SBA-15; an investigation into the synthesis solution's effect on formation dynamics and material properties

Bachelor of Science Thesis

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ABSTRACT

The aim of this thesis project was to study the reaction solution's effect on the formation dynamics and material properties of the mesoporous silica SBA-15.

The common synthesis procedure of SBA-15 was applied at 60°C, with 2.5 wt% Pluronic P104 dissolved in 1.6 M hydrochlorid acid. Simple sodium salts (NaCl, NaBr, NaI) or short to medium length alcohols (MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, 2-BuOH), in the concentration range 0-1 M, was added prior to the addition of the silica source, tetramethyl orthosilicate. The material was hydrothermally treated and approximately half of the sample was calcined.

UV-Vis spectrophotometry was used to establish the flocculation time. The spectrophotometric measurements showed a decrease in flocculation time for the salts and an increase in flocculation time for the alcohols. The different effects of the additives relate to their effect on the solubility of Pluronic. The salts increase the polarity of the solution, decreasing the solubility of the surfactant. Previous research shows an increased solubility of Pluronic on addition of sodium iodine, a trend not seen here. The added alcohols decrease the polarity of the solution, thus increasing the solubility of Pluronic, a trend not expected for the butanols which acts as cosurfactants.

Small angle x-ray diffraction was used to determine the structure of the products from the syntheses with additives. All, except the highest concentration of 1-butanol showed a hexagonal structure. The unit cell parameter decreased with increasing concentration for all additives.

The morphology of the particles was studied using scanning electron microscopy. The silica with added sodium salts resulted in fibrous particles at the higher concentrations, to different extent depending on the salt species. This oriented aggregation was not seen in the silica with added alcohols, leading to large undefinable particles randomly aggregated. As for the salts, the extent of the effect depends on the alcohol species and concentration, with the largest effect obtained by the alcohols with the longest alkylic chain.

The cause of the unexpected behavior of the sodium iodine and the two types of butanols was not studied in this project and further investigation is needed.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Tensider är en sorts molekyler som har en hydrofil- ("vatten-älskande") och en hydrofob ("vatten-hatande") del. Den här dubbla egenskapen gör att tensiderna är ytaktiva ämnen som har många användningsområden och vi stöter på dem dagligen, bland annat i tvättmedel, schampo och emulgeringsmedel i livsmedel. Även inom industrin och forskning används olika typer av tensider i stor utsträckning.

När man löser upp tensider i vatten klumpar de ihop sig i runda bollar, miceller, med de hydrofoba delarna i mitten skyddade från vattnet av de hydrofila delarna, se Figur 1. När man löser upp mer tensider i lösningen växer micellerna, men då de nått en viss storlek kan micell-bollen inte bli större och den ändrar form till exempel till en avlång cylindrisk struktur istället. De avlånga micellerna kan lägga sig bredvid varandra och bildar då en hexagonal packning. Andra strukturer kan också fås.
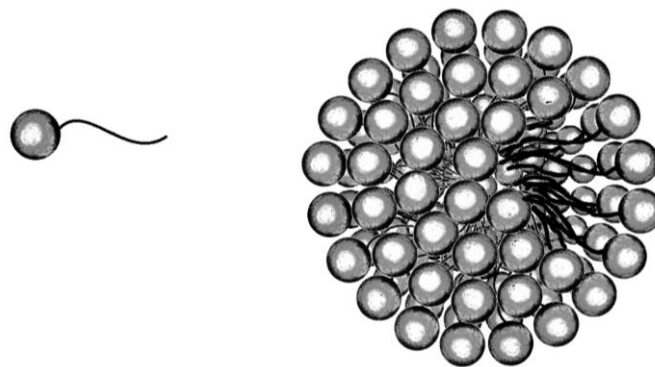
Figur 1. Vänster: tensid med hydrofilt "huvud" och hydrofob "svans", höger: tensider packade till micell; hydrofil utsida och hydrofob insida.

Genom att tillsätta en kiseldioxidkälla som lätt länkas samman till ett nätverk till micell-lösningen kan man bygga kiseldioxid runt micellerna. Denna kiseldioxid, en sorts glas, får då samma hexagonala form, se Figur 2. Genom att sedan bränna materialet i ugn bränns micellerna bort och man får en porös kiseldioxid som har en mycket stor yta i förhållande till sin vikt, 900 m^2 per gram. På grund av porositeten och den stora ytan har kiseldioxiden olika användningsområden, som till exempel för katalys, separationsprocesser eller som potentiella läkemedelsbärare.
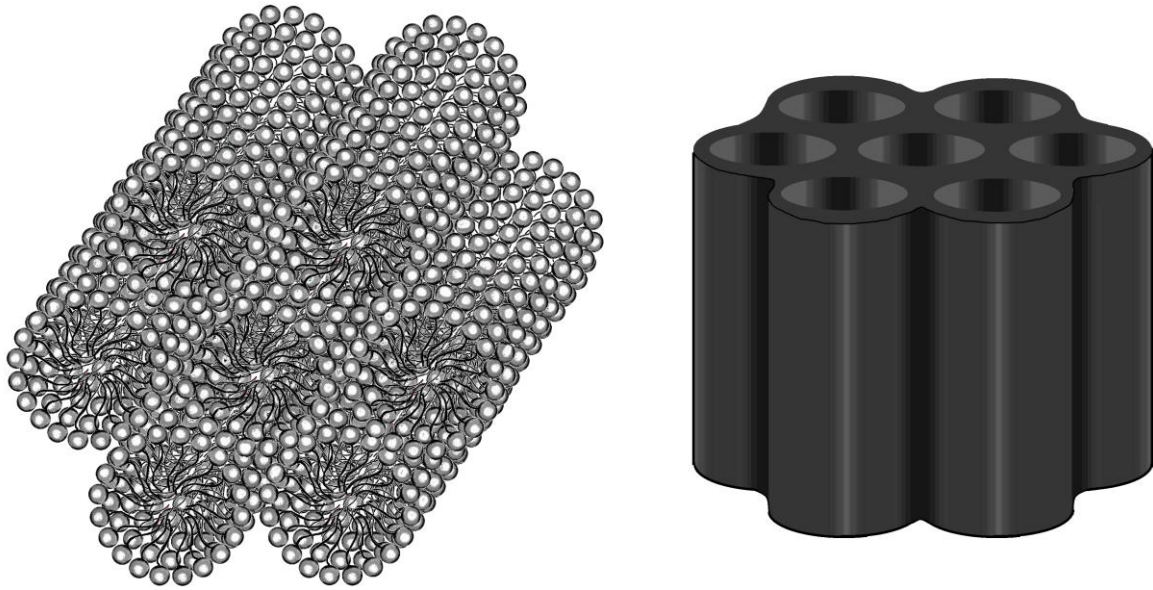
Figur 2. Vänster: cylindriska miceller packade hexagonalt, höger: hexagonal kiseldioxid.

Om man tillsätter andra ämnen i synteslösningen, till exempel salter eller alkoholer, så förändras tensidens egenskaper, exempelvis kan den hydrofila delen bli mer hydrofil eller den hydrofoba mer hydrofob. När dessa egenskaper förändras, så ändras också storleken på micellerna och vilka strukturer som bildas vid olika koncentrationer. Om man bygger kiseldioxid runt micellerna i de här lösningarna får man alltså skillnader i kiseldioxidens struktur.

De bildade partiklarna är mycket små, ungefär en tusendels millimeter, så för att kunna se dem använder man sig av en speciell sorts elektronmikroskop, och för att kunna se den inre hexagonala strukturen använder man sig av röntgenstrålning.

ABBREVIATIONS

CMC   critical micelle concentration

MCM-41   mesoporous silica first synthesized by the Mobil Research and Development Corporation

PEO   poly(ethylene oxide)

PPO   poly(propylene oxide)

SAXD   small angle x-ray diffraction

SBA-15   mesoporous silica first synthesized at the University of Santa Barbara (CA, USA)

SEM   scanning electron microscopy

TMOS   tetramethyl orthosilicate

UV-Vis   ultraviolet to visible light, 10 - 750 nm wavelength.

INTRODUCTION

When surfactants are dissolved in an aqueous solution, the molecules self-assemble into different structures to avoid unfavorable interactions between the hydrophobic parts of the surfactant molecules and the water molecules. By adding different species to the solution, the solubility of the surfactant can be altered and the preference for a certain structure changes. By adding a silica source, one can build mesoporous silica around these structures, and by altering the components of the system, silica with different types of structures can be synthesized. The exact mechanism of this synthesis is not known and therefore subject to present research. By studying the influence of different cosolutes and cosolvents on different aspects of the synthesized silica, i.e., morphology, internal and external structure, valuable information can be acquired. To get a better understanding on the subject we first go through some background on the surfactants and their self-assembly.

Surfactants

Amphiphiles are molecules that consist of two or more parts, where at least one is hydrophilic and one hydrophobic. In aqueous solutions, the hydrophobic part of some amphiphiles segregates to the water-air surface and thus gives a lower surface tension than pure water. This surface-active behavior of amphilphiles explains why they are often called surfactants.

