Modified Silica Sols as Emulsifiers

Master of Science Thesis in the Master Degree Programme

Materials and Nanotechnology

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Abstract

Silica surface was modified by grafting hydrophilic and hydrophobic moieties resulting in an amphiphilic silica.

(3-glycidoxypropyl) trimethoxysilane (3GTO) is reacted with hydrophilic poly(ethylene glycol) methyl ether (MPEG) group to produce 3GTO-MPEG which reacts readily with silanol groups on the silica surface. Hydrophobic isobutyl(trimethoxy)silane and propyl(trimethoxy)silane groups reacts directly with the silanols.

Surface modification of silica sol by hydrophilic and hydrophobic moieties was analyzed by Thermogravimetric analysis (TGA). Physicochemical properties namely surface tension measurement indicated that surface modified silica sols were surface active and the best surface activity was obtained when the silica sols were both hydrophobically and hydrophilically modified.

The surface active silica was used to prepare emulsions. The resulting stable dispersions, obtained at a very low ratio of silica sols (0.5 wt% of the oil phase), were oil in water. The droplets were polydisperse.

Emulsion stability results stated that emulsions were stable, the balance between MPEG and isobutyl was very important and it has to be in favor of isobutyl.

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1 INTRODUCTION

Emulsions are produced by many organisms in daily life and emulsion based products either natural or man-made have serious place in the market. [1] Since the applications of emulsions in industry and academic research are numerous, emulsion technology is regarded as a science field to be understood briefly and to be developed continuously.

In 1907 British scientist S.U. Pickering accomplished to stabilize emulsion with solid particles rather than surfactants and started the history of particle stabilized emulsion known as Pickering emulsions. [2] For more than 100 years, solid particles such as silica have been used as emulsifiers to provide long term stable emulsions.

Silica sols, namely aqueous colloidal silica dispersion, are suspension silica particles with particle size ranging from 1nm to 1µm in water. Sufficiently small particle size of this colloidal state of subdivision makes gravitational force negligible and also illustrates non-negligible deviations from characteristics of real solution through adequately large particle size. Throughout colloidal suspension, short-range forces such as electrostatic interactions and van der Waals attraction govern interactions. Random movement is occurred by colloidal particles as a consequence of collision with solvent molecules. This movement namely Brownian diffusion causes collusions that might result in aggregation and precipitation of the particles as long as enough time is given. [3] Silica sols are considered as stable due to the lack of significant rate of sedimentation or agglomeration.

The uses of colloidal silica in emulsion system are due to the fact that it is the most abundant mineral on the earth and therefore it is easy and cheap to be utilized. [4] Also it can be functionalized by modifying the surface area for different purposes.

Silica surface can be functionalized with hydrophilic polymer groups and hydrophobic molecules to obtain emulsifier with good performance. Hydrophilic polymers with oxyethylene chains have considerable effects on stabilization of emulsions providing steric stabilization through oxyethylene chains. [5] Hydrophobic molecules have stabilization effect on emulsion by the mechanism of particle stabilization.

One objective of this Master of Science study was to develop amphiphilic silica as a new family of emulsifier by modifying the silica surface with hydrophilic and hydrophobic groups. In order to achieve this purpose, firstly hydrophilic modifiers were synthesized and silica surface was grafted with both hydrophilic and hydrophobic molecules, as illustrated below.
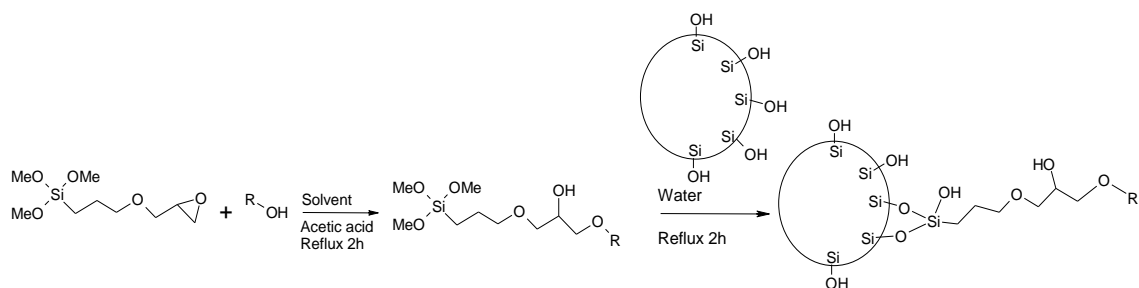
Another objective was the characterization of product and measurement of physicochemical properties. Finally the project was completed with emulsion tests.

This project was run in collaboration between Eka chemicals and Applied Surface Chemistry at Chalmers University of Technology.

2 THEORETICAL BACKGROUND

2.1 Emulsions

An emulsion is a thermodynamically unstable dispersion of two immiscible liquids. In emulsion system, one phase forms droplets (the dispersed phase) and as a result it is differentiated from the other liquid which is called the continuous phase. [6]

Emulsions mostly include organic liquid phase and water. The organic phase is generally referred as oil. However, it does not have to reflect the real meaning of the word. When mentioned water and oil in an emulsion, they might also refer to the derivatives of the substances. [6, 7]

From industrial aspects, emulsions have foremost importance in engineering of food, cosmetics, pharmaceuticals and petroleum products. The two types of emulsions which are oil in water (O/W) and water in oil (W/O) are used for different purposes. [7] For instance, butter is a kind of W/O emulsion and ice cream is O/W. [8] In pharmaceutical industry double emulsions such as O/W/O and W/O/W are very useful for drug delivery system. [6]

From a thermodynamic point of view, work units are used to express quantities. Since the surface tension of a liquid surface is a physicochemical property, it possesses the meaning of Helmholtz function. When drops coalesce, the area decreases. Consequently the change in the area ($\Delta A = A_{final} - A_{initial}$) is negative (at constant volume, temperature and composition) and expression of Helmholtz free energy is negative as well for the process of coalescence. Therefore the mixing of water and oil has insufficient stability and the addition of the third component, that will prevent spontaneous coalescence, is indispensable. In other words the third constituent ought to be surface active to acquire a stable emulsion. [9]

Stabilization of emulsions can be achieved by many emulsifying agents. For this purpose, surfactants and small particles are generally used. Powerful emulsifiers are anticipated to implement some necessities. First one is their ability to reduce the oil-water interfacial tension. The second and decisive one is that emulsifiers have to fill new interface quickly to avoid coalescence. [10] Moreover, different types of emulsifiers stabilize emulsions through

different types of mechanism. Types of emulsifier molecules are deterministic for stabilization process. For example electrostatic stabilization can be achieved by ionic surfactants whereas non-ionic surfactants with long polyoxyethylene chains provide steric stabilization. More than one mechanism is usually used in emulsion stabilization. [5]

2.2   Pickering Emulsions

The stabilization mechanism which relies on solid particles is called particle stabilization and the emulsion stabilized through these particles is referred as Pickering emulsion. This stabilization method was discovered by British scientist S.U. Pickering who achieved the stable emulsion with internal phase more than 99% in 1907. [11] From that time solid particles have been considered as effective emulsifiers similar to surface active molecules (surfactant) as they can locate at the oil-water interface. Besides, solid particles can hinder coalescence. When droplets are close to each other, the solid particles which are adsorbed at interface have the ability of lateral motion avoiding further contact. [12] As a second stabilization mechanism, solid particles can form three dimensional networks, mostly seen in clay particles, and prevent contact between droplets. [13]

However stabilization mechanisms behind Pickering emulsion still remains unclear. Therefore, generally two conditions are expected to be fulfilled. First one is that droplet size should be much bigger than particle size. Second one is that some part of particle surface must be wetted by water whereas some other parts must be wetted by oil. [14] Even though agitation is necessary so as to prepare Pickering emulsions, the size of droplets does not depend on the intensity of agitation. The particle size and the concentration are regarded as important factors on the droplet size. As long as there is no restriction in particle size, droplet diameters in most case are bigger than particle diameters by a number of varying between 30 and 300. [12] Moreover, there is a correlation between particle size and emulsion stability. Usually, when the particle size decreases, emulsion stability increases. [13]

Another correlation can also be established between the concentration of the particles and the emulsion stability. An increase in concentration of particle provides more stable emulsion. This result could be due to the decrease of the droplet size which uses more particles on interface and enable the formation of monolayer. [13]

When solid particles adsorbs at the oil-water interface, the contact angle is a beneficial tool to understand the wettability of the solid particles. It is usually regarded that if the particles have contact angle below 90º, they prefer the water phase and lead to oil in water (O/W) emulsion. On the contrary, if the particles have a contact angle bigger than 90º, they are located in the oil phase and form water in oil emulsion (W/O). [14] Nevertheless measuring contact angle of particles represents a very difficult task that will not be treated in this thesis.

As described before, the best stabilization in Pickering emulsion is achieved by particles which are partially wetted by both phases. Particles with desired contact angel are thus required. Nowadays, it is possible to supply various nanoparticles, particularly with silica, and alter them to reach desired contact angle. [15]

Since oil polarity has influence on hydrophobicity, it has effect on surface tension and contact angle. So, it is regarded as another factor that affects the stability of emulsion. [13]

2.3 Silica Particles

Silica is the most abundant mineral on the earth and it refers to any type of material with molecular formula SiO_2. Different forms of silica constitute many well-known materials such as glass and quartz and its applications have important place in nanomaterial chemistry. Generally, quartz is the one of the crystalline forms of silica, stable at room temperature whereas other crystalline forms of silica such as tridymite and cristobalite present as metastable forms at room temperature. [16, 17]

Silica can constitute colloidal dispersion, silica sols, and it has been marketable for more than 80 years, even though its application had not been found broadly until the 1950s. [18] With respect to other oxides materials, silica has unique characteristics and solubility of silica is fairly higher especially in its amorphous forms. Nevertheless, dissolution of silica is basically different from dissolution of other materials such as sugar. Whereas silica dissolves in water with a chemical reaction, sugar presents in water as its crystalline form. [19]

$$SiO_2 + 2H_2O \longrightarrow Si(OH)_4$$
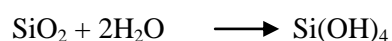
Silicic acid [Si(OH)$_4$], in its monomeric form, can be used so as to initiate silica synthesis. Colloidal silica particles can be produced by aggregation of the monomeric silicic acid under definite conditions mainly pH. During the process of silica synthesis, the effect of salt concentration in the reaction medium is very essential. For example; spherical particles are formed only in low salt concentration. Addition of electrolytes to the growing particles results in initiation of aggregation of primary particles. Subsequently irregular particles are formed. [16]

Silica sols also can be prepared by a method so called Stöber process. The reaction start with a tetraalkylortosilicate and ethanol is used as solvent together with water and ammonia. In this way silicic acid can be formed and aggregated to produce silica sols. [16]

$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + C_2H_5OH$$

2.4   Surface Modification of Silica

The silica surface is constituted mainly by silanol (Si-OH) groups and 8 μmol/m^2 of silanol groups is accessible at the silica surface. Chemistry on silica surface is well-known to be ruled by these groups. Chemical characteristics of silica surface can be temporarily changed by changing the amount of silanol groups on silica surface with some methods such as strong oxidizing acid or oxygen/air plasma. [20] However, new characteristics can be loaded onto silica surface by chemical modification. For instance, alumina layer on silica surface with thickness one or two molecules make silica sols behaving as if it is solid alumina particles. [21]

In another approach, silica particles can be used as stabilizer in emulsion study because of their surfactant behavior. Particularly, surface modified silica particles carrying hydrophilic and organophilic groups have adsorption ability at the oil-water interface. These types of modifications indicate greater stabilization ability at interface than surfactant and are used in industry to stabilize the emulsion system such as in the paints. [22]

3 MATERIALS

3.1 Silica Sols

Silica sols used are Bindzil grade of colloidal silica which was supplied from Eka chemicals. Colloidal silica has particles that are not polydisperse and have diameter of 25nm with surface area of 130 m^2/g. Also there are 8 μmol/m^2 silanol groups on the silica surface and pH of silica sol is 2.23 .
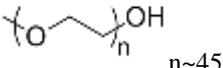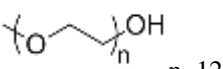
These silica sols are called "non-modified silica sols'' in this thesis.

3.2 Hydrophilic Molecules

The hydrophilic moieties used are poly(ethylene glycol) methyl ether, abbreviated as MPEG, groups with two different molecular weights. The structural difference of these hydrophilic moieties with poly(ethylene glycol) is that these hydrophilic moieties are end-capped with methoxy group to obtain a single reacting group.

MPEG were purchased from Sigma-Aldrich and their properties are described in the table below.

