	4.2405	0.2	
GPTE-8	0.1	10.01	-1250	200	4.1887	0.2	
GPTE-8	0.1	10.02	-1200	150	4.0380	0.2	
GPMDE-4	0.1	10.00	-1280	470	4.4127	0.2	
GPMDE-4	0.1	9.99	-1200	260	4.3570	0.2	
GPMDE-4	0.1	10.01	-1260	260	4.2169	0.2	
GPMDE-8	0.1	9.99	-1000	200	4.4467	0.2	
GPMDE-8	0.1	10.01	-960	140	4.2047	0.2	
GPMDE-8	0.1	10.00	-930	120	4.2112	0.2	

MPEGTM-2	0.1	10.00	-1300	130	4.1754	0.2	
MPEGTM-2	0.1	10.00	-1300	80	4.2139	0.2	
MPEGTM-2	0.1	10.01	-1300	16	3.9289	0.2	
MPEGTM-4	0.1	10.00	-1150	80	4.4364	0.2	
MPEGTM-4	0.1	10.00	-1150	140	4.2915	0.2	
MPEGTM-4	0.1	10.00	-100	100	4.1542	0.2	
GPTE2+APTE-2	0.1	9.99	-500	160	1.9556	0.2	
GPTE2+APTE-2	0.1	10.01	-400	120	2.0699	0.2	
GPTE2+APTE-2	0.1	10.00	-400	100	2.0250	0.2	
GPTE2+APTE-2	0.1	10.02	-300	95	0.0	0.2	Reached PZC without titrant
GPTE2+APTE-2	0.1	9.72	-220	60	1.087	0.2	
GPTE2+APTE-2	0.1	10.01	-540	n.a	0.0	0.2	pH 8.95 after PZC
GPTE2+APTE-2	0.5	10.00	-300	0.09	0.0	1.0	pH 8.98 after PZC
GPTE2+APTE-4	0.5	10.03	63	63	0.0	1.0	
GPTE2+APTE-4	0.5	10.00	75	75	0	1.0	
GPTE2+APTE-4	0.5	10.03	70	70	0	1.0	

D Results from the yield evaluations

Table D 1. Results from the total carbon (TC) and ethanol/methanol analyses of the ultrafiltration filtrate, as well as the yield calculated from the values. The samples marked with (30) were filtered through a 30 kDa filter, and the rest through a 5 kDa filter.

Name	TC [mg/l]	EtOH/ MeOH [%]	Added silane carbon [mg/l]	Yield [%]	Comment
GPTE-1	11000	1.8	8894.974	82	
GPTE-1 (30 kDa)	10000	1.9	8894.974	99	
GPTE-2	21000	3.6	16811.65	87	
GPTE-2 (30 kDa)	20000	3.7	16811.65	96	
GPTE-3	33000	5.4	23908.19	80	
GPTE-3 (30 kDa)	28000	5.3	23908.19	99	
GPTE-4	40000	7.0	30301.04	89	
GPTE-4 (30 kDa)	40000	6.9	30301.04	87	
GPTE-5	43000	7.7	36091.35	92	
GPTE-5 (30 kDa)	48000	7.7	36091.35	78	
GPTE-6	51000	9.2	41360.66	93	
GPTE-6 (30 kDa)	63000	9.0	41360.66	61	
GPTE-8	21000	3.9	50593.44	97	1:1 dilution
GPTE-8 (30 kDa)	71000	8.4	50593.44	46	
MPEGTM-0.5	8700	0.4 (MeOH)	19623.34	63	
MPEGTM-1	17000	0.7 (MeOH)	37754.99	62	
MPEGTM-2	36000	1.3 (MeOH)	70175.53	56	
MPEGTM-4	14000	1.7 (MeOH)	122975.9	75	1:3 dilution
MPEGTM-4 (30 kDa)	40000	1.2	122975.9	42	1:1 dilution
GPMDE-4	33000	4.5	35969.31	74	
GPMDE-8	49000	7.7	60769.05	85	
GPTE-2+APTE-2	39000	6.9	13509.71	46	
GPTE-2+APTE-4	60000	10	25612.25	78	
GPTE-2+CMTE-2 (30 kDa)	28000	5.5	2946.66	147	

Ultrafiltration with a 5 kDa filter resulted in very high yields, especially with larger amounts of added silane. This would mean that the more silane added, the more silane bound to the silica surface. This could be true for lower surface coverages, but it is not likely for higher surface coverages because it should be more sterically hindered to attach more and more silane to the particle surface when a saturation of the surface is approached. Therefore, ultrafiltration was investigated and validated as a method for determination of the synthesis yield.

