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A STUDY OF CONTROLLABLE AGGREGATION USING SILANE TREATED
SILICA NANOPARTICLES

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ABSTRACT

Colloidal silica particles were surface-treated with the silane coupling agent N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE). The aggregation behavior of TMPE-treated silica was then characterized as a function of silica volume fraction, grams of TMPE, and pH of the solution; the goal being to successfully manipulate these variables to establish a system of controllable aggregation. After surface modification, size measurements were recorded using Dynamic Light Scattering (DLS). Size measurements indicated that increasing the amount of TMPE led to slower aggregation rates and smaller final aggregate sizes. These results can be explained by the presence of excess TMPE in solution, which has a stabilizing effect on colloidal silica and reduces their need to form clusters. Results also showed that pH can be used to control the final size of aggregates by changing the zeta potential of the silica surface, in which a high zeta potential ($\sim > |20|$ mV) correlates to a stable colloidal dispersion. At high pH values (> 8.9), samples had low zeta potentials, formed unstable dispersions, and eventually aggregated to the point of complete gelation. At low pH values, the protonation of amino groups on silica surface created a high zeta potential and stabilized the silica particles in suspension through electrostatic repulsion. Results show that it is possible to control aggregation by manipulating the amount of TMPE used for surface treatment and the pH of the dispersion.

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Chapter 1

Introduction

Colloidal silica nanoparticles play an important role in a variety of applications including sensors, chromatography, pigments, and coatings (Egon, 2008). In medicine, drugs are placed inside silica particles, which act as transporting vessels for time-controlled drug delivery in the body. One common problem associated with colloidal dispersions is the tendency for particles to aggregate and settle out of solution. This behavior can negatively alter the electrical, optical, magnetic, chemical, or mechanical properties of the system (Khan et al, 2004). However, in some cases the ability to create stabilized aggregates in solution is an important aspect of enhancing specific system properties. One example of this phenomenon can be seen within nanofluids, where the formation of aggregates has been linked to large enhancements in thermal conductivity (Lee et al, 1999; Wong, et al, 2010; Eapen et al, 2007).

Nanofluids, fluids containing dispersed nano-sized particles, have become a promising new technology used to increase the thermal conductivity of base fluids such as oil or water, which alone act as poor heat transfer media. Nanofluids promote fast and efficient cooling in equipment such as high pressure reactors and microchips (Lee et al, 1999). In addition, nanoparticles have larger surface areas and a decreased tendency to settle out of solution, making them a preferred alternative to micro-sized metal particles. The formation of nanoparticle clusters, or aggregates, has been observed to have the largest measureable effect on thermal conductivity enhancement within fluids. These aggregates form long chains within the liquids and act as conduction channels enabling faster heat transfer, but more research is still needed to affirm the extent of this enhancement effect (Okeke, 2012).

Our lab group is interested in developing a deeper understanding of the possible linkage between nano-particle aggregation and increases in fluid thermal conductivity. To establish such an understanding, it becomes necessary to create a system of controllable aggregation. Previous studies in our lab have proven that it is possible to control the size of colloidal clusters and promote reversible aggregation through the use of *N*-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE), a silane coupling agent (SCA) that bonds to the surface of the silica. This surface modification enables the reversibility of aggregates by preventing chemical bond formation between silica nanoparticles and allowing only non-permanent physical interactions to form. The objective of this thesis is to characterize the behavior of surface treated colloidal silica and identify the factors affecting growth rate and final size of aggregates. This thesis focuses on how the dynamics of aggregation over time vary as a function of silica concentration (by volume), grams of TMPE, and pH of the solution. Ludox, a commercially prepared dispersion of silica in deionized water (40% by weight), is used to prepare all samples. The Ludox solution is diluted with deionized water to create lower silica concentrations. After forming the diluted silica solutions, surface modification is achieved through the addition of the TMPE. The effect of surface modification on aggregation is analyzed through size measurements using dynamic light scattering (DLS).

Chapter 2

Background

Synthesis of Silica Particles

Spherical silica nanoparticles are created through the repeated hydrolysis and condensation of alkyl silicates to create a polymeric species consisting of $[\text{Si-O-Si}]_n$ bonds (Aljama, 2010). The most common method, known as the Stober Method, involves the reaction of tetraethylorthosilicate (TEOS) in a mixture of alcohol, water, and ammonia, which act as the catalyst (Gellermann et. al, 1997). Figure 1 shows the chemical structure of TEOS.

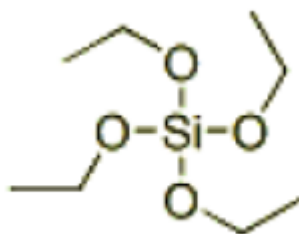
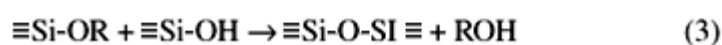
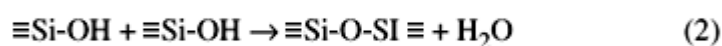
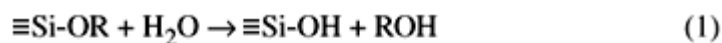


Figure 1: The Chemical Structure of TEOS (Aljama, 2010)

The chemical equations 1 through 3 demonstrate how the reaction proceeds, where R represents the ethyl group. In reaction 1, water performs a nucleophilic attack on the alkyl silicate to form silicic acid. This hydrolysis reaction is followed by subsequent water and alcohol condensation reactions to produce the silica nanoparticle. Figure 2 shows the final structure of the silica nanoparticle.



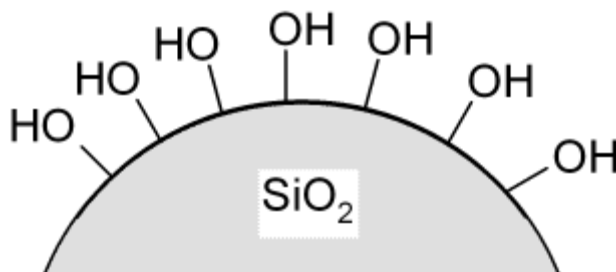


Figure 2: The chemical structure of a silica nanoparticle

Surface Modification of Silica using Silane Coupling Agents (SCA)

The final silica particle is covered with highly reactive hydroxyl groups, which can lead to the formation of bonds between silica molecules or other molecules. Therefore, the surface of the silica particles must be manipulated in order to create a system of reversible aggregation. This surface modification is achieved through the permanent chemical bonding of silane coupling agents (SCA) to the surface of the silica particle. The SCA layer forms a barrier that prevents the silica surface from sticking together and forming permanent chemical bonds. The structure of a silane contains the following functional groups:



where X represents a hydrolyzable group (i.e.-methoxy, ethoxy, or acetoxy) and Y is a nonhydrolyzable organofunctional group (i.e.-amino, epoxy, etc.). X groups react with the surface of the silica, while the Y groups are typically used to bond with organic materials such as polymers or resins (Honkanen et al, 2011). According to the company United Chemical Technologies, different silanes have different amounts of hydrolyzable and organofunctional groups which can affect the bond strength and degree of surface modification.

The structure of the SCA chosen for this thesis, TMPE, can be seen in Figure 3.

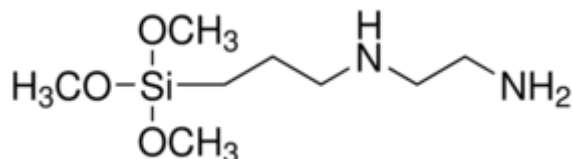


Figure 3: The chemical structure of *N*-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE) (Sigma-Aldrich)

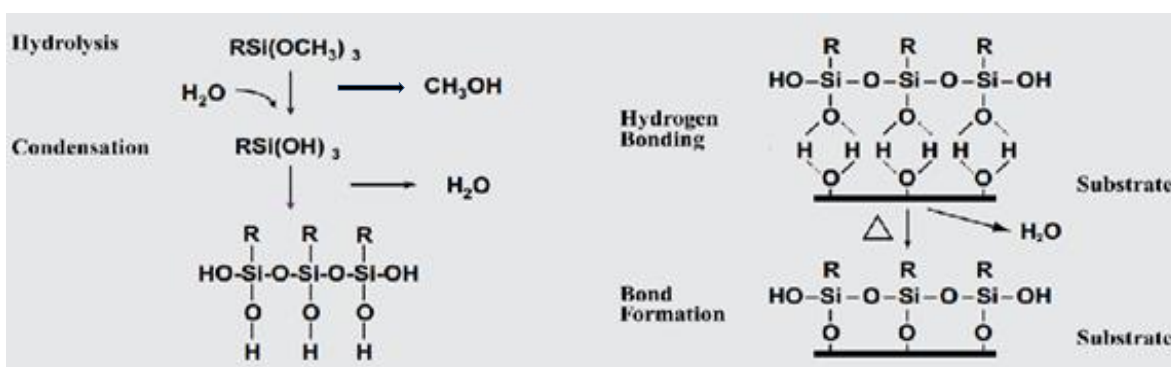


Figure 4: Schematic of the synthesis of surface treated silica nanoparticles with TMPE, where **R** represents a reactive organofunctional group, such as amino, methacryloxy, epoxy amino groups, etc. For TMPE the R group contains two amine groups. (Dow Corning, 2007)

TMPE has three reactive methoxy groups ($X=\text{CH}_3\text{O}$) which can be hydrolyzed to release methanol and produce a Si-OH groups. These newly formed –OH groups undergo a condensation reaction with the surface of the silica nanoparticle to form a Si-O-Si linkage. Figure 4 demonstrates the hydrolysis of the hydroxy groups and bond formation to the surface of the silica nanoparticle. TMPE also has 2 aminofunctional groups (Y groups) on the hydrocarbon chain. These non-reactive functional groups extend into solution and modify the charge density of the silica as a function of pH. The combined roles of the methoxy and amino groups allow SCA surface treatment to prevent permanent aggregation. The methoxy groups form permanent chemical bonds with the reactive hydroxyl groups on the silica particle; silica's reactive hydroxyl

groups would have otherwise chemically bonded with other molecules and lead to uncontrollable coagulation. In addition, the amino groups on the SCA hydrocarbon chain only allow for electrostatic and physical interactions between silica molecules rather than the formation of irreversible chemical bonds.