Surfactants can be divided into two classes; ionic and nonionic. The ionic surfactants can be anionic, cationic or zwitterionic, with the charge located on the hydrophilic part of the molecule. The nonionic surfactants often, as in the case of the Pluronic block copolymer mentioned later, consists of a short hydrophilic poly(ethylene oxide) chain and a hydrophobic hydrocarbon chain.[1]

Both natural and synthetic amphiphiles are common, e.g. phospholipids (the main part of cell membranes) and alcohol ethoxylate nonionic surfactants (widely used in detergents). The used surfactant in this project, Pluronic P104, is a synthetic nonionic surfactant commercially available with many uses, such as thickeners, emulsifiers or antifoaming agents. Pluronics are block copolymers consisting of two poly(ethylene oxide) (PEO) blocks separated by one poly(propylene oxide) (PPO) block. The solubility of Pluronics in aqueous solutions decreases with increasing temperature, a phenomenon called inversed solubility, which is caused by the increased hydrophobicity at higher temperatures of both types of segments in the polymer.[2]

The hydrophobic effect is the reason the surfactants segregates to the water-air surface, and is also the reason the surfactants at higher concentrations associates into micelles (above the critical micelle concentration, CMC). Micelles are spherical or elongated structures, with the hydrophobic parts of the surfactant molecules inside the core and the hydrophilic parts in the surrounding corona. Unfavorable interactions between the hydrophobic parts of the surfactant molecules and the water molecules are thus avoided. The size of the micelles is determined e.g. by the surfactant species, the association number, i.e. the number of molecules in a micelle, and the surfactants concentration. At higher concentrations the surfactants can self-assemble into different lyotropic liquid crystalline phases, such as lamellar (bilayer), 2D hexagonal (packing of rod-like micelles) and cubic (packed spherical micelles) phases (see Figure 1). The phases are called lyotropic because they are formed as a function of the surfactant concentration and temperature, and liquid crystalline because they are both ordered and fluid.[1]
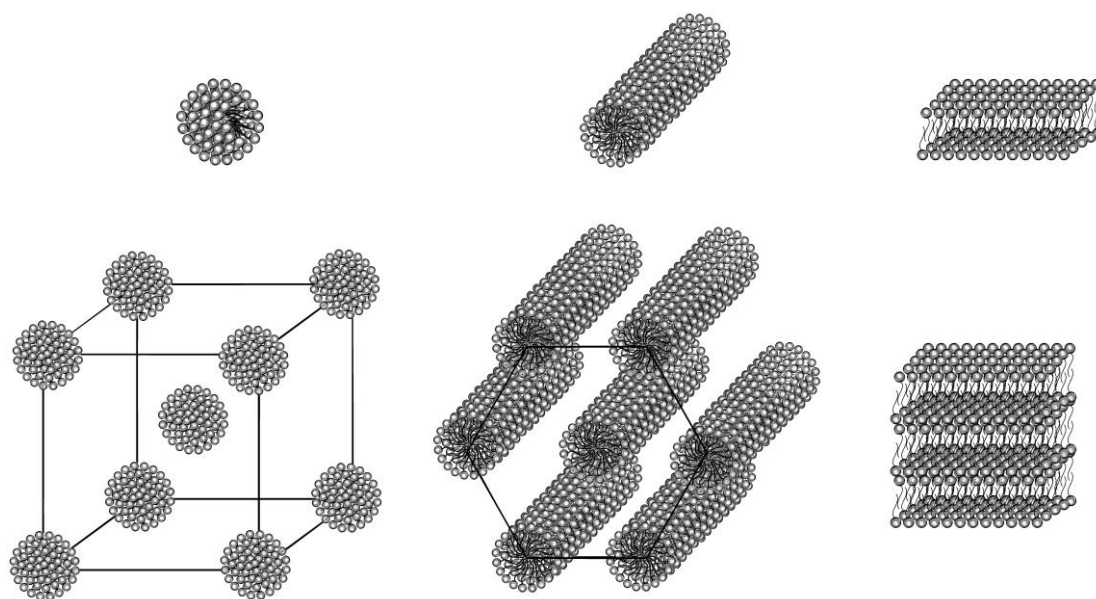

Figure 1. Self-assembled surfactants (hydrophilic head and hydrophobic tail), left to right; spherical micelle, cylindrical micelle, bilayer, cubic-, hexagonal- and lamellar phase.

Pluronics

In the micelles formed by Pluronic surfactants in aqueous solutions, the core consists mainly of the poly(propylene oxide) and the corona of the poly(ethylene oxide) and water. Some water molecules are still present to some extent in the core, but overall the unfavorable interactions between propylene oxide and water are diminished.[2] When adding a cosolute or cosolvent, such as electrolytes or organic compounds, the solvent quality of the water solution changes.

When the solvent quality changes, the surfactant's behavior in the solution and the solubility changes, hence the critical micelle concentration and/or the cloud point of the Pluronic solution changes.[3] The cloud point of a solution is the temperature where the solutes are no longer completely soluble and phase separate to some extent into a second phase, giving the solution a "cloudy" appearance. Inorganic salts are said to have a "salting-in" behavior on a solution containing organic solutes if they induce increased solubility, or a "salting-out" behavior if they induce decreased solubility. The Hofmeister series is a classification of anions according to their "salting-out" strength. For the halides this series is: $F^- > Cl^- > Br^- > I^-$. Ions with smaller radii have a greater effect on the cloud point. The "salting-in" and "salting-out" phenomena are caused by the absorption or depletion of the ions on the water-solute interface, which alter the phase equilibrium.[4]

On the addition of short chain alcohols; methanol, ethanol and 1-propanol, the cloud point of Pluronic have been shown to increase. For the medium length alcohols; 1-butanol, 2-butanol and 1-pentanol, on the other hand, a decrease in the cloud point has been observed.[5] The short chain alcohols, which are good solvents for both types of segments in Pluronic, increase the solubility and decrease the aggregation number of the micelles. The medium chain alcohols have the opposite effect because they dissolve into the micelles, increasing the mean volume per Pluronic molecule, resulting in larger micelles.[6]

The effect of the alcohols is related to the hydrophobic alkyl chain; for a homologous series, the longer the chain the larger effect and lower concentration is needed to obtain the same cloud point for Pluronic.[5] For all additives, cosolutes as well as cosolvents, the effect is proportional to the concentration, with the higher concentration giving a larger effect on the solubility of Pluronic.

Mesoporous Silica

In the early 1990's, the Mobil Research and Development Corporation produced a mechanically stable, porous silica material with well-defined 2D hexagonal structure and large surface area, MCM-41. The material was defined as mesoporous according to the International Union of Applied and Pure Chemistry's definition of mesoporous materials having pores with diameters between 2 and 50 nm. A few years later, at the University of Santa Barbara (CA, USA), a similar material was synthesized, called SBA-15. This, also 2D hexagonal material, has since become one of the most studied mesoporous silica. The walls of SBA-15 are thicker than the MCM-41, and the pores have a larger diameter. SBA-15 also has

two types of pores; primary mesopores interconnected by smaller intrawall pores. By changing different parameters in the synthesis, the pore size and the presence of intrawall pores can be altered. This gives the material a large number of applications, i.e., in drug delivery, catalysis, separation and adsorption[7].

Synthesis

The common synthesis procedure of SBA-15 used in this project, a dilute acidic micellar solution, was based on the seminal synthesis protocol.[8] When tetramethyl orthosilicate, the silica source, is added to the solution, the acidity triggers the polymerization of the siliceous species. The polymerization consists mainly of two steps; hydrolysis and water condensation, schematically presented below.

$$\equiv Si - OMe + H_2O \leftrightarrow \equiv Si - OH + MeOH$$

$$\equiv Si - OH + HO - Si \equiv \leftrightarrow \equiv Si - O - Si \equiv + H_2O$$
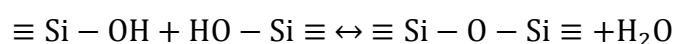
The interactions between the growing silica network and the micelles rearrange the spherical micelles into cylindrical micelles packed in a hexagonal arrangement. The exact nature of the interactions is not clear; it has been explained to be caused by hydrogen bonds or hydrophobic interactions. However, these interactions are the source of the formation of a precipitate. As the silica associates to the micelles, flocs start to form and the synthesis solution becomes turbid, an event called the flocculation time.

The formed particles after the synthesis can be both primary and secondary, depending on the synthesis parameters. The secondary particles normally consist of seven primary particles fused together to a single larger particle with approximately the same structure and thickness as the primary particles. When using Pluronic P104 (EO_{27}-PO_{61}-EO_{27}) as a structure director, the hexagonal structure is the only one observed, where the PPO segments form the primary pores and the PEO segments are responsible for the intrawall pores. To receive the pure mesoporous silica, the material is calcined after synthesis at 500°C, burning away the Pluronic.[7,9]

EXPERIMENTAL TECHNIQUES

The synthesized materials were studied with UV-Vis spectrophotometry to establish the flocculation time, with SAXD to identify the internal structure and with SEM to identify the particle morphology.

Chemicals

The used surfactant Pluronic P104; EO_{27}-PO_{61}-EO_{27} (M_{av}= 5900 g/mol), is commercially available from BASF and was used as received. Tetramethyl orthosilicate from Aldrich was used as the silica source. Sodium chloride from Merck, sodium bromide from VWR, sodium iodine from Merck, methanol from Merck, ethanol from Kemetyl, 1-propanol from Fluka, 2-propanol from Sigma-Aldrich, 1-butanol from Sigma and 2-butanol from Aldrich were all 99% pure or higher and used as received. The Milli Q water used was filtered through a 0.22 μm Millipore filter.

Syntheses

Mesoporous silica was synthesized with Pluronic P104 as structure directing agent. Pluronic P104 was dissolved in 1.6 M HCl to 2.5 wt%. Cosolute (NaCl, NaBr or NaI) or cosolvent (MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH or 2-BuOH) was added in 0, 0.1, 0.25, 0.5, 0.75 or 1.0 M concentration. The temperature was adjusted to 60°C and tetramethyl orthosilicate (TMOS) was added under vigorous stirring. After about two minutes 2.0 ml of the solution was transferred to a cuvette for UV-Vis analysis in a Varian Cary WinUV spectrophotometer at 500 nm and 60°C (measurement every 0.2 min until flocculation had occurred). After 24h of synthesis under stirring, the solution was hydrothermally treated under static conditions at 80°C for 24 h. The solid product was recovered, washed with Milli-Q H_2O and air-dried at room temperature. Approximately half of the sample was thereafter calcined at 500°C for 6h.

