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IMPROVED SURFACE COATING METHODS OF SILANE COUPLING AGENTS ON
SILICA NANOPARTICLES TO ENHANCE STABILITY AND SURFACE COVERAGE

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Abstract

The surface of silica colloidal particles in aqueous solution was modified with three silane coupling agents: 3-aminopropyltriethoxysilane (APES), aminopropyltrimethoxysilane (APMS), and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (TMPE). Two methods for the addition of the SCAs were employed. Either direct addition of pure SCA or dropwise addition of the SCA diluted to low concentrations in ethanol. In addition, the effect of timing of SCA addition was investigated by adding dilute SCA either quickly over 15-20 minutes or prolonged in stages over several days. The stability of the particles was measured with dynamic light scattering (DLS) and zeta potential measurements. In addition, the percentage of surface of the particles that had been covered with SCA was determined both qualitatively by comparing zeta potential profiles of samples with varying amounts of SCA added, and quantitatively by comparing the amount of SCA that had been added to a theoretically calculated maximum value for complete coverage.

In the direct addition of SCA, untreated silica showed the greatest stability at neutral pH as measured by DLS. The lowered stability when SCA is added is hypothesized to be caused by low surface coverage causing an overall decrease in the magnitude of zeta potential. The dilute addition of SCA in ethanol allows for much higher amounts of SCA to be added than in direct addition, resulting in much higher levels of surface coverage. The higher amount of surface coverage is confirmed by measuring zeta potential over a pH range for increasing amounts of SCA added, and TMPE allowed for the highest amount of addition compared with APES and APMS. TMPE dilute addition was also tested over a longer addition time of several days which resulted in higher coverage and the most stable treated particle dispersions achieved so far.

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Chapter 1: Introduction

In this thesis, silica nanoparticles dispersed in water were employed as model system to study stability in a nanofluid. A nanofluid is a dispersion of nanoparticles in a suspending fluid such as water or an organic solvent. There are many industrial applications of nanofluids, and one which is particularly relevant to this thesis is their use as a heat exchanger medium. Nanofluids of copper oxide particles dispersed in ethylene glycol with volume fractions of under 1% have been shown to increase the thermal conductivity of pure glycol by over 40%, which is much higher than predicted by theory, and this trend continues for other types of particles and fluids (Eastman 2004). There are several explanations which have been put forward to account for this phenomenon, including increased interfacial area and heat capacity of the fluid (Xuan 2000) and increased convection caused by Brownian motion of the particles (Kulkarni 2008).

However, one drawback to using nanofluids as a heat exchanger medium is potential for irreversible aggregation of the particles in the fluid. As shown in simulations, the thermal conductivity of a copper in water nanofluid is uniformly decreased upon aggregation of the copper particles and it can be expected this is the case for other similar systems (Xuan 2003). In addition, significant aggregation can cause large increases in viscosity to the point that the fluid becomes a solid gel, which would make it impossible to use in a heat exchanger, or in any other applications where it serves as a fluid. This aggregation can potentially be prevented or reduced through the addition of functional groups to the surface of the particles, whereby the surface charge can be increased and electrostatic repulsive forces can be enhanced to increase stability.

A nanofluid is more generally denoted as a colloidal suspension, and there is a rich theory of colloid science describing these dispersions. A colloid is a suspension of one substance in another such that they are evenly dispersed through one another. One common type of colloidal suspension is a

dispersion of solid particles in a liquid medium, and these are the only types of colloids encountered in this thesis. There are many forces that determine the dynamics and state of a colloid. All the particles in a suspension experience an attractive Van der Waals force that will cause irreversible aggregation of the particles if not opposed by other forces. There are many types of forces and interactions that can stabilize particles against aggregation, including electrostatic forces, steric repulsion and depletion forces (Wasan 2003). In this thesis, we focused on improving colloidal stability by increasing electrostatic repulsion between particles.

Specifically, in this thesis the colloidal system we use is monodisperse, spherical silica particles dispersed in water. Silica colloidal particles have a wide range of applications including ceramics, catalysis and chromatography (van Blaaderen 1993). A classic method for making very monodisperse, spherical silica particles was found by Stöber in 1968 and is still commonly used. In this reaction, a solution of tetraethyl orthosilicate (TEOS, depicted in Figure 1) in ethanol is mixed with another solution of ethanol, water and ammonia, with ammonia serving as a catalyst for the reaction (Stöber 1968).

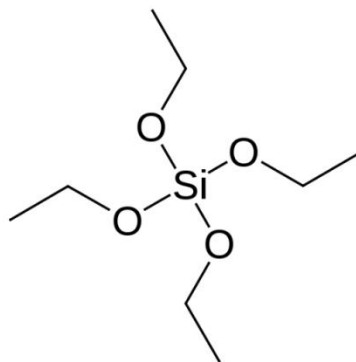


Figure 1: TEOS Chemical Structure

This reaction has been widely studied in the literature, and for instance by altering the concentrations of ethanol, water and ammonia, one can obtain varying sizes of particles (van Blaaderen

1993). However, since the final solution will contain the ammonia catalyst, upon destabilization, it could further contribute to particle aggregation. For this reason, in this thesis we only work with purchased pre-made Ludox silica. This is a dispersion of 30 nm silica particles in water, without any ethanol or ammonia present.

Surface coating is a commonly employed technique for enhancing or introducing desired properties to a material. In this thesis, a variety of silane coupling agents (SCA) were attached to the surface of silica nanoparticles in water. These SCAs were investigated as a way to increase the long term stability of the silica nanofluid and prevent aggregation, by increasing the electrostatic charge on the surface of the particles. Parameters such as the amount of total SCA added to the silica, the concentration of the SCA while being added and the pH of the nanofluid were varied to achieve better coverage of the surface treatment.

Chapter 2: Surface Coating Review

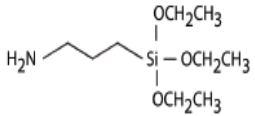
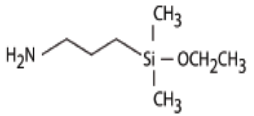
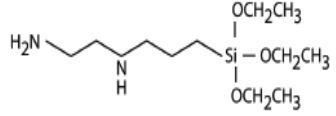
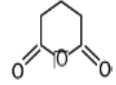
There has been a substantial and very varied amount of work done in the general area of applying chemicals to the surface of various substrates. In particular, silane coupling agents (SCA) have a long history of being employed to enhance desired properties of silica compounds. This includes the use of surface modified silica in protective paints and coatings (Pilz 1997), fabrication of fiber materials for photoconductors (Seog 1993), along with increasing physical properties such as thermal, chemical or mechanical stability (Caruso 2001).

Silane coupling agents are also often used to increase silica particle stability in various solvents and allow for the dispersion of the particles in these solvents without aggregation or precipitation. Since silica is naturally hydrophilic and water soluble, much of the work that has been done in this area has been in increasing the hydrophobicity of the particles to allow for dispersal in organic media. This can be done by covalently attaching long or short chain hydrocarbons, aromatics or other non-polar functional groups to the surface of the silica particles. Wu (2007) tested the hydrophobic properties of silica with carbon chains attached ranging in length from one carbon (methyl) to twelve carbons (dodecyl), along with a phenyl group and an alkene. One of the tests they performed to test the hydrophobicity of the modified silica was contact angle measurement, where a larger angle indicates a more hydrophobic particle. The coating agents they tested are summarized in Table 1; along with the measured contact angles (untreated silica had a contact angle of 86.7°). It can be seen that significant increases in the contact angle don't occur until the eight carbon length and twelve carbon length molecules are used, indicating it takes a relatively long hydrocarbon chain to cause a noticeable increase in hydrophobic behavior.

Table 1: Summary of Hydrocarbons used for Hydrophobic Silica (Wu 2007)

Molecule	Formula	Contact Angle
methyltriethoxysilane	$(C_2H_5O)_3SiCH_3$	92
vinyltriethoxysilane	$(C_2H_5O)_3SiCH=CH_2$	89
n-propyltriethoxysilane	$(C_2H_5O)_3Si(CH_2)_2CH_3$	94
bis(trimethoxysilyl)hexane	$(CH_3O)_3Si(CH_2)_6Si(OCH_3)_3$	88
phenyltriethoxysilane	$(C_2H_5O)_3SiC_6H_5$	92
n-octyltriethoxysilane	$(C_2H_5O)_3Si(CH_2)_7CH_3$	101
n-dodecyltriethoxysilane	$(C_2H_5O)_3Si(CH_2)_{11}CH_3$	109

In addition to increasing the dispersibility of silica in organic solvents, the use of water based systems is becoming more prevalent due to safety and environmental concerns (Sato 2009). Thus, there has recently been more work done on increasing stability in water by attaching functional groups to silica with the aim of increasing surface charge and achieving stability primarily through electrostatic repulsion. However this area has not been as widely explored and is the primary area of investigation in this thesis. There are three SCAs that were studied. 3-Aminopropyltriethoxy silane (APES), 3-aminopropyldimethylethoxy silane (APMS) and N[-3-(trimethoxysilyl)propyl-ethylenediamine (TMPE), along with glutaric anhydride as a further chemical additive in a two-step modification process. These were chosen because they have shown promising results for stabilization of silica in aqueous solution. The chemical structures of the SCA's used in the thesis are shown in Figure 2.