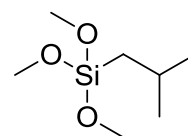**Table 1**: *Description of poly(ethylene glycol) methyl ether*

Name	Structure	Molecular Weight
MPEG(2000)	n~45	2000g/mol
MPEG(550)	n~12	550g/mol

3.3 Hydrophobic Molecules

Hydrophobic moieties chosen are isobutyl(trimethoxy)silane (Sigma-Aldrich) and propyl(trimethoxy)silane (Sigma-Aldrich). Both of these molecules include silyl ether groups that are able to react with silanol groups on the silica surface without using any linker molecules. Table 3 represents general characteristics of these hydrophobic molecules.
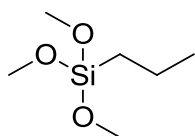

Figure 1: *Structure of isobutyl(trimethoxy)silane*   **Figure 2**: *Structure of propyl(trimethoxy)silane*

3.4 Linker

(3-glycidoxypropyl) trimethoxysilane (3GTO) is widely used as linker and coupling agent due to its bi-functional properties. [18] The epoxide ring can react with a nucleophile such as hydrophilic or hydrophobic moieties. The three alkoxy groups enable covalent bonding to the silanol groups on the silica surface.

GPTMS (3GTO)
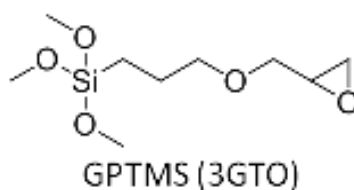
Figure 3: Structure of 3GTO

3.5 Other Materials

Acetonitrile (Merck) was used as a solvent in all coupling reactions between 3GTO and MPEG. Since acetonitrile is polar aprotic solvent, it does not form hydrogen bond and therefore it is convenient for this coupling reaction. Acetic acid (Sigma-Aldrich) was used as

catalyst because it is a hydrogen donor to oxygen in the epoxide ring. In this way, it makes the epoxide ring partially protonated and activates the ring. During emulsification tests, dodecane (Sigma-Aldrich) and Toluene (Fluka) were preferred as oil phases.

4 EXPERIMENTAL

4.1 Synthesis of Modifying Agents

Synthesis of 3GTO-MPEG(2000): MPEG(2000) (40g) and 3GTO (5.2g, excess of 10% molar) were added to acetonitrile (200ml) in a round bottomed flask. Acetic acid (12.50µl, 10% molar of 3GTO) was added and the mixture was refluxed at 80°C for 2h under stirring.

Synthesis of 3GTO-MPEG(550): MPEG(550) (5.0g) and 3GTO (2.58g, excess of 20% molar) were added to acetonitrile (50ml) in a round-bottomed flask. Acetic acid (62µl, 10% molar of 3GTO) was added finally and the mixture was refluxed at 80°C under stirring for 2h.

4.2 Surface Modification of Silica Sols

Silica surface modifications with 3GTO-hydrophilic and hydrophobic moieties were done by the following protocol.

Example of reaction of 3GTO-MPEG(2000) (to graft 0.8 µmol/m^2) and Isobutyl(trimethoxy) silane (to graft 1 µmol/m^2) with silica sol (8 µmol/m^2 SiOH): 3GTO-MPEG(2000) (3.9902g) and isobutyl(trimethoxy)silane (0.3975g) were added to silica sol (50g) in a round-bottomed flask at room temperature. The mixture was refluxed at 80°C for 2h.

Example of reaction of 3GTO-MPEG(550) (to graft 0.8 µmol/m^2) and Isobutyl(trimethoxy) silane (to graft 1 µmol/m^2) with silica sol (8 µmol/m^2 SiOH): 3GTO-MPEG(550) (0.2805g) and isobutyl(trimethoxy)silane (0.0795g) were added to silica sol (10g) in a round-bottomed flask at room temperature. The mixture was refluxed at 80°C for 2h.

4.3 Purification of Surface Modified Silica sols

4.3.1 Purification by Centrifugation:

Surface modified silica sols (4g) and distilled water (4ml) were mixed in the tube. The sample was vortexed to achieve a fine dispersion of silica into the water. Finally, sample was centrifuged at 2000rpm for 60 minutes and the supernatant was removed. This protocol was repeated 3 times.

4.3.2 Purification by Ultrafiltration:

Surface modified silica sols and distilled water were mixed in the Ultrafiltration cell. 4bar pressure was applied under stirring with nitrogen. The membrane cut-off was 100 kDa. Supernatant was removed (about 45ml for each trial). This protocol was repeated 5 times.

4.4 Surface Tension Measurement

Sigma 70 Tensiometer (KSV) was used to measure surface tension by du Noüy ring method. A cryostat Neslab RTE-200 was used to keep temperature constant (at $25^{\circ}C$ (±0.01) and at $15^{\circ}C$). The glassware was thoroughly clean prior to use. The ring was burned in order to remove surface active molecules.

4.5 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) basically relies on the monitoring of change in sample weight during temperature variation under a controlled atmosphere (N_2 gas). Description of temperature program used for characterization of dried silica sols is a follow

- ❖ Sample in the furnace was held at $50^{\circ}C$ for 1min.
- ❖ Furnace temperature was increased from $50^{\circ}C$ to $650^{\circ}C$ at the rate of $10^{\circ}C/min$.
- ❖ Sample in the furnace was held for 20min at $650^{\circ}C$.

Perkin Elmer Thermogravimetric analyzer was used for this characterization.

4.6   Emulsification

Following protocols were carried out for emulsification tests.

Example of emulsification including water (30%) and oil (dodecane (70%) and toluene (70%) respectively) using surface modified silica sol (0.5 wt% of oil phase): Silica sol (263.86mg and 19.8963 wt% of SiO_2) was added to tube containing water-dodecane (4.5g-10.5g) or water-toluene (4.5g-10.5g) respectively. Then the mixture was emulsified for 5min with a Heidolph DIAX 900 operating at 20000rpm.

 Example of emulsification including water (70%) and oil (dodecane (30%) and toluene (30%) respectively) using surface modified silica sol (0.5 wt% of oil phase): Silica sol (113.08mg and 19.8963 wt% of SiO_2) was added to tube containing water-dodecane (10.5g-4.5g) and water-toluene (10.5g-4.5g) respectively. Then the mixture was emulsified for 5min with a Heidolph DIAX 900 operating at 20000rpm.

For the preparation of colored emulsion methylene blue (miscible in mater) and oil red (miscible in oil) dies were used at a concentration of 1 mg/ml.

4.7   Light Microscopy-Monitoring the Size of Emulsion Droplets

The size of colorful emulsion droplets was monitored by olympus BH-2 optical light microscopy. The scale was calibrated with a calibration block (100 div/mm).

5 RESULTS AND DISCUSSION

First, the synthesis and the characterization of the amphiphilic silica will be presented. Then physicochemical properties of the amphiphilic silica will be discussed.

5.1 Synthesis

### 5.1.1 Synthesis Reaction of Hydrophilic Modifiers (3GTO-MPEG):

Since the amount of hydroxyl groups/g of MPEG is not precisely well known, an excess of 10% molar of 3GTO was used rather than stoichiometric reaction with MPEG. Catalyst acetic acid, which catalyzes ring opening reaction of epoxide, is 10% molar of the 3GTO used.
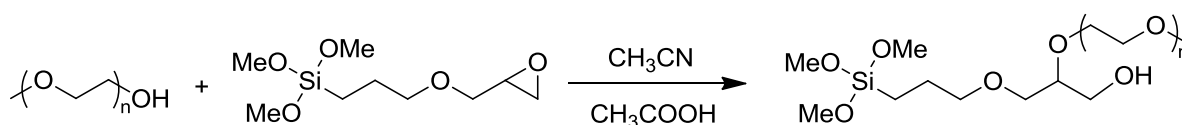
Figure 4: Reaction schemes illustrating reaction of the linker with hydrophilic molecules

5.1.2 Reactions of Hydrophilic Modifiers and Hydrophobic Molecules with Silica Surface:

Modification of silica surface with hydrophobic and hydrophilic moieties is demonstrated in the following figures. These reactions were conducted at $80^{\circ}C$ to avoid boiling that causes destabilization of the silica.
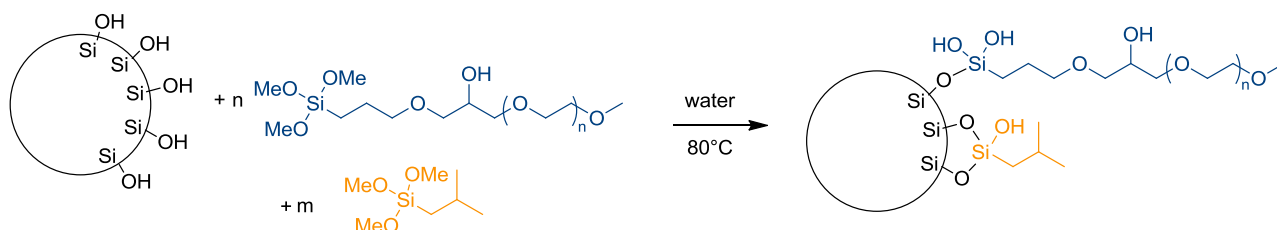
Figure 5: Reaction schemes illustrating the modification of silica surface

5.2 Observation of Centrifuged Silica Sols

In the centrifugation method, silica sols were dispersed and concentrated three times. After the first and the second centrifugations, two separated phases where silica cake was at the bottom and supernatant on the top were observed. However, after the third centrifugation some silica cake was still present at the bottom while some silica particles were seen as suspended phase on the top of the cake. This result indicated that the most of the unreacted polymer groups was rinsed away from the silica surface and consequently some silica suspension was obtained in the third centrifugation.

5.3 Calculation of Surface Coverage

It can be anticipated, there is a restriction in the amount of silica surface modification for hydrophilic and hydrophobic moieties. In order to calculate maximum coverage of silica surface by these modifiers, an approximation depending on some known values can be made. It is assumed, in this calculation, that linker 3GTO is small and has no effect on coverage of silica surface.

Isobutyl(trimethoxy)silane occupies the surface area of 32Å^2 when it is combined with silica surface.

As it is already known, there is 130 m^2/g SiO_2 and 8µmol Si-OH groups/m^2 on silica surface used in this study. Therefore according to calculation, maximum coverage of silica surface is 65% of the number of mol of silanol groups/m^2.

$$\frac{130}{32 \times 10^{-20} \times 6.022 \times 10^{23}} = 6.75 \times 10^{-4} \text{ mol isobutyl(trimethoxy)silane/g } SiO_2$$

$$\frac{6.75 \times 10^{-4}}{130 \times 8 \times 10^{-6}} \times 100 = 65\% \text{ of mol of silanol groups/m}^2$$

In the case of MPEG, it possesses a surface area of 120Å^2. The calculation is based on the area occupied by fatty alcohol ethoxylates $(nC_{16}H_{33}(OCH_4)_{21}OH)$ adsorbed at the water-air interface.

With the same approximation explained above, maximum coverage of silica surface is 17% of the number of mol of silanol groups/m^2.

$$\frac{130}{12.50 \times 10^{-20} \times 6.022 \times 10^{23}} = 1.8 \times 10^{-4} \text{ mol MPEG/g SiO}_2$$

$$\frac{1.8 \times 10^{-4}}{130 \times 8 \times 10^{-6}} \times 100 = 17\% \text{ of mol of silanol groups/m}^2$$

5.4 Surface Modification of the Silica Sols

Silica surface modification have been performed not only with various amounts of hydrophilic 3GTO-MPEG(2000) and 3GTO-MPEG(550) moieties but also with different amounts of hydrophobic isobutyl(trimetoxy)silane and propyl(trimethoxy)silane moieties by the protocols explained before.

First of all, the silica surface was modified only with linker 3GTO. Amount of 3GTO on the silica surface and visual observation of 3GTO linker loaded silica sol are reported in the following table 2.

Table 2: *Description of the 3GTO modified silica sols.*

Type of Silica Sols	Number of µmol of hydrophilic and hydrophobic moieties/m^2	Number of µmol of linker (3GTO)/m^2	Coverage of Silica Surface	Appearance of the modified silica sols
Silica sol 8 µmol SiOH	-	1 µmol	12.5% 3GTO	Same appearance as non-modified silica sol 8 µmol SiOH
Silica sol 8 µmol SiOH	-	2 µmol	25% 3GTO	Same appearance as non-modified silica sol 8 µmol SiOH
Silica sol 8 µmol SiOH	-	4 µmol	50% 3GTO	Same appearance as non-modified silica sol 8 µmol SiOH
Silica sol 8 µmol SiOH	-	8 µmol	100% 3GTO	Same appearance as non-modified silica sol 8 µmol SiOH

The modification by 3GTO does not influence the viscosity of the silica sols.

In addition, silica surface was modified with both hydrophilic and hydrophobic moieties separately in order to get characterization table. Amount of organics that was loaded on the silica surface was increased step by step and appearance of these modified silica surface is reported in the following table 3.