The aminofunctional groups on the TMPE create electrostatic interactions between particles because the charge of the amino groups can be altered as a function of pH. As the charge density around the silica particle changes, this affects the degree of electrostatic repulsion between particles; a characteristic known as the zeta potential. Zeta potential describes the degree of repulsion that exists between charged particles and determines the stability of a colloidal dispersion. A high positive or negative zeta potential correlates to a high degree of repulsion between particles and a well dispersed system. A zeta potential of zero describes the isoelectric point (IEP) at which no net charge exists in the system. The absence of electrostatic repulsions will cause the particles to aggregate uncontrollably. Depending on the pH of the system, TMPE creates a highly charged or neutral environment at the surface of the silica particles and changes the silica's zeta potential. Figure 5 displays how surface treatment of silica with TMPE changes the behavior of zeta potential as a function of pH. TMPE treated silica is changed to a pH of \approx 9.7- 9.9, which is very close to the isoelectric point; within this pH range aggregation occurs rapidly.

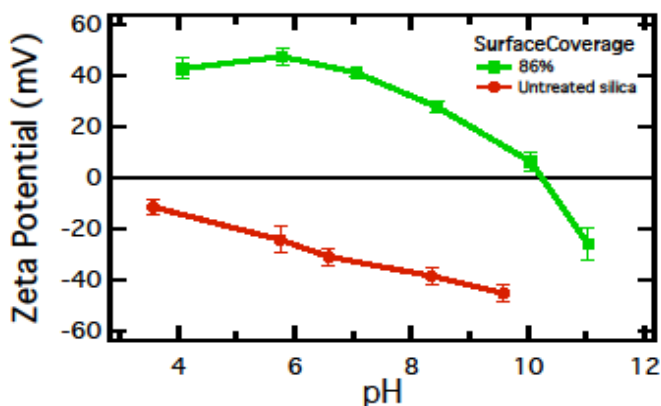
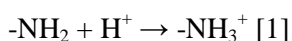


Figure 5: Comparison of the zeta potential vs. pH of TMPE surface treated silica (green) and untreated silica (red). (Lotfizadeh, 2014)

Figure 5 shows that the zeta potential or surface charge of the silica particle is a function of pH. It has also been explained that rate of aggregation is related to the degree of repulsion between particles. Therefore, pH can be used to control the extent of aggregation by controlling the degree of electrostatic repulsion between particles. The aggregation of silica particles is reversible because only electrostatic interactions can occur between particles rather than the formation of permanent chemical bonds. The following reactions take place among the aminofunctional groups on the surface of the particle:



Reaction [1] demonstrates that at low pH NH_2 becomes positively charged due to a large amount of H^+ ions present in solution. This creates a system of silica nanoparticles with like charges, causing them to electrostatically repel each other and disperse in the solution. This also creates a system with a high zeta potential. At high pH, the amine groups remain un-charged, which means the system is at the IEP. The amino groups begin to aggregate due to the absence of electrostatic repulsion between particles.

Previous studies of SCAs

A number of studies have demonstrated that it is possible to modify the surface of colloidal silica particles using silane coupling agents. Because untreated silica is hydrophilic, most literature focused on creating hydrophobic silica. Wu and coworkers' research on silanes led the discovery that the silica's hydrophobicity can be manipulated by changing the length of the hydrocarbon chain placed on the silica surface (Wu, 2006). Research studies also established that it is possible to modify the surface of silica with silanes without causing aggregation (van Blaaderen 1993, 1994; van Helden 1981; Wu 2006; Aljama, 2010). However, these studies have

not investigated: the stability of colloidal silica in aqueous solutions, colloidal stability after modification, and different degrees of silane coverage on the surface of the silica.

Due to limited research studies, previous work in our lab has been focused on improving the stability of silica in hydrophilic environments using the following silanes: aminopropyltriethoxysilane (APES) and 3-aminopropyldimethylmethoxysilane (APMS), and *N*-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE) (Aljama, 2010). These silanes have been identified to increase solubility in hydrophilic solvents. In his thesis, Aljama sought to determine the effects of different degrees of silane surface coverage and assess the stability of surface treated particles after modification (\approx two-week period). The following figures show the structures of APTS, APMS, and TMPE.

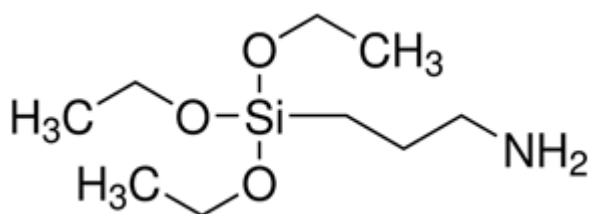


Figure 6: The chemical structure of aminopropyltriethoxysilane (APTES)

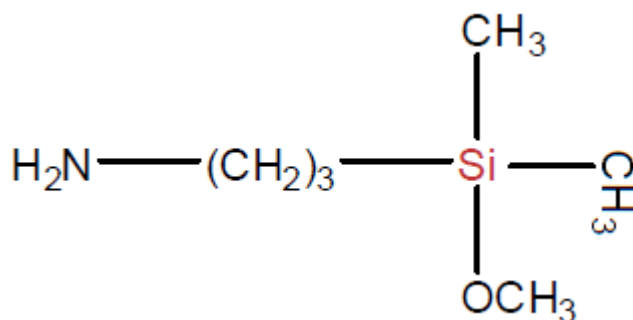


Figure 7: The Chemical Structure of 3-aminopropyldimethylmethoxysilane (APMS)

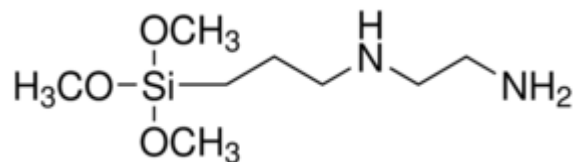


Figure 8:The chemical structure of N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE) (Sigma-Aldrich)

The structure of APES is very similar to that of TMPE, except it has 3 reactive ethoxy groups rather than 3 methoxy groups. Previous studies show that the presence of more than one reactive group increases the possibility of bridging between adjacent silica particles (see Figure 9).

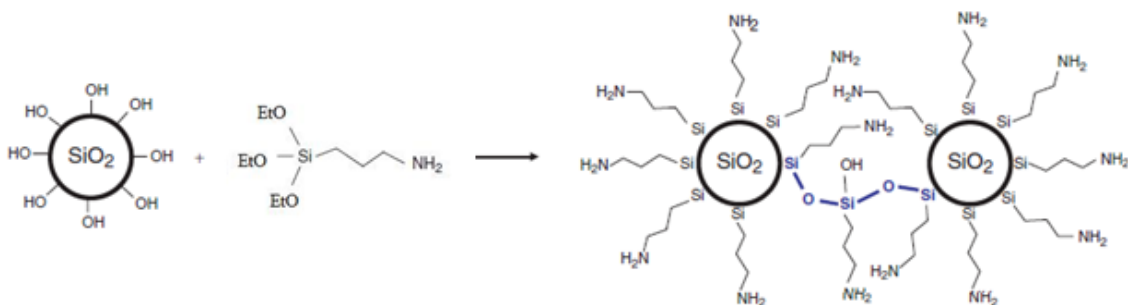


Figure 9: Schematic Showing the Possibility of Bridging between APES-treated Silica (Aljama, 2010)

Figure 9 shows that bridging is a chemical and irreversible linkage between two silica particles. A complex network of these linkages leads to uncontrollable aggregation and eventually complete gelation of the silica solution (Pham et al, 2007). In Aljama's thesis, he observed that high concentrations of APES led to gel formation with 48 hours and further testing confirmed APES-treated silica is less stable than untreated silica. In comparison to APES, APMS only has one methoxy group. APMS lead to no aggregation at any concentration because bridging can no longer occur. The disadvantage associated with APMS having only one reactive methoxy group is

the weak bond formation between APMS and the silica surface. Aljama discovered that TMPE's additional amino group had affected the zeta potential curve of the silica particle and concluded electrostatic forces are the dominant factor controlling colloidal stability rather than the formation of a steric layer on the surface of particles. TMPE was also the only silane that could fully coat the silica particle without generating aggregation at its native pH (≈ 10.7). Due to the results of preliminary research, TMPE was chosen for further analysis in this thesis for the following reasons: high reactivity due to its 3 methoxy groups, increased surface charge resulting from two amino groups, and ability to fully coat the silica particle with aggregation (or bridging).

Aljama's thesis also utilized various methods to modify the surface of silica particles. One method involved the synthesis of silica particles using the Stober method (explained in the introduction) followed by dilution of the silica with distilled water, and a dropwise addition of the SCA (Pham et al, 2007). In addition, surface modification of silica particles was also achieved through a modified version of Pham's method, in which TM-40 LUDOX was used as the source of silica. Lastly, Aljama analyzed a six-step surface treatment process in which a different functional group was introduced in each step (Mahalingam et. al, 2004). When using this method, Aljama saw slight increases in the magnitude of zeta potential of the silica particles near pH 7. Outside of Aljama's studies, other research studies show that silica particles (virginal silicas, product name: VN3) can be surface-treated by dipping the particles in a hydrolyzed silane solution (Park et. al, 2003). A summary of the varying types of silanes can be found in Table 1.