<p>3-aminopropyltriethoxysilane (APES)</p> 	<p>Aminopropyldimethylethoxysilane (APMS)</p> 
<p><i>N</i>-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMPE)</p> 	<p>Glutaric anhydrite (GA) (*)</p> 

(*) After treatment with silane first.

Figure 2: Silane Coupling Agents used in Thesis

Below is a summary of previous results that have been obtained with these chemicals.

2.1- APES Review

APES has been used extensively in the past to promote adhesion on silica and glass surfaces of various molecules such as polymer films, proteins, and metal nanoparticles (Howarter 2006). Particularly relevant to this thesis is that several studies have successfully modified the surface of colloidal silica with APES (Krysztafkiewicz 2000, Pham 2007). Wu (2006) modified the surface of Stöber silica with APES and measured its zeta potential as a function of pH, which is a commonly used method to characterize charging effects of a colloid in both positive and negative charge regimes, as well as to determine the isoelectric point, the pH at which the zeta potential is zero and positive and negative surface charges balance each other. Figure 3 shows these results from Wu's paper (TEOS is untreated silica and APTES is the name for APES from the paper).

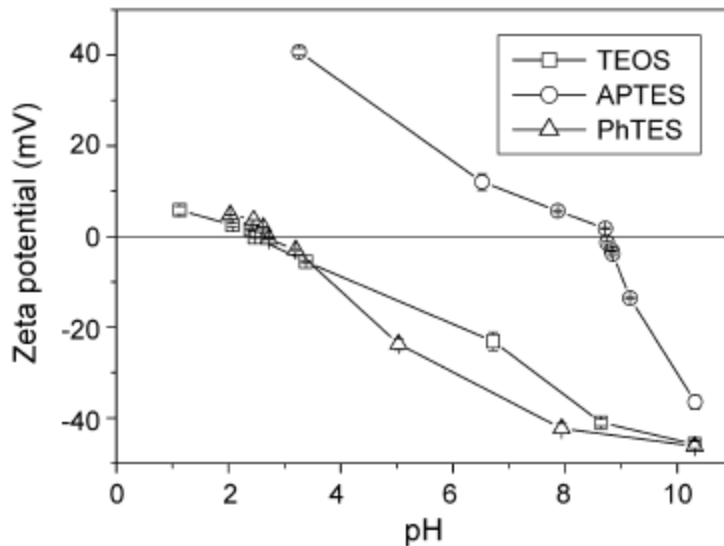


Figure 3: APES Zeta Potential Results from Wu (2006)

The large shift upward in the zeta potential curve from untreated to APES coated particles indicates a significant change in the properties of the silica. However, this treatment also causes a lower magnitude zeta potential near neutral pH, thereby destabilizing the particles compared with untreated

silica. This suggests that this specific treatment method would not be favorable for any application which requires stable silica dispersions at a pH near neutral pH, such as a nanofluid heat exchanger medium.

Previous work by our lab has also determined many properties of APES coated silica. In particular it has been observed that there is a critical concentration of APES that can be added to the silica, which depends on particle size, and above this concentration rapid aggregation of the silica occurs. This aggregation can be seen directly in TEM images of silica before and after the addition of APES. The images in Figure 4 were taken by a student Kolandra (2009) for her honor's thesis, and show the aggregation caused by the addition of too much APES.

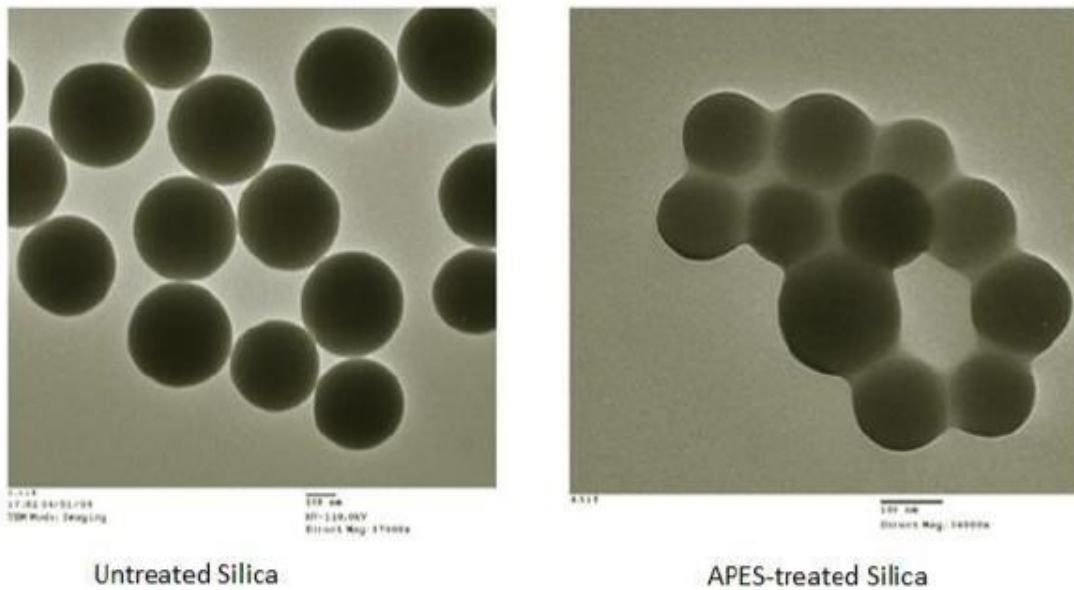


Figure 4: Aggregated Silica after APES Addition

Several studies have found evidence that this aggregation is caused by the hydrolysis of APES in the presence of water and subsequent self-polymerization of APES, causing bridging between the particles (Moon et al. 1997, Vrancken 1992). However, in order for the APES to covalently attach to the silica, there must be some water present to start hydrolysis (see Figure 5 for the reaction scheme).

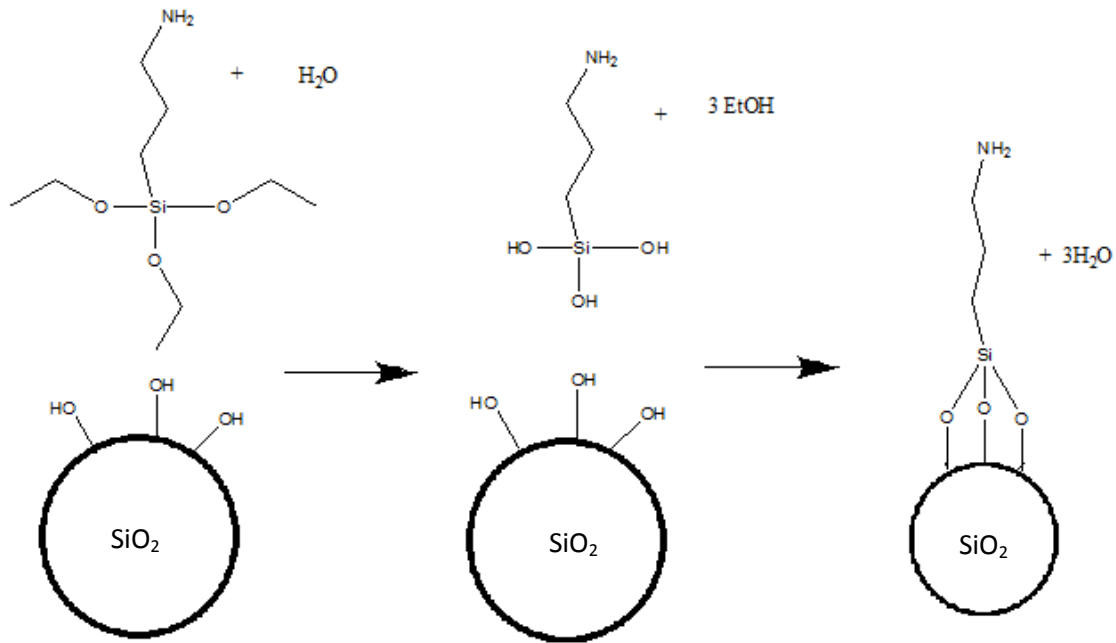


Figure 5: APES Coating Reaction Scheme

Zhang (2004) studied the deposition of APES on thin silica wafers and found a water concentration of .1% by volume in the APES solution led to optimal surface coverage. Thus, for successful APES coating of silica, there should be minimal amounts of water present, which is obviously difficult to impossible to achieve in an aqueous system.