The products synthesized with 0, 0.1, 0.5 and 1.0 M cosolute or cosolvent were analyzed with small angle x-ray diffraction (SAXD) and scanning electron microscope (SEM). The SAXD experiments were performed on an Anton Paar SAXSess with Cu-Kα radiation of wavelength 0.1542 nm and a CCD camera detector. The SEM images were obtained from a JEOL LSM-6700 microscope operated at 10 kV; the analyzed samples were sputter coated with Au-Pd before examination. The analyses were performed on "as synthesized" silica, except for the SEM micrographs of samples containing NaI, which were on calcined samples.

Analyses

UV-Vis spectrophotometry

When doing spectrophotometric measurements on a chromophore, the chosen wavelength of light should be one that gives the highest absorbance without disturbance from other possible chromophores in the sample. When it comes to the measurements on the mesoporous silica, the chosen wavelength is not as important. The mesoporous silica does not absorb the irradiance of the light, but reflects it and scatters it in different directions, preventing some of it from reaching the detector. A spectrophotometer can thus be used to detect the flocculation time in the synthesis of mesoporous silica.

In a spectrophotometer, the difference in irradiation is measured as monochromatic light passes through the sample. Some of the energy from the light is absorbed by the chromophores in the sample, causing a decrease in the irradiance. The fraction of light that passes through the sample, the transmittance, is defined as:

$$T = \frac{P}{P_0} \tag{1}$$

Where P_0 is the irradiance of the beam entering the sample and P is the irradiance of the beam emerging from the sample. The absorbance, A, of the sample is given by:

$$A = -\log T = \log \frac{P_0}{P} \tag{2}$$

The absorbance of the sample is directly proportional to the concentration, c, of the chromophores in the sample and the length, l, of the light's path through it, given by the Lambert-Beer's law:

$$A = \varepsilon l c \tag{3}$$

Where ε is the molar absorptivity, a parameter which describes how much light is absorbed at a given wavelength by a given substance. Absorbance is a dimensionless parameter, concentration has the unit M and the path length is often given in cm, hence the unit of the molar absorptivity is $M^{-1}cm^{-1}$.[10]

Small angle x-ray diffraction

To study objects with diffraction, the wavelength of the incident radiation must be much smaller than the objects themselves. The wavelength of x-rays are about 0.1 nm, which makes x-ray diffraction a suitable method to study the internal structure of mesoporous silica. For objects with large interplanar spacing, such as mesoporous silica or liquid crystals, small angle x-ray diffraction (SAXD) can be used.

When a monochromatic x-ray beam is reflected off a crystal plane, the reflected beams give rise to a distinctive diffraction pattern. The specific intensities of the diffraction pattern are caused by the constructive interference of the diffracted beams, the path lengths of which must differ by an integral number, n, of wavelengths, λ. The Bragg equation relates these parameters to the spacing between the crystal planes, d, and the Bragg angle, θ:

$$n\lambda = 2d \sin \theta \tag{4}$$
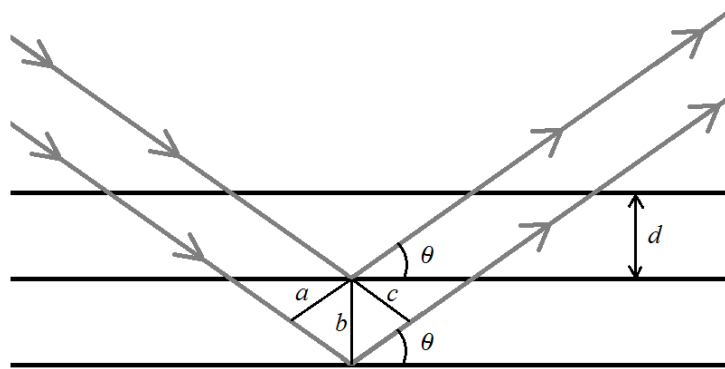
Figure 2. Schematic picture of the Bragg equation, constructive interference occurs when a, b and c are integrals numbers.

In a powder sample the individual crystals are oriented randomly, so when the incedent x-ray beam hits the sample diffraction will occur only from those crystals oriented in the angles that fulfill the Bragg condition. These reflections will lie on the surface of a cone with a reflection angle of *2θ* from the incedent beam.[11]

SAXD data is usually represented as a graph of intensity as a function of the scattering vector q. The intensity is given in arbitrary units, a.u., and the scattering vector is the difference between the diffracted and primary wave, given by:

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \tag{5}$$

The interplanar spacing d is related to the scattering vector by:

$$d = \frac{2\pi}{q} \tag{6}$$

To refer to faces and planes in ordered systems, such as crystals, Miller indices (*hkl*) are used. Since the Miller indices describe the planes in a crystal, they are related to the unit cell parameters and the interplanar spacing d. For a two dimensional hexagonal structure this relation is:

$$d = \sqrt{\left(\frac{3a^2}{4(h^2 + k^2 + hk)}\right)} \tag{7}$$

This provides the following specific conditions:

$$\frac{q_n}{q_1} = \sqrt{1}, \sqrt{3}, \sqrt{4}, \sqrt{7} \, ... \tag{8}$$

Each peak in the SAXD graph and its scattering vector corresponds to a specific interplanar spacing. The peaks in a SAXD graph therefore correspond to a specific crystal structure.[11]

Scanning electron microscopy

To study the topography of a solid sample scanning electron microscopy (SEM) can be used. The electron beam from a heated tungsten filament is focused by magnetic fields onto the sample in high vacuum, scanning the surface. The reflected electrons and emitted secondary electrons from the surface of the sample are detected and give a picture of the sample's surface topography. To stop charge building up on the surface of nonconductive materials, the samples are generally sputter coated with conductive metals such as gold or a mixture of palladium and gold.[11]

RESULTS AND DISCUSSION

UV-Vis spectrophotometry

The flocculation time for the syntheses containing different sodium salts decreased with increasing salt concentration (see Figure 3). A slight difference can be seen between the three different salts, but no qualitative difference can be observed due to the temperature fluctuations during the syntheses.
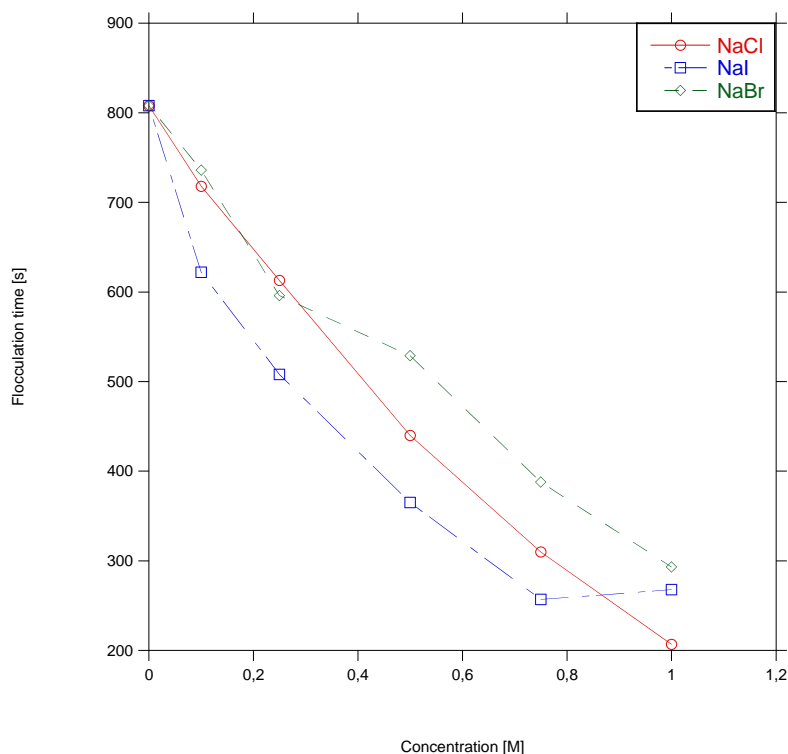

Figure 3. Flocculation time as a function of cosolute concentration. A decreased flocculation time with increasing cosolute concentration is observed.

The added salt increases the ionic strength and the polarity of the solution, leading to a decreased solubility of the Pluronic molecules. As a result, a faster association with the silica is observed. This trend is not as expected for NaI, since iodine ions interact with the Pluronic polymer in a different manner than the other two halides. The iodine ions absorbs on the PEO part of Pluronic, leaving it "effectively" charged, therefore increasing the repulsion between the segments and increasing the solubility.[4] A slower aggregation time is thus expected for the NaI, and further investigation is needed to understand why this trend is not observed.