Table 3: *Description of the characterization table*

Type of Silica Sols	Number of µmol of hydrophilic moieties/m^2	Number of µmol of hydrophobic moieties/m^2	Coverage of Silica Surface	Appearance of the modified silica sols
Silica sol 8 µmol SiOH	-	Isobutyl 0.16 µmol	2% Isobutyl	Viscous and turbid
Silica sol 8 µmol SiOH	-	Isobutyl 0.4 µmol	5% Isobutyl	Viscous and turbid
Silica sol 8 µmol SiOH	-	Isobutyl 1 µmol	12.5% Isobutyl	Viscous and turbid
Silica sol 8 µmol SiOH	-	Isobutyl 2 µmol	25% Isobutyl	Very viscous and turbid
Silica sol 8 µmol SiOH	-	Isobutyl 4 µmol	50% Isobutyl	Very viscous and turbid
Silica sol 8 µmol SiOH	-	Isopropyl 1 µmol	12.5% Isopropyl	Viscous and turbid
Silica sol 8 µmol SiOH	-	Isopropyl 2 µmol	25% Isopropyl	Viscous and turbid

Type of Silica Sols	Number of μmol of hydrophilic moieties/m^2	Number of μmol of hydrophobic moieties/m^2	Coverage of Silica Surface	Appearance of the modified silica sols
Silica sol 8 μmol SiOH	-	Isopropyl 4 μmol	50% Isopropyl	Viscous and turbid
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 00.8 μmol	-	1% 3GTO-MPEG(2000)	Viscous and turbid
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.16 μmol	-	2% 3GTO-MPEG(2000)	Viscous and turbid
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.4 μmol	-	5% 3GTO-MPEG(2000)	Viscous and turbid
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.64 μmol	-	8% 3GTO-MPEG(2000)	Viscous and turbid
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	-	10% 3GTO-MPEG(2000)	Very Viscous and turbid
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 1.2 μmol	-	15% 3GTO-MPEG(2000)	Very Viscous and turbid

Despite the fact that the hydrophobic modification induces an increase of the viscosity, the effect was more pronounced with MPEG modifiers.

In order to use amphiphilic silica particles as emulsifiers, it is already known that silica surface has to contain both hydrophilic and hydrophobic moieties. To achieve this purpose, silica surface was modified with these modifiers in one pot and to understand the effect of modifiers on the amphiphilic properties of silica particles, the amount of hydrophobic moieties on the silica surface was kept constant while the amount of hydrophilic moieties decreased stepwise and vice versa. These approaches are illustrated in the table 4 below.

Table 4: *Description of the emulsifiers*

Type of Silica Sols	Number of µmol of hydrophilic moieties/m^2	Number of µmol of hydrophobic moieties/m^2	Coverage of Silica Surface	Appearance of the modified silica sols
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.6 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 7.5% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.4 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 5% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.2 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 2.5% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.08 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 1% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 0.8 µmol	10% Isobutyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 0.6 µmol	7.5% Isobutyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 0.4 µmol	5.0% Isobutyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 0.2 µmol	2.5% Isobutyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 0.08 µmol	1.0% Isobutyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isopropyl 1 µmol	12.5% Isopropyl, 10% 3GTO-MPEG(2000)	Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(550) 0.8 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 10% 3GTO-MPEG(550)	Less viscous Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(550) 0.4 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 5.0% 3GTO-MPEG(550)	Less viscous Gel sedimentation and turbid liquid
Silica sol 8 µmol SiOH	3GTO-MPEG(550) 0.8 µmol	Isobutyl 0.5 µmol	6.25% Isobutyl, 10% 3GTO-MPEG(550)	Less viscous Gel sedimentation and turbid liquid

When the amount of hydrophilic and hydrophobic moieties on the silica surface was increased, viscosity of silica sols increased as well. Since the MPEG(2000) has longer polymer chain than MPEG(550), MPEG(2000) has bigger effect on the increasing of the viscosity.

5.5 Characterization of the Surface Modified Silica Sols

5.5.1 Thermogravimetric Analysis (TGA)

Perkin Elmer Thermogravimetric analyzer was used to evaluate whether or not modifications of silica surfaces were successfully achieved. By controlling the atmosphere, nature of thermal event occurred during the analysis was controlled to some extent. When the furnace was following over the adjusted temperature program that was described before in the protocol, silica samples underwent weight changes owing to losing moieties from surfaces and gave characteristic curves. The sizes of steps, where percentage changes in weight occurred, are used for quantitative evaluation of the curves.

The modification of silica surface with hydrophobic and hydrophilic groups are proven by analysis of some samples in TGA and results are shown as a % weight lost in the following table 5. The samples are depicted on the characterization table 3.

Table 5: *TGA results of surface modified silica sols*

Type of Silica Sols	Number of µmol of hydrophilic moieties/m^2	Number of µmol of hydrophobic moieties/m^2	Coverage of Silica Surface	% Weight Lost From Silica Surface
Silica sol 8 µmol SiOH	**-**	**-**	-	2.03
Silica sol 8 µmol SiOH	-	Isobutyl 0.16 µmol	2% Isobutyl	2.22
Silica sol 8 µmol SiOH	-	Isobutyl 0.4 µmol	5% Isobutyl	2.24
Silica sol 8 µmol SiOH	-	Isobutyl 1 µmol	12.5% Isobutyl	2.42
Silica sol 8 µmol SiOH	-	Isobutyl 2 µmol	25% Isobutyl	2.85

Type of Silica Sols	Number of μmol of hydrophilic moieties/m²	Number of μmol of hydrophobic moieties/m²	Coverage of Silica Surface	% Weight Lost From Silica Surface
Silica sol 8 μmol SiOH	-	Isobutyl 4 μmol	50% Isobutyl	4.21
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 00.8 μmol	-	1% 3GTO-MPEG(2000)	3.68
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.16 μmol	-	2% 3GTO-MPEG(2000)	5.58
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.4 μmol	-	5% 3GTO-MPEG(2000)	11.79
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.64 μmol	-	8% 3GTO-MPEG(2000)	13.89
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	-	10% 3GTO-MPEG(2000)	20.72
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 1.2 μmol	-	15% 3GTO-MPEG(2000)	57.52

It is obvious in the table 5 that when the percentage of hydrophilic and hydrophobic moieties on the silica surface increase, the percentage of sample lost from the silica surface also increases so the percentage of sample remaining on the surface decreases. This inverse relation between percentage of sample remaining on the silica surface and amount of organics that were loaded on the silica surface (only Isobutyl loaded silica sol and only MPEG(2000) loaded silica sol separately) are demonstrated in the following diagram 1 and diagram 2.
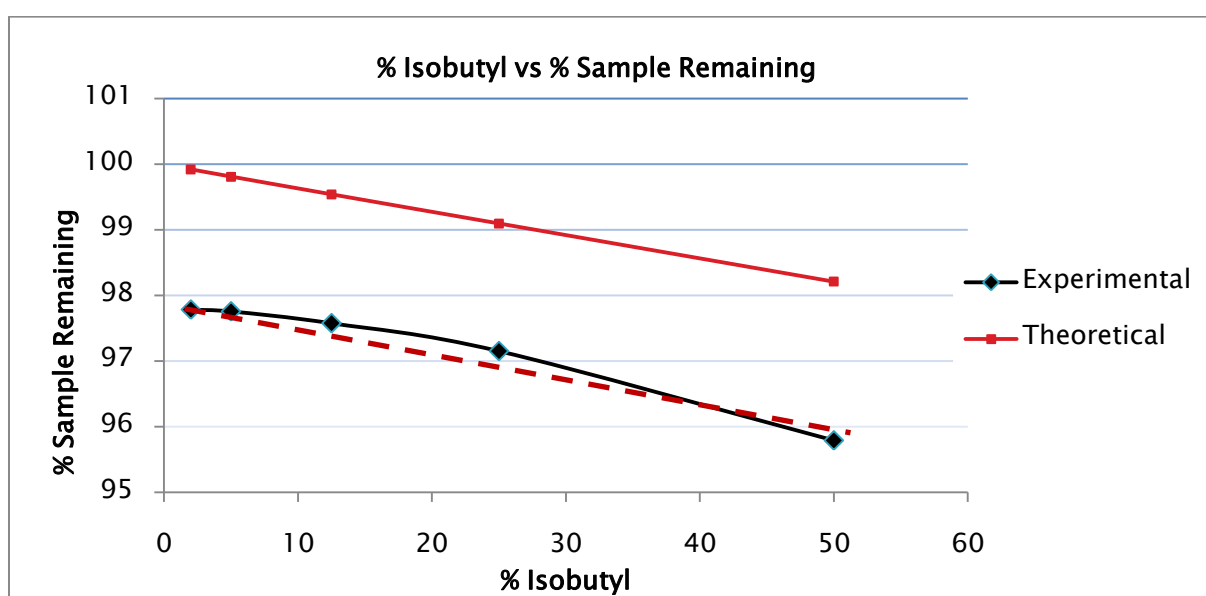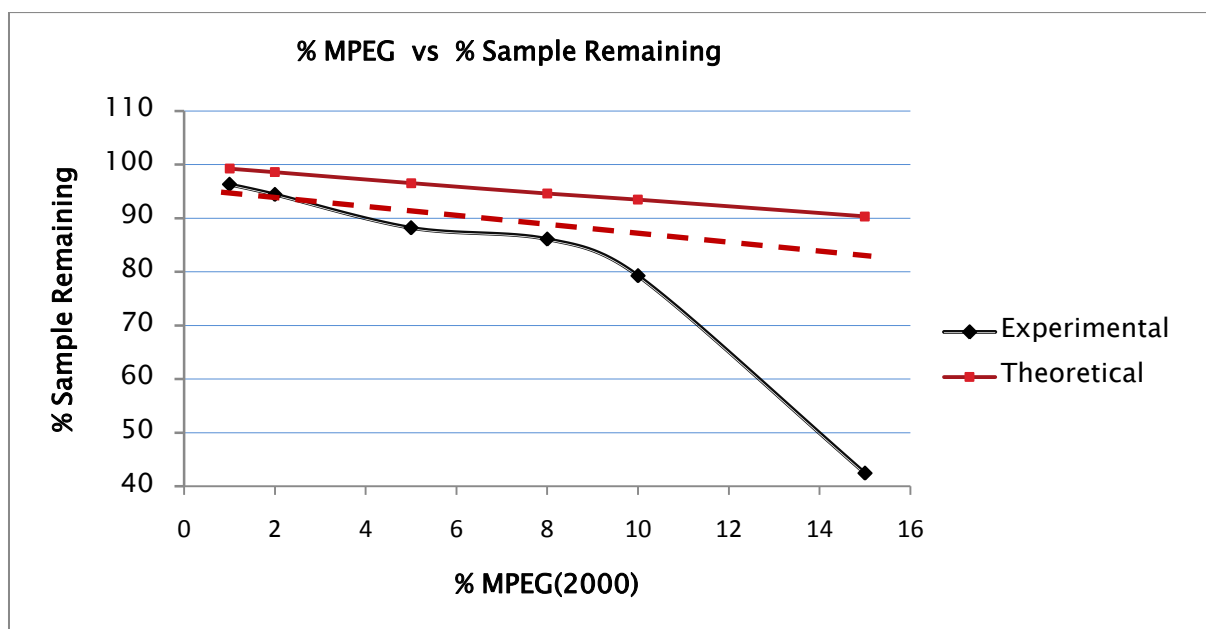

Diagram 1: *TGA graph of isobutyl modified silica sols*

In the diagram 1 even though both theoretical and experimental curves follow the same trend, there is almost 2% deviation of experimental curve with respect to theoretical one. This deviation is a consequence of water that bounded to silica surface.

Diagram 2: *TGA graph of MPEG(2000) modified silica sols*

Furthermore in the diagram 2, experimental curve for MPEG(2000) groups on silica surface start almost at the same point as theoretical curve but deviation from theoretical curve is more distinctive. This deviation is a consequence of the water up-taken by MPEG(2000).

TGA analysis was also done for samples which contain both hydrophilic and hydrophobic moieties. Results are illustrated in the table 6 below as % weight loss from silica surface.

Table 6: TGA results of some emulsifiers

Type of Silica Sols	Number of µmol of hydrophilic moieties/m^2	Number of µmol of hydrophobic moieties/m^2	Coverage of Silica Surface	% Weight Lost from Silica Surface
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 10% 3GTO-MPEG(2000)	6.55
Silica sol 8 µmol SiOH	3GTO-MPEG(2000) 0.8 µmol	Isobutyl 0.8 µmol	10% Isobutyl, 10% 3GTO-MPEG(2000)	5.82
Silica sol 8 µmol SiOH	3GTO-MPEG(550) 0.8 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 10% 3GTO-MPEG(550)	4.22
Silica sol 8 µmol SiOH	3GTO-MPEG(550) 0.4 µmol	Isobutyl 1 µmol	12.5% Isobutyl, 5.0% 3GTO-MPEG(550)	3.63
Silica sol 8 µmol SiOH	3GTO-MPEG(550) 0.8 µmol	Isobutyl 0.5 µmol	6.25% Isobutyl, 10% 3GTO-MPEG(550)	6.14

5.6   Efficiency Difference of Purification Methods

With the ultrafiltration, the method of silica sol filtration through a membrane with a cut-off at 100kDa was used. This method was believed not to be only more convenient and easy but also more efficient to get rid of the unreacted polymers from the modified silica surface. This statement was also proven by comparison of TGA results of same batch of non-purified silica sol, silica sols purified by centrifugation and silica sols purified by ultrafiltration. TGA results are indicated in the table 7.