The reason that APES is able to self-polymerize and lead to aggregation is explained by its three hydrolyzable ethoxy groups which can cause the molecules to attach to each other and form a three-

dimensional network. It is this that causes particle bridging and subsequent aggregation (see Figure 6 for a depiction of this process, image from Pham 2007).

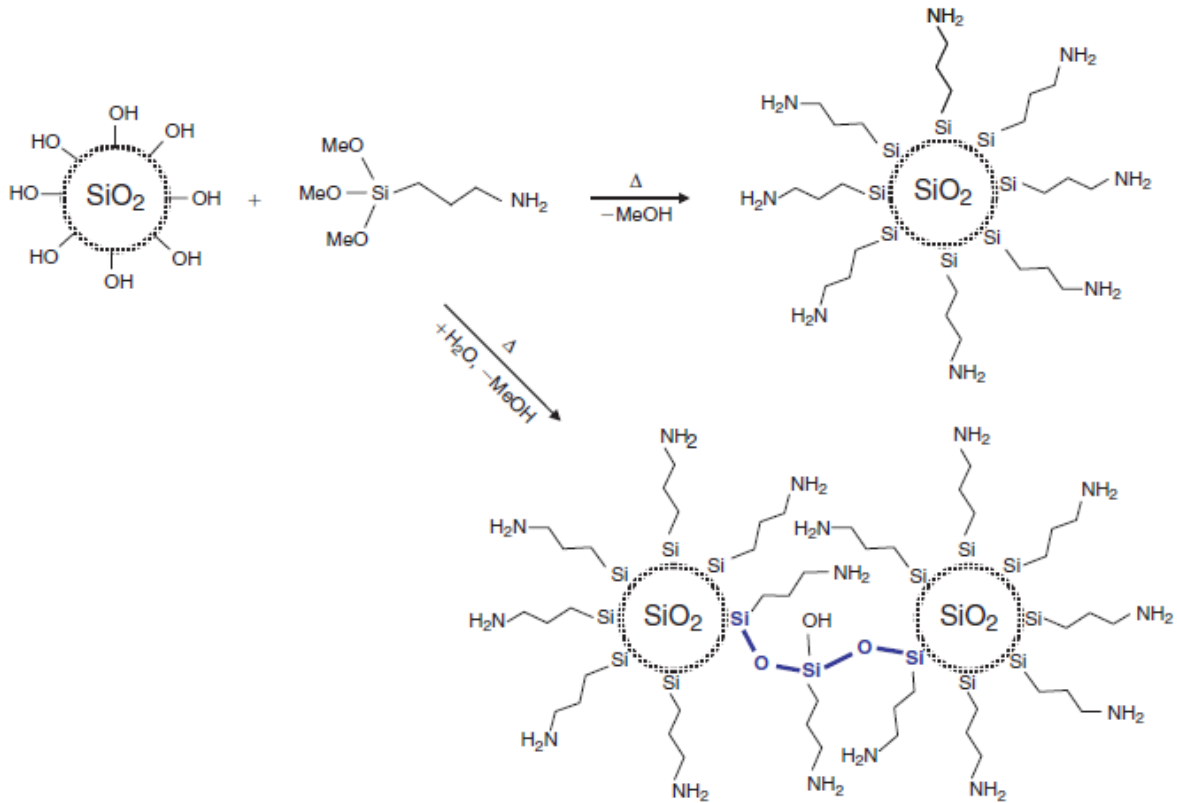


Figure 6: Particle Bridging Caused by APES (Pham 2007)

This effect can be reduced or eliminated by using a coating agent with only one hydrolyzable group, which is why APMS was studied in this thesis.

2.2- APMS Review

As can be seen in Figure 2, APMS has only one ethoxy group that can be hydrolyzed in the presence of water which eliminates the possibility of self-polymerization present with APES. Moon (1996) found that APMS forms much more uniform and controlled monolayer thickness as compared to APES when deposited on silica wafers. However, while it has been shown that APMS is able to coat silica and avoid problems associated with APES induced aggregation, its effects on surface charge modification and stability of silica has been less studied than with APES.

Pham (2007) measured the zeta potential of APES and APMS coated silica particles as a function of pH, the results of which are shown in Figure 7.

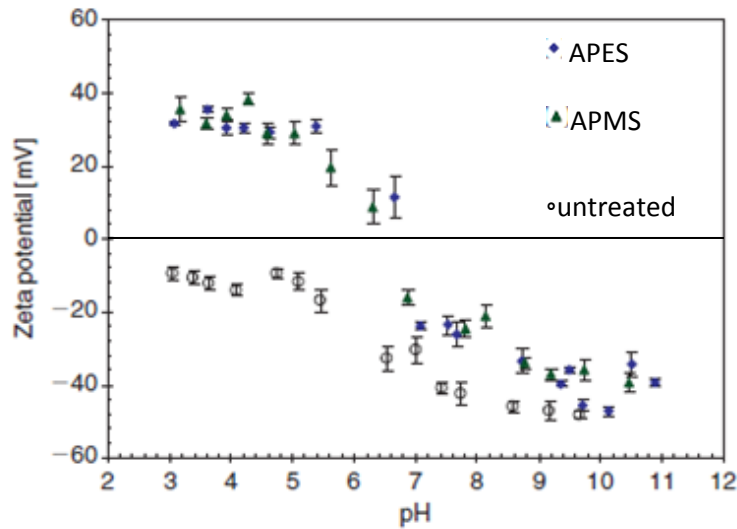


Figure 7: APES and APMS Zeta Potential Results from Pham (2007)

These results show a systematic and clear shift in zeta potential from the untreated silica. However, at the concentrations used, the shift in zeta potential is very similar for both APES and APMS, and the

APMS coated particles suffer from poor stability at neutral pH, as with the previously shown results for APES. In addition, Pham reports aggregation of the silica when the APES:silica weight ratio was in excess of 1:200, whereas this aggregation did not occur with any tested amount of APMS (although the paper does not report what amounts of APMS were tested). This supports the hypothesis that it is the three hydrolyzable ethoxy groups of APES that cause aggregation, since APMS, with only one of these groups, does not aggregate at similar amounts added.

2.3 TMPE Review

Since it is the amine functionality on APES and APMS that leads to the large shifts in zeta potential from untreated silica, it can be hypothesized that a diamine functionality would lead to larger changes, since it allows for a larger electric charge per molecule of SCA attached to the surface of the particle. For this reason, TMPE, with two amines in the backbone was used to coat the silica particles. TMPE has a very limited history of use as a coating agent of silica when compared with APMS and APES. However, one study reports that a high degree of coverage of silica is possible with TMPE, but the effects on the surface charge or stability were not examined (Krasnoslobodtsev 2002).

Previous work done by our lab investigated changes in zeta potential upon addition of APES, APMS and TMPE from untreated silica and found systematic changes with APES and APMS similar to previously presented results from literature (Figure 7) and found more pronounced changes with TMPE as was expected due to the diamine functionality of TMPE. These results, obtained by AlJama (2010), are summarized in Figure 8.

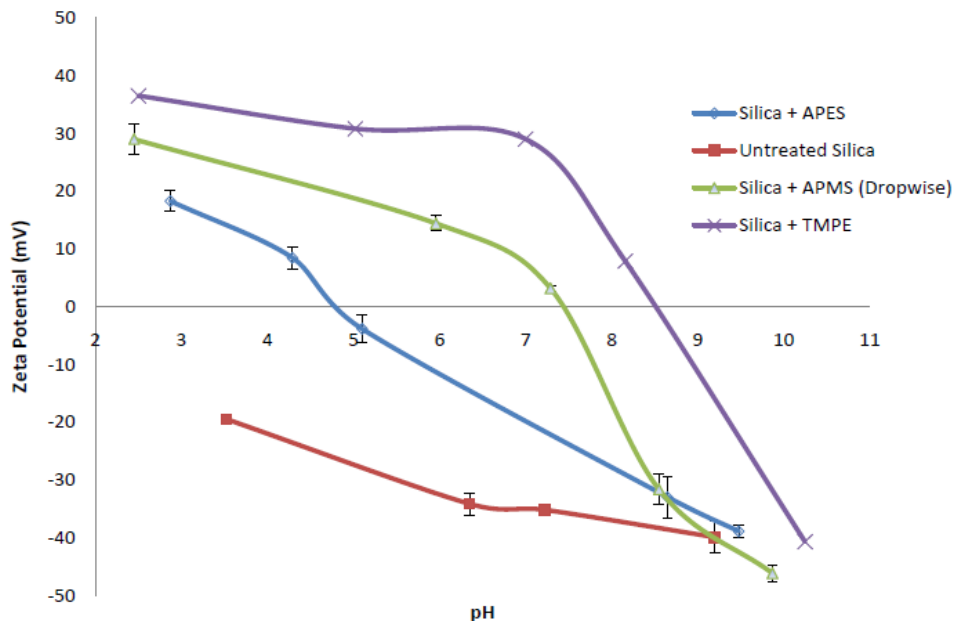


Figure 8: Zeta Potential Results from AlJama (2010)

These zeta potential results show a significant change in the zeta potential from untreated silica when TMPE is added, with enough of a shift that the TMPE treated silica is almost at the zeta potential range of a stable dispersion, with the magnitude of the potential approaching 40 mV, although not quite reaching it. Thus, TMPE appears to be a promising SCA for achieving a stable dispersion of silica in water.

