CHALMERS

Surface Active Silica Sols
Effect of PEG-Silica Interactions
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Surface Active Silica Sols: Effect of PEG-Silica interactions

ABSTRACT

Surface activity changes of silica nanoparticles caused by physical adsorption and covalent bonding of hydrophilic and hydrophobic molecules is the subject of this study. Interfacial tension and zeta potential measurements were also done during the research project.

Surface modifications were carried out by grafting different ratios of surface coverage by IsoButyl silane and 3GTO-MPEG which was produced by reacting (3-glycidoxypropyl) trimethoxysilane (3GTO) with hydrophilic poly(ethyleneglycol) methyl ether (MPEG) group. Also addition of MPEG2000 (polyethylene glycol methyl ether) to the sols at different pH has shown changes of the sols behavior resulting of the physical adsorption.

Surface activity difference resulting of the physical adsorption/covalent bonding of PEG polymers to silanols were investigated by the du Noüy ring method and with an optical tensiometer. Interfacial tension measurements were done with an optical tensiometer to investigate the difference for PEG adsorption in different media which were toluene and dodecane.

Surface tension values have shown significant changes by grafting of hydrophobic modifiers. Effect of physical adsorption of free MPEG2000 polymer to silanol groups was found to be significant in both surface and interfacial tension measurements. Zeta potential measurements were also investigated for all the systems and showed that the PEG adsorption influences the surface change density of the particles.

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1   INTRODUCTION

1.1   BACKGROUND

Emulsions are dispersions of immiscible liquids (usually oil and water) which are thermodynamically unstable leading to phase separation with time.

Stabilizing agent with an amphiphilic nature, such as a polymer or surfactant expand the lifetime of the emulsion by positioning themselves at the oil/water interface. Another way to stabilize emulsions is to use colloidal particles. The resulting dispersions are referred as Pickering emulsions. The particles used are usually not surface active and recent work have shown that by changing the nature of the surface of the particles, it was possible to increase their surface activity and thus to obtain better emulsification performances, [1]. These improvements were done by grafting polyethylene glycol and isobutyl moiety on silica particles. Silica is an abundant material, originally not surface active even if hydrophobized, that can be easily modified.

Silica is the most abundant material on earth covering 75 wt% of the Earth's surface as bound silicates and 12-14 wt% as free silica as quartz.[2] Silanols, (Si-OH) mostly covering the surface of silica nanoparticles (some can exist in the inner part) enables surface modifications.

Silica sol, also known as *colloidal silica* is a dispersed system, where SiO_2 is forming the discontinuous phase in continuous dispersion medium, such as water (hydrosols or aquasols). The particle diameters have to be between 1 nm and 100 nm by definition, in order to show differences from the typical behavior of the solution but without being affected by gravitational forces. The appearance depends on the particle size and also concentration.[3]

The solution is clear looking (colorless) when the particles are small and/or the concentration is sufficiently low. The colloidal silica becomes milky at high concentrations and bigger particle sizes. Particle size distribution is also another parameter about appearance of the sol which is affected by the production path used. Adjusting pH and temperature causes a deviation from the initial clear dispersion. It is possible to prepare aquasols as high up to 50 wt% silica content.[4,5] Most commercial silica sols are known to have particle sizes in between 5 nm and 100 nm. It is also possible to reach particle sizes around 130 nm, but the drawback is settling down of particles.[6]

As mentioned before, silica particles are not surface active. In previous work, surface modifications of the particles, both hydrophilic and hydrophobic, leading to amphiphilic colloids have shown promising results regarding the surface activity. In this case, the modifiers were covalently bonded to the surface. Isobutyl silane was used as hydrophobic modifiers while MPEG2000, an end-capped polyethylene glycol, was employed as a hydrophilic part, being grafted through a spacer, (3-glycidoxypropyl)trimethoxysilane.

It appeared that the interactions of the PEG chains with the surface of the silica particles, especially with the silanols groups as hydrogen bonds were very important.

The effect of MPEG2000 adsorption on silica nanoparticle surfaces is the main focus of this work.

Colloidal stability is another important parameter for each system for applications with different demands and also to store the colloidal silica for long periods of time. Zeta potential technique is used to measure of the electrical potential between charged solid particle surfaces and the liquid (e.g. water at different pH values) to have an idea of the aggregation tendency of charged particles.

1.2   AIM

This Master's Thesis project was started to evaluate the effect of the modification of the surface of silica particles on their surface activity. The general aim of the work was to compare the differences in surface activity between an MPEG2000 polymer covalently attached and MPEG2000 which is physically adsorbed. The effect of pH on this phenomenon was also another important point of this work.

The first investigation was done to understand the effect of concentration change of both bare silica (non-modified) and modified silica nanoparticles in sol on the surface activity. Improvement on surface activity by physical adsorption of MPEG2000 on modified (IsoButyl covalently bonded to silanols at different coverage) and bare particles were another subject of studies. After having significant results on surface activity by changing the parameters of free MPEG2000 in sol, interfacial tension in toluene and dodecane was studied to see the effect of MPEG2000 dissolution in different emulsion systems. The zeta potential measurements were carried out to assess the colloidal stability in the last part of the project.

This project was carried out with the collaboration between Eka Chemicals and Applied Surface Chemistry at Chalmers University of Technology.

2   SILICA SOLS

Early applications of silica sols were first used as binders in catalyst preparation process, ceramic glazing agents, coating materials, textile and paper treatment agents and some other applications in 1930s. Stability issues at higher concentrations were the drawback of silica sols until the 1950s. Colloidal silica sols became widely available in the 1970s when the sols started to be produced with better stabilities at higher silica contents.[7]

2.1   USES OF SILICA NANOPARTICLES

Total production of colloidal silica was around 83,000 tons in 2002. There are several manufacturers of colloidal silica in United States, where the largest amount is being produced, Germany, Sweden, France, Japan and United Kingdom.[8] Colloidal silica sols have very broad usage area for various purposes. Common applications of commercial silica sols are known as: binding materials in molds for casting of superalloys, to increase friction of different surfaces, anti-soiling finishes on surfaces, modifiers for hydrophilicity increase or decrease of surfaces, strength increasing additives for polymer goods, polishing silicon wafers used in electronics, dispersing agents, photographic emulsions and in photographic film industry as grain growth regulators and dye receptors, clarifying wines and gelatin.[9] Specific uses of Bindzil are: binding material for catalyst carrier, foundry, refractory applications, to disperse pigments, inks and minerals, for flocculation in wine and refractory fibre processes, as abrasive in lacquers, non-stick coating, to create friction for paper packages and as antiblocking agent for plastic films and for anti-soiling in cleaners and surface treatment processes. Inkjet printability and battery gelling are common uses of Bindzil related with computer industry.[10]

2.2   SURFACE OF SILICA NANOPARTICLES

The chemistry of surface active silica sols is mainly controlled by silanols (Si-OH groups) existing on the surface of each particle. Surfaces of the particles have 8 μmol/m^2 silanols accessible for surface interactions or modifications.[10]

The equilibrium between condensation and hydrolysis of Si-O bonds is strongly affected by temperature and pH, Figure 2.2.1. The pH is an important parameter for the equilibrium between silica surface and water molecules where acids and bases can break -Si-O-Si-bridges and increase the amount of free silanols (Si-OH) on the surface. Temperature and humidity were kept constant and the effect of pH on adsorption and self-assembly of silica nanoparticles was investigated in this project. Surface charges are driven by silanols (Si-OH groups) on the surface of each sphere-like silica nanoparticles.[11]

Hydration and dehydration reactions which are catalyzed by HO$^-$ ions take part in dissolution and deposition of silica.[12]

$$(SiO_2)_x + 2H_2O \underset{\text{condensation}}{\overset{\text{hydrolysis}}{\rightleftharpoons}} (SiO_2)_{x-1} + Si(OH)_4$$
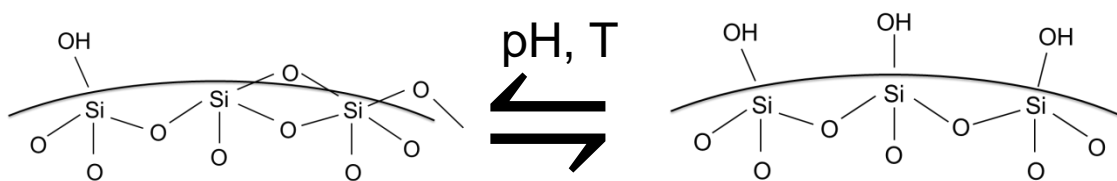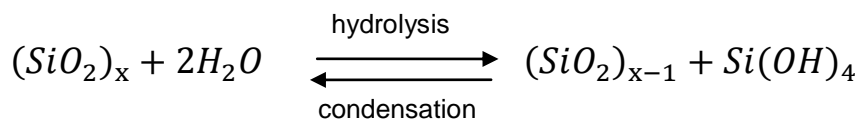

Figure 2.2.1. Effect of pH and temperature on silanols density on surface

2.3   COLLOIDAL STABILITY

Since silica particles when dispersed have charged surfaces there will be a competition between van der Waals forces which tries to aggregate particles and the repulsion created by the surface charges of each particle. Colloidal stability of dispersion depends on the nature of surfaces of particles (charges) and the short-range attraction by van der Waals force. This phenomenon is described by the DLVO (named after Derjaguin, Landau, Verwey and Overbeek) theory.[10] Long chain molecules or macromolecules (grafted or physically adsorbed) to the surface also play a role on steric stabilization of the colloidal sol to prevent aggregation of silica nanoparticles, which is also studied in this thesis work.[13]

Colloidal stability of silica aquasols is essential at every stage of silica nanoparticle processes from the production until the use in real applications. Desired particle size, concentration and pH values are achieved by stabilizing the sol after the growth by polymerization reaction where sodium is taken away from sodium silicate. There is a correlation in between particle size which affects surface charge and the maximum concentration of silica for a stable colloidal silica sol, Figure 2.3.1. Stability of colloidal silica depends on surface properties of silica and also particle size (particles smaller than 7 nm show spontaneous growth in storage).[13] The sols are stabilized by different ions depending on the requirements of the product such as particle size and pH. Ions in the solution are used for stabilizing the sol, but isoelectric point and pH range requirements vary. This is made possible by adding an alkali or acid and by surface treatments such as surface silicon substitution by tetrahedral aluminum. Furthermore the stability can be adjusted by pH for colloidal silica, Figure 2.3.2. There are also non-charged particles when the sol is in the range of pH 2-4 and the particles are ion exchanged to be deionized.
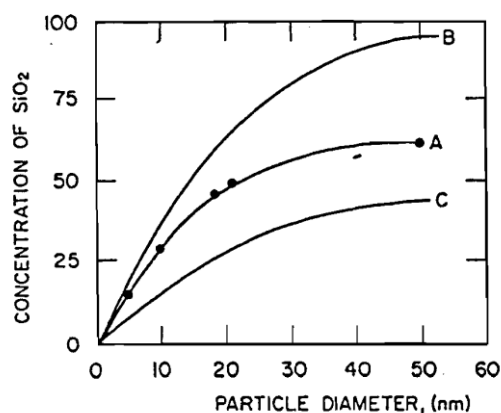