According to table 7, since non-purified silica sols consist of large amount of unreacted polymer groups (MPEG(2000) in this case) % weight lost from silica surface is very large. Moreover, % weight lost is smallest in the case of ultrafiltration method. The reason for this is that unreacted polymer groups the most efficiently rinsed away from silica surface in the ultrafiltration method.

Table 7: *TGA results of some emulsifiers purified by different methods.*

Type of Silica Sols	Number of μmol of hydrophilic moieties/m^2	Number of μmol of hydrophobic moieties/m^2	Coverage of Silica Surface	% Weight Lost from Silica Surface	% Weight Remaining on Silica Surface
Silica sol 8 μmol SiOH non-purified	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 1 μmol	10% 3GTO-MPEG(2000), 12.5% Isobutyl	16.0045	83.9954
Silica sol 8 μmol SiOH purified by Centrifugation	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 1 μmol	10% 3GTO-MPEG(2000), 12.5% Isobutyl	6.5572	93.4427
Silica sol 8 μmol SiOH purified by Ultrafiltration	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 1 μmol	10% 3GTO-MPEG(2000), 12.5% Isobutyl	5.3271	94.6728

5.7 Surface Tension Measurements

Surface activity of amphiphilic silica is very important criteria to find out whether they are suitable emulsifiers. De Noüy ring method was used to measure surface tension of surface modified silica sol. Surface tension values of 10 wt% of surface modified silica sols in water at 25°C are given in table 8.

Table 8: *Surface tension values of 10 wt% silica sols at 25°C*

Type of Silica Sols	Number of μmol of hydrophilic moieties/m²	Number of μmol of hydrophobic moieties/m²	Coverage of Silica Surface	Concentration in Water	Temperature(°C)	Surface Tension value (mN/m)
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	35.00
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.6 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 7.5% 3GTO-MPEG(2000)	10 wt% SiO₂	25	30.40
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.4 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 5.0% 3GTO-MPEG(2000)	10 wt% SiO₂	25	36.34
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.2 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 2.5% 3GTO-MPEG(2000)	10 wt% SiO₂	25	38.45
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.08 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 1.0% 3GTO-MPEG(2000)	10 wt% SiO₂	25	38.00
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.8 μmol	10% Isobutyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	36.35
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.6 μmol	7.5% Isobutyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	36.92
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.4 μmol	5.0% Isobutyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	55.29
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.2 μmol	2.5% Isobutyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	62.58
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.08 μmol	1.0% Isobutyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	62.87
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isopropyl 1 μmol	12.5% Isopropyl, 10% 3GTO-MPEG(2000)	10 wt% SiO₂	25	47.95

The surface tension of non-modified silica sols are known as 72.8 mN/m which is a very close value to surface tension quantity of water (72.4 mN/m). This indicates that non-modified silica sols do not have a proper surface activity.

The amount of surface active silica sols in solution also has non-negligible effect on surface tension. In order to demonstrate this effect, surface tension of 5 wt% of surface modified silica sols in water solutions were measured at 25°C. As expected, decrease in amount of silica sols in water causes increase in surface tension values. Results are reported in the table 9.

Table 9: *Surface tension values of 5wt% silica sols at 25°C*

Type of Silica Sols	Number of μmol of hydrophilic moieties/m²	Number of μmol of hydrophobic moieties/m²	% Coverage of Silica Surface	Concentration in Water	Temperature(°C)	Surface Tension value (mN/m)
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO₂	25	39.08
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.6 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 7.5% 3GTO-MPEG(2000)	5 wt% SiO₂	25	52.78
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.4 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 5.0% 3GTO-MPEG(2000)	5 wt% SiO₂	25	51.71
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.2 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 2.5% 3GTO-MPEG(2000)	5 wt% SiO₂	25	59.53
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.08 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 1.0% 3GTO-MPEG(2000)	5 wt% SiO₂	25	62.49
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.8 μmol	10% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO₂	25	44.92
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.6 μmol	7.5% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO₂	25	46.61
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.4 μmol	5.0% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO₂	25	59.47

Type of Silica Sols	Number of μmol of hydrophilic moieties/m^2	Number of μmol of hydrophobic moieties/m^2	% Coverage of Silica Surface	Concentration in Water	Temperature(°C)	Surface Tension value (mN/m)
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.2 μmol	2.5% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	25	64.74
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.08 μmol	1.0% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	25	64.71
Silica sol 8 μmol SiOH	-	Isobutyl 1 μmol	12.5% Isobutyl	5 wt% SiO$_2$	25	53

The amount of hydrophilic and hydrophobic moieties on silica surface have critical role on the surface activity of amphiphilic silica. When the amount of hydrophilic groups on the silica surface increases and the amount of hydrophobic groups are constant, surface tension decreases and vice versa. This expected inverse proportion between surface tension and amount of organics on the silica surface demonstrates that hydrophilic and hydrophobic moieties that covalently bounded to silica surface make silica sols surface active. These correlations are more obviously seen in the diagram 3 and diagram 4.

5% wt Silica Surface
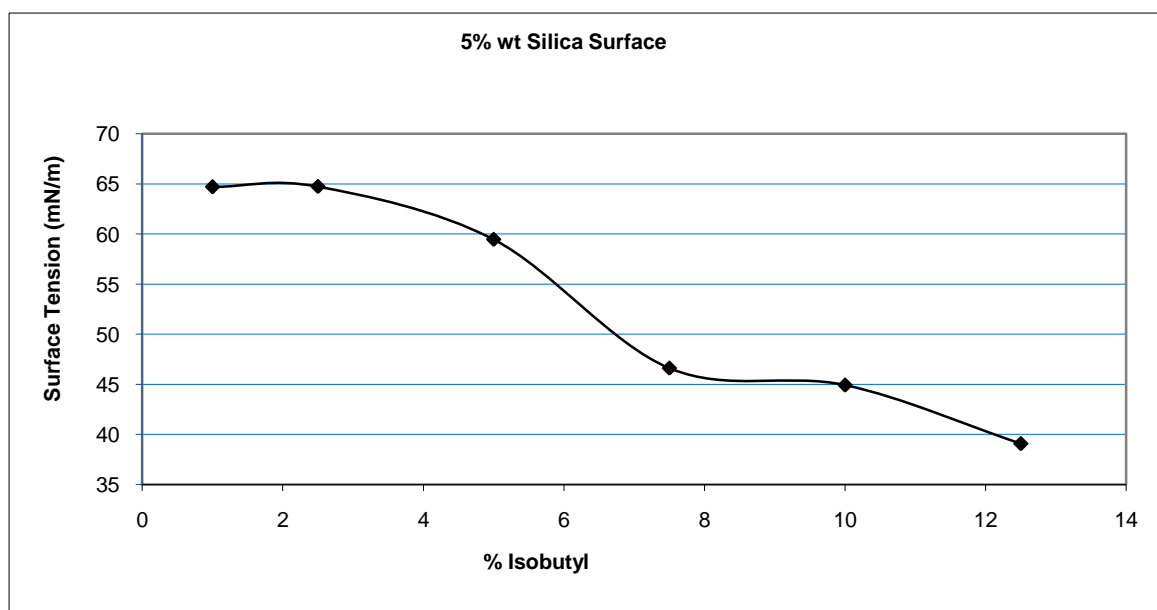
Diagram 3: *While the amount of hydrophilic 3GTO-MPEG(2000) is constant, surface tension decreases with increasing amounts of hydrophobic Isobutyl groups.*
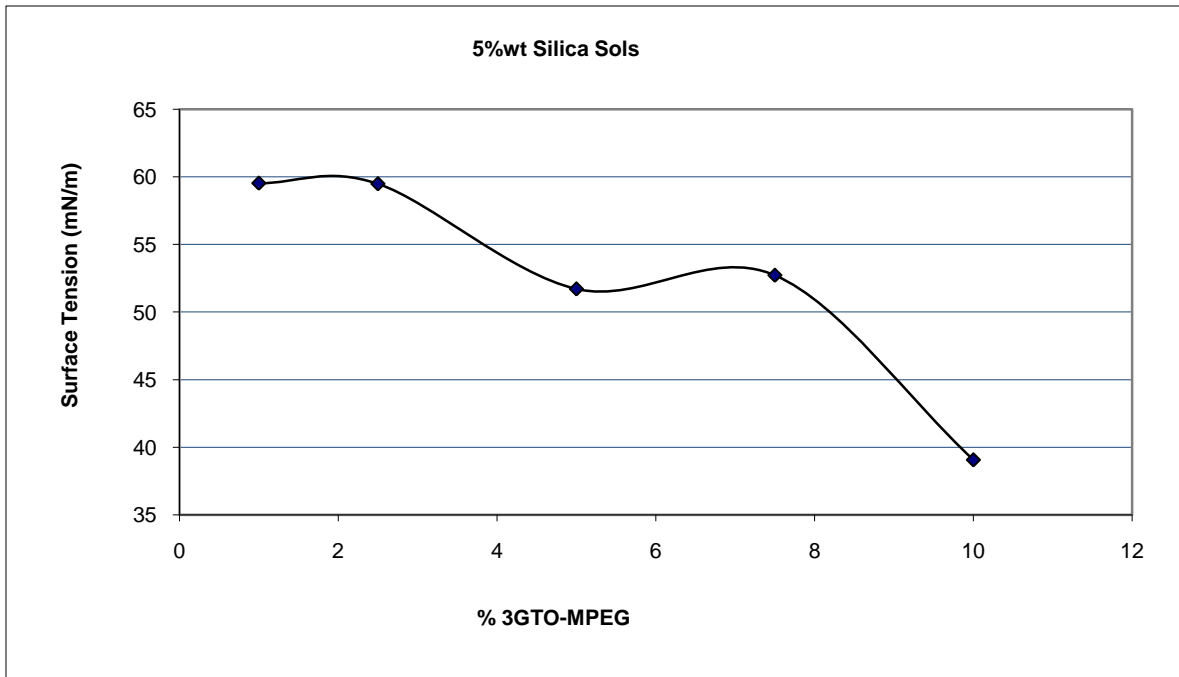
5%wt Silica Sols

Diagram 4: *While the amount of hydrophobic Isobutyl is constant, surface tension decreases with increasing amounts of hydrophilic 3GTO-MPEG(2000) groups.*

The role of temperature on surface activity of silica sols was clearly seen in the surface tension measurement curves. Because of the high surface dynamics at $25^{o}C$, there were lots of fluctuations through surface tension curve rather than any surface tension curve decreasing as straight line. Hence, surface tension measurements of same silica sols were done at $15^{o}C$. Even though surface tension curve decreased similarly to straight line, surface tension values increased due to decrease in surface activity of silica sols. Surface tension values at $15^{o}C$ are indicated in the table 10.

Table 10: *Surface tension values of 5wt% silica sols at 15°C*

Type of Silica Sols	Number of μmol of hydrophilic moieties/m²	Number of μmol of hydrophobic moieties/m²	Coverage of Silica Surface	Concentration in Water	Temperature(°C)	Surface Tension value (mN/m)
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	56.01
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.6 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 7.5% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	61.84
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.4 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 5.0% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	60.23
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.2 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 2.5% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	64.01
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.08 μmol	Isobutyl 1 μmol	12.5% Isobutyl, 1.0% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	66.15
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.8 μmol	10% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	48.38
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.6 μmol	7.5% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	58.02
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.4 μmol	5.0% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	63.39
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.2 μmol	2.5% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	63.04
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isobutyl 0.08 μmol	1.0% Isobutyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	65.64
Silica sol 8 μmol SiOH	3GTO-MPEG(2000) 0.8 μmol	Isopropyl 1 μmol	12.5% Isopropyl, 10% 3GTO-MPEG(2000)	5 wt% SiO$_2$	15	59.64

Surface tension of 3GTO at a concentration of 30 mmol/L was determined as 47.39 mN/m at 25°C and 53.95 mN/m at 15°C, these results show that 3GTO-MPEG has proper surface activity and temperature has effect on the surface activity of 3GTO-MPEG.

After the ultrafiltration of silica sols which contains 12.5% hydrophobic isobutyl and 10% of hydrophilic 3GTO-MPEG(2000), surface tension of this fifth supernatant was measured as 43.65 mN/m. This means that unreacted molecules were rinsed away through purification. The surface tension of even the fifth supernatant was very low so it can be deduced that after the purification it is possible for unreacted molecules to still be present in silica sols. Nevertheless it is admitted that small amount of surface active molecules can depress the surface tension efficiently.

5.8   Visual Observations of Surface Modified Silica Sols

It can be stated that modification of silica surface with 3GTO neither has any effects on appearance of silica sols nor colloidal behavior of silica sols. On the other hand, isobutyl(trimethoxy)silane modification causes an increase in viscosity similar to propyl(trimethoxy)silane. Therefore it can be noticed that hydrophobic molecules used in this study for modification of silica surface change the colloidal characteristics of silica sols.