2.4 Two-Step Modification Review

Glutaric anhydride (GA) is cyclic molecule which in the presence of water can open to form dicarboxylic acid and one of the acid groups can react with a primary or secondary amine to form an amide. Mahalingam et al. (2004) treated APES coated silica particles with GA in a two-step modification process which made a carboxylic acid functionalized silica (this silica was only a precursor to further modifications but the results obtained are applicable here). The schematic of this reaction is shown in Figure 9.

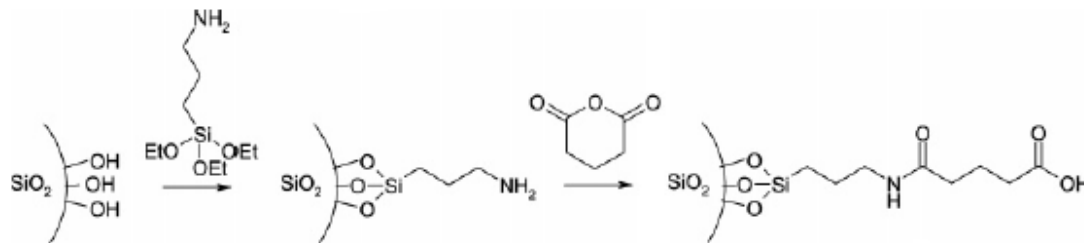


Figure 9: Schematic of Two-Step Modification Reaction

Mahalingam measured the zeta potential of the resulting particles, the results of which are shown in Figure 10, with the two-step modified silica shown as the triangles.

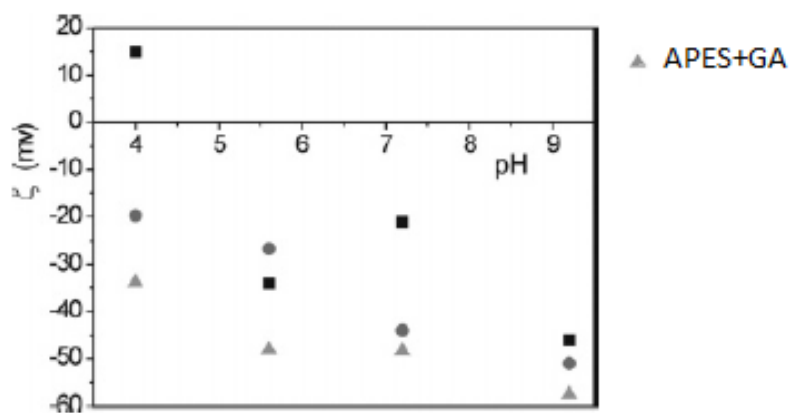


Figure 10: Zeta Potential of Two-Step Modification

These results show a very promising zeta potential, with a value of close to -50 mV at near neutral pH, indicating a stable dispersion.

Mahalingam only attempted to modify APES coated silica, although the reaction shown in Figure 9 suggests that GA could also successfully modify the surface of APMS and TMPE coated silica in addition to APES, since all of these terminate in an amine functional group. This was done previously in our lab and the results of this are shown in Figure 11 (AlJama 2010).

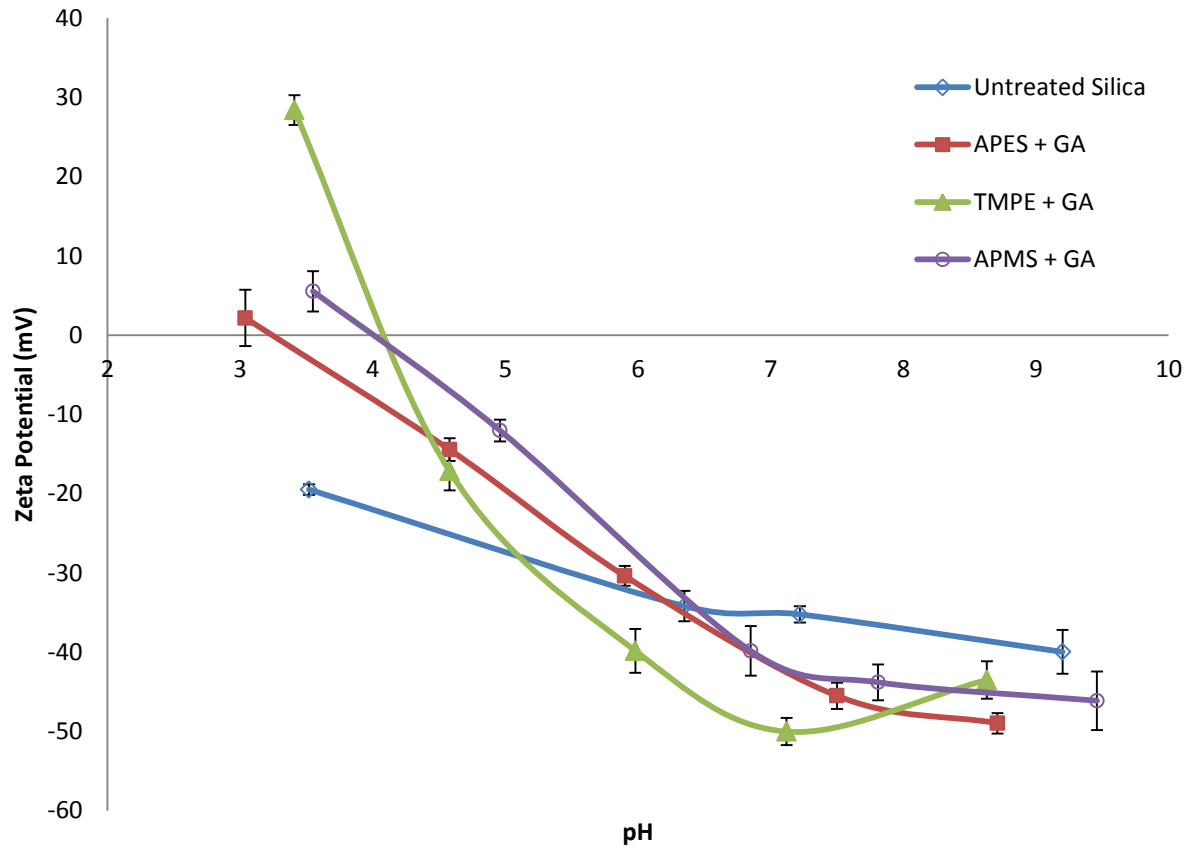


Figure 11: Zeta Potential Results for the Two-Step Modification of all SCAs

These results make it clear that GA is able to modify silica which has been coated with APES, APMS and TMPE since there is a shift in the zeta potential profile for all three. The best result from these treatments is the TMPE coated silica modified with GA, which shows a zeta potential of close to -50 mV at neutral pH.

Chapter 3: Methods and Materials

3.1 Zeta Potential

The zeta potential of a particle is defined as the electric potential difference between a point at the shear plane of the particle and a point in the bulk fluid away from the particle. The zeta potential of a particle dispersion can give some idea of its stability. A zeta potential of magnitude greater than 40 mV is often considered a good indicator of stability, and values below 20 mV in magnitude are very prone to aggregation.

One of the most common methods to measure zeta potential is with electrophoresis. In this method, an electric field E , is applied to the charged colloidal particle in solution, with net charge q . This imposes a net force on the particle

$$F_e = qE \quad (1)$$

and causes the particle to accelerate. However the particle also experiences a drag force due to fluid friction which is given by Stoke's Law

$$F_d = 6\pi\eta Rv \quad (2)$$

where v is the velocity. By dividing this velocity by the applied electric field, E , we obtain the electrophoretic mobility, μ . There are many theories which can relate μ to the zeta potential, ζ .

One commonly used model developed by Smoluchowski, which is valid for low Debye lengths, gives

$$\mu = \frac{\varepsilon\zeta}{\eta} \quad (3)$$

where ε is the dielectric constant of the solution (Hunter 1981).

In this thesis, the zeta potential measurements were made with a ZetaPlus analyzer manufactured by Brookhaven Instruments. To make a measurement, a small amount of sample is placed into a cuvette and diluted with DI water. Ten measurements were made for each sample, and any values which markedly deviated from the mean were not included in the reported averages.