Figure 2.3.1. Maximum concentration for a stable aqueous silica sol at about pH 9.5 versus particle size; A, concentration (wt%); B, concentration (grams Si02 per 100 ml); C, volume fraction of Si02 (x 100).[12]
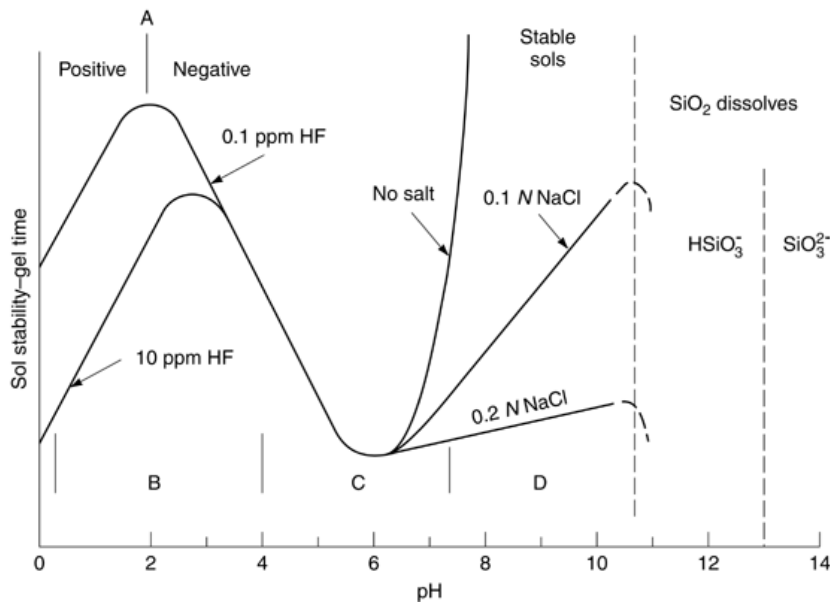
Figure 2.3.2 Effects of pH in the colloidal silica–water system, where A represents the point of zero charge; regions B, C, and D correspond to metastable gels, rapid aggregation, and particle growth, respectively. Positive and negative correspond to the charges on the surface of the silica particle.[12]

Since particle size is an important parameter affecting specific surface area for the same amount of solid silica content, total surface charge and the repulsion between particles change as well. Bigger particles are stabilized at higher concentrations due to less total surface area than the smaller particles. Particle size and temperature were kept at constant values (25 nm particle diameter and room temperature). Room temperature also reduces micro-organism growth.

2.4 SURFACE MODIFICATIONS

2.4.1 PHYSICAL ADSORPTION OF MPEG2000

PEG silica interaction depends both on MPEG-MPEG and MPEG-silica particle interactions in aqueous sol. It is known that when only MPEG chains are present in a solution they may arrange on liquid-gas (water-air) interface and decrease surface tension at very high concentrations.[14]

First interaction in between silica particle and MPEG2000, which is one of the main subjects of this study, is the physical adsorption of MPEG2000 chains on silanols. The interaction of MPEG2000 and silica nanoparticles by physical adsorption is driven by the interaction of long PEO part of the polymer and silanols on the surface where hydrogen bonds are formed,[14,15,16] Figure 2.4.1.1. The strength of the interaction depends on chain length as the PEO part and oxygen group interactions are increased.[15] The physical adsorption is also strongly affected by the pH of the sol. MPEG2000 chains are adsorbed on silica nanoparticles at low pH values.[17] Two different silica sols are used at the pH values of 2.23 and 9.00.

In this work, in order to keep entropic contribution constant, the size of the PEG and the size of the silica particles were kept constant. The MPEG-silanol interaction and physical adsorption contribution on the surface activity for modified/bare silica particles were studied. The effect was also studied when isobutyl(trimethoxy)silane groups were grafted on the particles in order to see the effect of the MPEG adsorption on modified silica sols.
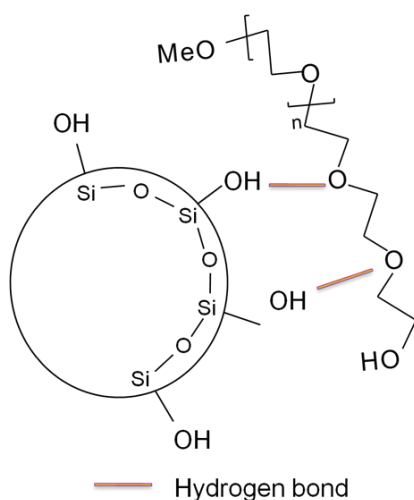

Figure 2.4.1.1 Physical adsorption of MPEG2000 on silica nanoparticles

2.4.2 COVALENT ATTACHMENT OF THE MODIFIERS

The second part of this work aimed at attaching MPGE2000 chains covalently and Isobutyl(trimethoxy)silane molecules to the particle. The linker molecule, (3-glycidoxypropyl) trimethoxysilane (3GTO) is used as linker for making covalent attachment of MPEG2000 possible.

The hydrophilic silanes are prepared by the reaction of the epoxide group of GPTMS (3GTO) with an end-capped polyethylene glycol (MPEG2000). TFA (Trifluoroacetic acid) having formula CF_3CO_2H, is a very strong acid which is used as a catalyst which is much more efficient than acetic acid used in the previous modifier synthesis,[18] Figure 2.4.2.1. 3GTO-MPEG2000 is used to covalently bond MPEG2000 to silica nanoparticle surface and the electrostatic repulsion in between the particles caused by certain type of modification (covalently bonding isobutyl(trimethoxy)silane or 3GTO-MPEG) increases surface activity.
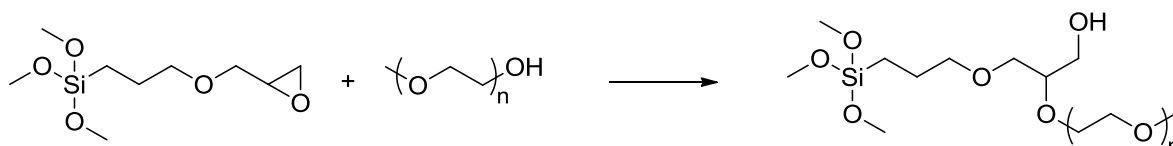

Figure 2.4.2.1 3GTO-MPEG modifier synthesis reaction

The surface activity of silica particles in colloidal aquasols depends on many parameters such as temperature, pH and particle size. Surface modifications or physical adsorption (creating electrostatic or steric repulsion) on silica particles change the ideal conditions and stability for each sample.[19]

Surface modifications are done by covalently bonding IBu [isobutyl(trimethoxy)silane], 3GTO-MPEG and both of them at the same time, Figure 2.4.2.2. The modifiers and silica nanoparticles are covalently attached in water at 80°C, Figure 2.4.2.3.
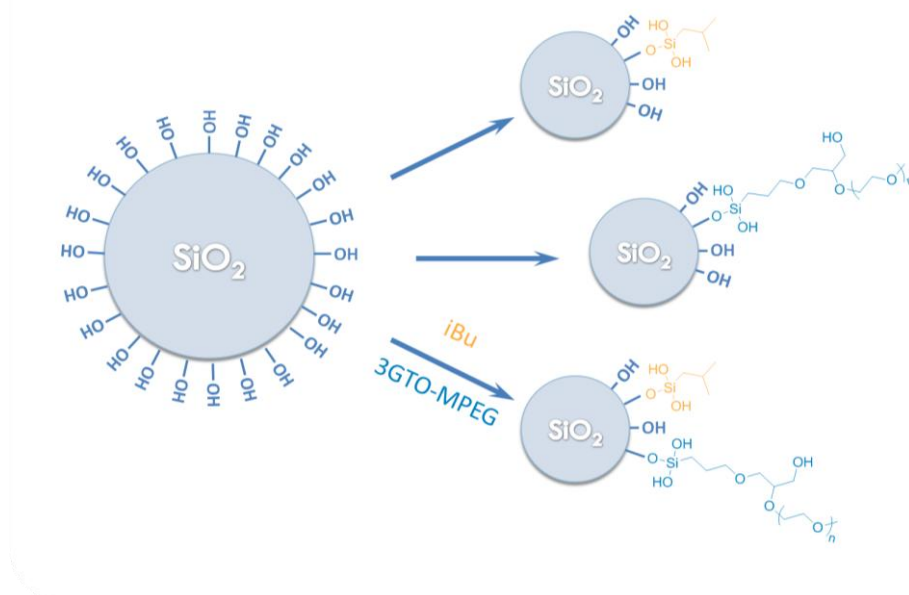

Figure 2.4.2.2 Modification paths for covalently bonded modifiers on silanols on the surface of silica nanoparticles.
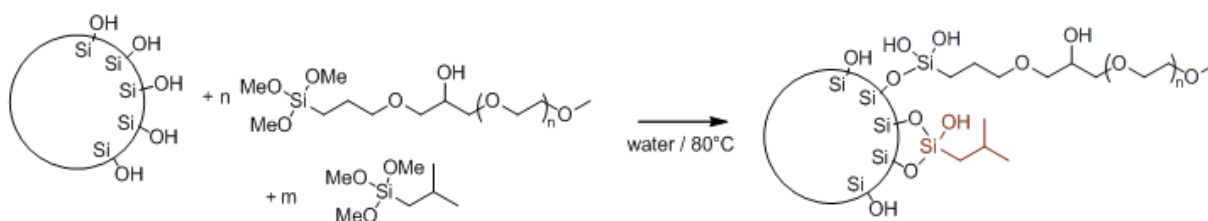
Figure 2.4.2.3 Surface modification reaction of silica with two types of modifiers covalently attached

The amphiphilic sols prepared by grafting both moieties exhibited a synergetic surface tension decrease. This phenomenon is important also when MPEG2000 polymers are adsorbed physically on the surface of modified silica nanoparticles. This synergy in between two different types of modifications is also studied by comparing physical adsorption of MPEG2000 chains instead of covalently bonding them to silica nanoparticles. It was shown that "isolated" silanols interactions were depending on both hydrophobization and hydrogen bonding.[20] Even though the mechanism of the hydrophobic association effect is not explained, hydrogen bonding is one of the main reasons for increased interaction and increased surface activity, Figure 2.4.2.4.
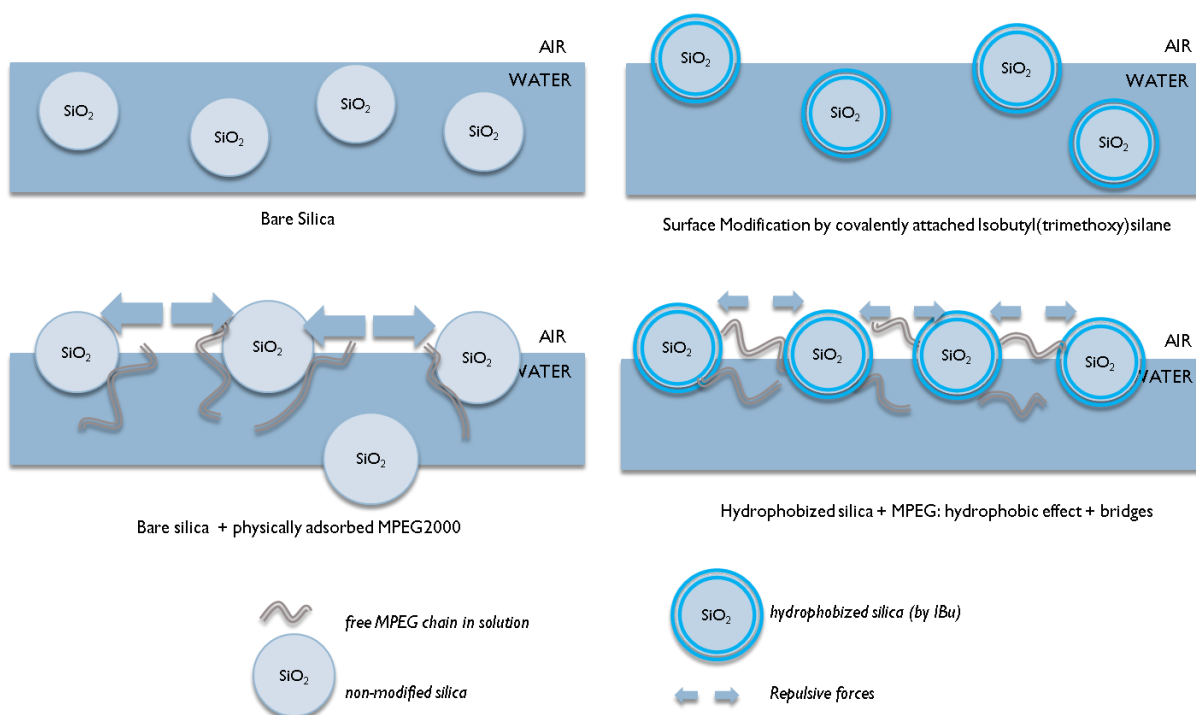

Figure 2.4.2.4 Illustration of Modified Silica and MPEG interaction

3 MATERIALS

3.1 BINDZIL®

The silica sol used was the Bindzil® grade of colloidal silica provided by Eka Chemicals with 25nm particle size and 0.343 solid silica content at pH=9. Values of pH for each sample were adjusted by using Bindzil and done by adding NaOH and HCl solutions in pure water. The appearance was milky liquid at the beginning.