One reason for the unexpectedly high yield could be that the filter pores becomes blocked from the silica particles and get too small to allow passage of the unattached silane. To evaluate this theory, the filter was changed and no remarkable visual difference in filtration rate was observed. The reproducibility of the ultrafiltration unit, TC-analysis and ethanol content analysis was investigated by analysis of three filtrates from the same sol and two measurements of the same filtrate, see Table D 2 and Table D 3. The result from the validation and investigation of the UF-method demonstrates that the method is reproducible and reliable within some margin of error.

Table D 2. The results from three filtrates of the same sol performed in UF.

	Filtrate 1	Filtrate 2	Filtrate 3
Yield (%)	90	93	91

Table D 3. Results from two identical filtrates analysed by TC.

	Sample 1	Sample 2
Yield (%)	91	91

A second hypothesis was either that the free silanes polymerize resulting in too big clusters to pass through the UF-filter, or that a double layer of free silane around the particle is created. To evaluate this, a 30 kDa filter was tested to see if the yield was changed. The comparison between the yields performed on a 5 kDa filter versus 30 kDa filter can be seen in Table D 4.

Table D 4. Comparison between 5 kDa and 30 kDa UF-filter.

	5 kDa			30 kDa		
	Functionalization (µmol silane/m^2 SiO$_2$)			Functionalization (µmol silane/m^2 SiO$_2$)		
Name	Added amount	Amount bound	Yield (%)	Added amount	Amount bound	Yield (%)
GPTE-1	1.0	0.82	82	1.0	0.99	99
GPTE-2	2.0	1.74	87	2.0	1.92	96
GPTE-3	3.0	2.40	80	3.0	2.97	99
GPTE-4	4.0	3.56	89	4.0	3.48	87
GPTE-5	5.0	4.60	92	5.0	3.90	78
GPTE-6	6.0	5.58	93	6.0	3.66	61
GPTE-8	8.0	7.76	97	8.0	4.56	57

The result from the comparison between 5 kDa and 30 kDa filters showed only a small difference for the modifications with low amounts of silane, but a remarkable difference when the sol was modified with high amounts of silane. This indicates that the free silane polymerizes to some extent and can therefore not be filtrated through pores too small such as 5 kDa filter but can pass through a 30 kDa filter. This would also support theories from previous studies, that there is a saturation of surface coverage of the silica surface around 4 µmol GPTE silane/m^2. After that point, the surface is completely covered by a silane monolayer and excess silane will end up free in solution and polymerize.

Ultrafiltration with 30 kDa filter for MPEGTM also resulted in lower yield compared to ultrafiltration with 5 kDa filter, which can be seen in Table D 5. For the same reason as for the comparison for GPTE between the filters, one hypothesis is that excess silane will end up free in solution and polymerize.

Table D 5. Comparison between 5 kDa and 30 kDa UF-filter.

	5 kDa			30 kDa		
	Functionalization (µmol silane/m^2 SiO_2)			Functionalization (µmol silane/m^2 SiO_2)		
Name	Added amount	Amount bound	Yield (%)	Added amount	Amount bound	Yield (%)
MPEGTM-4	4.0	3.0	75	4.0	1.68	42

E Calculations of yield

Constants:
Mw$_{\text{silane}}$ [g/mol] = Molecular weight of the silane.
Mw$_{\text{Chydrsilane}}$ [g/mol] = Molecular weight of carbon in the hydrolyzed silane.
Amount sol [g] = The weight of the sol used for the batch.
Density$_{\text{sol}}$ [g/ml] = The density of the sol used for the batch.
Mass silane [g] = The weight of the silane added to the modification.
Silane&water [ml] = The volume of silane and water added to the sol for the modificaton.
Mw$_{\text{ethanol}}$ [g/mol] = Molecular weight of ethanol.
Mw$_{\text{Cethanol}}$ [g/mol] = Molecular weight of carbon in ethanol.
Mwm$_{\text{ethanol}}$ [g/mol] = Molecular weight of methanol.
Mw$_{\text{Cmethanol}}$ [g/mol] = Molecular weight of carbon in methanol.
Ethanol content [%] = The percentage of ethanol in the filtrate from the ultrafiltration.
Total Carbon in filtrate [mg/l] = Total amount carbon in filtrate from ultrafiltration determined by TC.