3.2 Dynamic Light Scattering

Dynamic Light Scattering (DLS) is a very useful and commonly used method to determine the size of particles suspended in solution. In DLS, a laser is shown through a solution, and the particles scatter the light through all angles. A photon detector is offset from the sample by a certain angle, and this detector measures the intensity of incoming photons, denoted by I . Then, an autocorrelator is used to determine the dimensionless autocorrelation function

$$g(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} \quad (4)$$

where τ is a correlation time and the brackets denote a time average. It can be shown that the function

$$G(\tau) = g(\tau) - 1 \quad (5)$$

decays exponentially with a decay constant given by

$$\Gamma = Dq^2 \quad (6)$$

where D is the diffusion constant of the particles in the solution and q is the magnitude of scattering wave vector, given by

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (7)$$

By assuming the particles in solution are spherical, we can use the Stokes-Einstein law for D ,

$$D = \frac{k_B T}{6\pi\eta R} \quad (8)$$

Thus, by combining equations 1-4, we can find the diffusion constant D and with equation 5, we can solve for the particle radius, R (Goldburg 1999).

The light scattering apparatus used in this thesis consists of a He-Ne laser operating at 35 mW and a wavelength of 633 nm manufactured by Spectra Physics and a digital correlator manufactured by Brookhaven Instruments. To make a measurement, a small amount of the sample is diluted in a test tube with DI water. Several size measurements are made on each sample to ensure consistency, and results with a percent error greater than .1%, or with positive overflow (both reported by the software) are not accepted.

3.3 Stability Tests

One of the areas of investigation of this thesis research is in the long term stability of particle dispersions. However, this stability can be difficult to measure over a reasonable time scale if the particles are fairly stable. In order to perform tests of stability over a reasonable time scale, it is possible to increase the ionic strength of the dispersions by adding salt (NaCl is used in the thesis). This destabilizes the particles by decreasing the Debye length. The size of the particles as measured by DLS can then be tracked to determine relative stability between differently coated particles.

3.4 Surface Coating Methods

There are two distinct methods that are used to coat the silica particles in this thesis, which will be termed “direct addition” and “dilute addition”. In direct addition, a small amount of the pure SCA is added directly to the aqueous solution of silica and allowed to stir for 24 hours. In dilute addition, a desired amount of the SCA is diluted in pure ethanol, and this can then be added slowly to the aqueous

solution of silica. All the previous results shown from AlJama (2010) used the method of direct addition, although most of results in this thesis used dilute addition (it will be made clear which method was used as results are presented).

The main reason the dilute addition method was chosen was to minimize the concentration of SCA present at any time in the aqueous solution of particles. Since the SCA molecules require water to hydrolyze and cannot bond or polymerize with each other without first being hydrolyzed, by minimizing the concentration present, the rate of self-polymerization of the SCA's can be decreased, leaving more available for surface coating of the silica. It is hoped that this will lead to more complete surface coverage, as well as decrease the likelihood of particle aggregation caused by bridging.

3.5 Surface Coating Experimental Details

In the direct addition of SCA, a measured amount of APES, APMS or TMPE is added quickly and directly to a sample Ludox TM-40 silica particles, with the silica at a 12 wt. % in water (average size ~30 nm). The concentrations of the SCA that were used in the direct addition method are shown in Table 2.

Table 2: Concentrations of SCA in the Silica Suspension used in Direct Addition

SCA added to silica	Concentration (mM)
APES + SiO ₂	2.26
APMS + SiO ₂	3.11
TMPE+ SiO ₂	6.75

After addition of any SCA, the sample was allowed to stir for at least 24 hours before any measurements were taken or further modification.

The two step modification procedure involved the addition of GA to silica particles already coated with either APES, APMS or TMPE. In this procedure, a solution of .175 M GA in DMF is made, and variable amounts are added to a sample of silica already modified with TMPE (based on the results shown in Figure 11, we only continued testing of the two-step process with TMPE).

In the dilute addition procedure, a solution of APES, APMS or TMPE in ethanol is made at the concentrations shown in Table 3.

Table 3: Concentrations of Diluted SCA in EtOH

SCA used	Concentration in EtOH (M)
APES	0.090
APMS	0.124
TMPE	0.180

Then, varying quantities of these solutions are added dropwise over a period of roughly fifteen to twenty minutes in order to achieve a desired concentration of SCA in the silica solution, and left to stir for 24 hours.

3.6 Surface Percent Coverage Calculations

One of the goals of the surface treatments is to achieve a coverage as close as possible to the theoretical maximum, where every open site on the silica would be occupied by an SCA molecule. In order to quantify this, we must first find the theoretical maximum amount of SCA that can be added to achieve complete coverage. For this we use a surface area of 110 m²/ gram of silica particles, which is reported by the manufacturer. For the area taken up by a single SCA molecule bound to the surface, we

use a value of 25 Å²/ molecule, which was reported in a patent by Iler (1957) for a typical value of an aminoorganosilane.

We first need to find the weight per unit volume of silica solution in a sample using the known density (reported by manufacturer) and concentration. Multiplying this by 110 m²/gram gives the effective surface area per unit volume of the particles in solution, which I'll call A_m. Then,

$$w = A_m * \frac{1 \text{ molecule}}{25 * 10^{-20} \text{ m}^2} * \frac{1 \text{ mol}}{6.022 * 10^{23} \text{ molecules}} * MW_{SCA} \quad (9)$$

gives the weight in grams of SCA needed to achieve theoretical maximum coverage per mL of silica solution, by the given SCA. These are reported in Table 4.

Table 4: Theoretically Calculated Max Weight of SCA for Complete Coverage

SCA	Theoretical Max Weight (g/mL solution)
APES	0.0211
APMS	0.0153
TMPE	0.0211

Multiplying the appropriate number from Table 4 by the total solution volume gives the maximum weight of SCA that can theoretically be added to achieve full coverage. Then, dividing the amount of SCA that has been added by that maximum amount gives the percent of theoretical maximum coverage that has been added, denoted by percent coverage.

However, it should be noted that the calculations which lead to theoretical maximum coverage and percent coverage are subject to assumptions, such as the area taken by one molecule equal to 25

\AA^2 / molecule. Thus, the values of percent coverage that are reported are better used as relative measures of coverage to compare between different samples rather than absolute quantities.

Chapter 4: Results and Discussion

4.1 Stability Tests with Direct Addition

The first tests that were done in this thesis were to determine the stability of particle dispersions shown in Figure 8 and Figure 11 (one step and two step modifications with direct addition of SCA). Figure 12 shows the size of silica modified with APES, APMS, TMPE along with untreated silica and Figure 13 shows the size of silica modified with APES + GA, APMS + GA and TMPE + GA. These stability tests were done at the native pH of the silica after modification (see Table 5 for these pH values), with equal amounts of NaCl added to each sample (.2 g NaCl), and all sizes were measured with DLS.

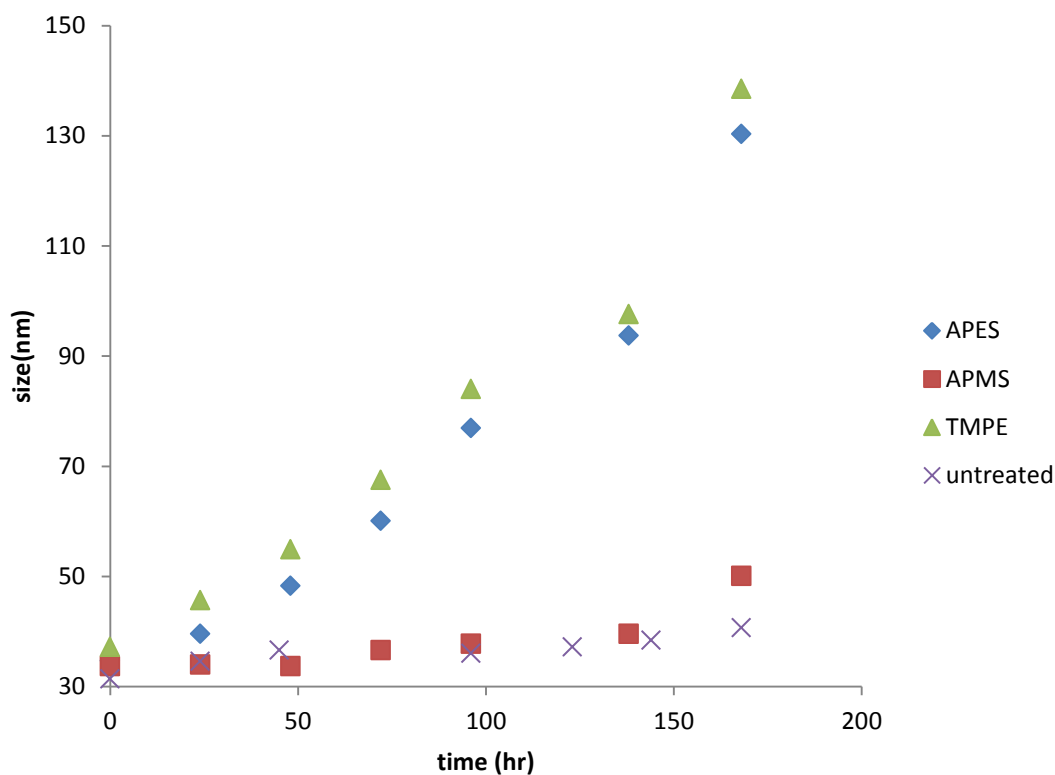


Figure 12: Stability Test- One Step Modification at Native pH with .2g NaCl added