Bindzil has 8 μmol SiOH groups per m^2 and a specific surface area of 130 m^2/g.

3.2 ISOBUTYL(TRIMETHOXY)SILANE

Isobutyl(trimethoxy)silane was used directly for hydrophobic modification since the reaction in between the silanols and silyl ether groups does not require any linker, as in 3GTO-MPEG. Hydrophobization is favorable for increasing emulsion stability. There is also a synergetic effect of having this hydrophobic modification and MPEG adsorption to increase surface activity.
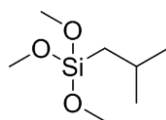

Figure 2.2.1 IsoButyl(trimethoxy)silane structure

3.3 LINKER (3GTO)

The epoxide ring of (3-glycidoxypropyl) trimethoxysilane (3GTO) which opens during the reaction with MPEG2000 is able to couple both hydrophilic and hydrophobic moieties. Three alkoxy groups make it possible to react with the silanols on silica nanoparticles.
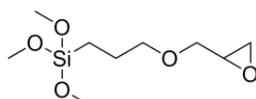
Figure 3.3.1 3GTO structure

3.4 MPEG2000

The polymer used for adsorption to the surface was *poly(ethyleneglycol) methyl ether* also named as MPEG2000 which is produced by Sigma Aldrich. The structure of MPEG2000 is consisting of one MeO group at one and a long oxyethylene chain, Fig.3.4.1.
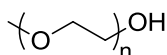
Figure 3.4.1 MPEG2000 structure

The real molecular weight was calculated by NMR titration with acetone as an internal standard. The results of the titration are displayed, Figure 3.4.2.

$y = 9{,}5835x + 0{,}0183$

Figure 3.4.2 NMR-titration adsorption plots & trendline

The plot has given the value for 1 g MPEG powder having 3.04823×10^{20} CH_3 groups. So, the average molecular weight of MPEG2000 has been found as 1975.5752 g/mol.

4 EXPERIMENTAL

4.1 SYNTHESIS OF HYDROPHILIC MODIFIER (3GTO-MPEG)

The stoichiometry of the reaction is calculated with 1 equivalent hydroxyl group per MPEG2000, 2 equivalent TFA and 25 mL Toluene per gram of 3GTO. The reaction is carried out in one-pot at 65°C for 5 hours. TFA and solvent are removed under reduced pressure.
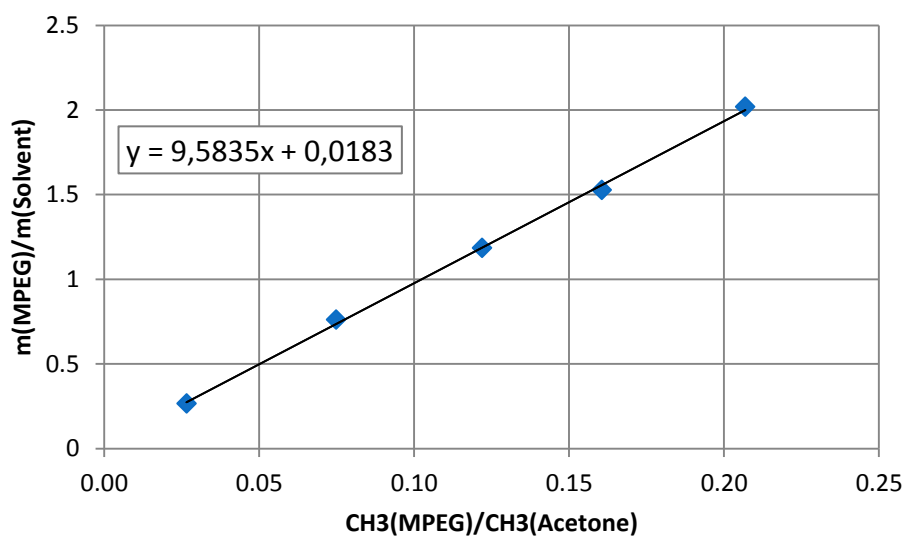
4.2 SURFACE MODIFICATION

The surface modification is carried out in a round bottomed flask at 80°C for 2 hours by cooling the evaporated water by a reflux system for 50 g silica sol with 0.343 solid silica content.

The stoichiometry of the reaction is based on theoretical surface silanols and their ideal coverage. Since the surface area of 1 g SiO_2 is known as 130 m^2 and the silanol density as 8 $\mu mol/m^2$.

All the pH adjustments were done by addition of NaOH and HCl solutions at very low amounts for the preparation of each sample.

4.3 ULTRAFILTRATION

After the surface is modified the sample is expected to be free of impurities in order to be able to adjust the pH and observe the effect of parametric changes correctly. To do so, ultrafiltration techniques have been used for over 20 years.[12] The process is basically moving the ions away from the colloidal sol by stirring the filter under high nitrogen (N_2) gas pressure which creates a flow of liquid through the membrane. Air pressure is not used to avoid the pH drop caused by CO_2 solubilization.

Even though the system is energy efficient and easy to use, there is a drawback called "concentration polarization".[12] As the ions are filtered through the membrane with solvent, concentration of the colloidal sol is increased in the ultrafiltration system interactions in between the particles are increased and the movement of silica nanoparticles due to the flux create a microgel layer on the membrane. This microlayer does not stop the filtration process completely. Since the viscosity is changed, more energy and time is consumed. Since, the process of microgel formation is completely reversible. Decreasing the silica nanoparticle concentration or increasing the temperature solves the problem. This batch process was repeated 5 times in order to reach a required surface activity free from impurities, under the conditions of 4 bar pressure by N_2 gas pumped into the chamber fitted with a membrane that had a cut-off value of 100 kDa.
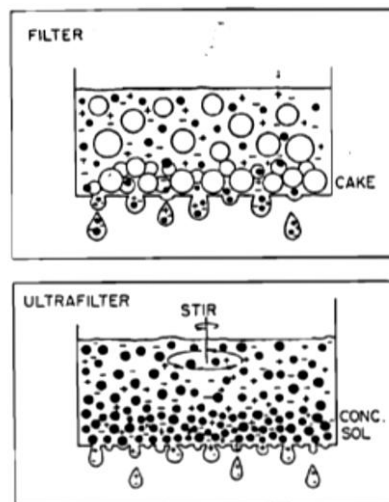

Figure 3.3.1 Filter retains large particles as a filter cake but salts and colloidal particles can pass through. Ultrafiltration keeps colloidal sol particles but the ions can pass and the purification is achieved.[12]

4.4 DRY CONTENT OF THE SOL

The initial concentration of the solid silica content was changed during the ultrafiltration step as the filtered water was passed through the membrane. The sol was diluted with the addition of pH-adjusted water into the ultrafiltration system to acquire lower viscosity. The solid silica content of the sol was calculated from the weight ratio of the solid which remained in the container after centrifugation of the sample under vacuum condition with a SpeedVac vacuum concentrator (Savant).

The remaining solid consisting of silica was weighed and the value was assumed to be the solid content for the ultrafiltrated aquasol. The adjustment to reach the desired solid silica content was done by dilution of the aquasol with various volumes of pH adjusted MilliQ water, depending on the ultrafiltrated sample.

4.5 SURFACE ACTIVITY OF SOLS

The surface activity is affected by the temperature, so the temperature was kept stable at 20°C for *ring method* and at 23°C for *pendant drop* measurements. Two different instruments utilizing different methods were used; Force tensiometer with du Noüy ring method, and optical tensiometry. Interfacial tension measurements were done with the Attension Theta optical tensiometer instrument (Biolin Scientific). Water used to prepare sols and cleaning is purified with a MilliQ device (Millipore).

4.5.1 RING METHOD (du Noüy Method)

The du Noüy ring is a force tensiometry method which is used to measure static surface tension of liquids. It is also possible to measure interfacial tension with this method.

The system (Sigma 70 tensiometer) is consisting of a sample holder cooled with 15°C cold liquid flowing inside a cooling jacket which keeps the sample at 20°C during measurement, Figure 4.5.1.1. The stability of measurements which repeat 40 to 80 times depends highly on temperature and colloidal stability change due to temperature change and time. Figure 4.5.1.2 shows a measurement with little deviations created by temperature gradient or sedimentation. The platinum ring is cleaned by water-ethanol-water and flamed between each measurement.

The ring is submerged below the air-liquid interface and continuously raised upwards where a meniscus is formed. As the ring is pulled upwards the interface the meniscus returns to the previous state. The measurement is based on the maximum force exerted while the meniscus volume reaches and passes through a maximum value during this detachment process. The surface tension is measured by the ratio of the force measured to the length of the ring.
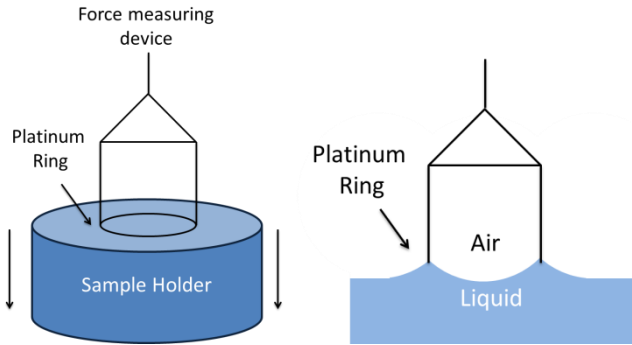

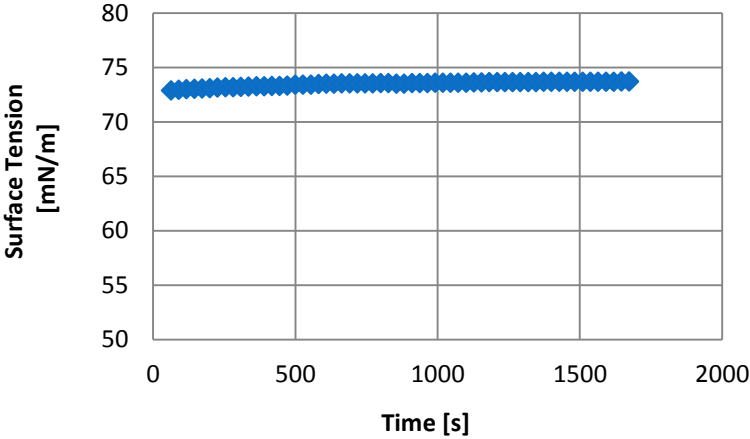
Figure 4.5.1.1 du Noüy ring method

Figure 4.5.1.2 Surface tension plot of sample DD50

4.5.2 PENDANT DROP

An Attension Theta optical tensiometer (Biolin Scientific) was used for the pendant (or reverse when required) drop shape analysis. The calculations of surface tension are based on the analysis of the shape of a drop of one liquid hanging from a tip of syringe which is 0.71 mm in diameter, Figure 4.5.2.1. The equation used for the surface tension calculation is as follows:

$$\gamma = \Delta\rho \cdot g \cdot R_0^2 / \beta$$

γ = surface tension

$\Delta\rho$ = density difference in between fluids at interface

g = gravitational constant

R_0 = radius of drop curvature at apex

β = shape factor which is defined by Young-Laplace equation which is expressed as 3 dimensionless first order equation.