Calculations for ethoxy silanes:
Sol volume [ml] = Amount sol [g] / Density$_{\text{sol}}$ [g/ml]
Total volume [ml] = Sol volume [ml] + Silane&water [ml]
Total volume [l] = Total volume [ml] / 1000
Silane [mol] = Mass silane [g] / Mw$_{\text{silane}}$ [g/mol]
Mass carbon in silanes after hydrolysis [g] = Mw$_{\text{Chydrsilane}}$ [g/mol] * Silane [mol]
Carbon added from hydrolyzed silane [g/l] = Mass carbon in silanes after hydrolysis [g] / Total volume [l]
Carbon added from hydrolyzed silane [mg/l] = Carbon added from hydrolyzed silane [g/l] * 1000
Carbon content in ethanol [%] = Mw$_{\text{Cethanol}}$ [g/mol] / Mw$_{\text{ethanol}}$ [g/mol]
Ethanol content [mg/g] = Ethanol content [%] * 1000
Carbon from ethanol [mg/g] = Ethanol content [mg/g] * Carbon content in ethanol [%]
Carbon from ethanol [mg/l] = Carbon from ethanol [mg/g] * 1000
Yield [%] = 1 - ((Total carbon in filtrate [mg/l] - Carbon from ethanol [mg/l]) / Carbon added from hydrolyzed silane [mg/l]

Calculations for methoxy silanes:
Sol volume [ml] = Amount sol [g] / Density$_{\text{sol}}$ [g/ml]
Total volume [ml] = Sol volume [ml] + Silane&water [ml]
Total volume [l] = Total volume [ml] / 1000
Silane [mol] = Mass silane [g] / Mw$_{\text{silane}}$ [g/mol]
Mass carbon in silanes after hydrolysis [g] = Mw$_{\text{Chydrsilane}}$ [g/mol] * Silane [mol]
Carbon added from hydrolyzed silane [g/l] = Mass carbon in silanes after hydrolysis [g] / Total volume [l]
Carbon added from hydrolyzed silane [mg/l] = Carbon added from hydrolyzed silane [g/l] * 1000
Carbon content in methanol [%] = Mw$_{\text{Cmethanol}}$ [g/mol] / Mw$_{\text{methanol}}$ [g/mol]
Methanol content [mg/g] = Methanol content [%] * 1000
Carbon from methanol [mg/g] = Methanol content [mg/g] * Carbon content in methanol [%]
Carbon from methanol [mg/l] = Carbon from methanol [mg/g] * 1000
Yield [%] = 1 - ((Total carbon in filtrate [mg/l] - Carbon from methanol [mg/l]) / Carbon added from hydrolyzed silane [mg/l])

F All modifications attempted during the project

Table F 1. List of all modifications attempted during the project, including some characterization results.

Name	Density [g/cm^3]	% SiO_2 (from density measurement)	% SiO_2 (from XRF)	Turbidity [NTU]	Diameter [nm] (from electro spray)	Comment
Bare sol	1.221	30.99	-	14.9	20.7	
GPTE-1	1.211	30.82	-	16.6	-	
GPTE-2	1.204	29.94	-	18.5	19.7	
GPTE-3	1.196	28.97	-	22.3	-	
GPTE-4	1.186	27.75	27.9	24.4	-	
GPTE-5	1.186	27.71	-	27.2	-	
GPTE-6	1.180	26.99	-	26.0	20.5	
GPTE-8	1.183	27.39	27.0	25.8	17.9	
GPMDE-4	1.189	28.15	28.6	27.8	-	
GPMDE-8	1.168	25.46	26.5	25.9	-	
MPEGTM-0.5	1.215	30.34	-	17.5	-	
MPEGTM-1	1.218	30.65	-	21.1	-	
MPEGTM-2	1.214	30.24	29.2	24.9	-	
MPEGTM-4	1.206	29.29	26.3	45.5	-	
APTE-4	-	-	-	-	-	Gel
GPTE-2+APTE-2	1.207	30.33	-	41.0	-	
GPTE-2+APTE-4	1.192	28.50	29.0	46.9	-	
MPTM-4	-	-	-	-	-	Gel
CPTE-2	-	-	-	-	-	Gel
GPTE-2+CPTE-2	1.275	-	36.7	376	-	
CMTE-2	1.219	31.76	30.9	28.4	-	
GPTE-2+CMTE-2	1.204	30.00	-	25.2	-	
GPTE-2+MPEGTM-2	1.203	28.91	27.1	29.6	-	