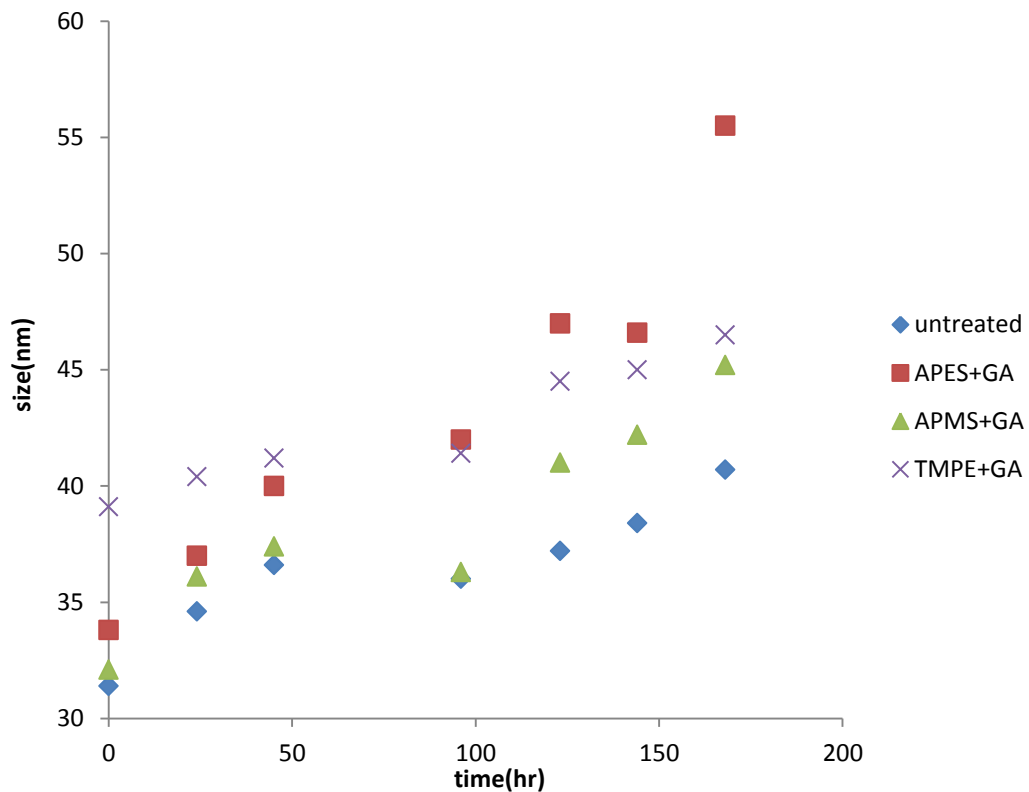


Figure 13: Stability Test- Two Step Modification at Native pH with .2 g NaCl added

The concentrations of SCA used for these tests along with the native pH values are summarized in Table 5. The concentrations of GA used were determined from the best zeta potential results from previous research done in our lab in this area (AlJama 2010).

Table 5: Summary of Concentrations used and Size Increase in Native pH Stability Test

SCA used	Concentration of SCA(mM)	Concentration of GA (mM)	Native pH	% size Increase over experiment
Untreated	-	-	9.4	30
APES	2.26	-	9.51	276
APMS	3.11	-	9.57	49
TMPE	6.75	-	9.7	272
APES + GA	2.26	4.28	8.56	64
APMS + GA	3.11	3.75	9.09	41
TMPE + GA	6.75	5.84	8.65	19

It can be seen in Table 5 that in the one-step modification, APMS coated silica showed greater stability than compared with APES and TMPE while untreated silica was more stable than any of the one-step treatments. Over all the treatments including untreated silica, TMPE + GA showed the greatest stability. The fact that TMPE alone shows such poor stability while TMPE + GA is the most stable treatment may seem surprising, but can be easily explained by examining the reaction scheme of the two step modification in Figure 9: Schematic of Two-Step Modification Reaction. Since a molecule of GA attaches directly to an SCA molecule, the higher the concentration of SCA on the surface of the silica will allow for a higher concentration of GA, causing greater potential stability. This is supported by the fact that the ordering of stability in the two step modification is equal to the ordering of amounts of SCA present before addition of GA, as seen in the column in Table 5 labeled concentration of SCA.

Since a potential application for the particle dispersions in this thesis is as a medium in a heat exchanger which would be run at a near neutral pH, the previous stability tests were repeated at pH =7,

with all concentrations the same as in Table 5. Since zeta potential and surface charging are very much affected by solution pH, it is expected that stability would also be. The method of pH adjustment used for these tests is by the addition of pH=4 buffer solution. The reason this was chosen instead of the more common method of pH adjustment (adding small quantities of dilute acid or base) was that it allowed for the final pH to be better controlled and exactly 7. However, since this method requires large volumes of buffer compared with acid addition, it will dilute the samples which could also affect stability.

The stability test results for the one step modification at neutral pH are shown in Figure 14.

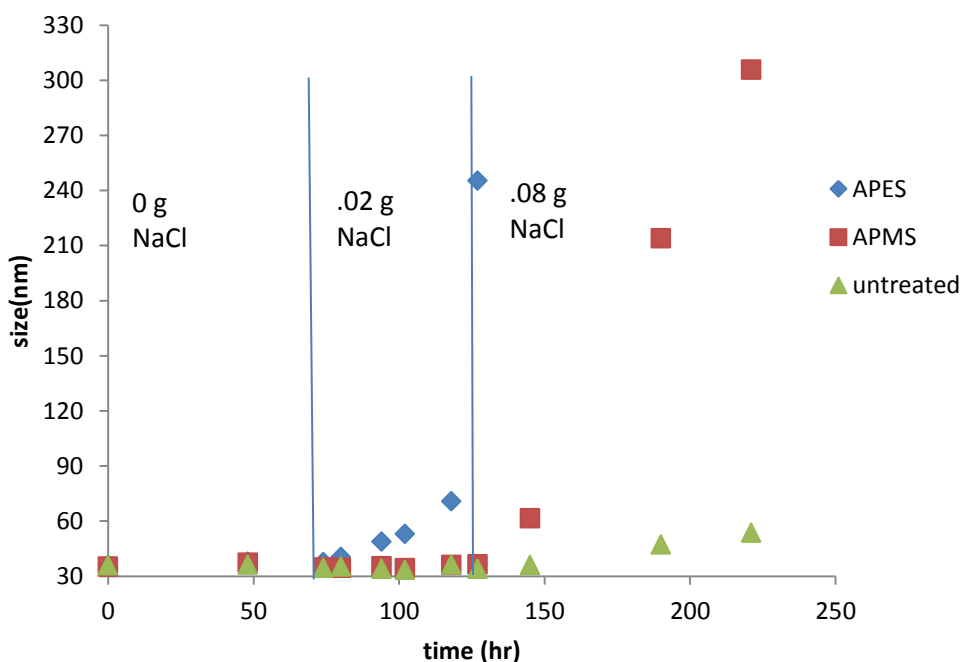


Figure 14: Stability Test- One Step Modification at Neutral pH

In this graph, the results for TMPE are not shown because it aggregated immediately upon pH adjustment to neutral, meaning that it approached or crossed its isoelectric point during the process of adjusting the pH from native to 7. The blue lines in the graph indicate the total amount of salt that had been added up to the time where the blue line crosses the x-axis. From this graph, it can be seen that

upon addition of .02g of NaCl to all samples, the APES coated silica destabilized whereas the APMS and untreated silica did not. Upon addition of an additional .06 g (to bring the total to .08 g), APMS and untreated silica both started to grow, but with the untreated growing at a slower rate, indicating higher stability.

Figure 15 shows the stability test conducted for APES + GA and APMS + GA, with TMPE + GA not shown because it also aggregated immediately upon pH adjustment to neutral as with TMPE alone.