Figure 4.5.2.1 Pendant drop shape sample

The shape of the droplet is spherical in order to minimize the contact area between the liquid and the environment (another liquid or a gas). Gravitational or buoyancy forces elongate the drops during measurements so a hanging "pendant" one is taken into account with a silhouette type image which is taken 100 times in a second repeatedly. Mean values of the measurements are calculated by the help of software which determines the borders of the image and calculates the volume. This method has an advantage of high accuracy but it is required to clean the syringe after the change of liquid inside by washing with ethanol, MilliQ water and evaporating them with N_2 gas. Surface tension calibrations are done by using a metal calibration sphere.

4.6 INTERFACIAL TENSION

Interfacial tension measurements are important to have information on the emulsifier adsorption at an interface with different types of liquids. Dodecane and toluene are used for the measurements.

There is a need for changing the direction of the drop and the environment-sample types where environment has a higher density than the drop for interfacial tension measurements. The first reason was the difficulty of having a good contrast for curve fitting and the other was the ease of cleaning the syringe for several samples. A hooked ring type of syringe was used for using the buoyancy force to elongate the drops.

The difference between dissolution of MPEG2000 chains which move towards the interface during surface tension measurements in dodecane and toluene are studied.[21] So, the MPEG2000 physical adsorption characteristics at an interface (toluene-water) where the chains can be dissolved (in toluene) can be compared to dodecane-water interface.[21]

Temperature conditions and cleaning procedures were the same as pendant drop surface tension measurements. Dodecane needs purification and that is done by passing the dodecane through Al_2O_3 before each measurement.[22] Calibrations of samples were done by syringe diameter.

4.7 PARTICLE SIZE & ZETA POTENTIAL

A ZETA PALS zeta potential analyzer from Brookhaven Instruments Corporation was used for both particle size and zeta-potential measurements. Even though the particle sizes are known to be 25 nm in diameter, particle size measurements have shown sizes from 30-35 nm diameters. This result differs due to having a counter ion layer around each silica nanoparticle (generally increased by 10nm due to chemisorption/physisorption of water).[11]

Electrostatic force in between silica surface and ions are affecting colloidal stability.[23,24] Electrostatic self-assembly is depending on this interaction. Electrostatic potential (ψ_0) is generally assumed equal to the zeta potential (ζ).

Zeta potential value is calculated by electromobility measurements and the results were affected by pH (different counter-ions and concentrations) and gave the surface charge density on the silica nanoparticle surface. Zeta potential measurements were done at

different pH with different modified silica. For the sake of the measurement, they are repeated at least 10 times. Electrostatic potential at the plane of shear is assumed to be close to the surface of silica nanoparticles and depend on viscosity, permittivity of free space and dielectric constant.[10] Zeta-potential varies by dissociation of surface silanol groups in a wide range of electrolyte conditions. The measurement parameters (conductance, current, electric field and count rate values) were adjusted by the software of the instrument for each sample.

5 RESULTS & DISCUSSION

5.1 EFFECT OF ULTRAFILTRATION OF MPEG ON THE SURFACE ACTIVITY

Ultrafiltration filters impurities and unwanted ions from the first synthesis product after the addition of MPEG2000 and dilution of the sample. Surface tension measurements were done both on *non-ultrafiltrated* and *ultrafiltrated* MPEG2000 solutions in MilliQ water.

The results were 65.5 mN/m for non-ultrafiltrated solution, and 67.5 mN/m for ultrafiltrated solution with 0.5 wt% SiO_2 sols. There was a slight surface activity decrease after filtration which might be caused by small amount of ions but the results have shown that MPEG2000 polymers are not filtered out of the solution by ultrafiltration, at the pH of the experiment, i.e. pH 2.

5.2 EFFECT OF COVALENT ATTACHMENT ON THE SURFACE ACTIVITY

Surface activity at the air/water interface is both affected by covalently attached and physically adsorbed MPEG2000 on bare and modified silica nanoparticles. Three different syntheses of silica sols modified by covalently attached moieties were compared.

The measurements of modified silica nanoparticles started at 5 wt% solid content of SiO_2, Table 5.1.1. Three different samples with covalently bonded isobutyl(trimethoxy)silane and 3GTO-MPEG2000 have been synthesized to see the effect of MPEG2000 coverage on bare silica nanoparticles and the synergetic effect of having two different moieties at the same time. The pH of the solutions was at pH=2.23.

Table 5.2.1 Surface tension measurements of the covalently bonded surface active silica sols

Name of the sample	SiO$_2$/sol concentration [wt%]	3GTO-mPEG Theoretical surface silanol coverage	iBu Theoretical surface silanol coverage	Average ST [mN/m]
DD7	5.0%	10.0%	12.5%	45.51
DD8	5.0%	5.0%	0%	66.66
DD9	5.0%	10.0%	0%	66.30

The effect of 3GTO-MPEG2000 modification on bare particles has not shown big differences from 5% to 10% theoretical coverage ratios, Table 5.2.1.

The highest surface activity has been observed with the sample having theoretical 10.0% 3GTO-MPEG and 12.5% isobutyl(trimethoxy)silane surface silanol coverage. These results are in agreement with previous observations for which the most surface active particles were the one both hydrophobically and hydrophilically modified. Sample DD7 from Table 5.2.1 was also taken as the reference for the comparison of the effect of physically adsorbed MPEG on silica nanoparticle modified by isobutyl(trimethoxy)silane with the same theoretical surface coverage.

5.3 EFFECT OF PARTICLE CONCENTRATION ON THE SURFACE ACTIVITY

The effect of bare silica concentration on surface activity was investigated. The concentration was increased until having 25 wt% bare silica concentration in aquasols at pH=2.23, Figure 5.3.1.
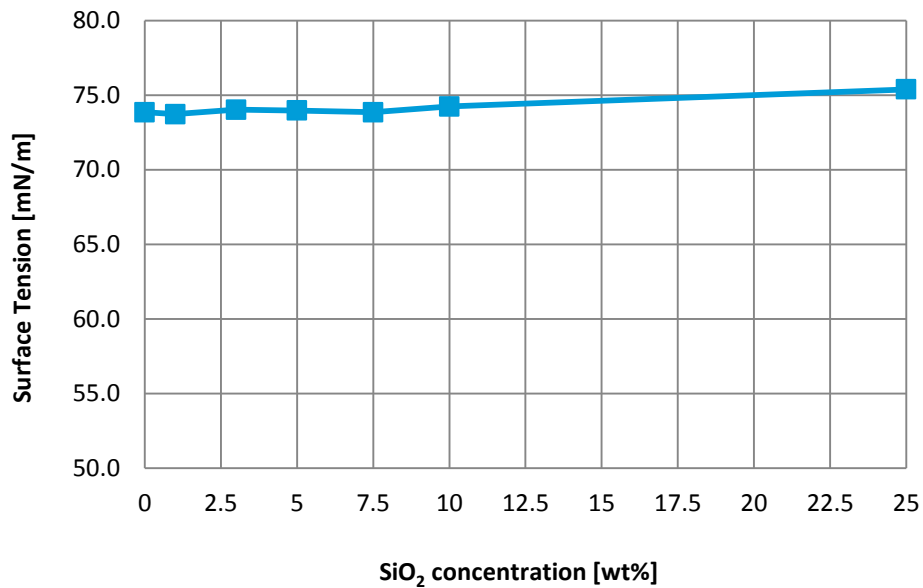

Figure 5.3.1 Surface tension values vs. bare SiO$_2$ concentration [wt%] at pH=2.23

The results have shown that the effect of bare silica nanoparticles has no effect on the surface activity of the sol. There was no force driving the bare silica nanoparticles to air water interface due to having only silanols and no hydrophobization on the surface, Figure 5.3.1.

The effect of concentration is then observed on modified particles and the adsorption of MPEG2000 on the interfaces. Two different concentrations for modified silica sols were selected, 0.5 wt% and 5 wt% respectively. Each concentration had 4 different samples starting from Bare Silica sol and continued by three different modifications having theoretical 12.5%, 25% and 50% isobutyl(trimethoxy)silane coverage on surface silanols at pH=2.23, Figure 5.3.2.
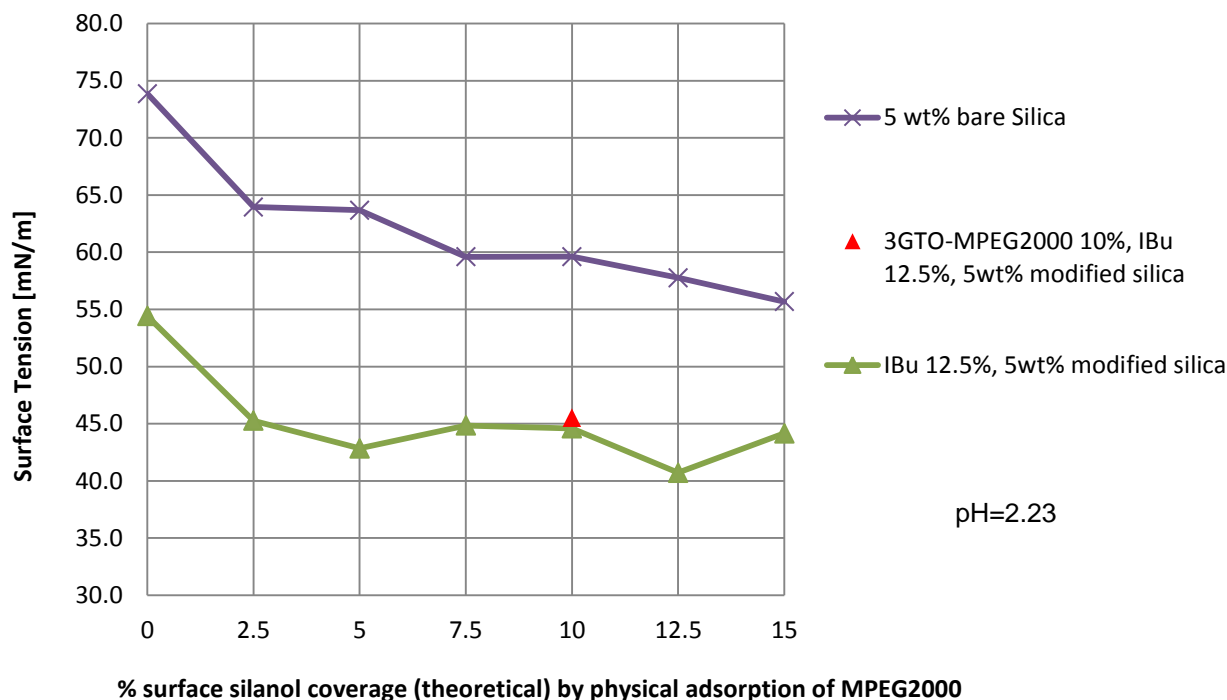
Figure 5.3.2 Surface tension values of 0.5 wt% silica solid content samples in comparison with 5 wt% samples by means of % MPEG coverage by physical adsorption at pH=2.23.