Molecular Formula	Name	Reference
$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$	Aminopropyltriethoxysilane (APES)	Wu et al, 2007; Gellermann et. al, 1997
$(\text{CH}_3\text{O})(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{NH}_2$	3-aminopropyldimethylmethoxy silane (APMS)	Pham et al 2007
$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	3-aminopropyltrimethoxy silane	Pham et al 2007
$\text{H}_2\text{C}=\text{CHSi}(\text{OCH}_3)_3$	vinyltrimethoxysilane	Gellermann et. al, 1997
$\text{C}_{10}\text{H}_{22}\text{O}_4\text{Si}$	3-methacryloxypropyltrimethoxysilane	Gellermann et. al, 1997
$\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$	3-glycidoxypropyltrimethoxysilane	Gellermann et. al, 1997
$\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$	γ -aminopropyl triethoxysilane	Park et. al, 2003
$\text{C}_6\text{H}_{15}\text{ClO}_3\text{Si}$	γ -chloropropyl trimethoxysilane	Park et. al, 2003
$\text{C}_{10}\text{H}_{20}\text{O}_5\text{Si}$	γ -methacryloxypropyl trimethoxysilane	Park et. al, 2003
$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$	<i>N</i> -[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE)	Aljama, 2010

Table 1: Summary of Studied Silane Coupling Agents (SCA)

Dynamic Light Scattering (Theory)

The size of the silica nanoparticles are measured using (DLS), a very common technique used to determine the diameter of particles. Light in the form of a laser is passed through solution of suspended particles. The particles intercept the path of the light and cause it to scatter. The

fluctuations of the light scattering is detected and measured by a sensor and sent to a correlator, which relates the scattering of light to the particle size based on two mathematic functions. The equipment setup is shown in Figure 10.

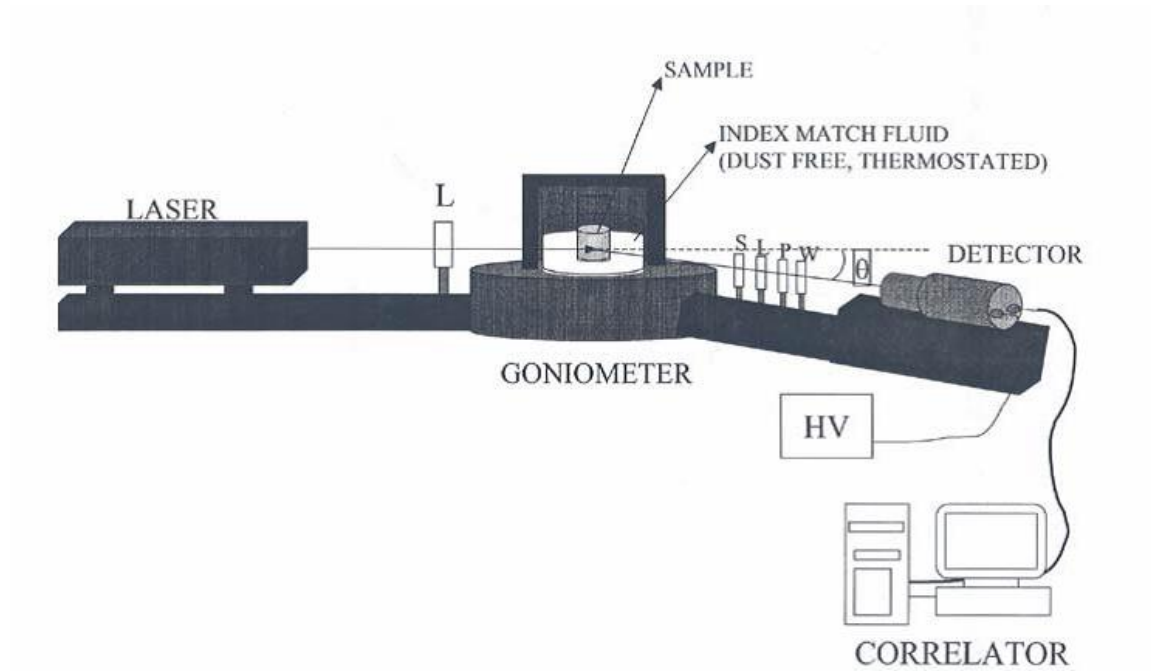


Figure 10: The Dynamic Light Scattering Equipment Setup (Weitz, 2014)

The Intensity Correlation Function ($G_2(\tau)$) measures the change in the scattering intensity by comparing the intensity at time (t) to the intensity at a later time ($t + \tau$) through the following equation:

$$G_2(\tau) = \frac{1}{T} \int_0^T I(t)I(t + \tau)dt \quad (5)$$

where (τ) is the delay time, (I) is the measured intensity, and (t) is the total time. The changes in the scattering intensity are due to the random motion of the particles in the solution known as Brownian motion. This constant motion will constantly change the scattering pattern of the light (Weitz, 2014).

The correlation function typically follows an exponential decay as shown in Figure 11.

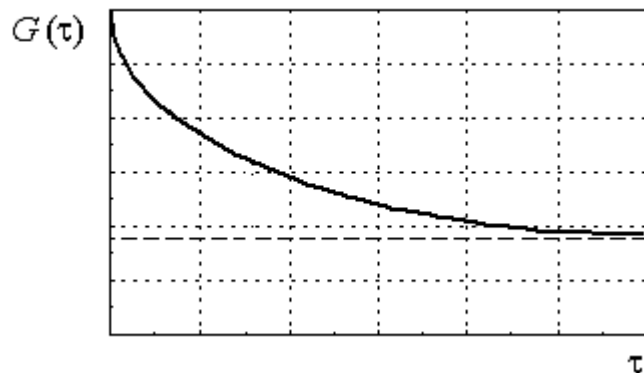


Figure 11: The Exponential Relationship Between the Correlator Function, $G(\tau)$, and the Delay Time (τ). (Aljama, 2010)

It is not possible to determine the motion of particles by analyzing the changes in scattering light, as a result, the motion of particles must be correlated relative to one another through the Electric Field Correlation Function ($G_1(\tau)$). The equation is as follows:

$$G_1(\tau) = \exp^{-\Gamma\tau} \quad (6)$$

where (Γ) is the decay constant. Equation 3 demonstrates that the decay constant can be written as a function of the diffusivity. Because diffusivity is a function of the particle size, the decay constant can be re-written in terms of the particle size through the Stokes-Einstein Equation (equation 4). The equations are as follows:

$$\Gamma = -Dq^2 \quad (7)$$

$$D = \frac{kT}{6\pi\mu r} \quad (8)$$

where (D) is the diffusion coefficient and (q) is the distance that the particle travels. The diffusion coefficient describes the motion of a spherical particle of radius (r) in a fluid with a dynamic viscosity (μ) at an absolute temperature (T).

The two correlation functions are then related through the Siegert Relationship, which allows the scattering of light to be related to the size of diffusing particles. The following relationship holds:

$$G_2(\tau) = B[1 + \beta|G_1(\tau)|^2] \quad (9)$$

where (B) is the baseline and (β) is an instrumental response, both of which are constants (Weitz, 2014).

Chapter 3

Experimental Procedure

In this thesis, the rate of aggregation and final particle size of silica nanoparticles was analyzed as a function of three parameters: volume fraction of silica, amount of TMPE, and pH of the solution. The analysis was separated into two different experiment sets. In set one, the rate of aggregation was observed against different amounts of TMPE. Two different amounts of TMPE (0.096 g TMPE/g silica & 0.11 g TMPE/g silica) were each added to three different volume fractions of silica (3%, 5%, and 7%) for a total of six samples. In set two, the rate of aggregation was tested across a pH range (5-9) using the same three concentrations of silica, but keeping the amount of TMPE constant. For each experiment set, the particle size was measured using DLS.

Surface Modification Process

TM-40 LUDOX colloidal silica (diameter of about 30 nm) was purchased from Sigma-Aldrich. The LUDOX product contains silica nanoparticles (40% by weight) dispersed in water. The silica was diluted with distilled water to make silica solutions of three different volume fractions (3%, 5%, and 7%). Each sample has a total volume of 20 mL. The experiment set determined the specific amount of TMPE that was added. TMPE was added dropwise to each solution and all solutions were mixed for 24 hours using a magnetic stirrer. The pH of the treated silica was then changed from its native pH (around 10.7) to a pH of 9.7. The pH range of 9.7-9.8 represents the isoelectric point within the system, in which the particles have no electrostatic

repulsion and begin to aggregate uncontrollably. Size measurements were recorded over a 2-month period using Dynamic Light Scattering (DLS).

Effects of TMPE on Aggregation Rate (Experiment Set 1)

Two sets of untreated silica solutions with volume fractions of 3%, 5%, and 7% were prepared following the above surface modification process. Each set was treated with a different amount of TMPE (0.096 g TMPE/g silica and 0.11 g TMPE/g silica) for a total of six samples. The rate of aggregation was observed over a 2-month period. Size measurements were recorded using Dynamic Light Scattering (DLS).

Effects of pH on Aggregation Rate (Experiment Set 2)

One set of untreated silica solutions with volume fractions of 3%, 5%, and 7% were prepared following the above surface modification process and treated with TMPE (0.086 g TMPE/g silica). The solutions were left for 24 hours to allow for aggregation and complete gelation. Each solution was then separated into five solutions with distinct pH values (5, 6.5, 7.5, 8.1, and 8.8), creating a total of 15 samples. All of the samples were sonicated for 30 minutes each at 50 Amperes using the QSonica Sonicator Model Q55. Sonication is the use of sound energy in attempts to agitate and, in this case, deaggregate the particles back to their original size ($\approx 30\text{nm}$). After pH modifications and sonication, size measurements were recorded using Dynamic Light Scattering (DLS) over a 1.5 month period.