For the alcohols, the effect is opposite; the flocculation time increases with increased concentration (see Figure 4). The extent of the increase depends on the identity of the alcohol.
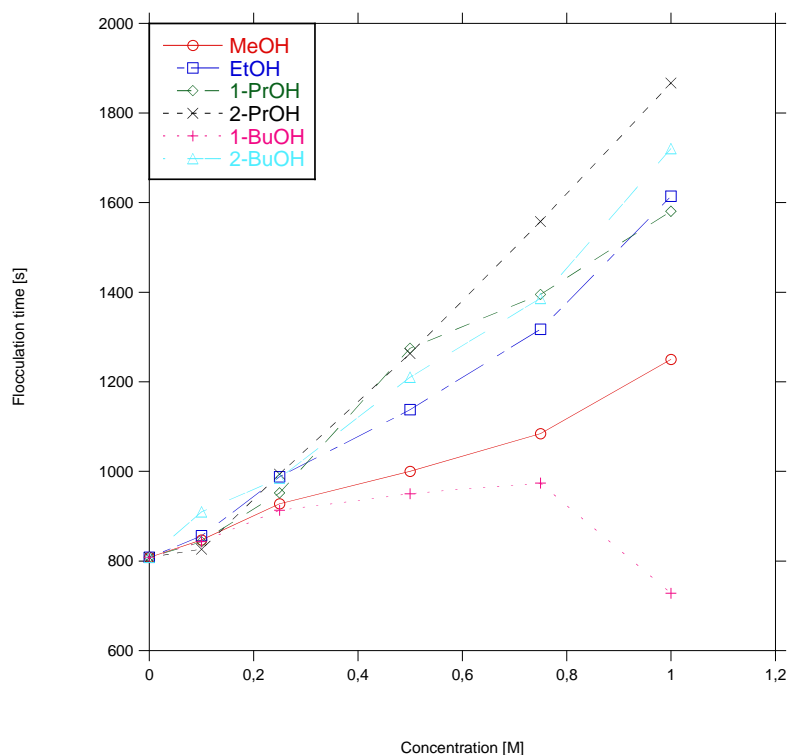
Figure 4. Flocculation time as a function of concentration of cosolvent. An increased flocculation time with increasing cosolvent concentration is observed, except for 1.0 M 1-BuOH which caused a phase separation prior to addition of the silica source.

By adding alcohols to the solution, the polarity decreases and the solubility of Pluronic increases. By increasing the solubility of the Pluronic, the aggregation time also increases and the association with silica is observed to occur at a slower rate. In aqueous solution, the short chain alcohols increase the cloud point of the Pluronic[5], the addition of these alcohols to the acidic synthesis-solution decreases the polarity of the solution and an increased solubility of the Pluronic is observed.

The two types of butanol are expected to decrease the solubility of Pluronic by acting as cosurfactants, thus giving a faster aggregation time.[5,6] This is only seen for the higher concentration of 1-butanol, which caused a phase separation at 60°C prior to addition of TMOS in the beginning of the synthesis. This unexpected behavior suggests that the butanols also have another effect on the system, which needs further investigation.

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Small angle x-ray diffraction

Internal structure

A selection of the samples, 0, 0.1, 0.5 and 1.0 M of each cosolute or cosolvent, was measured with SAXD (see Appendix 1). The intensities of the peaks in the SAXD-plots are different in each plot, which depend on different parameters, a subject we will not go into further in this thesis. All samples showed a hexagonal internal structure, except 1.0 M 1-BuOH; which showed no structure (see Table 1).

Table 1. Control of hexagonal internal structure, according to equation 8. The relation between the scattering vectors of the second and first peak, and the relation between the third and first peak for the different concentrations of cosolutes or cosolvents.

Cosolute/cosolvent	Concentration [M]	q_2/q_1	q_3/q_1
-	0	2.01	2.66
NaCl	0.1	2.01	2.66
	0.5	2.00	2.63
	1.0	1.75	2.01
NaI	0.1	1.74	2.01
	0.5	1.74	2.01
	1.0	1.73	2.01
NaBr	0.1	2.01	2.66
	0.5	2.01	2.66
	1.0	1.70	2.02
MeOH	0.1	2.01	2.66
	0.5	2.01	2.67
	1.0	2.01	2.66
EtOH	0.1	1.73	2.00
	0.5	2.01	2.66
	1.0	2.00	2.65
1-PrOH	0.1	2.01	2.67
	0.5	2.01	2.67
	1.0	2.01	2.65
2-PrOH	0.1	2.01	2.64
	0.5	2.01	2.67
	1.0	2.01	2.67
1-BuOH	0.1	1.74	2.02
	0.5	1.74	2.01
	1.0	-	-
2-BuOH	0.1	2.01	2.66
	0.5	1.74	2.01
	1.0	1.74	2.01

The unexpected behavior of 1.0 M 1-BuOH is seen in the other analyses as well; this alcohol has some other effect on the system and needs further investigation to explain how and why this happens. The butanols act as cosurfactants instead of cosolutes, dissolving into the micellar core[6] and changing the geometry of them.

Unit cell parameter

No significant change in the lattice spacing was observed for the silica with different concentrations of NaCl added to the synthesis. For the syntheses with added NaBr or NaI, the lattice spacing of the silica decreases, with the largest effect for NaI (see Figure 5).
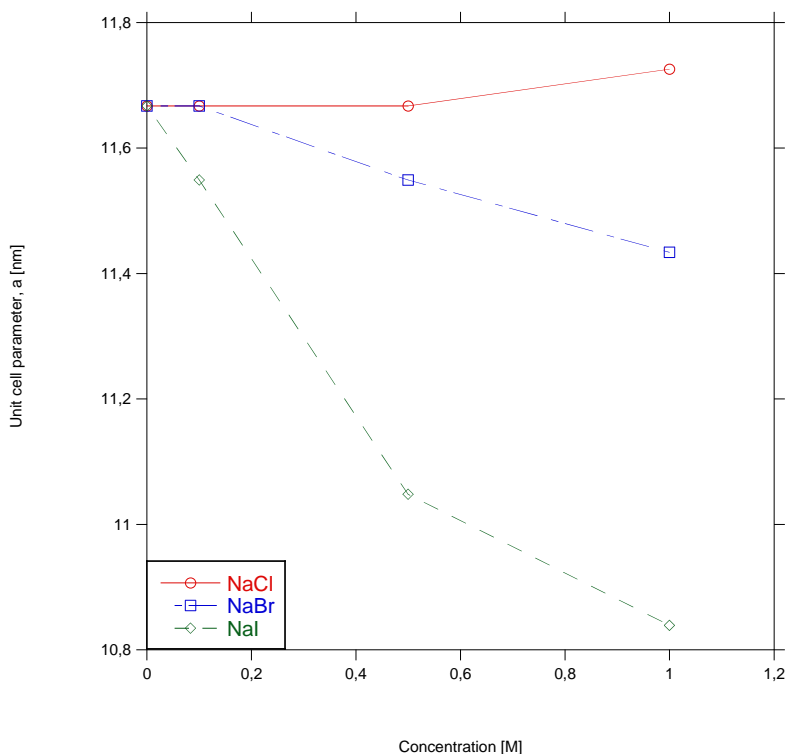
Figure 5. Unit cell parameter as a function of cosolute concentration. The unit cell parameter of the silica synthesized with NaBr and NaI decreases with increased cosolute concentration, while the unit cell parameter of the silica synthesized with NaCl does not show a significant change.

The unit cell parameter of the silica synthesized with NaI and NaBr decreases with increased cosolute concentration, while the unit cell parameter of silica synthesized with NaCl shows no significant change, trends consistent with previous research.[2] The decreased unit cell parameter is probably caused by smaller micelles, which can be a result of less solubility of the Pluronic or a lower association number. For Pluronic in aqueous solution, it has been shown that added chloride or bromide ions are depleted from the corona of the micelles, which leads to an osmotic effect dehydrating the corona, decreasing its thickness. The addition of ions to the Pluronic solution increases the polarity of the aqueous solution, making the Pluronic more solvophobic. The increased solvophobicity increases the tendency to aggregate, thus increases the core size.[2] For these two ions, chloride and bromide, the two effects seems to almost cancel each other out, since the effect on the unit cell parameter is not that significant. The iodine ions however, affect the solubility of the Pluronic molecules in a different manner or to a different extent.

When it comes to the alcohols, the unit cell parameter does not change significantly for MeOH. The EtOH has an odd effect, with fluctuations in the unit cell parameter, and the cause of this is not clear. For the primary alcohols, the longer the alkyl chain, the smaller the unit cell parameter. The same trend goes for the secondary alcohols, however not to the same extent (see Figure 6).
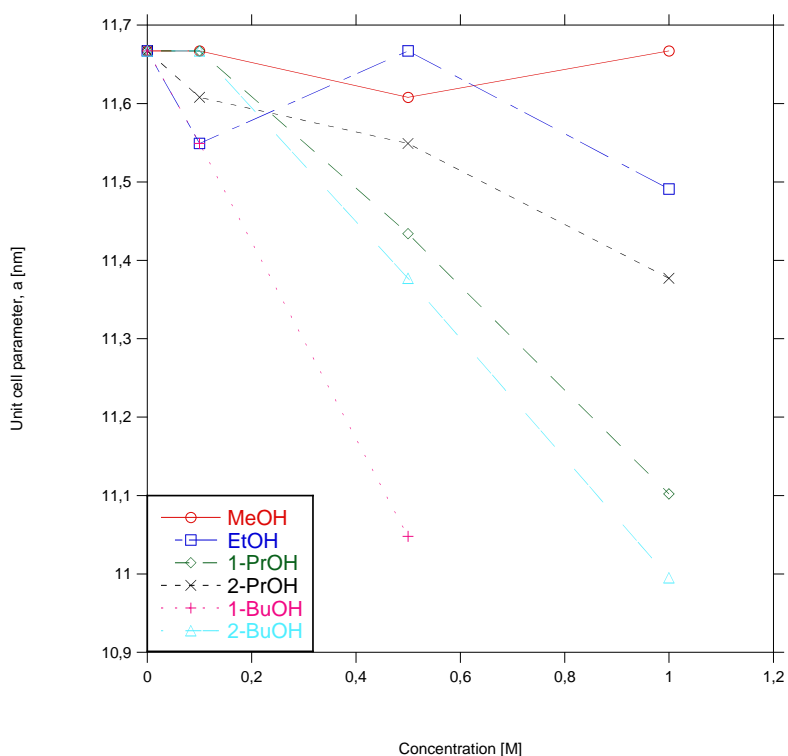
Figure 6. Unit cell parameter as a function of cosolvent concentration. The unit cell parameter generally decrease with increased cosolvent concentration, with the exception of MeOH (which shows no significant change) and EtOH (which fluctuates in size).