IBu 12.5%, refers to the modification by covalent attachment of isobutyl(trimethoxy)silane at 12.5% theoretical surface silanols coverage. 3GTO-MPEG2000 10%, IBu 12.5%, refers to the modification by covalent attachment of 3GTO-MPEG2000 isobutyl(trimethoxy)silane at 12.5% theoretical surface silanols coverage.

Surface activity of the sol containing bare silica at 5 wt% concentration increased with the increasing free MPEG2000 concentration at pH=2.23. The surface tension value with 10% theoretical surface silanols coverage by free MPEG2000 adsorption was 59.62 mN/m, lower than the initial value of 73.86 mN/m as no MPEG2000 chains were adsorbed to the surface, Figure 5.3.2. Free MPEG2000 chains were adsorbed at the surface silanols of bare silica and reduced repulsive interactions.

The MPEG2000 adsorption also increased the surface activity of hydrophobically modified silica, as the surface tension was 44.59 mN/m with 10% theoretical surface silanols coverage by MPEG2000 physical adsorption, Figure 5.3.2

Surface coverage of 10% free MPEG2000 physically adsorbed on modified silica with isobutyl(trimethoxy)silane had almost the same surface activity decrease with the covalently bonded 3GTO-MPEG2000 on the surface which had the same amount of isobutyl(trimethoxy)silane coverage (12.5%). The surface tension value with 10% theoretical surface silanols coverage by the 3GTO-MPEG2000 was 45.51 mN/m. Figure 5.3.3 shows the effect of physical MPEG2000 adsorption on the surface activities of 5 wt% bare silica and 0.5 wt% hydrophobically modified silica sols. The aim was to see the effect of the increase in surface hydrophobization and the effect of synergistic compatibility with a lower concentration of silica sol at pH=2.23, Figure 5.3.3.
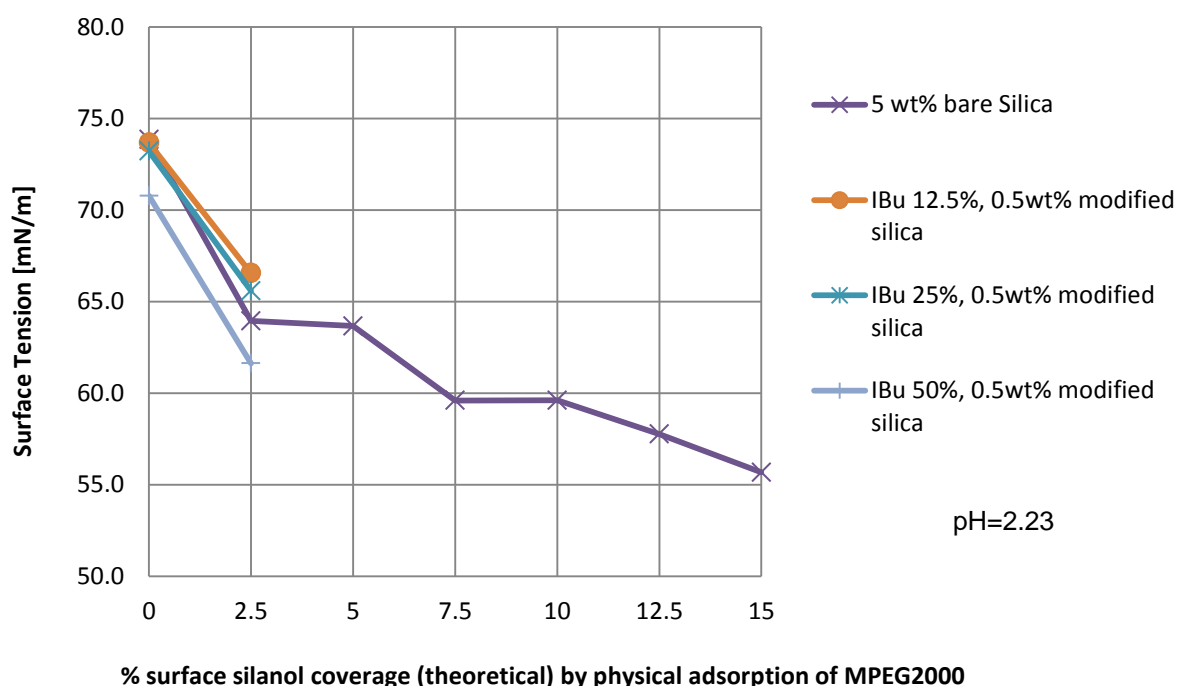

Figure 5.3.3 Surface tension values of 0.5 wt% silica solid content samples in comparison with 5 wt% samples by means of % MPEG coverage by physical adsorption at pH=2.23.

IBu 12.5%, IBu 25% and IBu 50% refer to the modifications by covalent attachment of isobutyl(trimethoxy)silane at 12.5%, 25% and 50% theoretical surface silanols coverage respectively.

The effect of MPEG2000 physical adsorption of the sols having 0.5 wt% solid silica content was similar for all the surface coverage values of isobutyl(trimethoxy)silane, Figure 5.3.3. The surface activities were increased by the physical adsorption of free MPEG2000 chains. Synergetic effect of free MPEG2000 chains and covalently attached isobutyl(trimethoxy)silane was not observed at this low solid silica content. The following experimental set was designed to determine the effective solid silica content in the sample sols where the free MPEG2000 chains and hydrophobization by covalent attachment were synergistically effective on surface activity.

Figure 5.3.4 shows the effect of silica concentrations of two sols modified by isobutyl(trimethoxy)silane at theoretical surface silanols coverage of 25% and 50% on surface activity while the concentration values for the solid silica content in the sol were increased from 0 to 10 wt% to reach the most efficient concentration to work with, Figure 5.3.4.

Theoretical surface coverage by physically adsorbed MPEG2000 was chosen as 5% for each sol to have compatibility of two different moieties at the surface of silica nanoparticles.
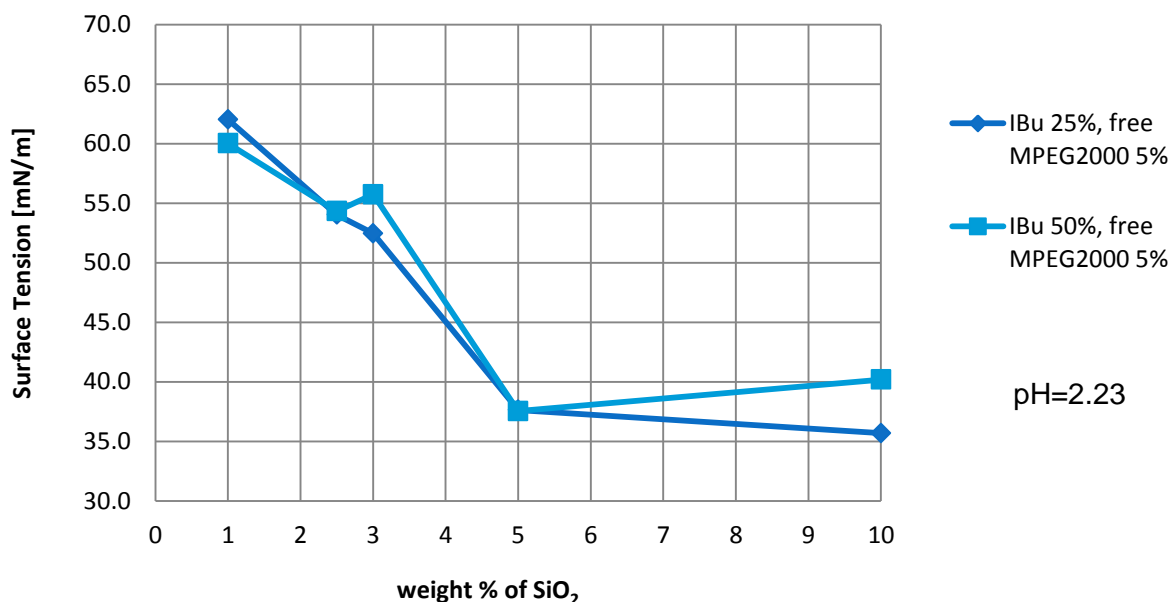

Figure 5.3.4 Surface tension values vs. wt% modified by covalently bonding isobutyl(trimethoxy)silane.

IBu25 and IBu50 refer to the modifications by covalent attachment of isobutyl(trimethoxy)silane at 25% and 50% theoretical surface silanols coverage respectively.

A decrease of surface tension values was observed as the solid silica concentration increased until 5 wt%. The decrease of surface activity shows that more surface active silica nanoparticles were adsorbed at the air-water interface by hydrophobization. A plateau was observed for both of the modified silica sols at 5 wt% concentration as the concentration was increased. The surface tension values were 37.64 mN/m and and 37.54 mN/m for 25% and 50% isobutyl(trimethoxy)silane modification theoretical surface coverage respectively.

This trend of surface tension decrease shows that silica nanoparticles have a limitation as they are arranged at the air-water interface. The particles are surface active and behave like surfactants as the increase of their concentration decreases surface tension values. This surfactant-like behavior shows that the air water interface was saturated at a concentration around 5 wt% solid silica content and surface activity did not decrease further. This plateau value was taken as the concentration value reference for the following samples prepared for the measurements.

5.4 EFFECT OF ISOBUTYL COVERAGE ON THE SURFACE ACTIVITY

Covalent attachment of isobutyl(trimethoxy)silane hydrophobized the silica nanoparticles and drove them to the interface. The effect has been found to be more efficient with MPEG2000 while the film of particles at the interface was stabilized. The effect of surface modification by isobutyl(trimethoxy)silane on surface activity was investigated with 5% theoretical surface silanol covered by physical adsorption of MPEG2000 at 5 wt% solid silica containing aquasol, Figure.5.4.1.

pH=2.23

5 wt% SiO_2

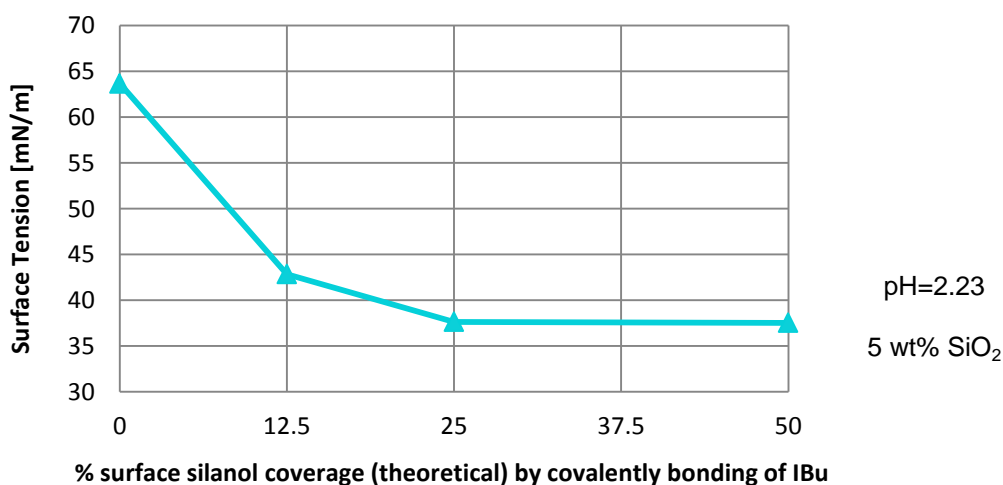**% surface silanol coverage (theoretical) by covalently bonding of IBu**

Figure 5.4.1 Surface tension values vs. surface IBu theoretical coverage value and 5% theoretical MPEG2000 coverage by physical adsorption at SiO_2 concentration of 5 wt%.