Dynamic Light Scattering

For this measurement, the Brookhaven Instrument Corporation's Digital Correlator and the Spectra-Physics Model 127 35 mW Helium-Neon Laser were used. Certain parameters such as the wavelength setting (633 nm) and the angle between the laser and the detector (90°) were kept constant throughout the experiment. The viscosity parameter was adjusted according to the temperature at the time of the measurement. Samples were prepared for the DLS measurement by adding one or two drops of the sample to a test tube and diluting it with distilled water. At least three measurements are recorded per sample to assess the precision of the measurements. The accuracy of the measurements is determined by the percent error provided by the correlator and only measurements with a percentage error of <0.1% was recorded.

Chapter 4

Results and Discussion

Effects of TMPE on Aggregation Rate (Experiment Set 1)

The purpose of experiment set 1 is to determine how the amount of TMPE (g) and volume fraction of silica affects the evolution of particle size over time. Two sets of untreated silica solutions, with volume fractions 3%, 5%, and 7%, were prepared according to the experimental procedure (surface modification process). Two different amounts of TMPE were then added to each of set of solutions. Table 2 summarizes the conditions of experiment set 1. To better differentiate the amount of TMPE added to each sample set, 0.096g TMPE/g silica will be referred to as the low TMPE sample and 0.11 g TMPE/g silica will be referred to as the high TMPE sample throughout the remaining sections of this thesis.

Outline of Experiment Set 1		
Particle Concentration (%Volume)	Low Amount of TMPE Run 1 (g TMP/g silica)	High Amount of TMPE Run 2 (g TMP/g silica)
3	0.096	0.11
5		
7		

Table 2: Outline of Experiment Set 1

After 24 hours from the addition of TMPE, the pH of all samples was changed to pH 9.7, and the size of the nanoparticles was measured using DLS. This specific pH was chosen because it is close to the IEP and will create an environment that promotes the most aggregation. Therefore, pH 9.7 creates the best

conditions for observing how the amount of TMPE affects the dynamics aggregation and the final size of aggregates. A summary of the results for runs 1 and 2 are shown in figure 12.

Figure 12 shows that the low TMPE silica particles grow about two times faster than the high TMPE silica particles. In addition, the low TMPE silica particles also have a significantly larger final particle size. The particles treated with low TMPE formed a solid gel, whereas the high TMPE silica particles remained dispersed in solution (final size ≈ 100 nm).

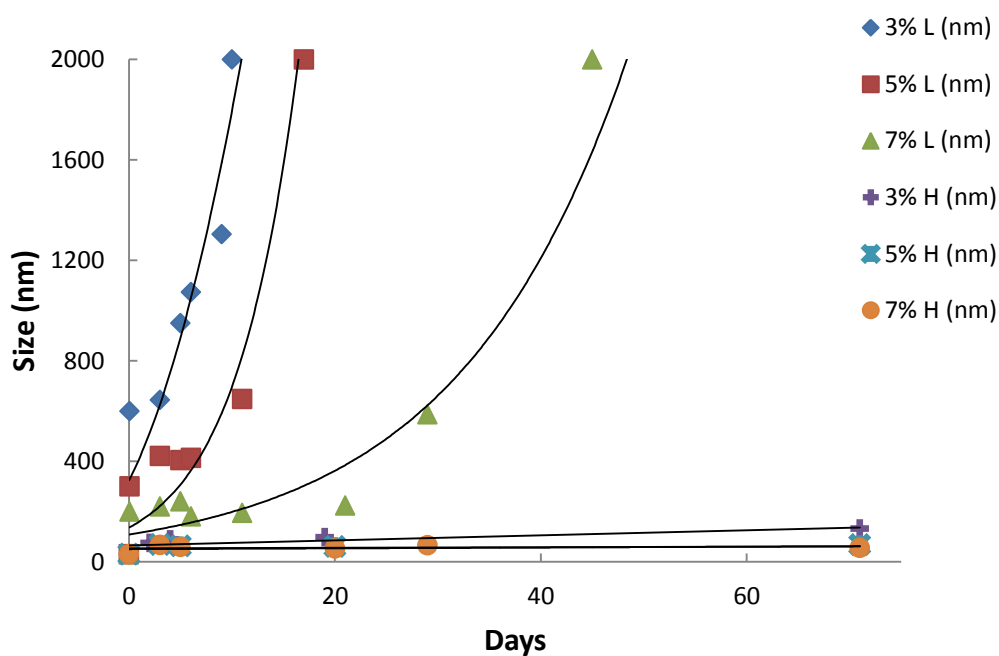


Figure 12: Summary of Size vs. Time Measurements for Low and High-TMPE-treated Silica Nanoparticles at pH 9.7

To further understand how the dynamics of aggregation change with volume fraction of silica, it is necessary to analyze the low TMPE and high TMPE samples exclusively (see figures 13 and 14).

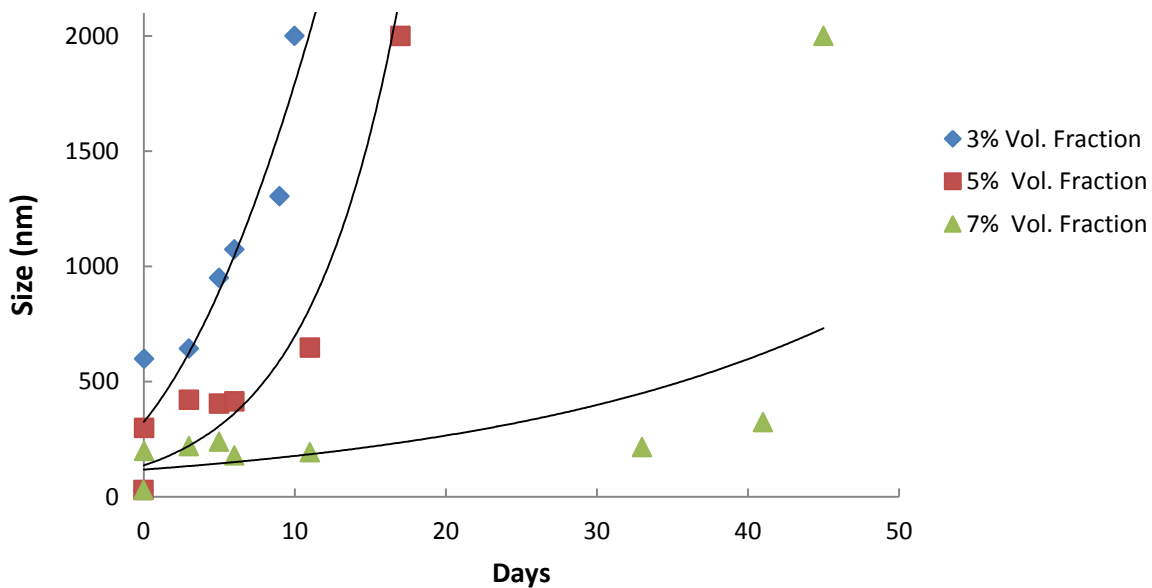


Figure 13: Size vs. Time Measurements for Low TMPE-treated Silica Nanoparticles at pH 9.7

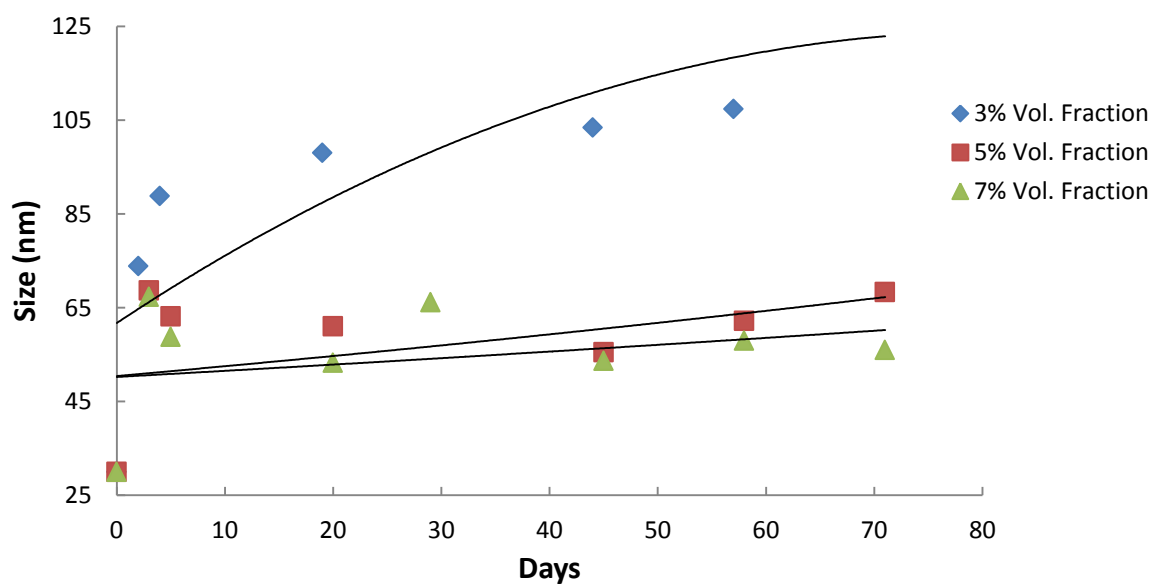


Figure 14: Size vs. Time Measurements for High TMPE-treated Silica Nanoparticles at pH 9.7

Figure 13 shows that all the samples reach the same final particle size (complete gelation), but the lowest volume fraction of silica aggregates at a faster rate, followed by the 5%, and then the 7% sample. Contrastingly, high TMPE samples do not all reach the same final particle size (Figure 14). The 3% sample has the largest final particle size and fastest growth rate, while the final sizes and growth rate of the 5% and 7% samples are almost equivalent.