As mentioned in the introduction, the short chain alcohols increase the solubility of Pluronic and decrease the aggregation number of the micelles, thus making them smaller.[6] This trend is seen, as the unit cell parameter decreases. For the medium chain alcohols, however, the opposite effect is expected, as they dissolve into the micelles. 1-Butanol and 2-butanol have been shown to dissolve into the PPO core of the micelles, and to some extent also in the corona. The solubilization of these alcohols causes dehydration in the intermediate region of the corona[12] and affects the geometry of the micelles. The results from the SAXD experiments imply that the micelles decreases in size, as the unit cell parameter for these medium chain alcohols decrease.

Scanning electron microscopy

Particle morphology

To study the morphology of the synthesized particles, scanning electron microscopy was used. A collection of the SEM micrographs can be seen in Figure 7-16 below.
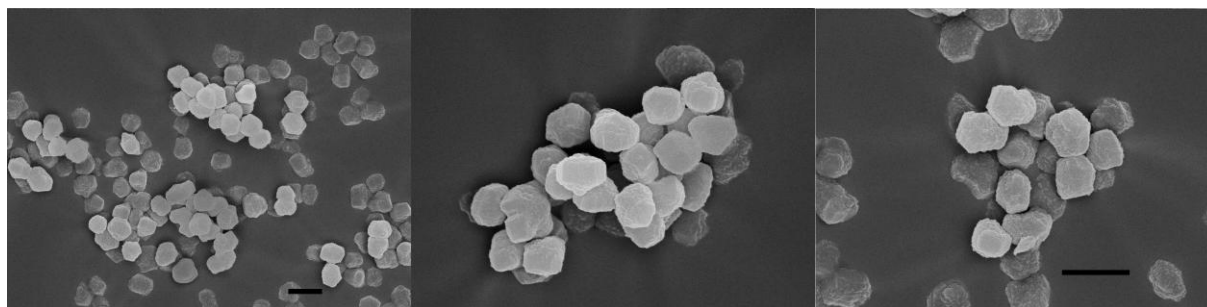
Figure 7. SEM micrographs of SBA-15. Scale bar valid for pictures left of it, corresponding to 1µm.
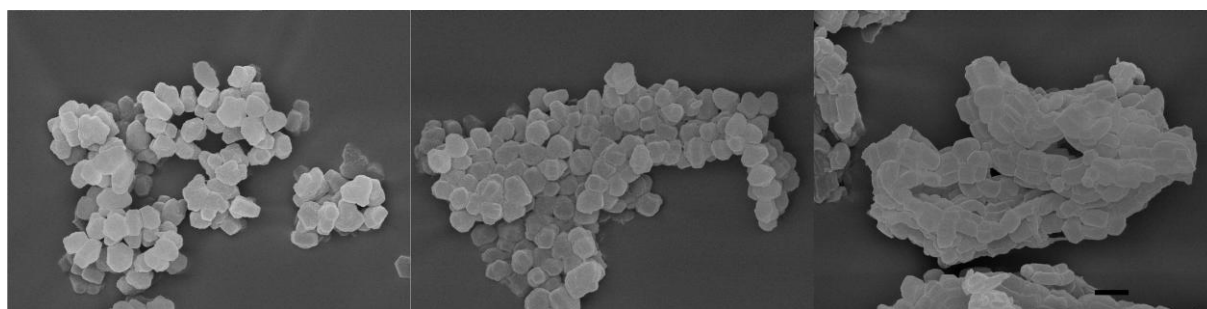
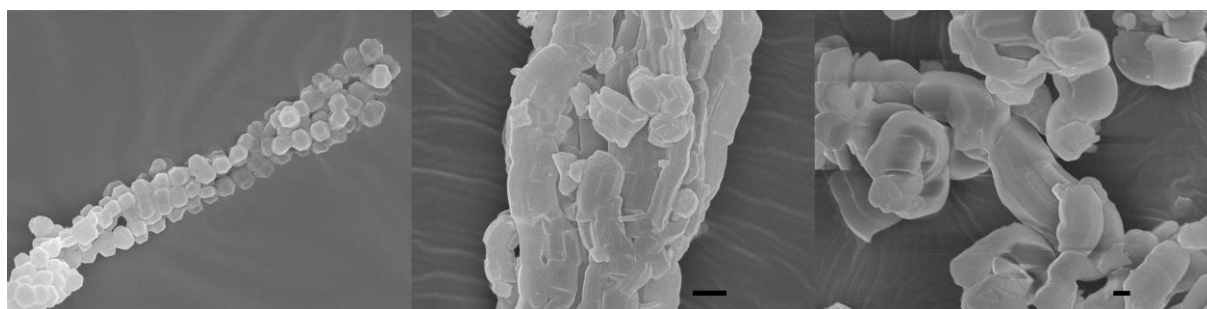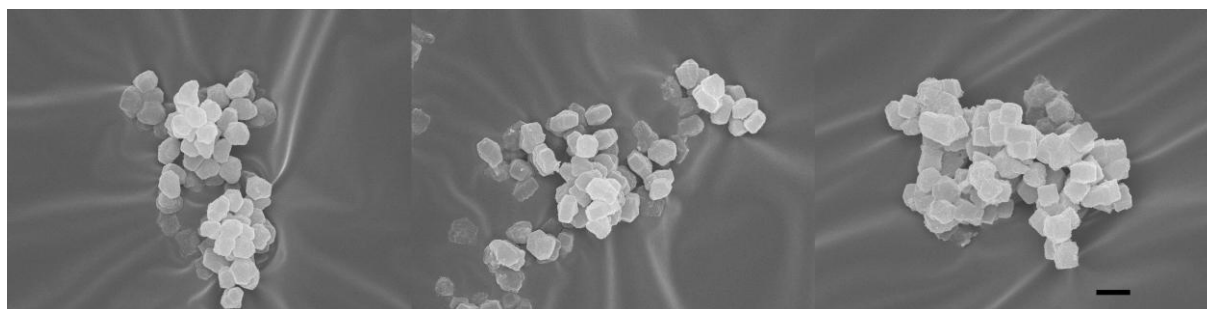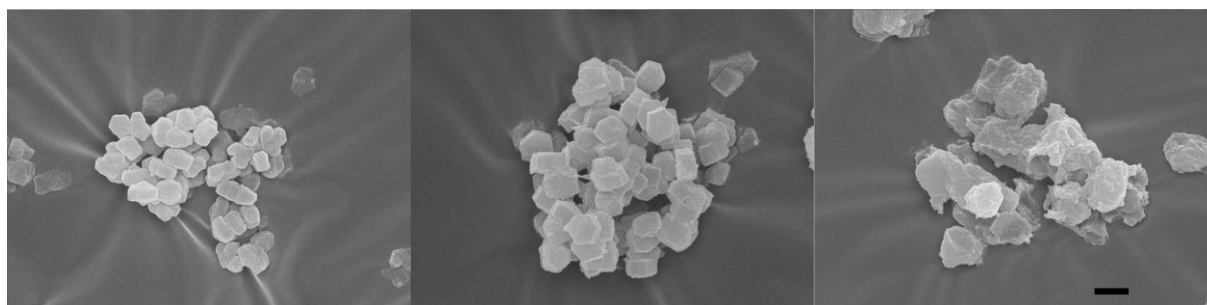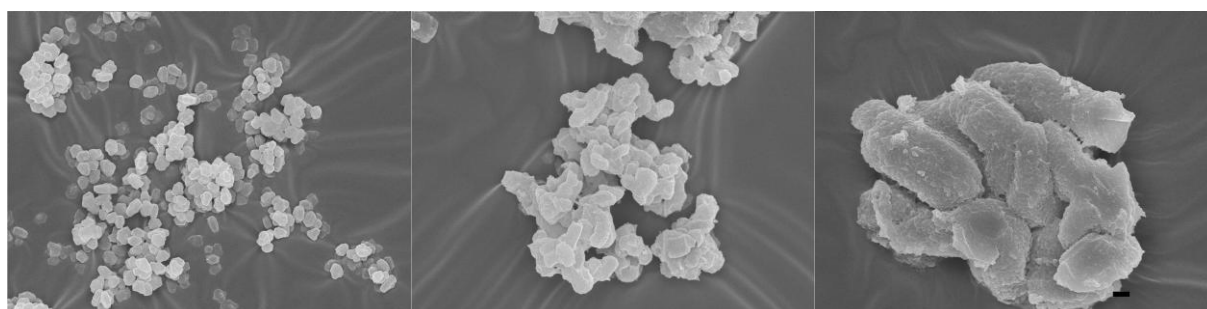**Figure 8.** SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M NaCl. Scale bar valid for all pictures, corresponding to 1µm.
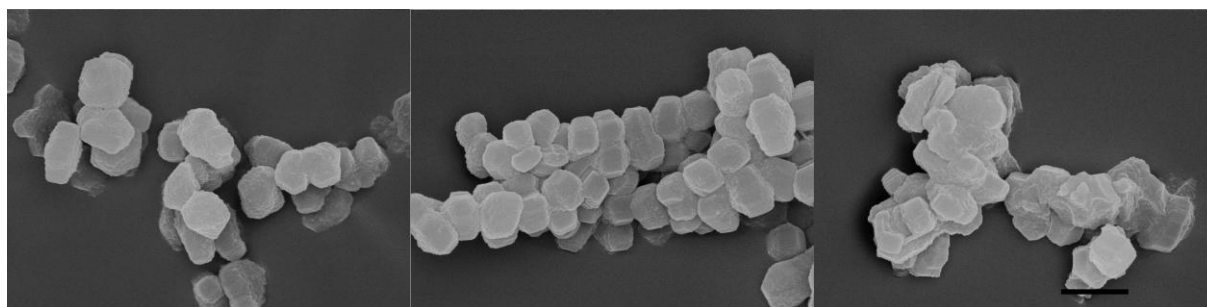
Figure 9. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M NaBr. Scale bar valid for all pictures, corresponding to 1µm.
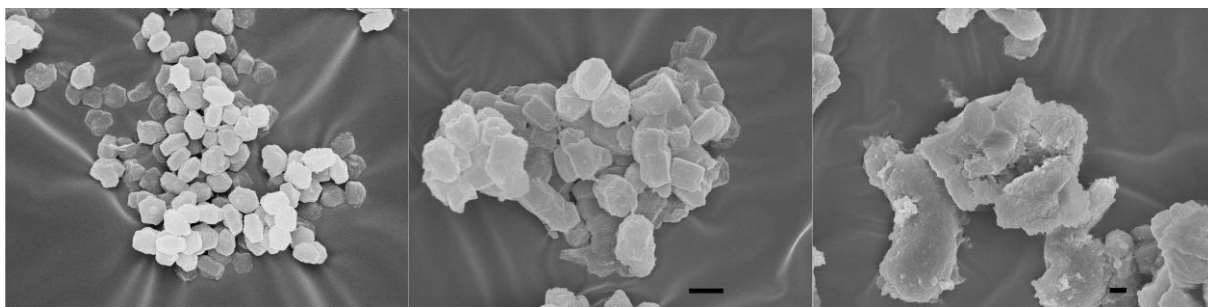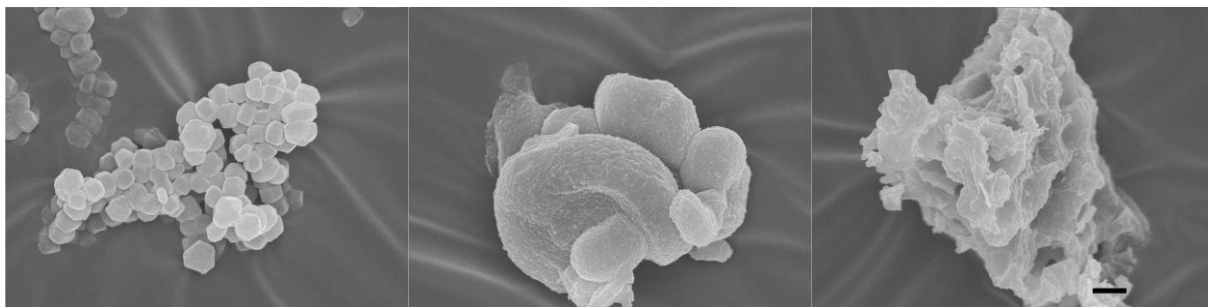