The surface tension continuously decreased up to 25% theoretical surface silanols coverage by isobutyl(trimethoxy)silane covalently bound in presence of physical adsorbed MPEG2000. The hydrophobization effect was highly effective for the particles up to 25% surface modification of isobutyl(trimethoxy)silane reaching the plateau value, Figure 5.4.1. The surface tension decrease was limited since there was a limitation of surface coverage by isobutyl(trimethoxy)silane. The theoretical amount of added isobutyl(trimethoxy)silane in the synthesis may not be totally covalently bonded to the surface of bare silica nanoparticles due to steric hindrance.

5.5 EFFECT OF THE PRESENCE OF FREE MPEG2000 CONCENTRATION ON THE SURFACE ACTIVITY ON HYDROPHOBICALLY MODIFIED & BARE SILICA NANOPARTICLES

The effect of physically adsorbed MPEG2000 on bare and hydrophobized silica on the surface activity was investigated. Two different surface coverage values by physical adsorption were studied as 0% and 2.5% for MPEG2000 chains on 5 wt% solid silica containing aquasols, Figure 5.5.1.
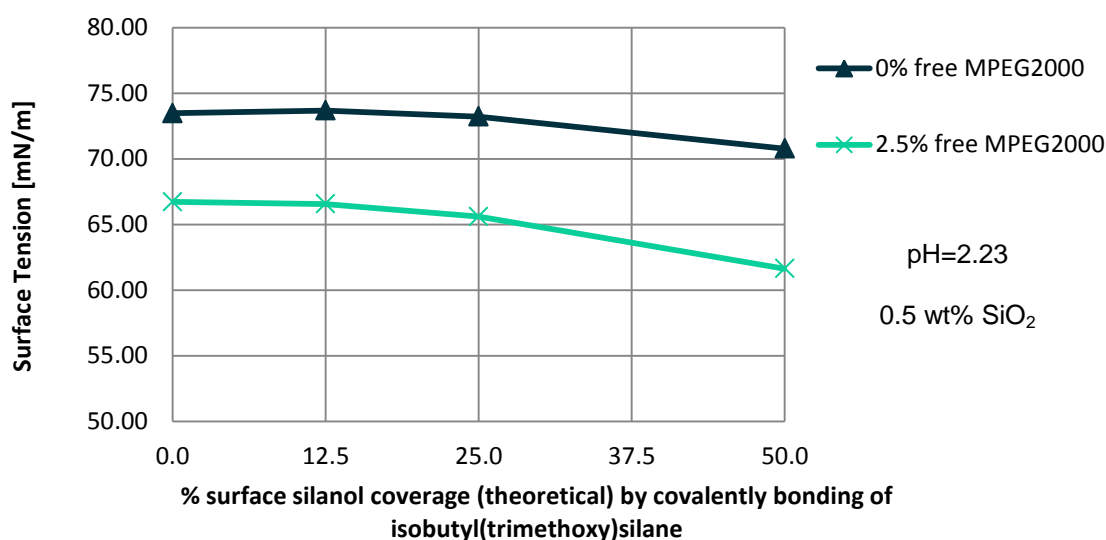

Figure 5.5.1 Effect of the presence of physically adsorbed MPEG2000 on the surface activity of bare and hydrophobized silica nanoparticles

0% free MPEG2000 and 2.5% free MPEG2000 refer to the modifications by physical adsorption of MPEG2000 at 0% and 2.5% theoretical surface silanols coverage respectively.

Free MPEG2000 addition to the sols resulted in 7-10 mN/m surface tension decrease on bare silica, at pH2.23. The synergy in between MPEG2000 physical adsorption and covalently bonded isobutyl(trimethoxy)silane did not change surface activity significantly as the amounts of isobutyl(trimethoxy)silane by covalent attachment on the surfaces were increased. MPEG2000 presence has shown the same effect on both modified and non-modified silica nanoparticles. The effect of physically adsorbed MPEG2000 concentration on the hydrophobized surfaces by covalent attachment of isobutyl(trimethoxy)silane was the subject of the next investigation to see the limitations of physical adsorption.

The effect of surface activity increase and the increased repulsion of particles at the interface by physical adsorption of MPEG2000 polymers were observed by surface tension measurements done by du Noüy ring method. Solid silica content was chosen as 0.5 wt% and the amount of IBu added during synthesis was corresponding to the theoretical surface coverage of 50% of surface silanols, Figure 5.5.2.
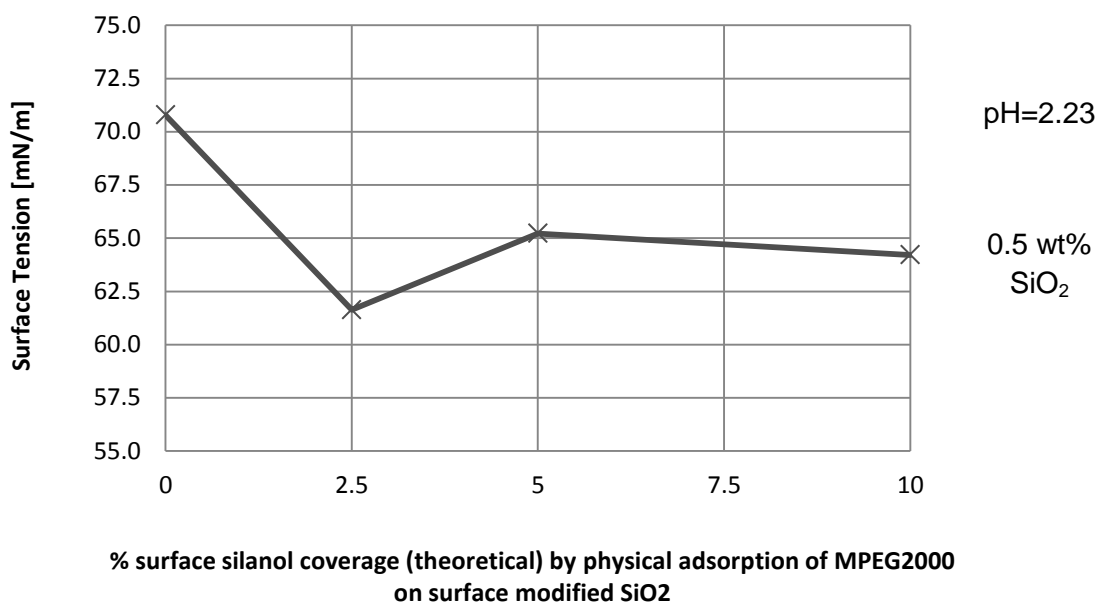

Figure 5.5.2 Effect of the concentration of physically adsorbed MPEG2000 on the surface activity on bare and hydrophobized (by covalently attached isobutyl(trimethoxy)silane with 50% theoretical surface silanol coverage) silica nanoparticles

Addition of the MPEG2000 chains up to 2.5% theoretical surface coverage on hydrophobized silica nanoparticles decreased the surface tension value by 10 mN/m as it was shown on Figure 5.5.1. The surface tension value was then increased by 3 mN/m at 5% theoretical coverage of surface silanols by introducing more free MPEG2000 chains to the new sample prepared. The particles did not become more surface active as the amount of MPEG2000 chains was increased and a plateau value was observed after 5% surface coverage.

5.6 EFFECT OF pH ON SURFACE ACTIVITY

Physical adsorption mechanism is affected by several parameters such as temperature, pH, and concentration values. Since the adsorption mechanism is related with surface charges and electrostatic attraction the effect of pH was studied. The pH values were adjusted by the addition of 0.1M HCl and 0.1 M NaOH solutions to the silica sols for the pH related measurements.

The silica sols at two different pH values of 2.2 and 9.0 with 5 wt% solid silica content were compared to see the differences of the effects of physically adsorbed MPEG2000 on surface activity, Figure 5.6.1.
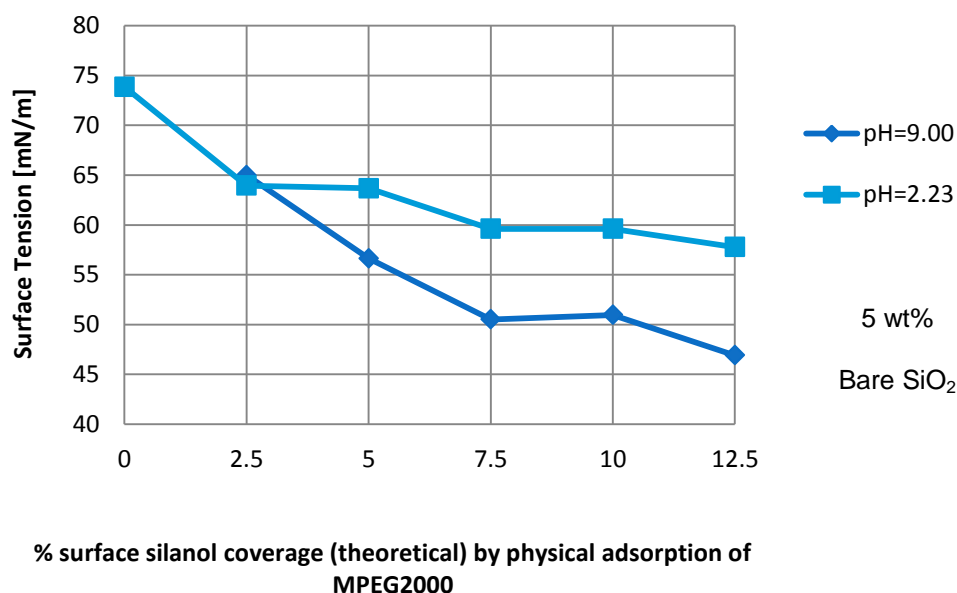

% surface silanol coverage (theoretical) by physical adsorption of MPEG2000

Figure 5.6.1 Surface tension vs. theoretical MPEG coverage for two different silica sols having pH values of 9.00 and 2.27.

Increasing the concentration of free MPEG2000 increased the surface activity by physical adsorption on surface silanols for each sol with different pH values. The effect of physical adsorption of MPEG2000 chains on surface activity on bare silica nanoparticles was more effective for the sample having pH=9, Figure 5.6.1.

This result was unexpected; as the value of 46.91 mN/m obtained at pH=9 was surprisingly low, Figure 5.6.1. The interactions driven by H-bonds between MPEG2000 and the silanols at higher pH values are almost negligible.