Figures 13 and 14 further justify that more TMPE in solution ambiguously stabilizes silica particles in solution. The plots show that aggregation decreases even as the volume fraction of silica particles increases. These results conflict with the von Smoluchowski theory (Dobias et al, 2005), which states that the coming together of two particles to form an aggregate is defined by the following second order equation:

$$-\frac{dN_t}{dt} = k_D N_t^2 \quad (10)$$

Where N_t is the number of single particles at time t , N_0 is the initial number of single particles, and k_D is the rate coefficient of doublet formation. This theory assumes the particles are undergoing Brownian motion, which describes the random motion of particles in a fluid. It also assumes aggregation is limited by either the diffusion of particles through the fluid or is reaction limited. The theory also assumes there is no repulsion between interacting particles; so each interaction results in aggregation. This equation suggests that as the number of particles in solution doubles, the rate of aggregation should quadruple because particles will collide more frequently. Because this system does not exhibit this trend, it means that aggregation is not diffusion limited and that there is something present in the solution that is stabilizing these particles and slowing aggregation. TMPE is the only other variable within the system. Therefore it is possible these results can also be explained by the amount of excess TMPE in solution.

These differences in growth rate and final particle size can be a result of a stabilizing effect induced by excess TMPE in solution. Excess TMPE is suspected to be in solution because when TMPE is added to the sample to coat the silica, there is a certain amount of additional TMPE in the solution that did not react with the silica surface. When a higher amount of TMPE is added to the sample to coat the

silica, there is also a higher amount of excess TMPE in solution. Because these silanes are highly reactive, if TMPE cannot react with silica, it will instead quickly react with other TMPE to form a complex polymer –like network in solution. Once the TMPE have reacted to form this chain-like structure they are no longer available to react with the silica. However, TMPE can still form favorable physical interactions with the silica surface.

One possible physical mechanism responsible for the stabilization of silica particles in solution is chemical compatibility between the silica and TMPE. TMPE-treated silica particles are hydrophobic, so it is expected that the particles will cluster together to minimize unfavorable interactions with water. Because this clustering is not occurring at high amounts of TMPE, it is possible that TMPE acts to stabilize the particles in solution by forming favorable non-polar interactions with the silica surface. TMPE in solution makes the solvent more compatible for TMPE-treated silica particles, and as a result, reduces their rate of aggregation and sustains smaller aggregates.

Another possible physical mechanism hypothesized to slow aggregation rates is steric hindrance. Steric hindrance would be caused by the chains of TMPE that extend from the surface of the silica particle into solution and act as a physical obstruction that prevents particles from sticking together. However, due to the dominating hydrophobic characteristics of TMPE-treated silica, steric hindrance was determined not to be the cause of reduced aggregation in high TMPE samples. Silica particles minimize interactions with water through aggregation. As a result, the non-polar hydrocarbon chains on TMPE actually acts as an attractive force between particles. Particles will aggregate to maximize non-polar interactions and exclude water. Figure 12 also demonstrates how sensitive the silica system is to changes in TMPE. The difference in the amount of TMPE between the high TMPE and low TMPE samples is about .01 grams. However, this small change in TMPE led to drastic changes in the rates of growth and final particle sizes.

Yet another possible mechanism that can explain the stabilization of colloidal silica particles is the depletion effect, which is traditionally known to create attraction between colloidal particles in

suspension. However, several research studies show that certain conditions can generate both attractive and repulsive forces (Rudhardt et al, 1999; Crocker et al, 1998; Walz et al, 1994). According to the Asakura and Oosawa (AO) theory, depletion forces occur between two larger colloidal spheres of radius R that are surrounded by smaller fluid spheres with radius r , known as macromolecules. When the distance between the two colloidal spheres is smaller than the diameter of the macromolecule, it creates a “depletion zone” in which the macromolecules can no longer enter. The exclusion of macromolecules from this region leads to an osmotic pressure generating an attraction between the colloidal spheres. This generated attraction, however, is relative to the concentration of macromolecules. Studies show that as the concentration of the macromolecules increase they will begin to form layers around the colloidal spheres. Because the concentration of the macromolecules is now higher between the colloidal spheres, an osmotic pressure is created that forces the colloidal spheres apart. Within our experiment, it was assumed that TMPE-treated silica particles represented the colloidal spheres and the excess TMPE in solution represented the macromolecules. Figures 15 and 16 show the formation of the depletion zone associated with attraction and the formation of layers around colloidal spheres associated with repulsion respectively.

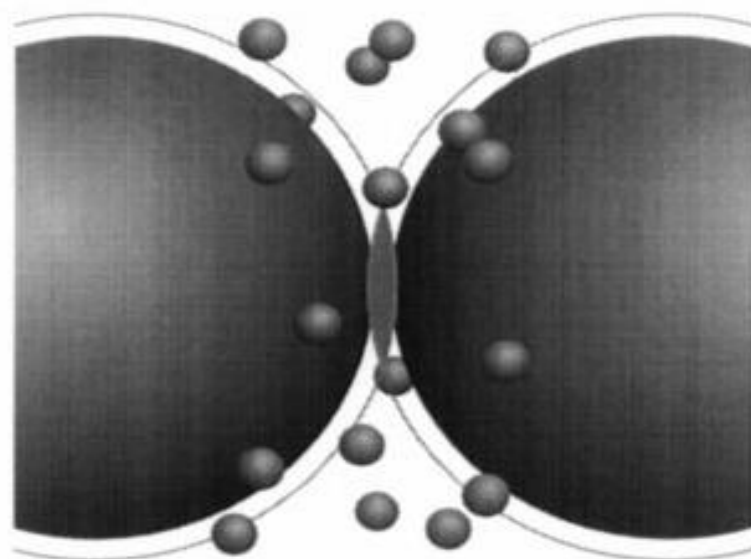


Figure 15: The formation of the depletion zone (shaded area) between two colloidal spheres generates an osmotic pressure that leads to an attraction between the colloidal spheres (Crocker et al, 1998)

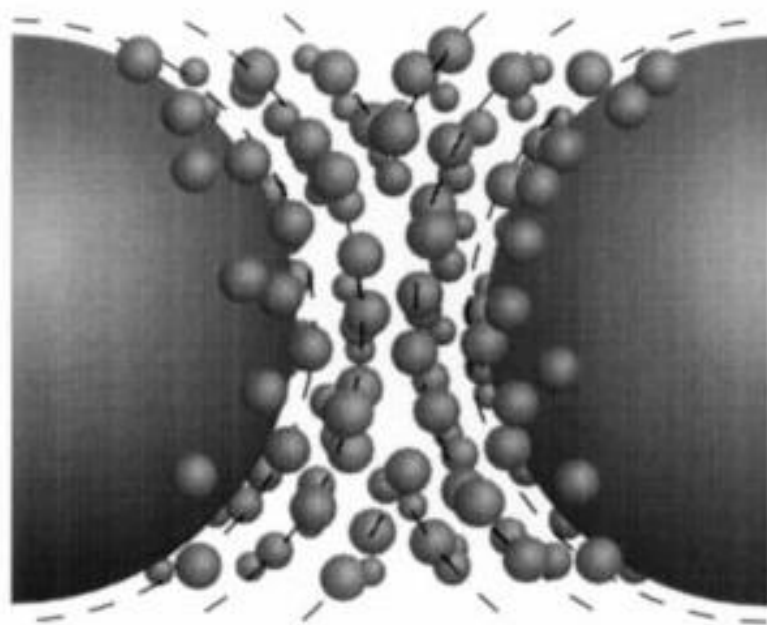


Figure 16: The smaller spheres form layers around the larger colloidal spheres generating an osmotic pressure that forces the colloidal spheres apart (Crocker et al, 1998)

The available literatures have all come to a very similar conclusion that increasing the concentration of the macromolecules generates a repulsive depletion force, but the exact volume % of macromolecules necessary to promote repulsion between particles is still unclear; findings ranged from 1-10% volume (Rudhardt et al, 1999; Crocker et al, 1998; Walz et al, 1994). Despite this numerical discrepancy, the results shown in figure 12 are in agreement with the conclusions found in the literature and suggest that increasing concentrations of excess TMPE could stabilize colloidal dispersions through repulsive depletion forces. Due to the conditions of this experiment, it is not possible to calculate the exact concentration of excess TMPE in solution; it is only hypothesized that the total concentration of excess TMPE in solution increases when more TMPE is added to a sample.

Among the literature studies, experiments involved colloidal dispersions of polymer spheres (≈ 1 micron) dispersed in a solvent containing smaller polymer spheres (≈ 100 nm) as macromolecules (Rudhardt et al, 1999; Crocker et al, 1998; Walz et al, 1994). By comparison, most samples of TMPE-

treated silica with high amounts of excess TMPE only grow to ≈ 100 nm. In addition, the size and structure of excess TMPE in solution is unknown. Walz and colleagues determined that the size, structure (i.e.-sphere vs. polymer), and surface charge, and presence of other forces in solution can affect the magnitude and range of depletion forces. First, increasing the size of the colloidal sphere will also increase the magnitude of repulsive and attractive forces. Second, charged spherical particles and spherical macromolecules generate higher magnitudes and ranges of the depletion forces than dispersions containing polymers. Lastly, the magnitude of depletion forces must be significant in comparison to other forces present in the dispersion (i.e.-van der Waals, electrostatic repulsion, etc.); otherwise, depletion forces will have no effect on colloidal stability. Research studies show that repulsive depletion forces are a possible mechanism to explain colloidal stability of TMPE-treated silica particles. However, more research is needed to understand how the size, structure, charge of TMPE-treated silica particles and excess TMPE may affect the final magnitude of depletion forces. It is also necessary to determine if the magnitude of depletion forces are significant in comparison to other forces within the dispersion.