Figure 10. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M NaI. Scale bar valid for pictures left of it, corresponding to 1µm.

As seen in the Figures 8-10 above, the salts are qualitatively similar, but quantitatively different. Addition of salt to the reaction solution leads to oriented association and fibrous particles, to different extent depending on the salt. The effect of NaI is more pronounced then the other salts, leading to oriented aggregation at the low concentration and bent and twisted undefinable particles at the higher concentration.
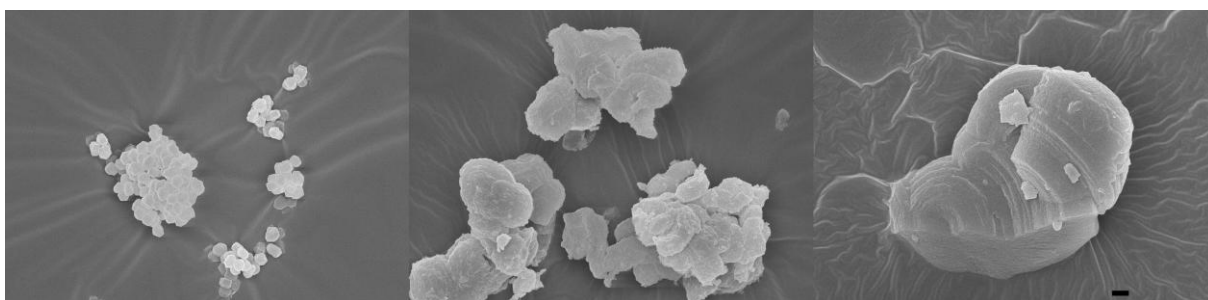

Figure 11. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M MeOH. Scale bar valid for all pictures, corresponding to 1µm.

Figure 12. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M EtOH. Scale bar valid for all pictures, corresponding to 1µm.

Figure 13. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M 1-PrOH. Scale bar valid for all pictures, corresponding to 1µm.

Figure 14. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M 2-PrOH. Scale bar valid for pictures left of it, corresponding to 1µm.

Figure 15. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M 1-BuOH. Scale bar valid for all pictures, corresponding to 1µm.

Figure 16. SEM micrographs of SBA-15 synthesized with (left to right) 0.1, 0.5 and 1.0 M 2-BuOH. Scale bar valid for all pictures, corresponding to 1µm.

For the addition of short chain alcohols to the synthesis solution (Figure 11-14), the effect is less pronounced than for the longer alcohols (Figure 15-16), but the effect is similar in all systems. The additions of alcohols lead to large undefinable particles.

For all additives, the particles with clear hexagonal morphology are still present in the system with the lowest concentration. For the increased concentrations, salts lead to a defined association while the alcohols lead to random association.

Particle size and categorization

The sizes of the particles were measured from the SEM micrographs (see Table 2). The sizes and thickness of the particles vary a bit, but no obvious trends are seen.

Table 2. Sizes of the particles, measured from the SEM micrographs.

Cosolvent/cosolute		Dominating particle	Primary particles		Secondary particles		Fibrous partices	
Species	Conc. [M]		Diameter [μm]	Hight [μm]	Diameter [μm]	Hight [μm]	Diameter [μm]	Length [μm]
-	-	Primary	0.63	0.28	0.81	0.29	-	-
NaCl	0.1	Primary	0.69	0.31	1.0	0.30	-	-
NaCl	0.5	Both primary and secondary	0.72	0.31	1.1	0.34	-	-
NaCl	1.0	Fibrous	0.59	0.30	0.75	0.24	0.37	0.88
NaBr	0.1	Both primary and secondary	0.68	0.32	1.1	0.32	-	-
NaBr	0.5	Both primary and secondary	0.54	0.25	1.1	0.30	0.31	0.61
NaBr	1.0	Secondary	0.59	0.26	1.1	0.30	-	-
NaI	0.1	Primary	0.59	0.28	0.91	0.29	-	-
NaI	0.5	Fibrous	1.0	0.47	1.4	0.49	0.77	2.1
NaI	1.0	Undefined	0.94	-	1.4	0.42	2.7	4.3
MeOH	0.1	Both primary and secondary	-	-	0.83	0.29	-	-
MeOH	0.5	Secondary	-	-	0.90	0.32	-	-
MeOH	1.0	Primary	-	-	0.81	0.49	-	-
EtOH	0.1	Secondary	-	-	0.98	0.32	-	-
EtOH	0.5	Secondary	-	-	1.0	0.46	-	-
1-PrOH	0.1	Secondary	0.68	0.28	1.1	0.31	-	-
1-PrOH	0.5	Undefined	1.4	-	1.9	0.60	1.4	1.6
2-PrOH	0.1	Secondary	-	-	0.91	0.30	-	-
1-BuOH	0.1	Both primary and secondary	-	-	0.90	0.32	-	-
2-BuOH	0.1	Both primary and secondary	-	-	0.89	0.37	-	-

Previous research has shown that synthesis of SBA-15 at 50°C results in secondary particles and synthesis at 60°C gives primary particles.[13] All syntheses in this project were performed at 60°C, but secondary particles are still present. The better solvent quality on addition of alcohols counteracts the temperature effect, and secondary particles are still formed.

By categorization of the particles (see Appendix 2) general trends on the morphology and aggregation are seen. The particles retain their hexagonal or altered/deformed hexagonal shape on addition of low concentrations of salts or alcohols. The aggregation of the particles increases and becomes more compact at higher concentrations, and the addition of salt leads to ordered concrescence while addition of alcohol leads to random concrescence.

SUMMARY AND CONCLUSIONS

The UV-Vis experiment showed that for the salts, the flocculation time decreases with increased concentration. If the addition of salt does not affect the polymerization of the silica source, this means that the silica in the flocs is not as polymerized in the syntheses containing salts as in the regular synthesis. The polymerization of silica continues after the formation of flocs, thus the addition of salts should typically result in a more well ordered structure. The synthesis containing NaI does not behave as expected in one aspect, it decreases the flocculation time. The iodine ions of NaI have another effect on the synthesis system, not studied or detected in this project.

For the alcohols, the flocculation time in the UV-Vis experiment increases with increased concentration. Again, assuming that the polymerization of the silica source is not affected by the added species, this means that the silica has longer time to polymerize before the flocs form and should thus result in a less well ordered system. However, the analysis of the SAXD data shows no general difference between the salts and the alcohols; they all have an internal hexagonal structure and the unit cell parameter decreases.

Both of the butanols does not behave as expected; only the highest concentration of 1-butanol shows the expected decrease in flocculation time, but the SAXD data for the material from this synthesis show no internal hexagonal structure. This shows that the butanols, like the NaI, have some other effect on the synthesis system and needs additional investigation.