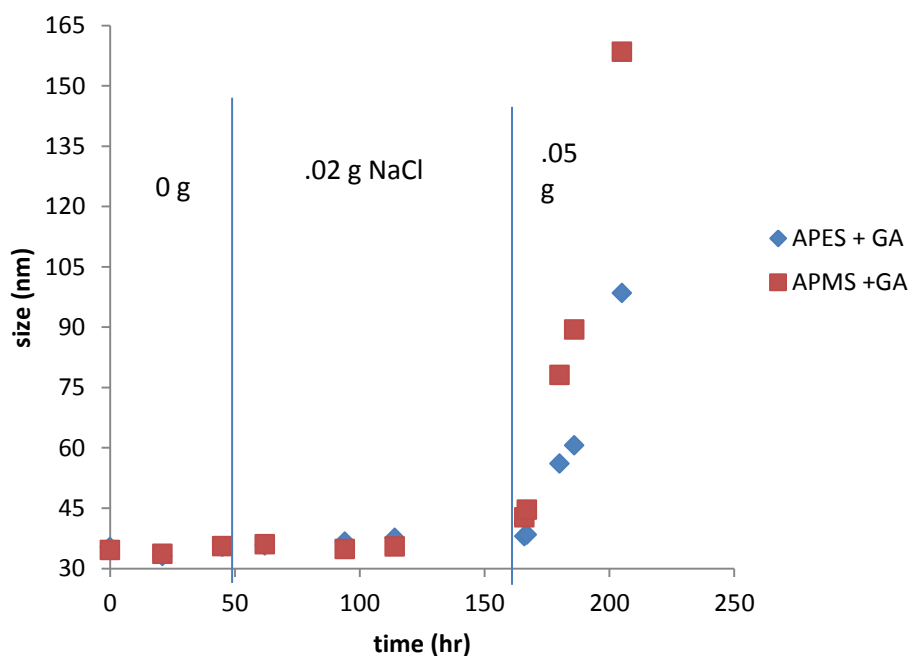


Figure 15: Stability Test- Two Step Modification at Neutral pH

It can be seen in this graph that both samples are stable until the addition of NaCl reaches .05 g, at which point both destabilize, with APMS + GA destabilizing at a slightly faster rate.

The results of these stability tests show that at native pH of solution, the only coating method that achieves a greater stability than untreated silica is the two step modification with TMPE + GA, and at neutral pH untreated silica is the most stable. One reason that untreated silica shows so much better

stability than the majority of the treated samples is that silica is naturally negatively charged at the pH ranges explored whereas the SCAs, upon attachment to the silica will become positively charged due to protonation of the terminating amine group. Thus, if the silica particles are less than fully coated with SCA, the negatively charged terminal hydroxyls from uncoated sections of the particles will partially cancel some of the positive charges from the coated sections of the particles, thereby lowering the magnitude of the overall zeta potential. Thus, one way to potentially achieve greater stability with the coated silica than with the uncoated is to try to achieve greater surface coverage by increasing the amounts of SCA that are added. As explained before, this is difficult to achieve with direct addition because of hydrolysis of the SCA when present in high concentrations in water, so the following experiments use the dilute addition method of coating.

4.2 APES Dilute Addition

The basic idea behind the dilute addition tests of SCA is that controlled amounts of SCA can be added in excess of what can be added with direct addition. Then, the zeta potential of samples with increasing amounts of SCA can be monitored, with a larger deviation from untreated silica indicating higher surface coverage of the SCA on the silica. If the zeta potential eventually shows no more change with increasing amounts of SCA, this gives evidence that complete or maximum surface coverage of the SCA on silica has been achieved.

APES was the first SCA used in the dilute addition tests. First, APES was diluted in pure ethanol at the concentration indicated in Table 3. This diluted APES solution was then added dropwise (over roughly 15-20 minutes) to samples of untreated silica in varying quantities to achieve the concentrations shown in Table 6. In addition, Table 6 also lists the percent coverage, computed by dividing the amount of APES added by the theoretical maximum listed in Table 4.

Table 6: Concentrations and Percent Coverage of APES Dilute Additions

Sample Descriptor	Concentration (mM)	Percent Coverage
APES-1	1.10	1.19
APES-2	2.15	2.37
APES-3	3.27	3.56
APES-4	4.30	4.76
APES-5	5.31	5.94
APES-6	6.30	7.13

Figure 16 shows the size of each of the above samples after addition of the APES, with 0 percent coverage indicating untreated silica. All the sizes were measured 24 hours after addition of APES, with the dotted line indicating the initial size before APES addition.

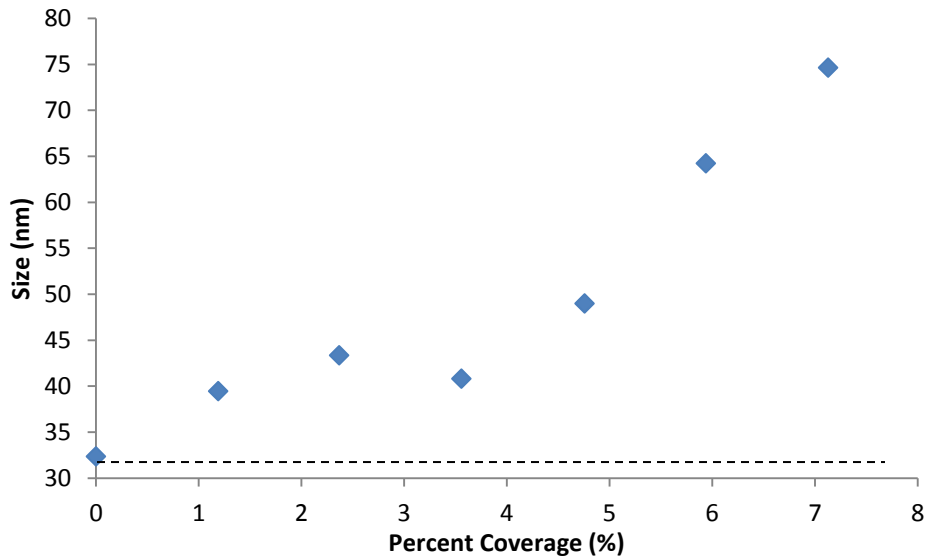


Figure 16: Size of APES Dilute Additions Measured 24 Hours after Treatment

This graph shows a large increase in size with increasing amounts of APES added, indicating the particles are either becoming unstable electrostatically due to increasing amounts of APES or they are aggregating due to the bridging effect caused by APES. Visually, the particles show aggregation, with a small sol-gel layer forming at the bottom of the samples within a couple days of SCA addition, and the thickness of the layer being roughly proportional to the amount of APES added. However, the volume of the sol-gel layer has remained roughly constant over a period of several months, with no more aggregation occurring after the initial formation, and no appreciable size increases over time. This suggests that the initial formation of the sol-gel layer may have been caused by bridging due to some of the APES self-polymerizing, because if it was caused by electrostatic instability, the size of the sol-gel layer would keep growing over time, as would the particle size. In order to determine if any of the APES successfully coated the surface of the silica, the zeta potential of the still liquid part of the samples was determined as a function of pH. These results are shown in Figure 17.