The grams of TMPE per grams of silica, remains constant within each sample set, but the total concentration of TMPE in the sample increases with increasing volume fraction of silica. Therefore, the 7% solution is more likely to have the highest amount of excess TMPE in solution, which leads to the slowest aggregation rate. The 5% solution has the second highest concentration of TMPE, which means it experiences less stabilizing effects of excess TMPE and will gel faster than the 7% solution.

One important difference between the low TMPE samples and the high TMPE samples is the final size of the aggregates. In Figure 13, all the low TMPE samples eventually reached the same final aggregate size (complete gelation). However, the high TMPE samples have varying final sizes (see Figure 14). In the high TMPE samples, the 3% sample has the lowest concentration of TMPE. These silica particles experience less stabilizing interactions with TMPE and are more likely to succumb to hydrophobic forces and form larger aggregates. Following this trend, it is expected that the 5% sample will have larger aggregates than the 7% sample. However, the sizes of the 5% and 7% samples remain

almost identical throughout a 2-month observation period. This occurrence can be explained by analyzing the size of mono-dispersed silica. The size of one silica particle is about ≈ 30 nm, which means the smallest possible aggregate is a dimer (≈ 60 nm). Figure 14 shows that the 5% and 7% samples both reach a maximum particle size of ≈ 60 nm. This means that the concentration of TMPE in the 5% sample is already high enough to maintain the aggregates at their smallest size (dimers). Remembering that all of the samples are at the IEP, a condition that promotes the most aggregation, it is highly unlikely that more TMPE will significantly reduce aggregation enough to form a mono-dispersed solution of silica particles.

The growth rate of the 5% and 7% high TMPE samples are also close to identical. The 5% sample has minimal sized aggregates, which means TMPE has a high stabilizing effect and significantly slows the rate of aggregation. Seeing as how the growth rate in the 5% sample is already very slow, any further increases in TMPE concentration may lead to an unnoticeable change in the rate of growth. As a result, there is no clear distinction between the growth rates of the 5% and 7% samples. The high TMPE samples are expected to eventually aggregate and form a solid gel. Size measurements should be taken over a prolonged period of time (more than two months) to confirm these expectations.

An additional experiment was performed to validate the existence of excess TMPE in solution and its stabilizing effects on silica particles. In the experiment, three different samples of TMPE-treated silica solutions were diluted with water, methanol-water mix, and a TMPE-water mix. A sample of silica particles (5% volume fraction) was treated with TMPE (0.086 g TMPE/g silica) as explained in the experimental procedure (surface modification process). The 20 mL sample was split into 3 vials, each contained 5 mL of sample. In the first vial (sample 1), 5 ml of water was added. Sample 1 was the control during the experiment and was expected to aggregate aggressively. The methanol-water mix (5 ml water/0.1 mL methanol) was added to sample 2. Methanol is also suspected as a possible cause for silica stabilization because methanol is released when the methoxy groups on TMPE are hydrolyzed. Methanol is also partially hydrophobic and can form non-polar interactions with the treated silica particles. For sample 3, 0.2 grams of TMPE was added to 60 mL of water and mixed for 10 minutes using a magnetic

stirrer. As explained previously, TMPE is highly reactive and will irreversibly react with itself; 10 minutes of mixing was chosen to ensure that TMPE had sufficient time to react to completion. This ensures that the TMPE added to the modified silica solution will not react with the silica surface and form only physical interactions with the silica. 5 mL of this TMPE-water mix was then added to sample 3. Purposely adding extra TMPE to the sample after it was coated ensures that excess TMPE is in solution and can also prove that excess TMPE is responsible for slower aggregation rates. All 3 samples were then mixed for an additional 5 minutes before changing the pH to 9.7. Figures 17 through 19 show pictures of the samples: before the pH change, immediately after the pH change, and 24 hours after the pH change.

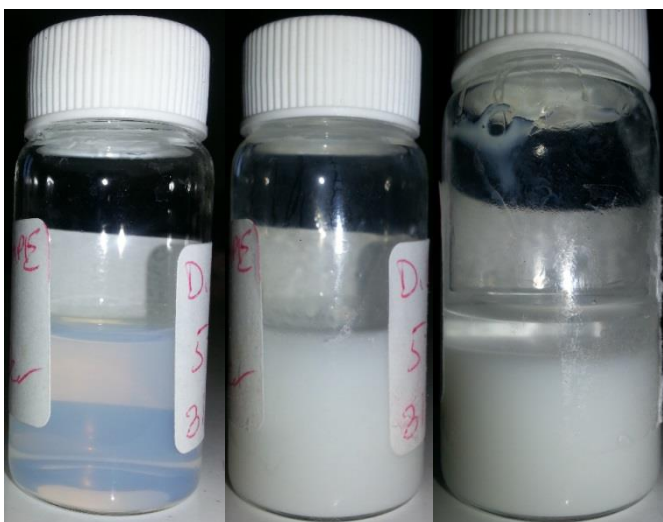


Figure 17: (Sample 1) 5mL of TMPE-treated silica particles mixed with 5 mL of water. From left to right: before pH change, immediately after pH change, 24 hours after pH change

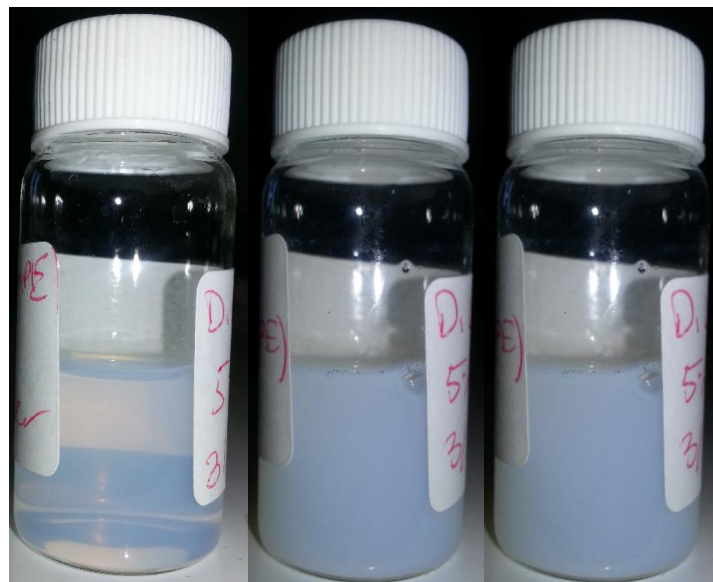


Figure 18: (Sample 3) 5mL of TMPE-treated silica particles mixed with 5 mL of TMPE-water mix. From left to right: before pH change, immediately after pH change, 24 hours after pH change



Figure 19: (Sample 2) 5 mL of TMPE-treated silica particles mixed with 5 mL of methanol-water mix. From left to right: before pH change, immediately after pH change, 24 hours after pH change

Figures 17 and 18 show that samples 1 and 2 coagulated immediately after the pH change and settled out of solution after 24 hours. The final size of the particles in samples 1 and 2 were ≈ 1 micron. In contrast, Figure 19 shows that silica particles in sample 3 did not aggregate as aggressively or settle out of solution. The color of sample 3 became slightly more opaque, signifying that particles did grow slightly, but remained dispersed in solution. After one week, the particles within sample 3 had reached a size of only ≈ 200 nm. These results validate that excess TMPE in solution is responsible for the stabilizing effect on TMPE-treated silica particles and leads to a reduction in the aggregation rate. The magnitude in which the rate of aggregation is reduced is related to the amount of excess TMPE in solution, with more TMPE causing slower aggregation and smaller final aggregates. More research is needed to determine the specific physical mechanism by which TMPE stabilizes silica particles in solution.

Effects of pH on Aggregation Rate (Experiment Set 2)

While experiment set 1 observed the evolution of particle size at one specific pH, the purpose of experiment 2 is to test the hypothesis that at a fixed amount of TMPE, the final size of aggregates is only a function of pH. One set of untreated silica solutions with volume fractions of 3%, 5%, and 7% were prepared according to the experimental procedure (surface modification process) and were treated with TMPE (0.086 g TMPE/g silica). After the solutions achieved complete gelation (≈ 24 hrs), each solution was then separated into five solutions with a distinct pH value. Table 3 summarizes the conditions of experiment set 2. All of the samples were then deaggregated using sonication. As samples began to reaggregate, now at a new pH, the effects of pH on the dynamics of aggregation could be observed. Size measurements were recorded using DLS. A summary of the results for all 3 volume fractions are shown in figure 20.