Even though the morphology effect on the material is quite different on the addition of salts and alcohols, the SAXD data shows a similar trend; both are still hexagonal and they cause a decrease in the unit cell parameter. The porosity, however, can still be very different in the materials; no data on the porosity has been collected. Hence, two materials with the same unit cell parameter can have very different wall thicknesses and pore sizes.

By adding different species, one can not only influence the internal structure of the silica, but also the morphology. The additives affect the size, growth and association of the material, allowing one to tune the parameters in the synthesis to form a specific material.

FUTURE WORK

The future work relevant for thesis project would be to investigate the porosity of the synthesized material. By receiving this data, one would gain more knowledge about the structure of the synthesized silica and the effect of the different additives. Nitrogen sorption experiments as a compliment to the performed SAXD analyses is an example of a technique that would give this information.

It would also be relevant to further investigate the effects of NaI and the butanols on the synthesis system. This could be done by studying how these additives, as well as the others, affect the geometry of the Pluronic micelles and their solubility in 1.6 M hydrochloric acid. The available literature data on the effects of salts and alcohols in the Pluronic micelles are mostly in a pure aqueous solution, thus the behavior in a solution similar to the synthesis solution is not properly investigated. For the purpose of measuring the size of the Pluronic micelles, light scattering could be used, and measurements of the cloud point would give information about the solubility.

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A big thank you to everyone in the group, my office-mates and everyone at the Physical Chemistry Department for making me feel welcome and making my stay a pleasant time.

Last, but not least; a special thanks to friends and family for love and support.

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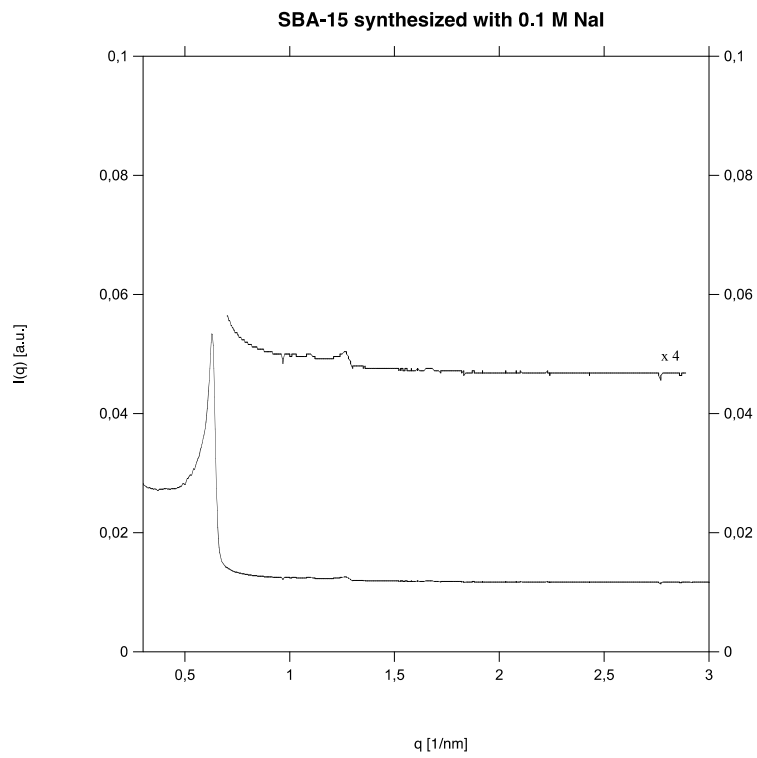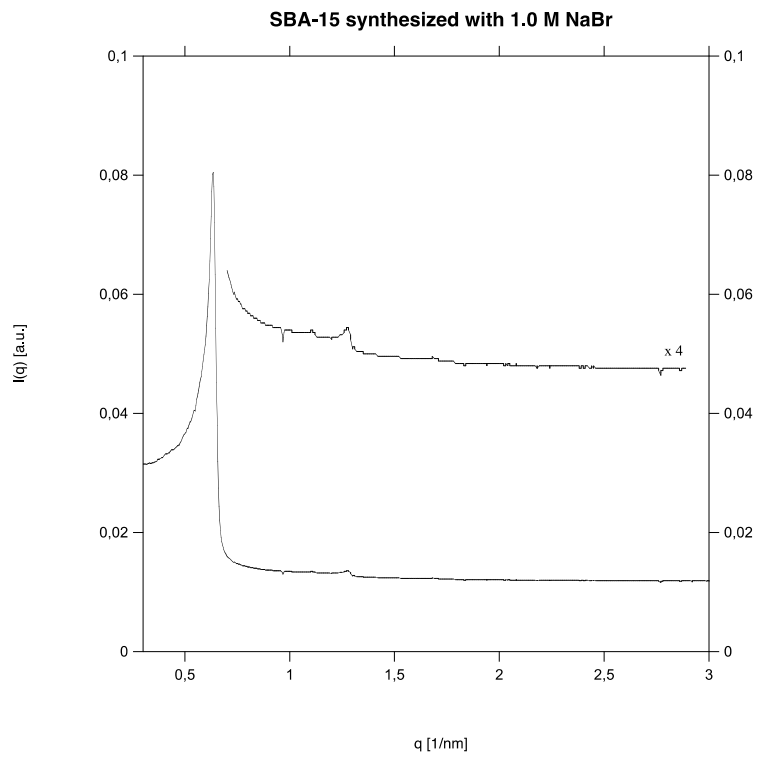[9]   Flodström K., *Mesoporous Silica Formed with Triblock Copolymers.* Doctoral Thesis, Lund University, 2004.

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APPENDIX 1; SAXD-Plots

SBA-15

q [1/nm]

SBA-15 synthesized with 0.1 M NaCl

q [1/nm]

SBA-15 synthesized with 0.5 M NaCl

SBA-15 synthesized with 1.0 M NaCl

30

SBA-15 synthesized with 0.1 M NaBr

I(q) [a.u.]

x 4

q [1/nm]

SBA-15 synthesized with 0.5 M NaBr

I(q) [a.u.]

x 4

q [1/nm]

SBA-15 synthesized with 1.0 M NaBr

I(q) [a.u.]

q [1/nm]

x 4

SBA-15 synthesized with 0.1 M NaI

I(q) [a.u.]

q [1/nm]

x 4

SBA-15 synthesized with 0.5 M NaI

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 1.0 M NaI

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.1 M MeOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.5 M MeOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 1.0 M MeOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.1 M EtOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.5 M EtOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 1.0 M EtOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.1 M 1-PrOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.5 M 1-PrOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 1.0 M 1-PrOH

x 4

q [1/nm]

I(q) [a.u.]

SBA-15 synthesized with 0.1 M 2-PrOH

x 4

q [1/nm]

I(q) [a.u.]

SBA-15 synthesized with 0.5 M 2-PrOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 1.0 M 2-PrOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.1 M 1-BuOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.5 M 1-BuOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 1.0 M 1-BuOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.1 M 2-BuOH

x 4

I(q) [a.u.]

q [1/nm]

SBA-15 synthesized with 0.5 M 2-BuOH
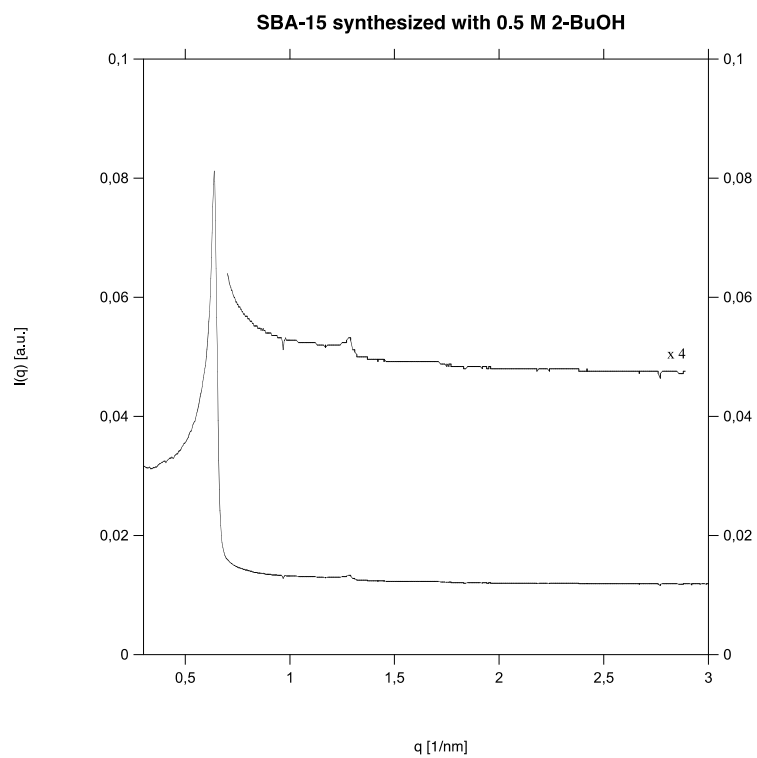

SBA-15 synthesized with 1.0 M 2-BuOH

APPENDIX 2; SEM categorization

Bellow, in Figure 17-22, the six categories used for categorization of the materials are listed and shortly described in the caption. All scale bars corresponds to 1 µm.
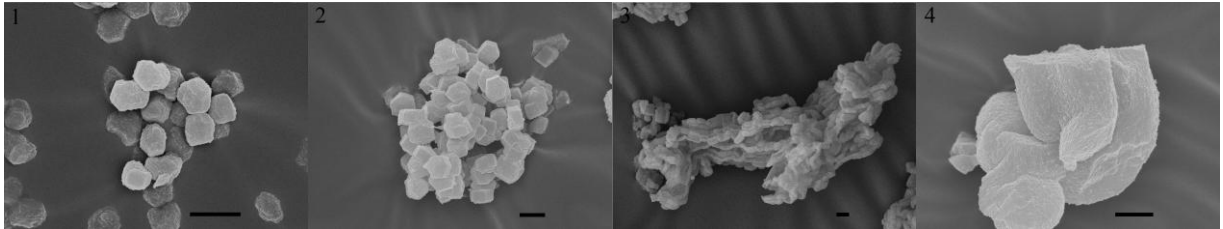