Determination of the effective pH range for physical adsorption was the next step to be measured. Figure 5.6.2 shows the evolution of surface activity for two different silica sols containing 10% and 20% theoretical surface silanols covered by MPEG2000 chains adsorbed at different pH values.
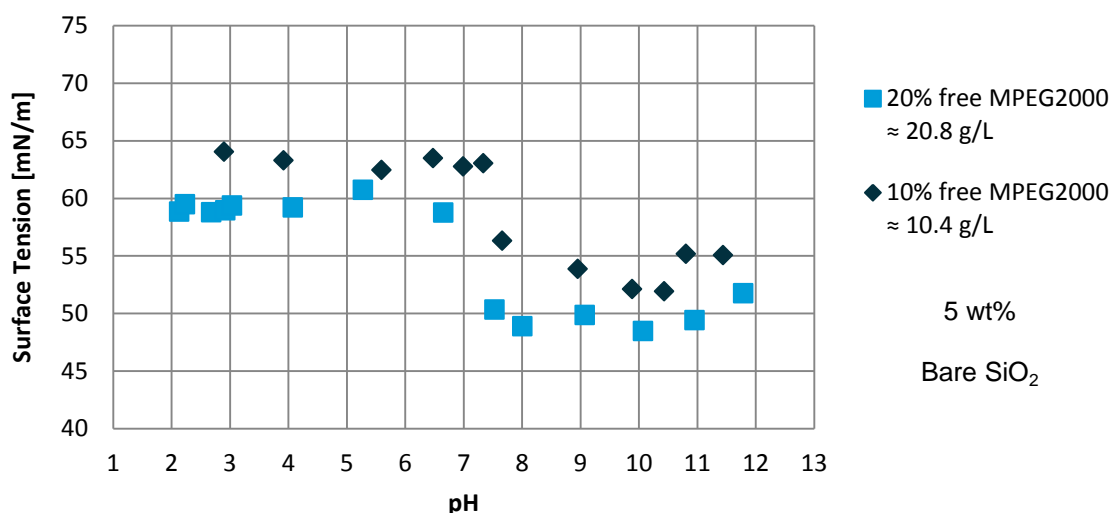

Figure 5.6.2.Surface tension values at different pH values for comparison of two different surface coverage values of physically adsorbed MPEG2000 chains.

The surface tension measurements with different concentrations of MPEG2000 have shown that physical adsorption of free MPEG2000 to surface silanols occurs at a very broad range of pH. The surface activity for the sample with 20% theoretical surface silanols coverage had a surface activity increase with an average of 5 mN/m, Figure 5.6.2.

Another important observation from the measurement was the surface tension decrease depending on pH for both samples. The surface activities had a rapid increase around pH=7 with a surface tension decrease of 10 mN/m. The MPEG2000 concentrations were around 20.8 g/L and 10.4 g/L for 20% and 10% theoretical surface silanols coverage values by

physical adsorption, respectively. The resulting increase in surface activity can eventually be attributed to the MPEG2000 chains that were freed from the surface of the particles.

After the pH effect on MPEG2000 physical adsorption on bare silica surface was studied, the next question was to understand the effect of pH on bare silica and bare MPEG2000 to see which is mostly affected by the pH.

For this study, the surface tension values of two different sols with pH ranging from 2 to 12 were measured. The first sample had 10 wt% bare silica solid content and the second sample had only bare MPEG2000 without any silica nanoparticle as if the theoretical surface coverage would be 10% of the first sol containing bare silica nanoparticles. The concentration of the second bare MPEG2000 was 5g/L, Figure 5.6.3.
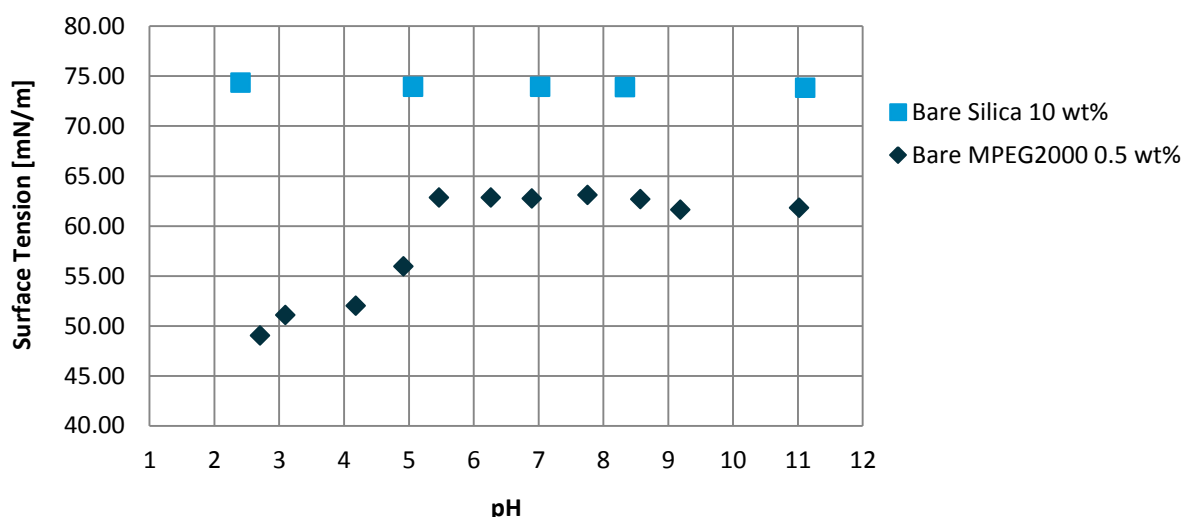

Figure 5.6.3 Surface tension values vs. pH for bare silica and bare MPEG2000

The surface activity for bare silica nanoparticles remained constant in the whole measured pH range, from pH=2 to pH=11. Even though the counter ions are interacting with the surface silanols of silica nanoparticles, the particles has not shown any increase of surface activity, Figure 5.6.3.

For MPEG2000 chains, the increase of acidity caused the chains to become more surface active. This behavior is different from the ones physically adsorbed to silica nanoparticles as seen on Figure 5.6.2 & Figure 5.6.3.

5.7 EFFECT OF MEASUREMENT TIME ON INTERFACIAL ACTIVITY

Interfacial tension measurements were carried out with an Attension Theta instrument (Biolin Scientific). The temperature was kept stable at 23°C. Toluene and dodecane were used for the determination of interfacial tension.

During the measurements by pendant drop technique to determine interfacial tension, the drop has been hanging at the tip of the needle for a maximum time interval of 600 seconds.

For understanding the effect of the kinetics of the adsorption repeated interfacial tension measurements were repeated at short time intervals until 1800 seconds were reached. The surface active sol (water phase) had 12.5% theoretical surface silanols coverage by isobutyl(trimethoxy)silane and 10% theoretical surface silanols coverage by MPEG2000 by physical adsorption on 5 wt% solid silica concentration and pH=9, Figure 5.7.1. The measurement was done at the interface of toluene-water (surface active sol).

5 wt% modified SiO$_2$ (12,5% IBu, 10% free MPEG2000), pH=9
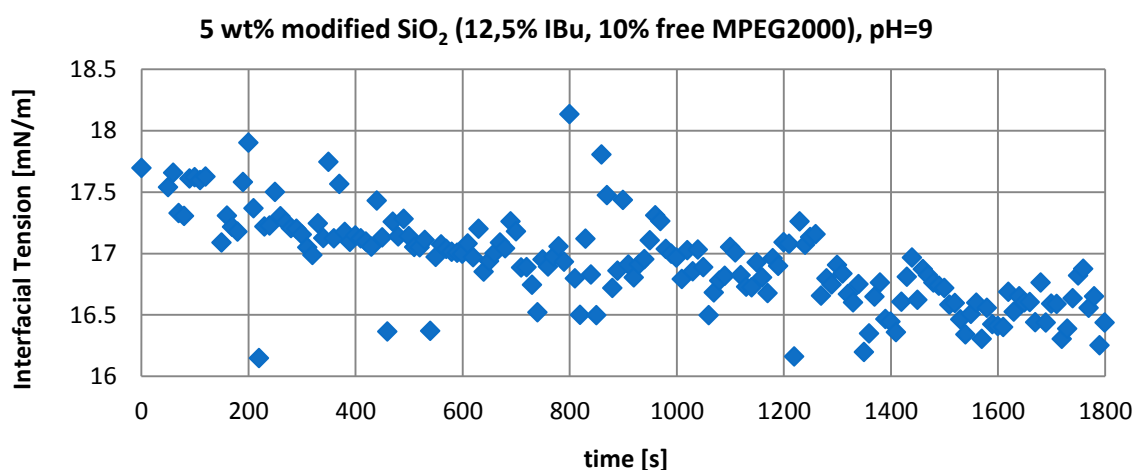

Figure 5.7.1 Interfacial tension(toluene-water) values vs theoretical surface silanol coverage by physically adsorbed MPEG2000 chains. 12.5% IBu corresponds to theoretical surface silanol coverage by covalently attachment of isobutyl(trimethoxy)silane and 10% free MPEG2000 corresponds to the theoretical surface silanol coverage of MPEG2000 by physical adsorption.

The increase of interfacial activity versus the time passed can be observed on Figure 5.7.1. The interfacial tension was decreased by 1 mN/m during the measurement, corresponding to a time interval which was longer than the regular measurement time interval. The variation is small and was neglected in the interfacial tension measurements, Figure 5.7.1.

5.8 INTERFACIAL TENSION & MPEG2000

The interfacial tension versus MPEG2000 coverage for aquasols containing bare silica was chosen as the initial interfacial activity comparison for the interface between water (silica containing aquasols phase) and two different oil phases, which were dodecane and toluene.

The reference values on the Figures 5.8.1 and 5.8.2 are values for pure-water/toluene and pure-water/dodecane interfaces and the aquasols containing silica nanoparticles were plotted as dodecane-water and toluene-water interfaces.

Toluene is relatively more polar than dodecane and MPEG2000 chains dissolve in toluene so MPEG2000 physical adsorptions were compared for these two oil phases in order to have an idea for the adsorption effect and the behavior at the interface for surface active silica nanoparticles.

Non-modified (bare) silica at 5 wt% concentration was used for determination of the effect of MPEG2000 adsorption on interfacial activities of dodecane-water and toluene-water interfaces, Figure 5.8.1.

The interfacial tension values for toluene/water and dodecane/water interfaces are 28.4 mN/m and 43.0 mN/m at 20°C, respectively. The pH of the sols was 9, Figure 5.8.1.
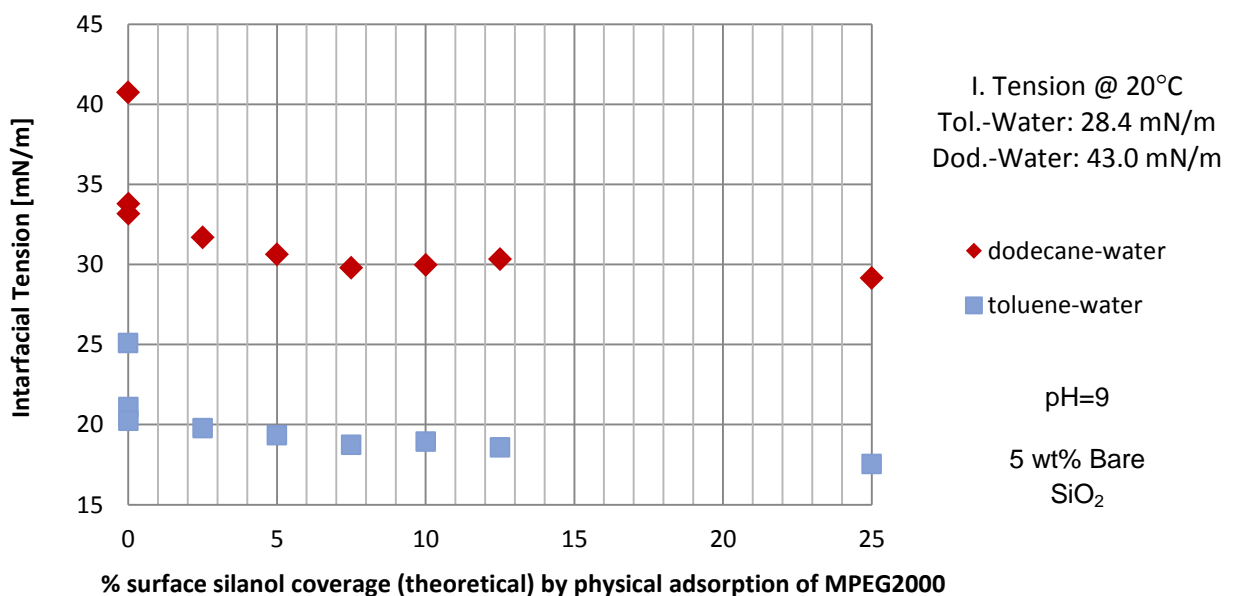

Figure 5.8.1 Interfacial tension values of water (aquasol) and toluene/dodecane interfaces versus physically adsorbed MPEG2000 chains on surface silanols of bare (non-modified) silica nanoparticles. Dodecane-water and toluene-water plots refer to bare silica sol at 5 wt% concentration.