Silica surface modification with hydrophilic 3GTO-MPEG induces gel sedimentation of particles and formation of turbid liquid. It can be taken into consideration that SiO_2 particles in silica sols have 34.3 wt% causing proximity of high concentration silica particles to one another. Also 3GTO-MPEG is a long polymer group known to interact strongly with silica surface resulting in a bridge flocculation leading to sedimentation. [23]

Purification plays an important role in the colloidal behavior and appearance of particles. When there is an increase in unreacted groups that are rinsed away from the silica sols, the amount of silica particles dispersed in water increases as well. Especially purified silica sols, which are well dispersed in a tube, keep its colloidal behavior for longer period of time than same sample which is not purified. The higher the amount of hydrophilic and hydrophobic moieties on silica surface, the longer the colloidal stability.

5.9 Emulsion Tests

Amphiphilic silica sols were used as emulsifiers to stabilize emulsion prepared with oil and water. Since unreacted groups have effects on the stability of emulsions, purification of emulsifiers before use is a critical step for the reliability of the emulsion tests.

Aliphatic dodecane and polar aromatic toluene were used as oil phases. Both proportions of 70 wt% of oil - 30 wt% of water and 70 wt% of water - 30 wt% of oil were used. Only surface modified silica sols were used as emulsifier and stabilizer, in order to evaluate their performances.

As indicated in table 11, only linker 3GTO modified silica surface does not have a proper emulsifying effect.

Table 11: Emulsification results of 3GTO modified silica sols

Amount of Organics on Silica Surface	Type of Oil	Water Phase	Time of Mixing (min)	Results
25% 3GTO	Dodecane (70 wt%)	30 wt%	5	Not Fine Emulsion
25% 3GTO	Toluene (70 wt%)	30 wt%	5	Not Fine Emulsion

"Fine Emulsion refers that emulsion was obtained''
"Not Fine Emulsion refers that emulsion was not obtained"

The results of emulsification tests which were performed for all emulsifiers containing hydrophilic 3GTO-MPEG(2000) and hydrophobic isobutyl, are represented in table 12. Here, the role of hydrophilic 3GTO-MPEG(2000) and hydrophobic Isobutyl groups on emulsifying can clearly be seen. All Silica sols modified with different percentages of these groups achieved to form fine emulsion when 70 wt% oil (both toluene and dodecane) and 30 wt% water proportions were used.

Table 12: Results of emulsification using different oil and different quantity of silica sols.

Amount of silica sols	Coverage by Hydrophobic Molecules	Coverage by Hydrophilic Molecules	Time of Mixing (min)	Oil phase (wt%)	Water phase (wt%)	Results
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	7.5% 3GTO-MPEG(2000)	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	7.5% 3GTO-MPEG(2000)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	7.5% 3GTO-MPEG(2000)	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	7.5% 3GTO-MPEG(2000)	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	5.0% 3GTO-MPEG(2000)	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	5.0% 3GTO-MPEG(2000)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	5.0% 3GTO-MPEG(2000)	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	5.0% 3GTO-MPEG(2000)	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	2.5% 3GTO-MPEG(2000)	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	2.5% 3GTO-MPEG(2000)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	2.5% 3GTO-MPEG(2000)	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	2.5% 3GTO-MPEG(2000)	5	Dodecane (30)	70	Not good emulsion

Amount of silica sols	Coverage by Hydrophobic Molecules	Coverage by Hydrophilic Molecules	Time of Mixing (min)	Oil phase (wt%)	Water phase (wt%)	Results
0.5 wt% of Oil phase	**12.5% Isobutyl**	1.0% 3GTO-MPEG(2000)	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	**12.5% Isobutyl**	1.0% 3GTO-MPEG(2000)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	**12.5% Isobutyl**	1.0% 3GTO-MPEG(2000)	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	**12.5% Isobutyl**	1.0% 3GTO-MPEG(2000)	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	10% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	10% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	10% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	10% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	7.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	7.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	7.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	7.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	5.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	5.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	5.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	5.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (30)	70	Not good emulsion

| Amount of silica sols	Coverage by Hydrophobic Molecules	Coverage by Hydrophilic Molecules	Time of Mixing (min)	Oil phase (wt%)	Water phase (wt%)	Results
0.5 wt% of Oil phase	2.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	2.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	2.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	2.5% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	1.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	1.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	1.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Toluene (30)	70	Not good emulsion
0.5 wt% of Oil phase	1.0% Isobutyl	**10% 3GTO-MPEG(2000)**	5	Dodecane (30)	70	Not good emulsion

Also all silica sols modified with different percentage of 3GTO-MPEG(550) and isobutyl gave fine emulsion only when the 70 wt% dodecane and 30 wt% water used. Results of emulsification tests are given in table 13.

Table 13: Results of emulsification using different oil and different quantity of silica sols.

Amount of silica sols	% of hydrophobic part on surface	% of hyrophilic part on surface	Time of Mixing (min)	Oil phase (wt%)	Water phase (wt%)	Results
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(550)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(550)	5	Toluene (70)	30	Not good emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	5% 3GTO-MPEG(550)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isobutyl	5% 3GTO-MPEG(550)	5	Toluene (70)	30	Not good emulsion
0.5 wt% of Oil phase	6.25% Isobutyl	10% 3GTO-MPEG(550)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	6.25% Isobutyl	10% 3GTO-MPEG(550)	5	Toluene (70)	30	Not good emulsion

The nature of the hydrophobic group on silica surface was changed to propyl(trimethoxy)silane (12.5%) while hydrophilic group was still 10% 3GTO-MPEG(2000). As illustrated in the table 14, similar results as for isobutyl were obtained with isopropyl modifiers.

Table 14: Results of emulsification using Isopropyl as hydrophobic group

Amount of silica sols	% of hydrophobic part on surface	% of hyrophilic part on surface	Time of Mixing (min)	Oil phase (wt%)	Water phase (wt%)	Results
0.5 wt% of Oil phase	12.5% Isopropyl	10% 3GTO-MPEG(2000)	5	Dodecane (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isopropyl	10% 3GTO-MPEG(2000)	5	Toluene (70)	30	Fine Emulsion
0.5 wt% of Oil phase	12.5% Isopropyl	10% 3GTO-MPEG(2000)	5	Dodecane (30)	70	Not good emulsion
0.5 wt% of Oil phase	12.5% Isopropyl	10% 3GTO-MPEG(2000)	5	Toluene (30)	70	Not good emulsion

It must be noted that when the tube was moved up and down during the emulsification test to reach convenient stirring, the result was a fine emulsion for both dodecane and toluene oils and each of them includes very small amount of oil to be measured. On the other hand, as the probe of mixer was fixed at a constant height from the bottom of the tube, toluene seems to give better emulsions than dodecane. For the emulsions with oil on the top of the tube, the amount of non-emulsified oil was less for toluene than for dodecane.

5.10 Texture of the Emulsions

In emulsion technology, particularly from an industrial point of view, and since different types of emulsions, (oil in water (O/W) or water in oil (W/O)) are used to prepare different types of products, determination of emulsion types is essential. In this work, basically two strategies were used to investigate the nature of emulsions:

- ✓ Red dye dissolved in dodecane and toluene oils. Then emulsions with prepared by red stained oil and water.
- ✓ Methylene blue dissolved in water. Then emulsions were prepared by blue stained water and oil.

The emulsions are described in table 15. The prepared emulsions were monitored by light microscope. In all cases, oil was the dispersed phase while water was the continuous phase.

Table 15: Descriptions of emulsions pictures

Amount of silica sols	Coverage by Hydrophobic Molecules	Coverage by Hydrophilic Molecules	Time of Mixing (min)	Dispersed Oil phase (wt%)	Continious Water phase	Picture nᵒ
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (70) red color	30 wt%	1
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (70) red color	30 wt%	2
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (70)	30 wt% blue color	3
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (70)	30 wt% blue color	4

Amount of silica sols	% Coverage by Hydrophobic Molecules	% Coverage by Hydrophilic Molecules	Time of Mixing (min)	Dispersed Oil phase (wt%)	Continious Water phase	Picture n°
0.5 wt% of Oil phase	10% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (70) red color	30 wt%	5
0.5 wt% of Oil phase	10% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (70) red color	30 wt%	6
0.5 wt% of Oil phase	10% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (70)	30 wt% blue color	7
0.5 wt% of Oil phase	10% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (70)	30 wt% blue color	8
0.5 wt% of Oil phase	12.5% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (30) red color	70 wt%	9
0.5 wt% of Oil phase	5.0% Isobutyl	10% 3GTO-MPEG(2000)	5	Toluene (30)	70 wt% blue color	10
0.5 wt% of Oil phase	5.0% Isobutyl	10% 3GTO-MPEG(2000)	5	Dodecane (30) red color	70 wt%	11
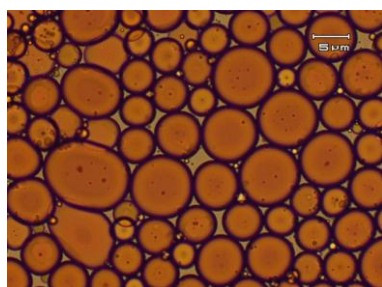
1
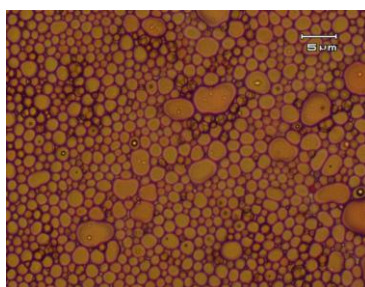
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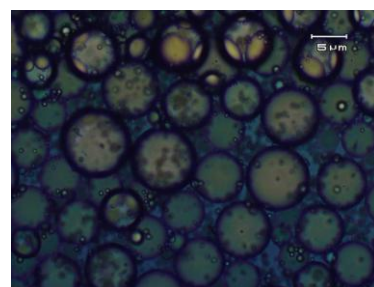
3
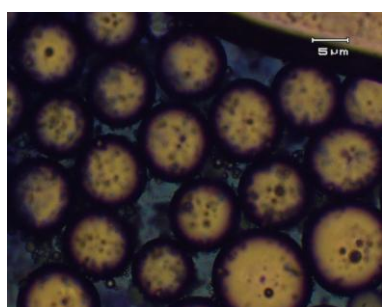
4
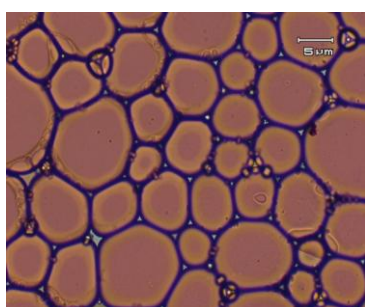
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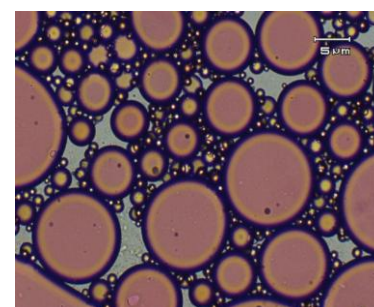
6
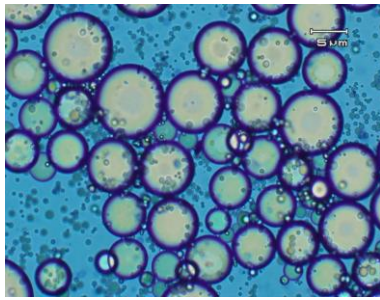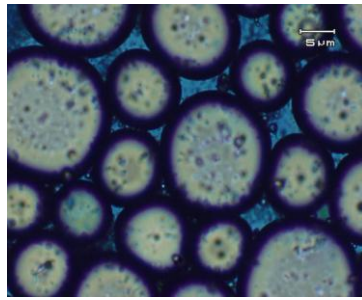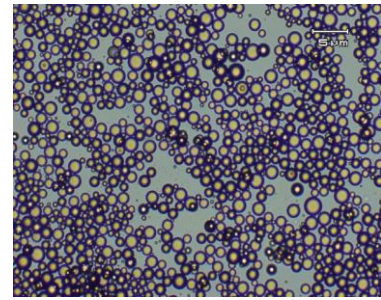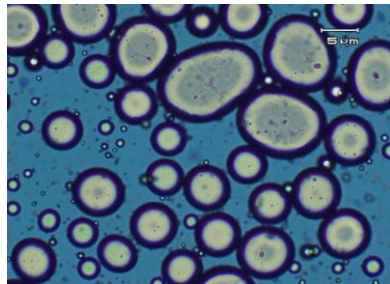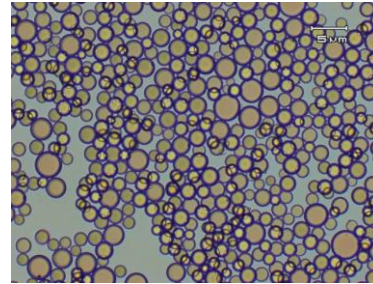
| 7 | 8 | 9 |

| 10 | 11 |

In the emulsified systems, an old and totally qualitative method namely Bancroft's rule is mainly used for prediction of what type of emulsion is formed. According to this concept, water miscible emulsifiers lead to formation of O/W emulsions and oil miscible emulsifiers w/o emulsions. If an explanation is made based on the Bancroft's rule for emulsions in this study, it can be stated that surface modified silica sols is soluble in water and because of this reason emulsions are O/W emulsions. However there are such factors as electrolyte concentration in water, oil polarity and water-to-oil ratio that may affect the emulsion type. [24]

5.11 Size Distribution Graphs of Emulsion Droplets

In an emulsion, the droplet size is important to achieve a stable dispersion.