Outline of Experiment Set 2	
0.086 g TMPE/g silica	
Sample pH	Sample Concentration (%Volume)
5	3, 5, and 7
6.5	
7.5	
8.1	
8.9	

Table 3: Outline of Experiment Set 2

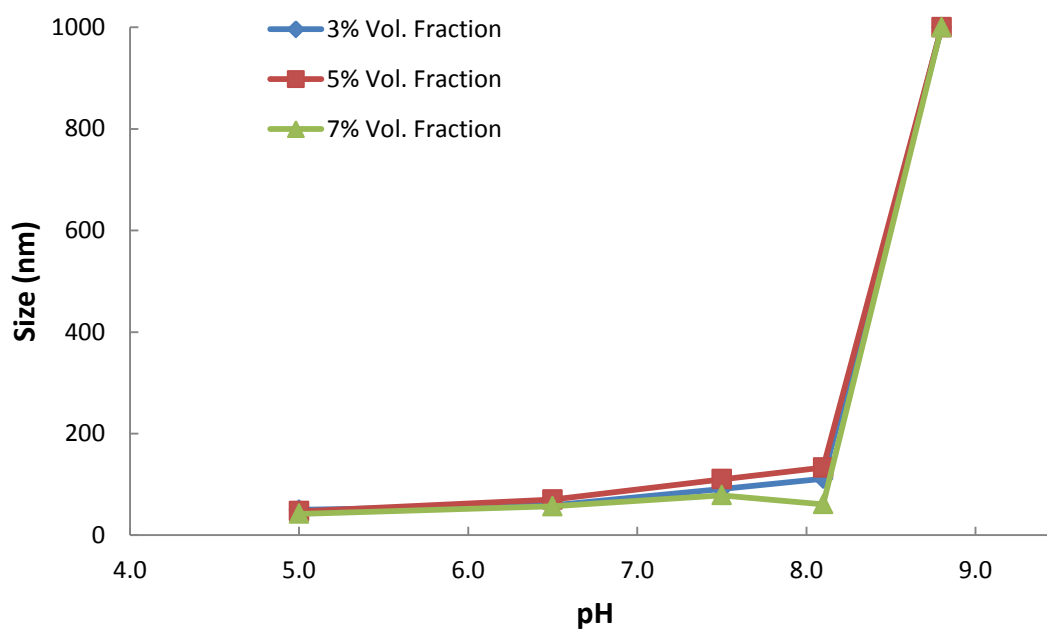


Figure 20: Final Size vs. pH Measurements for TMPE-treated Silica Nanoparticles at pH Values: 8.9, 8.1, 7.5, 6.5, and 5

Figure 20 shows that all the volume fractions have almost identical final sizes at each pH value. The general trend of the data shows that particle size remains relatively constant below pH 8. However, as pH increases above 8.1, the particles size increases significantly, indicating that particles are aggregating

aggressively. Silica particles at pH 8.9 completely gelled, reaching a final size of ≈ 1 micron, while samples at pH 8.1 and below formed much smaller aggregates (≈ 100 nm) that remained dispersed in solution.

Because of the significant difference in size between particles at pH 8.9 and those below 8.1, it is necessary to analyze the final size of aggregates at lower pH values independently to get a more accurate depiction of how pH affects the evolution of particle size. Figure 21 shows the results of aggregates size for pH values of 8.1 and below.

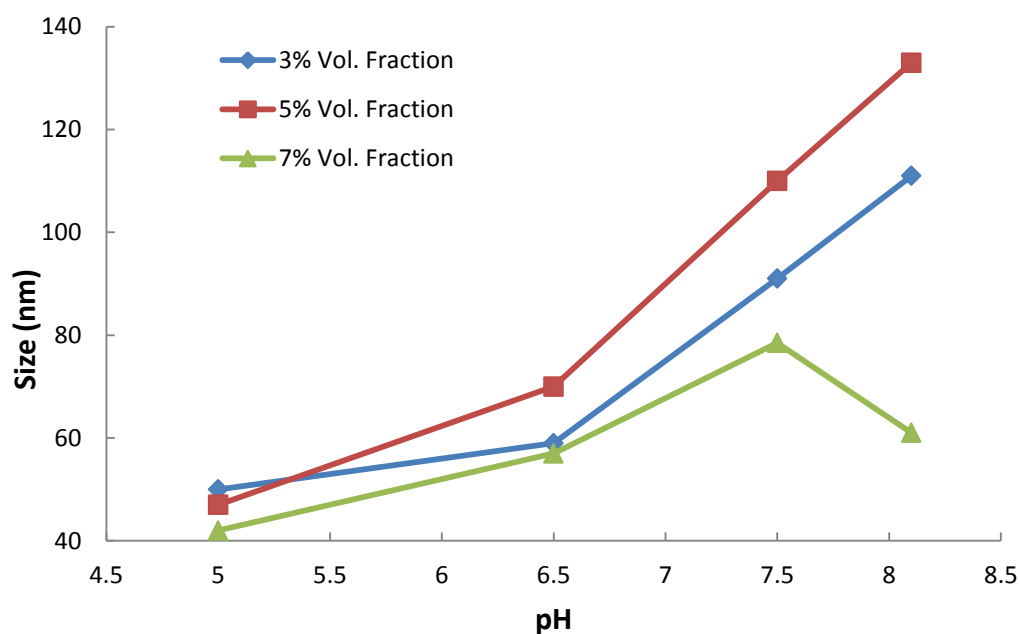


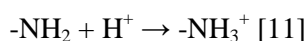
Figure 21: Final Size vs. pH Measurements for TMPE-treated Silica Nanoparticles at pH values: 8.1, 7.5, 6.5, and 5

Result in figure 21 shows that the sizes of aggregates generally grow larger with increasing pH. The 7% sample seems to deviate from this trend at pH 8.1. It is possible this deviation is due to variation in the degree of sonication across each sample. All 15 samples were sonicated individually so it is difficult to make sure that every sample is set up exactly the same. As a result, it is likely that some

samples were sonicated more or less vigorously. A more vigorous sonication would lead to a further deaggregation of particles, which would explain the small particle size of the 7% sample at pH 8.1. Size measurements of the 7% samples immediately after sonication show that particles at pH 8.1 began at a size of ≈ 65 nm. Figure 21 also shows that the 5% sample has a slightly higher final aggregate size at most of the pH values. This size difference becomes progressively more pronounced as the pH increases.

These results prove that at a fixed amount of TMPE, the final size of aggregates can almost exclusively be controlled by manipulating the pH of the solution. Within this experiment, all samples were originally made at a pH of 9.7; a pH set point that led to complete gelation (particle size ≈ 1 micron) within 24 hours. The samples were then deaggregated using sonication before being changed to a new pH values. Figure 20 shows that at these new pH values, all samples below pH 8.1 did not form solid gels similar to the original samples at pH 9.7. Therefore, it can be concluded that the pH of the solution determines the size of its aggregates regardless of the original pH. The effects of sonication are still unclear. Results show that if the pH is changed, the size of the aggregates will also change in accordance to this new pH value. Similarly, if aggregates are separated by physical means such as sonication, aggregates will reform somewhat relative to the pH of the solution. Overall, pH acts as an equilibrium point that corresponds to a certain aggregate size; so despite the original conditions and outside disturbances, the silica particles will return to the aggregate size that corresponds with the current pH of the solution.

Figure 20 shows that smaller aggregates are observed at lower pH values. This is a result of aminofunctional groups on the TMPE. The presence of amino groups on the surface of silica particles increases their positive charge at low pH. The following reactions take place amongst the aminofunctional groups on the surface of the particle:



Reaction [11] demonstrates that at low pH, the amino groups are protonated and become positively charged. These positive charges increase the zeta potential and generate an electrostatic

repulsion between particles, which decreases their ability to aggregate. Previous work in our lab has determined the unstable zeta potential range to be $\sim < |20|$ mV (Aljama, 2010). Within this range, the colloidal dispersion is unstable and particles will coagulate to form large aggregates. Figure 22 shows that TMPE-treated silica particles with pH values $\sim \leq 8$ have zeta potentials $\sim \geq +25$ mV. This indicates that samples with pH values of 8.1 form stable dispersion, which leads to the formation of smaller aggregates.

In contrast, at high pH values the amino groups remain neutral and bring the system closer to the IEP, in which the zeta potential is 0. This lower degree of electrostatic repulsion causes particles to aggregate and form a gel, as observed at pH 8.9 (see figure 20). Figure 22 demonstrates the samples made at a pH of 8.9 form unstable dispersions because their zeta potentials are lower than 20 mV. As result of their colloidal instability, these solutions aggregated aggressively to form much larger aggregates and eventually a solid gel.

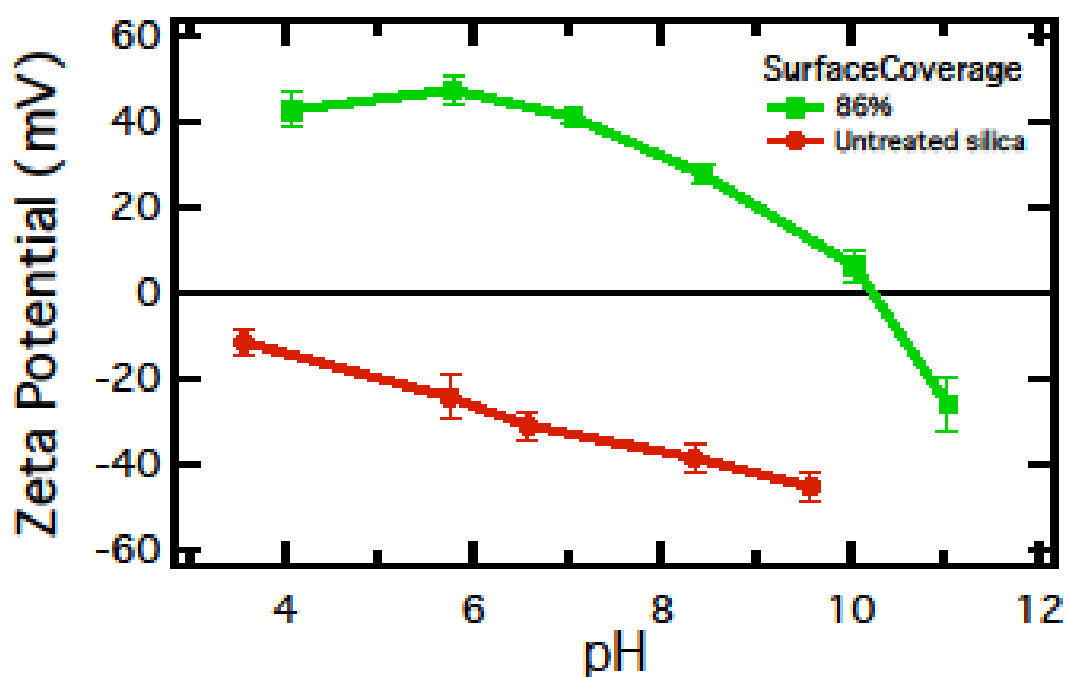


Figure 22: Comparison of The Zeta Potential vs. pH Of TMPE Surface Treated Silica (Green) and Untreated Silica (Red). (Loffizadeh, 2014)