Having bare silica in the aquasols at 5 wt% concentration had almost no effect on interfacial activity in comparison of the reference pure water-toluene and pure water-dodecane interfacial tension values, Figure 5.8.1.

The MPEG2000 chains adsorbed on the silica nanoparticles and increased the interfacial tension of both toluene-water and dodecane-water interfaces. The interfacial tension values were decreased by a margin of 10 mN/m for dodecane-water interface and 6 mN/m for toluene-water interface. The interfacial activity increase was more efficient for dodecane-water interface. Toluene is more polar than dodecane and capable of dissolving MPEG2000. The interaction of MPEG2000 chains and silica nanoparticles were more dominant than toluene-MPEG2000 chains interaction, Figure 5.8.1.

The measurements to determine the effect of MPEG2000 coverage on interfacial tension by physical adsorption were also repeated for the sols containing silica nanoparticles modified by covalently attached isobutyl(trimethoxy)silane. The measurement conditions were the same as the previous bare silica interfacial activity measurements; aquasols with 5 wt% solid silica content at pH=9, Figure 5.8.2.

I. Tension @ 20°C
Tol.-Water: 28.4 mN/m
Dod.-Water: 43.0 mN/m

■ tol-water (IBu 12.5%)
◆ tol-water (IBu 25%)
▲ dod-water (IBu 12.5%)
✕ dod-water (IBu 25%)

pH=9

5 wt% SiO$_2$

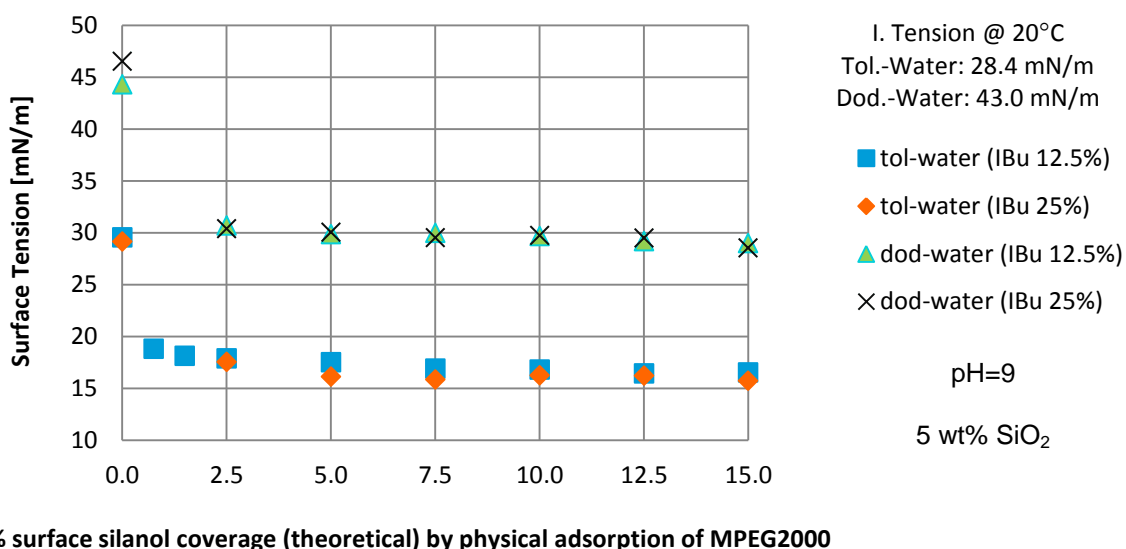**% surface silanol coverage (theoretical) by physical adsorption of MPEG2000**

Figure 5.8.2 Interfacial tension values of water (aquasol) and toluene/dodecane interfaces versus isobutyl(trimethoxy)silane covalently bonded on surface silanols of silica nanoparticles. Tol-water and dod-water plots refer to modified sols at 5 wt% concentration at toluene and dodecane interfaces.

Covalent attachment of isobutyl(trimethoxy)silane on silica nanoparticles have not created an increase on interfacial activity without having MPEG2000 physically adsorbed on silica as the initial values were not different than the pure water-oil interface reference values, Figure 5.8.2.

MPEG2000 chains physically adsorbed on silica nanoparticles and the hydrophobization effect moved the particles to both interfaces of dodecane-water and toluene-water. Interfacial activity increase was more significant when the theoretical surface silanols coverage of MPEG2000 by physical adsorption reached 5% at both interfaces. Interfacial tension values have shown a very similar trend of the effect of MPEG2000 physical adsorption on bare silica nanoparticles, Figure 5.8.2 & 5.8.3.

Covalent attachment of isobutyl(trimethoxy)silane had no synergetic effect on increasing the interfacial activity. This can be explained by the incompatibility of isobutyl(trimethoxy)silane modification with oil interfaces. Even though surface tension values and hydrophobization worked synergistically, emulsion stability of toluene-water and dodecane-water systems are expected to be depending on the physical adsorption of MPEG2000 more than isobutyl(trimethoxy)silane covalent attachment on silica nanoparticles, Figure 5.8.2.

5.9 ZETA POTENTIAL & pH

Zeta potential measurements were done with Zeta Pals (Brookhaven Instruments) and the trends were measured for the solutions of bare silica, 1% and 5% theoretical surface coverage of silanols by physically adsorbed MPEG2000 chains, Figure 5.9.1.

The sols have been prepared at 4 wt% Bindzil solid content and the measurements have been started after checking the validity of results for the concentration. All the samples were found to be in the measurement range for the instrument.
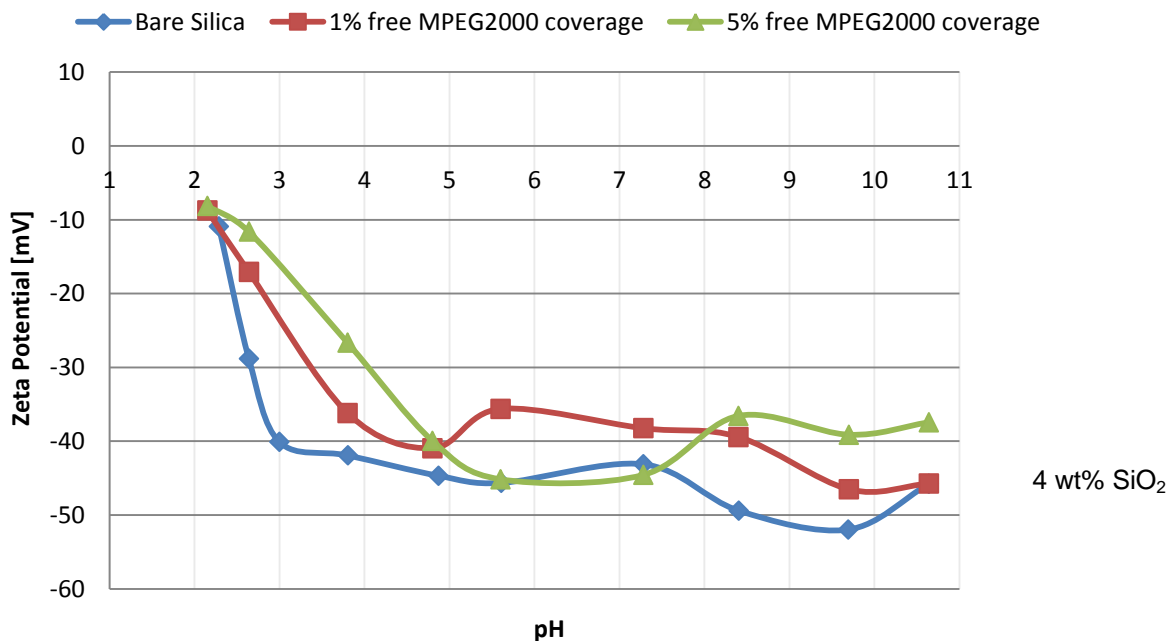
Figure 5.9.1 Zeta potentials of non-modified and modified silica sols

The samples were modified at 1% and 5% theoretical surface silanols coverage by physical adsorption of MPEG2000 chains.

All the zeta potential curves had the same isoelectric point but the pH range in between 2 and 5 has shown the most interesting results. In this pH range, the interactions between MPEG2000 and surface silanols are known to be strong. This interaction influences the surface charges. This explains why the zeta potential of the silica particles in presence of MPEG2000 at pH around 4 is higher than for the bare particles, Figure 5.9.1.

Above pH=5, the surface silanols could not form H-bonds with MPEG2000 any longer, leading to the more or less constant zeta potential values independently of the MPEG2000 coverage, around -40 mV. The results obtained are in agreement with the previous surface tension measurements in the same pH range, Figure 5.6.3.

6 CONCLUSIONS

The theory of hydrophobizing surface by isobutyl(trimethoxy)silane coverage works well but with limitations of surface silanols coverage.

The effect of hydrophobization on surface activity works efficiently at silica concentrations of 5 wt% solid content. This value is important since the surface activity was increased mostly by physical adsorption of MPEG2000 chains at lower solid content concentrations.

There is almost no difference in between the surface activities of nanoparticles with covalently bonded and physically adsorbed MPEG2000 to the surface. The surface activity increase is thought to be related with the electrostatic interactions on the surface of silica nanoparticles.

The difference of adding MPEG2000 to the solution increases the surface activity by reducing the repulsion between particles caused by the charge.

Ultrafiltration results did not change much by means of surface tension (from 67,5 mN/m to 65,5 mN/m). MPEG2000 adsorption is strong enough to stay at the surface for the ultrafiltration process conditions. (The values are really close to MPEG2000 adsorption values, 10 mN/m different from bare silica which would be the case if ultra-filtration took away all the MPEG2000 on the surface).

Increasing the concentration of bare silica did not affect surface activity, as expected.

Adding MPEG2000 to a bare silica containing aquasol decreased the surface tension. Interfacial tensions were also affected significantly when MPEG2000 is present in aquasols while dissolution of MPEG2000 in toluene results with a lower surface activity decrease.

Changing the pH value of colloidal sol affected the surface and interfacial tension values significantly.

7 FUTURE WORK

The effects of time and pH on zeta potential measurements were in agreement with the literature. Further parametric measurements are possible and can be carried out.

The size of silica nanoparticles was not studied but is an important parameter as well as the length of MPEG chains. Adsorption characteristics for different particle sizes can be studied.

Size and surface coverage ratios of different modifiers will give different surface activity decreases. The order of the modifications is also another important parameter to be investigated for the future.

8 ACKNOWLEDGEMENTS

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