- ✓ The smaller the droplet size, the slower the droplet moves. So it is important to make droplet small to increase stability. [6]
- ✓ For particle stabilized emulsions, particle size must be much smaller than the droplet size. [14]

In this work, the emulsion droplet size was resulting from the processing of images from the optical microscopy. The size distributions graphs correspond to the pictures above. In the graphs it can clearly be seen that the second condition is already fulfilled by all emulsions because size scale of emulsion droplets started at μm level whereas particle size is 25nm. In all cases droplets of emulsions are polydisperse. All of them include both very small droplets in the size range ≤10μm and large droplets in the size range of hundreds μm. Nevertheless this size may lead to a weak stability. This is why the stability of emulsions was also investigated.
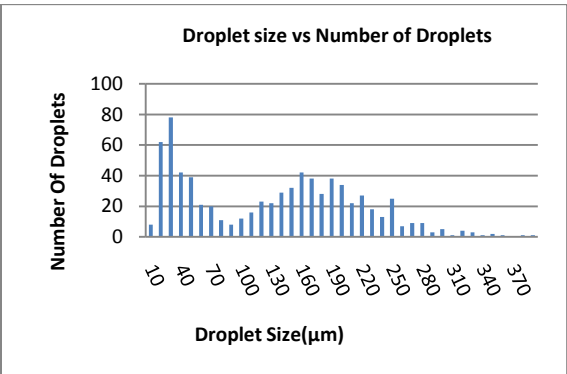
The graph corresponding to the emulsion in Picture 1
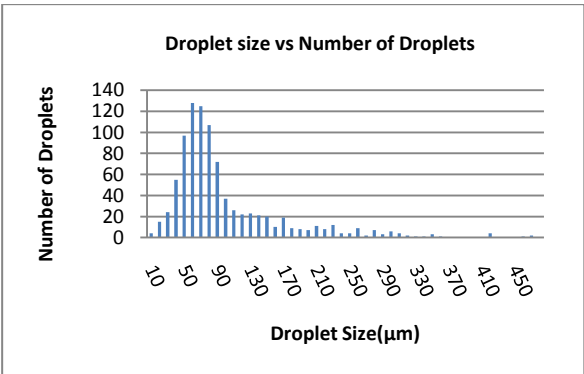
The graph corresponding to the emulsion in Picture 2
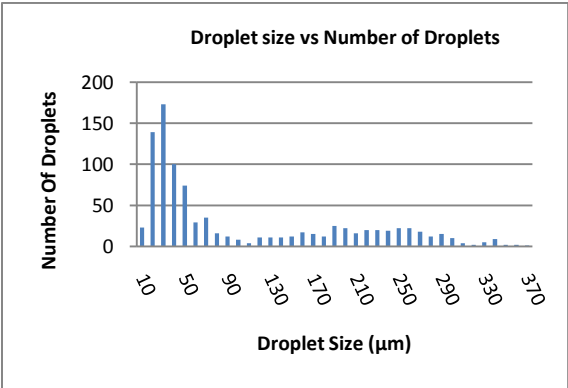
The graph corresponding to the emulsion in Picture 3
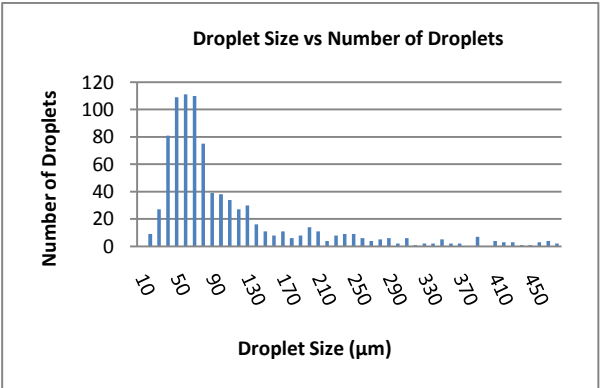
The graph corresponding to the emulsion in Picture 4
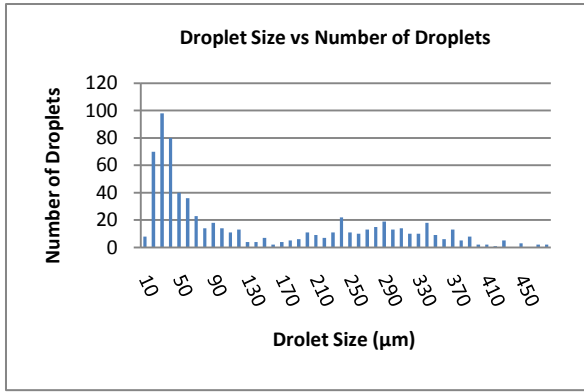
The graph corresponding to the emulsion in Picture 5
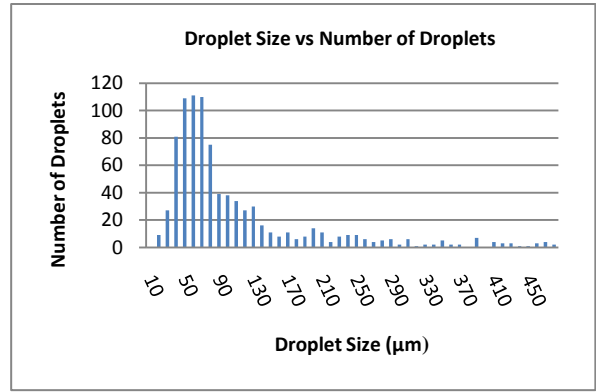
The graph corresponding to the emulsion in Picture 6
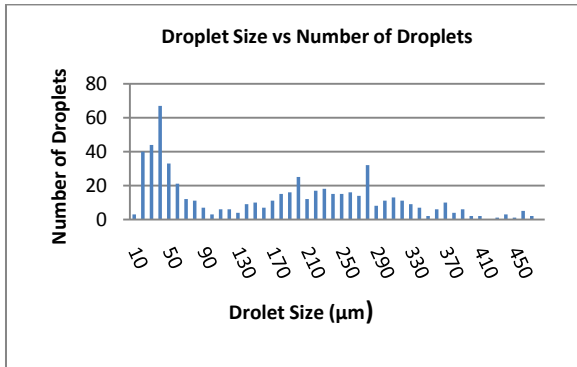
The graph corresponding to the emulsion in Picture 7
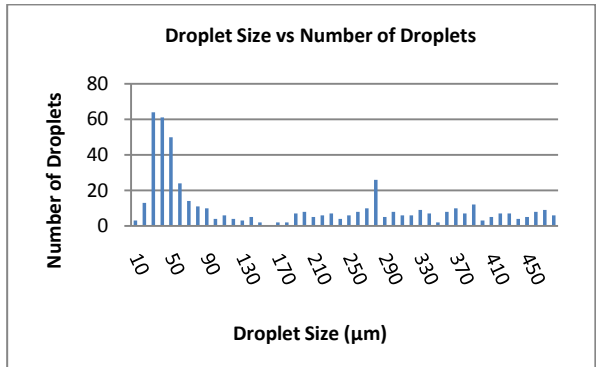
The graph corresponding to the emulsion in Picture 8
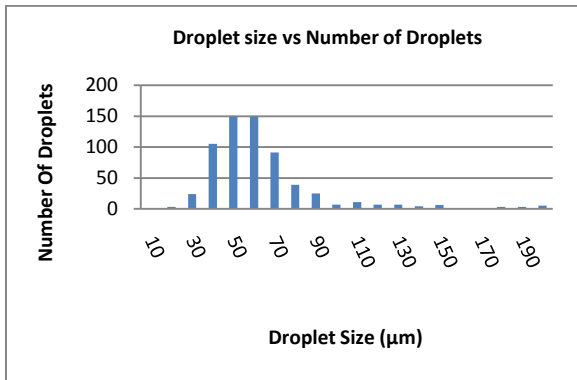
The graph corresponding to the emulsion in Picture 9
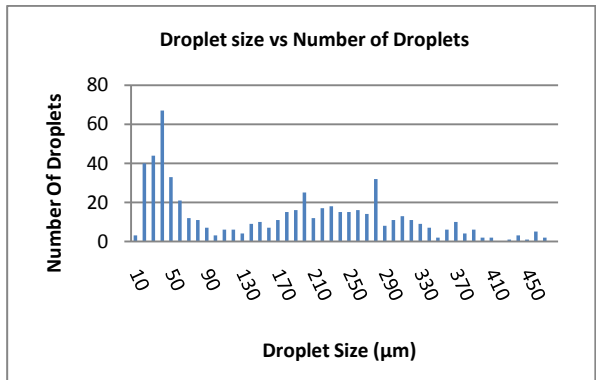
The graph corresponding to the emulsion in Picture 10
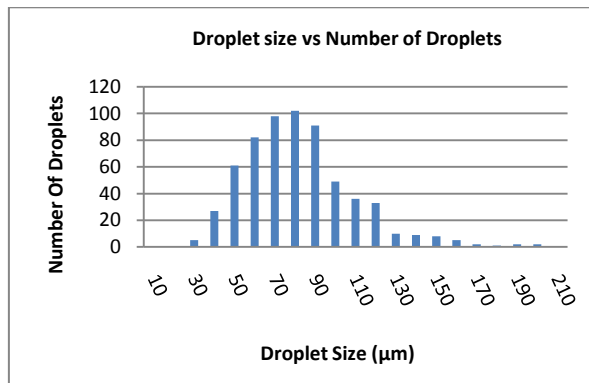
The graph corresponding to the emulsion in Picture 11

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5.12 Effect of the Nature of the Emulsifiers on Stability of Emulsion

The phase separation of emulsions with respect to time is an important factor to evaluate the effect of hydrophilic and hydrophobic moieties on the stability of the emulsions. In order to understand this effect, the measurement of the amount of water separated was evaluated. Observations at different times are reported for each emulsifier as a function of % total separation of water vs. time (minutes).

The study of phase separation was not carried out for the silica sol solely covered with 12.5% isobutyl because no proper emulsion was obtained. This results that hydrophilic MPEG group is important factor for the emulsion stability.

Effects of hydrophilic 3GTO-MPEG(2000) on stability of emulsions were evaluated. Therefore, silica surface was modified with different amounts of hydrophilic moieties whereas amount hydrophobic Isobutyl groups on silica surface were constant. Descriptions of surface modified silica sols are indicated table 16.

Table 16: Description of Surface Modified Silica Sols

Emulsifier code	Coverage by 3GTO-MPEG(2000)	Coverage by Isobutyl	MPEG/Isobutyl
EA 25	10%	12.5%	0.8
EA 15	7.5%	12.5%	0.6
EA16	5.0%	12.5%	0.4
EA 17	2.5%	12.5%	0.2
EA 18	1.0%	12.5%	0.08

Percentage phase separation of emulsions which were prepared with 70 wt% toluene and 30 wt% water represent that the most stable emulsion was given by emulsifier EA18 while emulsifier EA25 gave the least stable emulsion. In addition, there is an inverse correlation

between the amount of hydrophilic moieties and stability of emulsion with respect to time. This correlation is indicated in diagram 5.
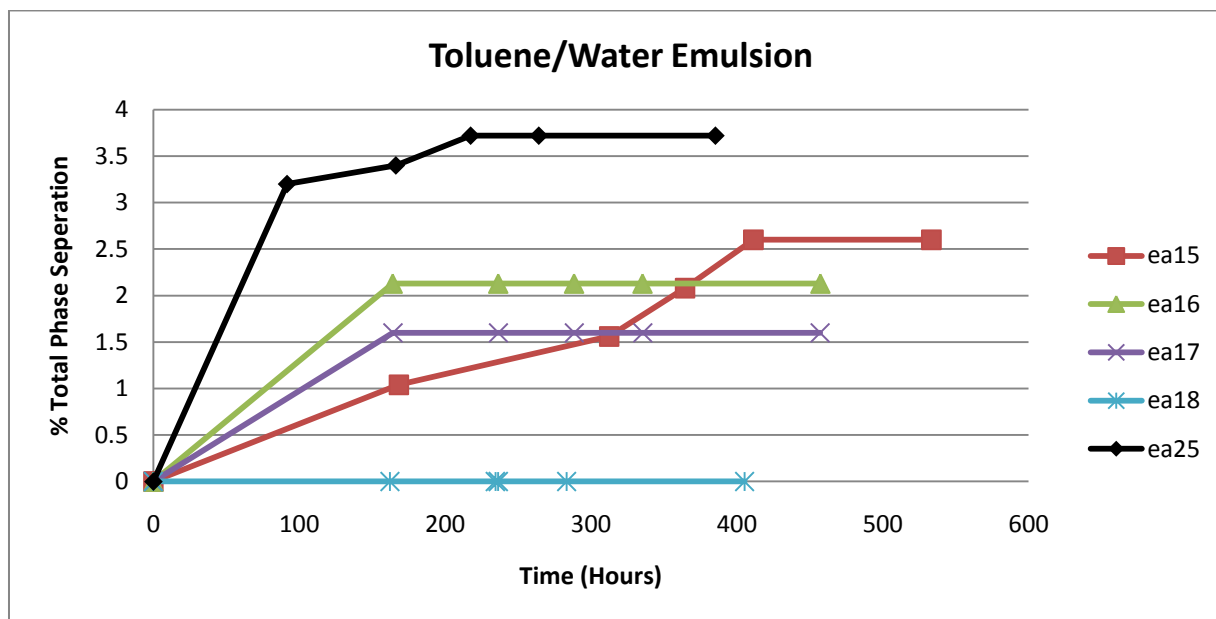