Figure 17. Morphology; 1:hexagonal, 2: altered/deformed hexagonal, 3: fibrous and 4: undefined particles.
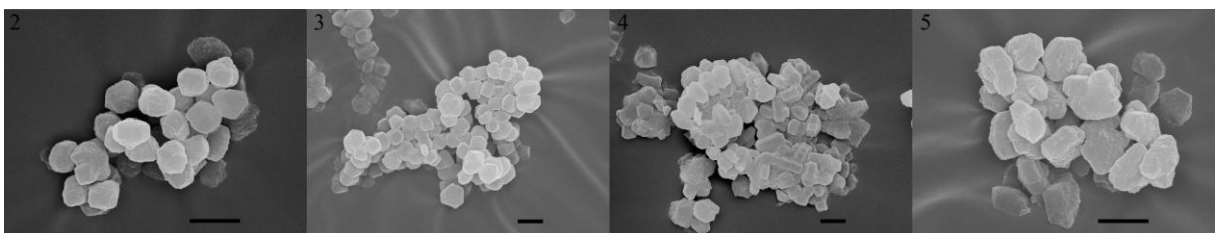

Figure 18. Particles, 1 (not pictured): primary, 2: both, predominantly primary, 3: both, 4: both, predominantly secondary and 5: secondary particles.
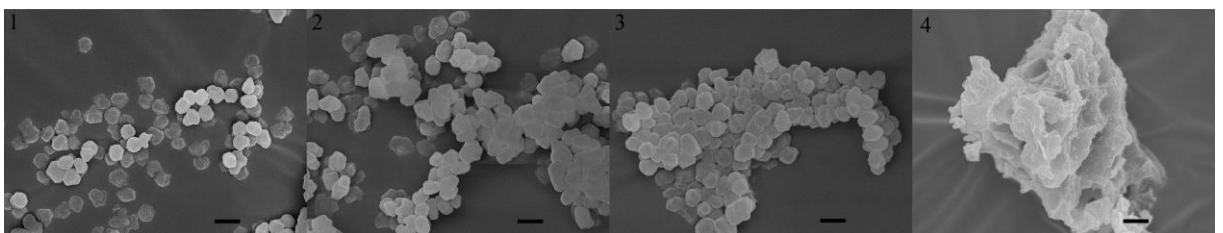

Figure 19. Aggregation; 1: loose packing, 2: intermediate packing, 3: compact packing and 4: particles not distinguishable.
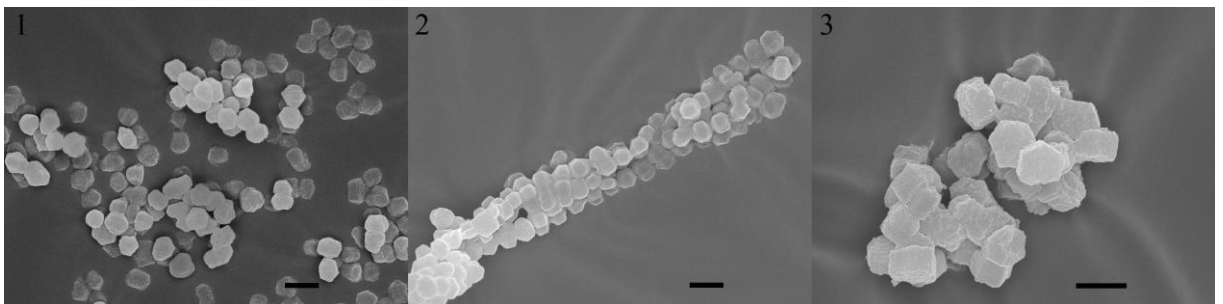

Figure 20. Concrescence, 1: no concrescence, 2: ordered concrescence and 3: random concrescence.
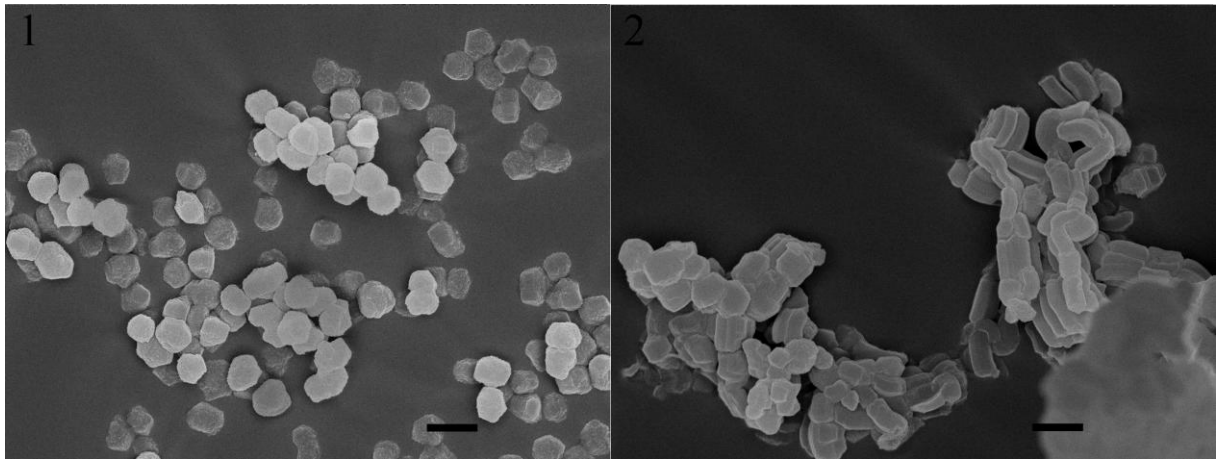
Figure 21. Diversity; 1: homogeneous particles and 2: heterogeneous particles.
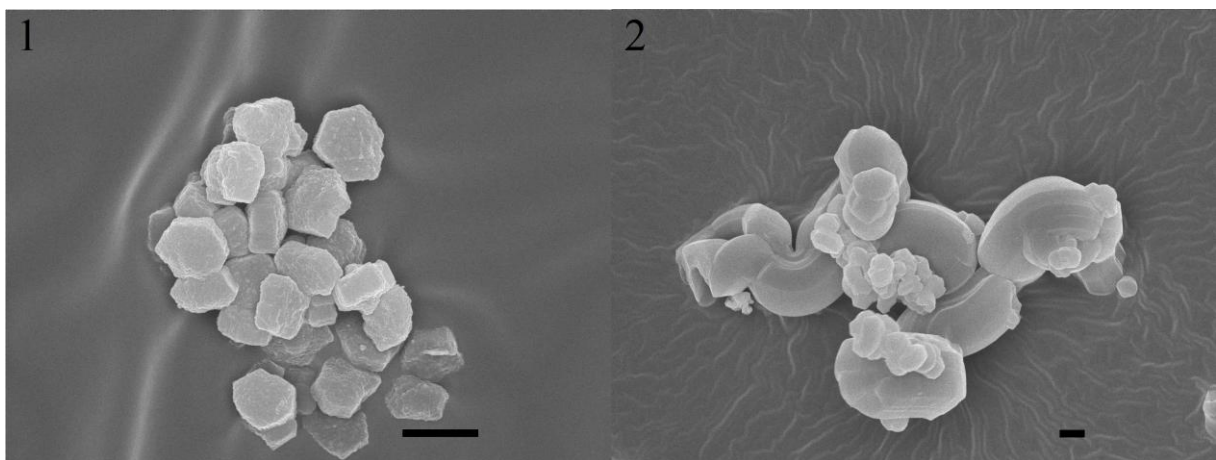

Figure 22. Populations; 1: homogeneous aggregates and 2: heterogeneous aggregates.

Table 3. Categorization of the SEM-pictures, for key see Figure 17-22.

Sample	Morphology	Particles	Aggregation	Concrescence	Diversity	Populations
SBA-15	1	2	2	1	1	1
0.1 M NaCl	1	2	3	3	1	1
0.5 M NaCl	2	3	4	3	1	1
1.0 M NaCl	3	-	4	2	2	2
0.1 M NaBr	2	3	3	3	1	1
0.5 M NaBr	2	3	4	2	2	2
1.0 M NaBr	2	4	4	3	1	1
0.1 M NaI	2	2	3	2	1	1
0.5 M NaI	3	-	4	2	2	2
1.0 M NaI	4	-	3	3	2	2
0.1 M MeOH	2	3	2	1	1	1
0.5 M MeOH	2	4	3	3	1	1
1.0 M MeOH	2	2	4	3	1	1
0.1 M EtOH	2	5	3	3	1	1
0.5 M EtOH	2	5	4	3	1	1
1.0 M EtOH	4	-	4	3	1	1
0.1 M 1-PrOH	2	4	3	3	1	1
0.5 M 1-PrOH	4	-	4	3	1	1
1.0 M 1-PrOH	4	-	4	3	1	1
0.1 M 2-PrOH	2	5	3	3	1	1
0.5 M 2-PrOH	2	-	4	3	1	1
1.0 M 2-PrOH	4	-	5	3	1	1
0.1 M 1-BuOH	2	3	3	2	1	1
0.5 M 1-BuOH	4	-	4	3	1	1
1.0 M 1-BuOH	4	-	5	3	1	1
0.1 M 2-BuOH	2	3	3	3	1	1
0.5 M 2-BuOH	4	-	4	3	1	1
1.0 M 2-BuOH	4	-	4	3	1	1