Results show that pH can be used to control the size of aggregates, but figure 21 shows that not all samples do have the same final aggregate size. Although the samples are all pretty close in particle size, the size difference does depend to some extent on the volume fraction. However, the size difference does not correlate to the volume fraction as would be expected. It is anticipated that the size of the aggregates would increase with decreasing volume fraction. This inverse correlation is a result of the excess TMPE in solution, which has a stabilizing effect on the silica particles and reduces their tendency to aggregate. More TMPE is added to the higher volume fractions to keep the g TMPE/g silica constant, which in turn also increases the total concentration of excess TMPE in solution. Therefore, it was expected that the 3% sample would have the highest particle size, followed by the 5% sample, and then the 7% sample. Because these results are not observed, another factor must be responsible for this size difference. Variation in sonication was determined not to be cause for these larger aggregates because this would lead to a more dramatic difference in the aggregate size of one or two samples as seen for the 7% at pH 8.1. Figure 21 shows that the size of the 7% samples are steadily increasing with pH, as expected, but then the size drops drastically at pH 8.1. This indicates that this sample was sonicated more vigorously and experienced more deaggregation than the other 7% samples. Contrastingly, all the size of the 5% samples steadily increases with pH with no drastic deviations; another variable must be responsible that could have affected all the 5% samples equally.

Therefore, it is possible that when making the original 5% sample an experimental error occurred and less than the required amount of TMPE (<0.086 g TMPE/g silica) was added to the silica dispersion. If less TMPE was added to the 5% sample, this would lead to the formation of larger aggregates because there is less TMPE in solution to stabilize the silica. These results show that the stabilizing effects of TMPE can still affect the final size of aggregates in addition to the pH. It is also possible that these samples simply need more time to grow upon which they will reach the same final size. Size measurements should be taken over a prolonged period of time (>1 month) to confirm these expectations.

Chapter 5

Conclusions

In this thesis, the dynamics of aggregation of TMPE-treated colloidal silica was investigated with respect to the following variables: the volume fraction of silica (3%, 5% and 7%), grams of TMPE used for surface treatment, and the pH of the colloidal dispersion. Experiment results showed that samples with larger higher amounts of TMPE aggregated at slower rates and had smaller final aggregates. In addition, if the amount of TMPE (g TMPE/g silica) was fixed, samples with higher volume fractions of silica also had slower aggregations rates, and in some cases smaller final aggregates. It was determined that excess TMPE in solution has a stabilizing effect on colloidal silica and reduces their tendency to aggregate, resulting in slower aggregation rates or smaller final aggregates. A repulsive depletion force was identified as one physical mechanism that could be responsible for maintaining particles in suspension. In this mechanism, excess TMPE would form layers around the treated silica particles. As the concentration of excess TMPE between particles became larger than in the surrounding solution, an osmotic pressure would be created and force the particles apart. It is also possible that excess TMPE in solution makes the water (solvent) more compatible with the hydrophobic surface of the silica particles. Silica particles form clusters to reduce interactions with water. The presence of excess TMPE in solution can form favorable non-polar interactions with the surface of the particle, which reduces the need for silica particles to flocculate.

The effects of pH were also investigated at fixed amounts of TMPE and using the same three volume fractions of silica. All samples were originally a solid gel at pH 9.7. They were then deaggregated through sonication and changed to the following pH values: 5.1, 6.5, 7.5, 8.1, and 8.9. After the pH change, only the sample with a pH of 8.9 returned to a solid gel, while all other samples contained silica

particles that remained dispersed in solution (≈ 100 nm). Experiment results demonstrated that pH can be used to control the final size of the aggregates no matter the original pH. The effect of sonication on the final size of aggregates is still unclear. pH can control the size of aggregates because it changes the zeta potential at the surface of the silica. A high zeta potential ($\sim > |20|$ mV) correlates to a stable dispersion. At pH values ≤ 8.1 , the amino groups on the silica surface become protonated, creating an electrostatic repulsion that prevents particle from sticking together. This high charge density on the amino group correlates to a high zeta potential. Contrastingly, samples at pH 8.9 are close to the isoelectric point, which means they have a zeta potential lower than $|20|$ mV and form an unstable dispersion that leads to aggregation. Overall, a trend of decreasing aggregate size with decreasing pH was observed. Across the different volume fractions, the final size of the aggregates was not exactly the same at each pH value; 3% and 7% samples had smaller final aggregate sizes than the 5% sample. These differences in aggregates size can be a result of varying degrees of sonication that the samples may have received, with more vigorous sonication leading to a smaller initial particle size. It is anticipated, that given more time, all samples will eventually reach the same final size. Size measurements need to be recorded over a longer period of time (> 1 month) to confirm these expectations. Overall, results show it is possible to establish a system of controllable aggregation by manipulating the amount of TMPE used for surface treatment and the pH of the dispersion.

References

- Aljama, H. Surface Modification of Silica Nanoparticles using Surface Coupling Agents. Honors Thesis, Pennsylvania State University, 2010.
- Crocker, J. C., et al. "Entropic attraction and repulsion in binary colloids probed with a line optical tweezer." *Physical review letters* 82.21 (1999): 4352.
- Dobias, Bohuslav, ed. *Coagulation and flocculation: theory and applications*. CRC Press, 1993.
- Eapen, Jacob, Ju Li, and Sidney Yip. "Beyond the Maxwell limit: Thermal conduction in nanofluids with percolating fluid structures." *arXiv preprint arXiv:0707.2164* (2007).
- Gellermann, C., W. Storch, and H. Wolter. "Synthesis and characterization of the organic surface modifications of monodisperse colloidal silica." *Journal of Sol-Gel Science and Technology* 8.1-3 (1997): 173-176.
- Honkanen, Mari, et al. "Aminofunctional silane layers for improved copper–polymer interface adhesion." *Journal of materials science* 46.20 (2011): 6618-6626.
- Khan, Saif A., et al. "Microfluidic synthesis of colloidal silica." *Langmuir* 20.20 (2004): 8604-8611.
- Lee, S., et al. "Measuring thermal conductivity of fluids containing oxide nanoparticles." *Journal of Heat Transfer* 121.2 (1999).
- Mahalingam, V, et al. "Directed Self-Assembly of Functionalized Silica Nanoparticles on Molecular Printboards through Multivalent Supramolecular Interactions." *Langmuir* (2004): 11756-11762.
- Park, Soo-Jin, and Ki-Sook Cho. "Filler–elastomer interactions: influence of silane coupling agent on crosslink density and thermal stability of silica/rubber composites." *Journal of*

colloid and interface science 267.1 (2003): 86-91.

Pham, Khoa N., Damian Fullston, and Kwesi Sagoe-Crentsil. "Surface charge modification of nano-sized silica colloid." *Australian Journal of Chemistry* 60.9 (2007): 662-666.

Rudhardt, Daniel, Clemens Bechinger, and Paul Leiderer. "Repulsive depletion interactions in colloid-polymer mixtures." *Journal of Physics: Condensed Matter* 11.50 (1999): 10073.

Matijevic, Egon. *Medical applications of colloids*. Springer, 2008.

Okeke, George, et al. "Computational Analysis of Factors Influencing Enhancement of Thermal Conductivity of Nanofluids." *arXiv preprint arXiv:1205.2032* (2012).

van Blaaderen A, et al. "Synthesis and Characterization of Monodisperse Colloidal Organosilica Spheres", *Journal of Colloid and Interface Science*, 156, (1993).

van Blaaderen A, et al. "Model Particles from Organosilanes" *The colloid chemistry of silica. Chapter 4. American Chemical Society, 1994.*

Van Helden, A, et al. "Preparation and characterization of spherical monodisperse silica dispersions in nonaqueous solvents." *Journal of Colloid and Interface Science*, 81(2):354–368, 6 (1981).

Walz, John Y., and Amber Sharma. "Effect of long range interactions on the depletion force between colloidal particles." *Journal of colloid and interface science* 168.2 (1994): 485-496.

Weitz, David. *Dynamic Light Scattering*. Harvard University. School of Engineering and Applied Sciences. Web. 4 March 2014.

<<http://weitzlab.seas.harvard.edu/links/tutorials/dynamiclightsattering.pdf>>

Wong, Kaufui V., and Omar De Leon. "Applications of nanofluids: current and future." *Advances in Mechanical Engineering* 2010 (2010).

Wu, Zhijian, et al. "Surface properties of submicrometer silica spheres modified with aminopropyltriethoxysilane and phenyltriethoxysilane." *Journal of colloid and interface*

science 304.1 (2006): 119-124.

Wu, Zhijian, et al. "Controlling the hydrophobicity of submicrometer silica spheres via surface modification for nanocomposite applications." *Langmuir* 23.14 (2007): 7799-7803.

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