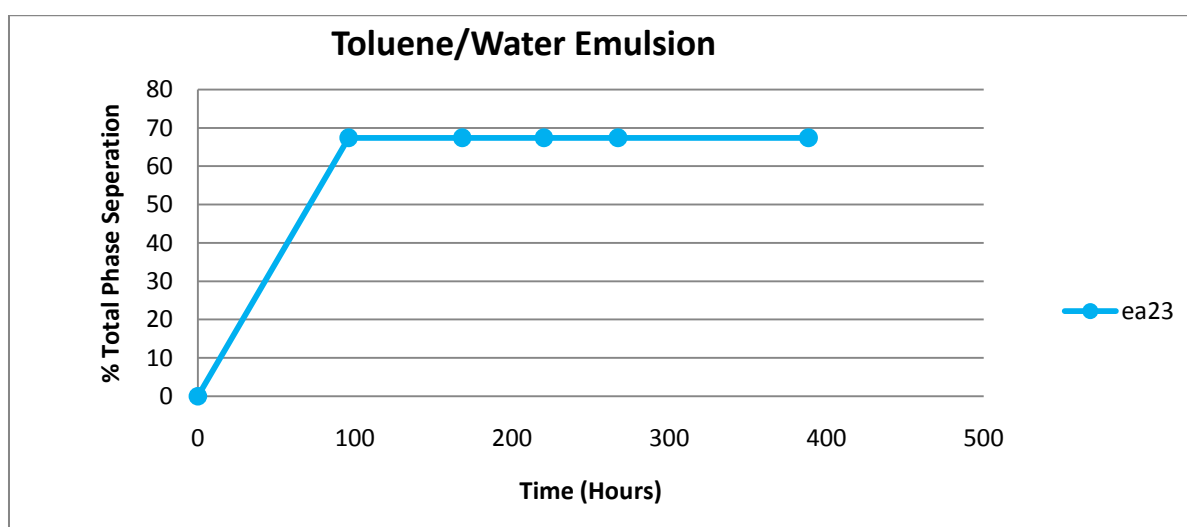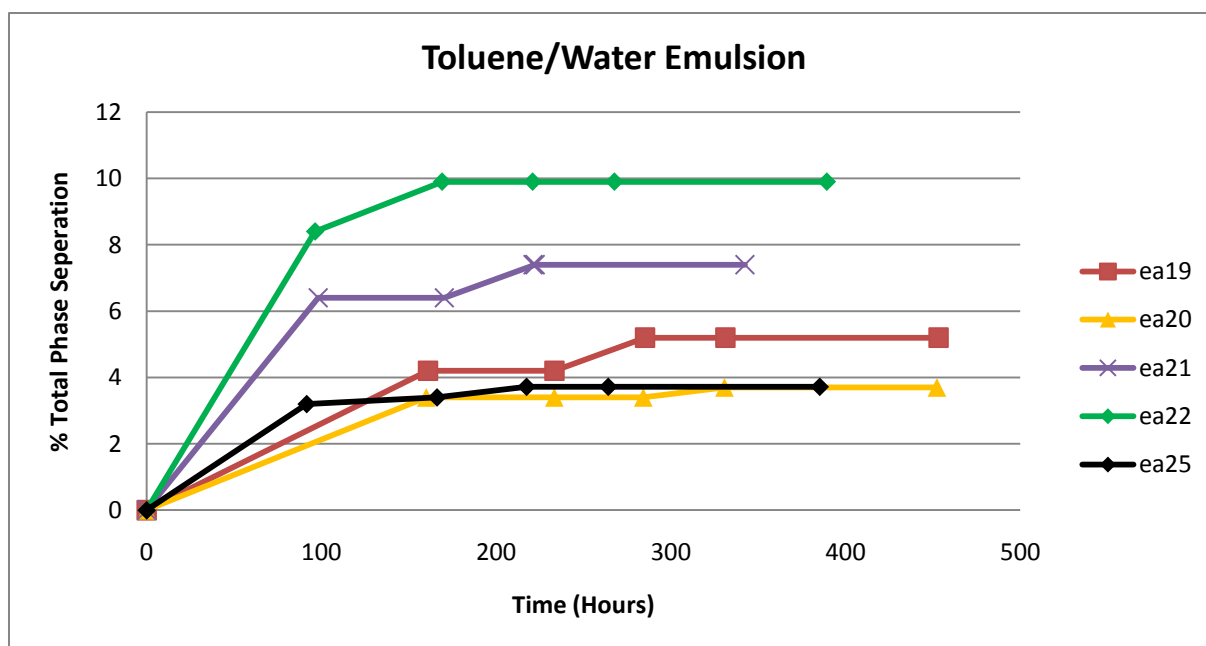*Diagram 5: Time vs. % Total Phase Separations*

As aforementioned, silica sol solely modified with hydrophobic isobutyl group does not have emulsifier effect. Therefore, silica surface has to be modified both with hydrophilic MPEG and hydrophobic isobutyl groups. In addition, diagram 5 indicates that ratio between MPEG and isobutyl is important for the emulsifier with good performance. MPEG/Isobutyl ratio has to be in favor of isobutyl.

Effects of hydrophobic Isobutyl on stability of emulsions were also studied. Silica surface was modified with constant amounts of hydrophilic moieties whereas the amounts of hydrophobic isobutyl groups on silica surface were changed. Table 17 represents the characteristics of silica sols.

Table 17 Descriptions of surface modified silica sols

Emulsifier code	Coverage by 3GTO-MPEG(2000)	Coverage by Isobutyl	MPEG/Isobutyl
EA 25	10%	12.5%	0.8
EA 19	10%	10%	1.0
EA 20	10%	7.5%	1.3
EA 21	10%	5.0%	2
EA 22	10%	2.5%	4
EA 23	10%	1.0%	10

Stabilization effects of emulsifiers on emulsions which were prepared by 70 wt% of toluene and 30 wt% of water were observed. It can be noticed that emulsifier EA23 containing the smallest amount of hydrophobic groups provided the least stable emulsion whereas emulsifiers EA19 and EA20 which include the highest amount of hydrophobic moieties provided the most stable emulsion. Therefore, there is a direct relation between the amount of hydrophobic moieties and stability of emulsion. This relation is demonstrated in the diagram 6 and diagram 7.

Diagram 6: Time vs. % Total Phase Separations

Diagram 7: Time vs. % Total Phase Separations

Diagram 6 and diagram 7 state parallel results with diagram 5. The ratio between MPEG and isobutyl is very important and it has to be in favor of isobutyl.

One possible reason can be asserted for the direct relation between the amount of hydrophobic moieties and stability of emulsion is as follows; the more amount of hydrophobic group on silica surface, the higher the amphiphilic characteristic of silica sols. That is why the silica sol becomes more convenient emulsifier hence making the emulsion less prone to phase separate.

Stability effects of emulsifiers indicated in table 16 were also observed for different type of oil phase. In this case, 70 wt% of dodecane and 30 wt% of water were used for each emulsion. It is important to note that the largest phase separation occurred with emulsifiers EA25 and EA15. On the contrary, no phase separation was observed in emulsifiers of EA17 and EA18. It can be again stated that the ratio between MPEG and isobutyl is very important and it has to be in favor of isobutyl. This relation is represented in diagram 8.
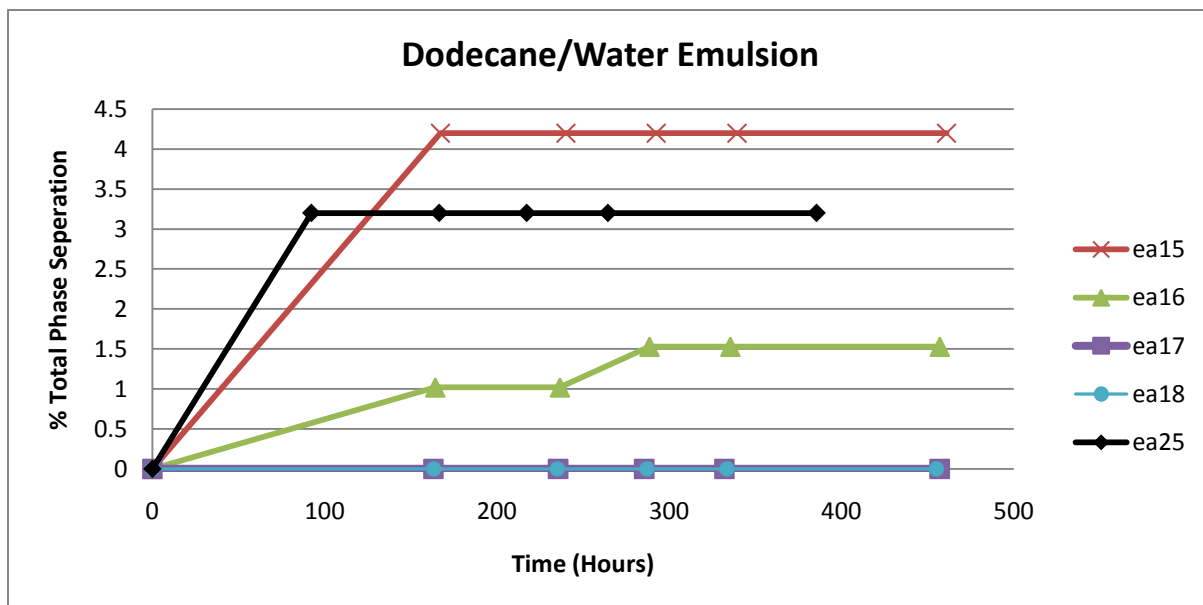
Diagram 8: Time vs. % Total Phase Separations

The stability of the emulsions prepared with the products in table 17 was tested with dodecane as well. It is observed that both dodecane and toluene follow almost the same trends for these emulsifiers. So, the more hydrophobic moieties on the silica surface, the smaller ratio between MPEG and isobutyl is obtained. This ratio is in favor of isobutyl and provides more stable emulsions. Diagram 9 illustrates this.
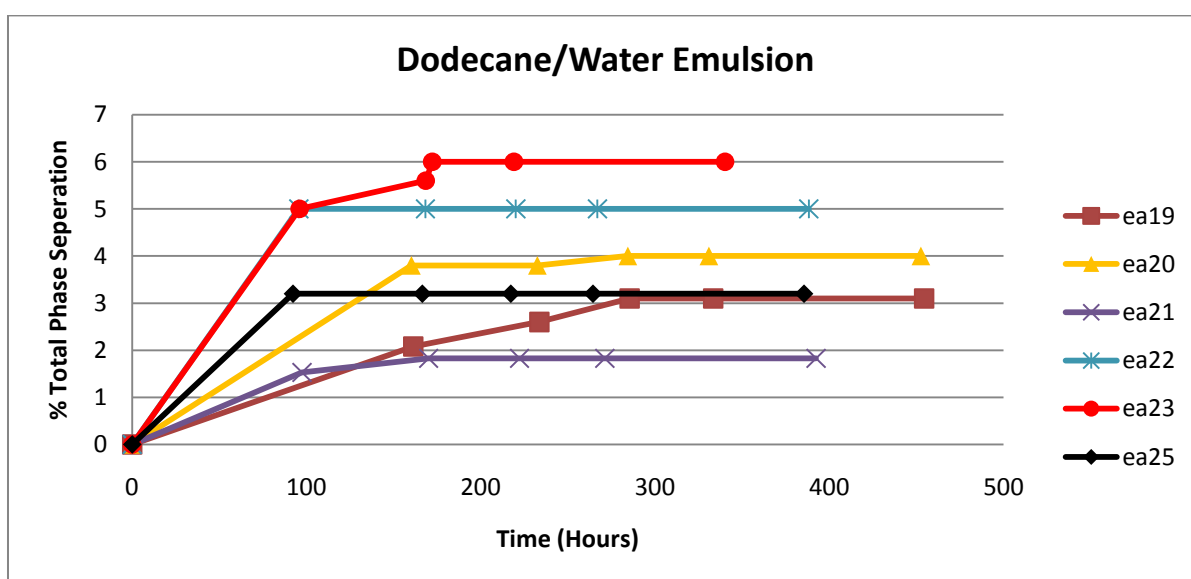

Diagram 9: Time vs. % Total Phase Separations

Type of hydrophobic groups on the silica surface has non-negligible effect on the stability of the emulsion. In order to see this effect, the silica surface is modified with propyl(trimethoxy)silane (12.5% of silica surface) as a hydrophobic group rather than isobutyl(trimethoxy)silane (12.5% of silica surface). However, amount of 3GTO-MPEG(2000) was kept constant (10% of silica surface). It was noticed that stability of emulsion prepared with emulsifier containing isobutyl(trimethoxy)silane provided better stability than emulsifier containing propyl(trimethoxy)silane, as seen in diagram 9 and diagram 10 for toluene and dodecane respectively.
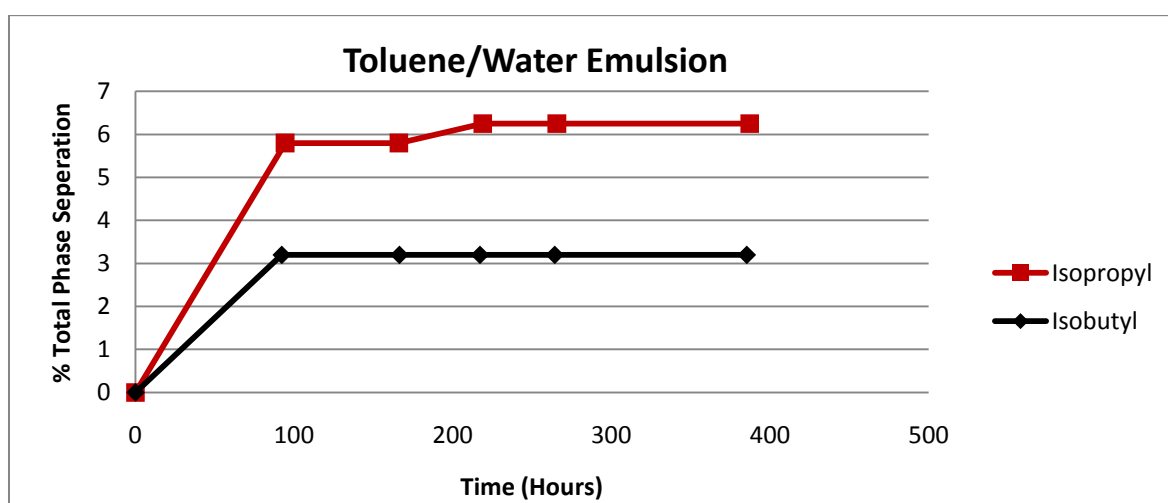
Diagram 9: Toluene/Water Emulsion
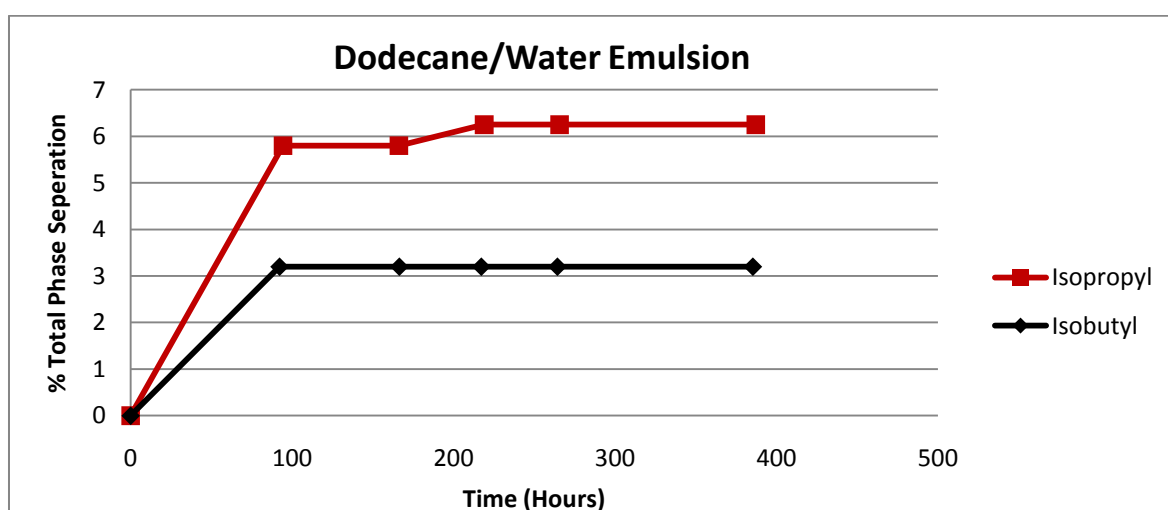
Diagram 10: Dodecane/Water Emulsion

The reason why isobutyl provided better emulsion than isopropyl is that isobutyl could possibly possess more hydrophobic character than isopropyl.

On the other hand, the effect of hydrophilic moieties on the stability of the emulsion was also observed by changing the type of hydrophilic groups. Surface of silica was modified by 3GTO-MPEG(550) (10% of silica surface) instead of 3GTO-MPEG(2000) (10% of silica surface) while amount of isobutyl was kept constant (12.5% of silica surface). Related results are given in diagram 11 for dodecane and toluene. The graphs clearly indicate that the emulsion containing dodecane has better stability with 3GTO-MPEG(550).
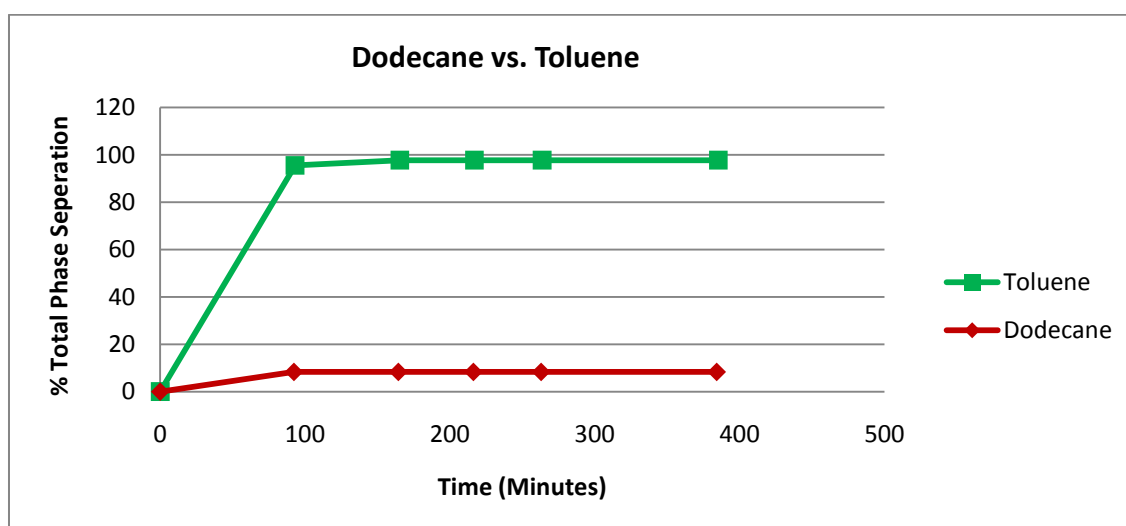
Diagram 11: Efficiency difference of MPEG(550) for Dodecane and Toluene

The consequence of dodecane providing better emulsion than toluene is that PEG pending groups are partly soluble in toluene. This can affect the surface character of emulsifier.

The comparison of hydrophilic 3GTO-MPEG(2000) and 3GTO-MPEG(550) are made in order to understand which one is better stability effect on emulsion. Two silica based emulsifiers, in which one of them includes 3GTO-MPEG(2000) (10% of surface coverage) and another consists of 3GTO-MPEG(550). Nevertheless, both of them include constant amount of isobutyl (12.5% silica surface). Stability of these emulsifiers is given in diagram 12.
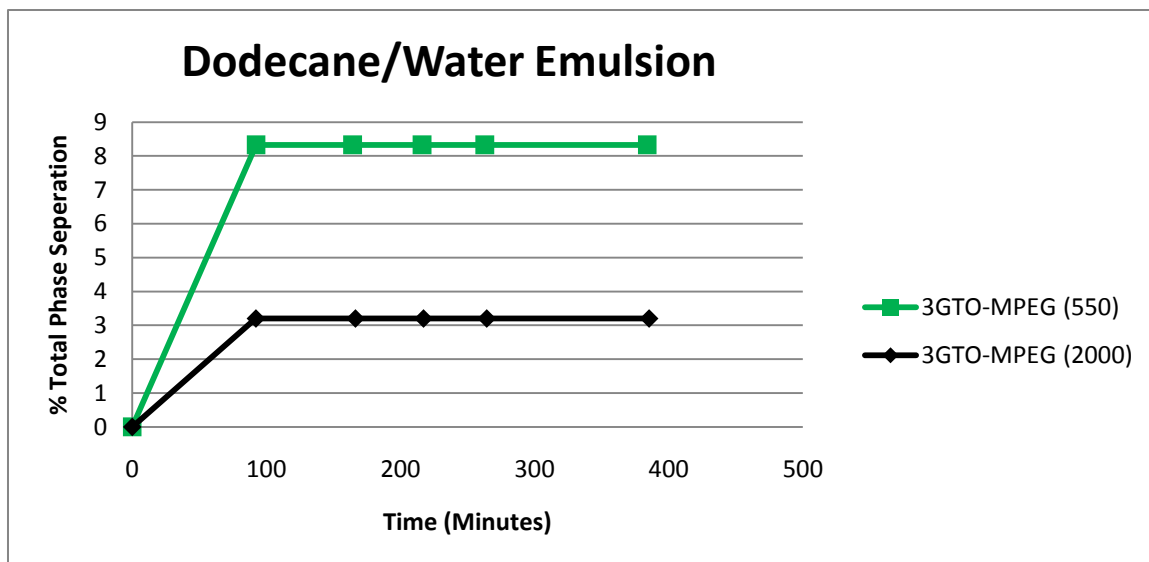
Diagram 12: 3GTO-MPEG(2000) vs. 3GTO-MPEG(550)

According to graphs 3GTO-MPEG(2000) provides better stability. The reason for this could be the fact that 3GTO-MPEG(2000) has longer polymer chain than 3GTO-MPEG(550). Therefore it could have better steric stabilization effect.

6 CONCLUSION

The investigation of surface modified colloidal silica particles by hydrophobic and hydrophilic groups was carried out. Afterwards, surface grafted silica sols were used as emulsifiers to prepare the oil-water emulsion system.

The synthesis of hydrophilic modifiers was implemented through linking of hydrophilic moieties to 3GTO. Since 3GTO possesses silyl ether group, it is possible to link hydrophilic 3GTO-MPEG group to silica surface through reaction between the silyl ether and the silanol groups.

The possibility of silica surface grafting was proven by TGA analysis for each hydrophilic and hydrophobic group separately. Besides, TGA analyses were carried out for silica sols possessing different proportion of both hydrophilic and hydrophobic moieties. Furthermore, TGA also indicates that purification by ultrafiltration has to be preferred.

Surface tension measurements were performed after purification of surface modified silica sols to understand their physicochemical properties. Surface active characters of modified silica sols were proven by du Noüy ring method and the best surface activity was obtained when the silica sols were both hydrophobically and hydrophilically modified.

The emulsification performances of the surface modified silica sols were evaluated. Pickering emulsion systems were prepared for different proportions of oil and water phases. Weight of surface modified silica sols were always kept as 0.5 wt% of oil phases and time of mixing was kept as 5(min.) for each emulsion tests. Following results were obtained.

➢ To be efficient the silica sols have to be hydrophobically and hydrophilically modified.

➢ For all 3GTO-MPEG(2000) and Isobutyl modified emulsifiers provided fine emulsions for 70 wt% of oil phases (dodecane and toluene) and 30 wt% of water phases. However, same emulsion tests were failed in the case of 30 wt% of oil phases (dodecane and toluene) and 70 wt% of water phase were used.

➢ For all 3GTO-MPEG(550) and isobutyl modified emulsifiers provided fine emulsions for 70 wt% of oil phase dodecane and 30 wt% of water phases. However, same emulsion tests were failed in the case of 70 wt% of toluene and 30 wt% of water phase.

Texture of emulsions was determined by light microscopy. All emulsions were oil in water (O/W) the size of the droplet was ranging from ten to hundreds of μm. The droplets were polydisperse.

Emulsions have long term stability and phase separation results illustrated the requirement of a balance between MPEG and isobutyl.

This thesis work proved that it is feasible to customize silica surface with both hydrophilic and hydrophobic moieties with a versatile approach. This has led to the preparation of new emulsifier with good performances. In similar manner, the modification technique could find application in other field, such as the preparation of stationary phases for HPLC.

7 ACKNOWLEDGEMENTS

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