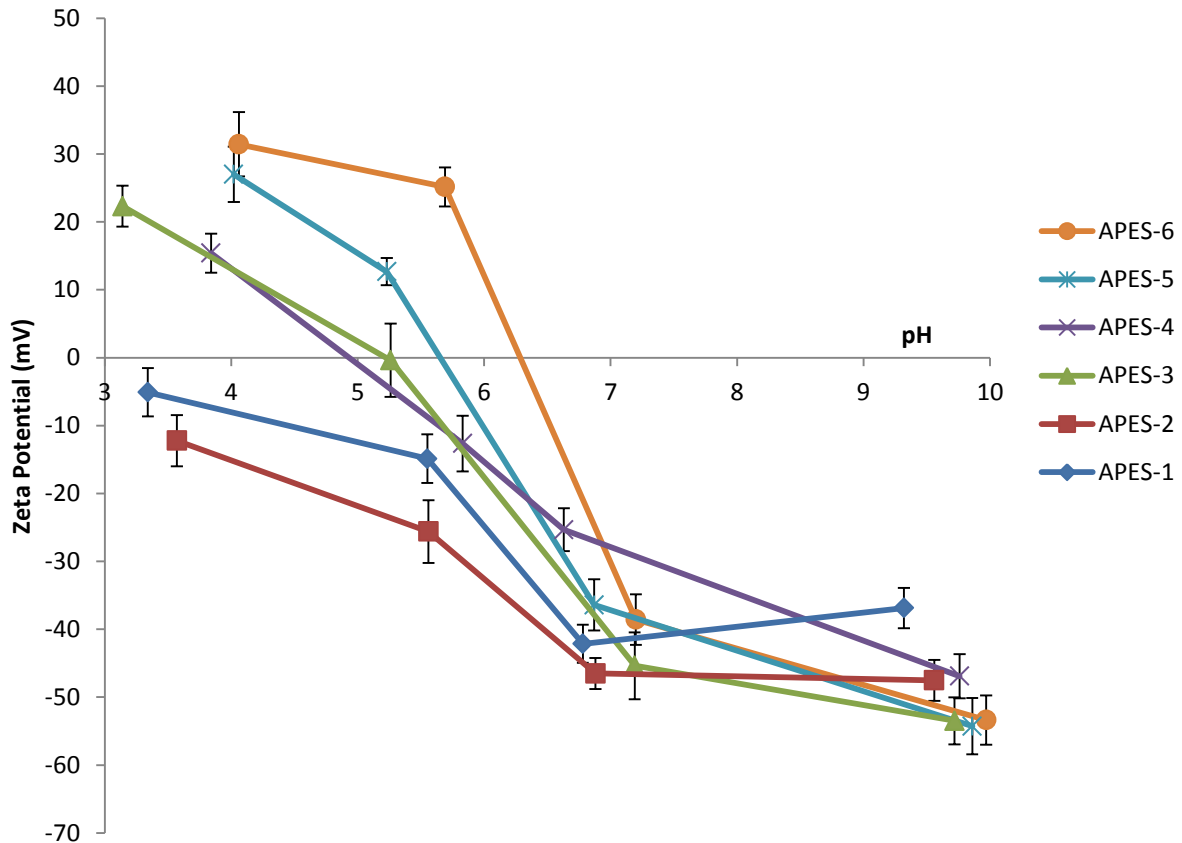


Figure 17: Zeta Potential Results for Dilute APES Addition

There can be seen a significant shift in the zeta potential profile and isoelectric point with increasing amounts of APES being added. Thus, the APES is clearly bonding to the surface of the silica and having an effect on its surface charging. However, this behavior is not exactly what is desired because there is not enough APES bonded to the surface to bring the silica to a positive zeta potential that is more stable than untreated silica at neutral pH. This could be resolved if more APES were able to coat the surface, but as Figure 16 suggests, the addition of more APES is rapidly causing the size of the silica to increase and approach aggregation. Thus, these tests were repeated with APMS, since the presence of only one hydrolyzable in APMS may allow for the addition of larger amounts than APES with three hydrolyzable groups.

4.3 APMS Dilute Addition

As with the tests with APES, APMS was diluted in pure ethanol to the concentration indicated in Table 3. This was then added dropwise, over roughly 15-20 minutes, to untreated silica in varying quantities to achieve the concentrations shown in Table 7.

Table 7: Concentrations and Percent Coverage of APMS Dilute Additions

Sample Descriptor	Concentration (mM)	Percent Coverage
APMS-1	1.91	2.04
APMS-2	3.76	4.08
APMS-3	7.29	8.16
APMS-4	10.63	12.24
APMS-5	19.58	24.47
APMS-6	29.44	38.75

Figure 18 shows the size of each of the above APMS samples after addition of the APMS. All the sizes were measured 24 hours after addition of APMS, with the dotted line indicating the initial size before APMS addition.

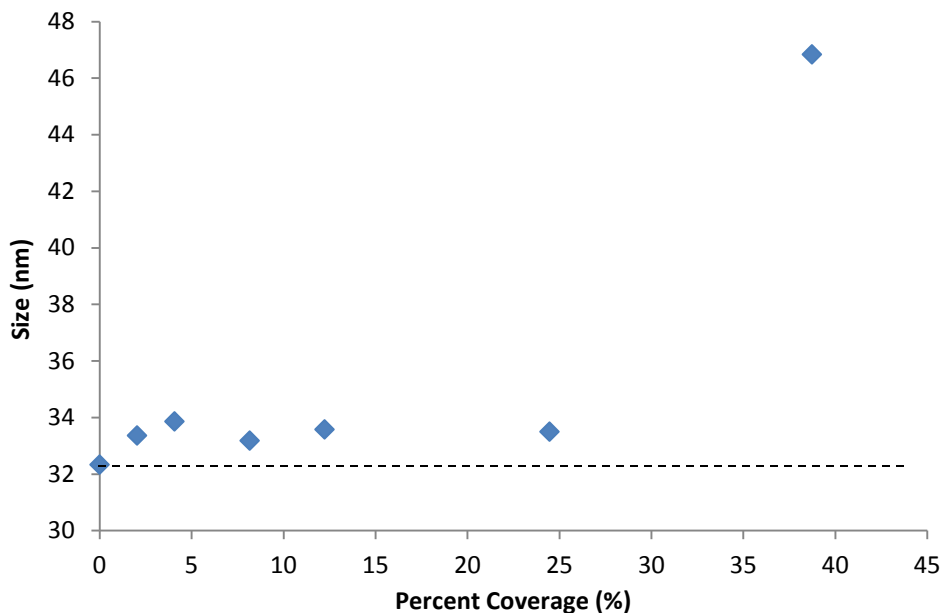


Figure 18: Size of APMS Dilution Treated Samples Measured 24 Hours after Treatment

It can be seen in Figure 18 that the size of the particles is relatively constant until the final sample with 38.75% coverage. One higher amount of APMS was tested at 48.95% coverage which completely aggregated within one day of addition, so these results are not included. Thus, the amount of APMS added in sample AMPS-6 is close to the maximum amount that can be added with the dilute addition method without aggregation occurring.

It is noteworthy that there are much larger quantities of APMS that can be added than APES without causing aggregation. This confirms the previous expectation that the one hydrolyzable group of APMS compared with three for APES would allow for larger amounts to be added without problems arising from particle bridging. Since the percent coverage of APMS is higher than APES, it is expected that the zeta potential would show larger deviations from untreated silica than with APES. The zeta potential results for the dilute APMS additions are shown in Figure 19.

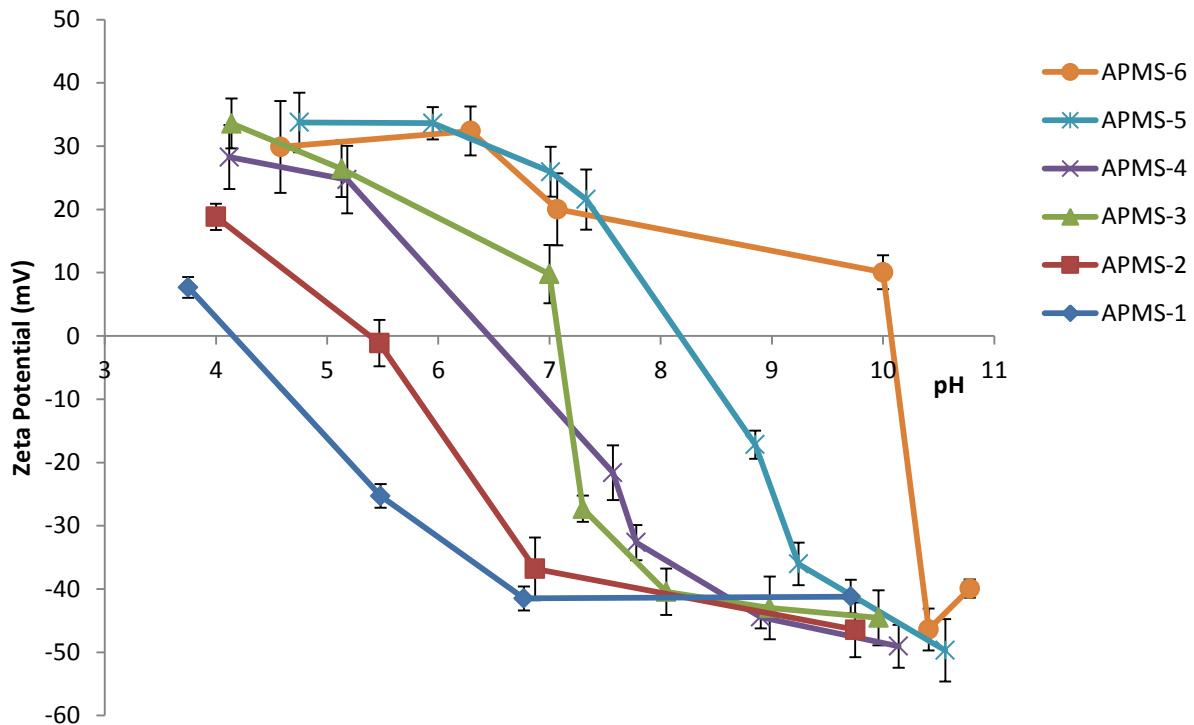


Figure 19: Zeta Potential Results for Dilute APMS Addition

This graph shows a larger shift in the zeta potential and isoelectric point over the amounts of APMS that can be added before aggregation than is seen in Figure 17 with APES. In addition, at close to neutral pH, there is a shift from fairly negative value of zeta potential to positive values above 20 mV. Thus, there is indeed more surface coverage surface charging effects occurring with the larger amounts of APMS that are added. In comparing the zeta potential results for APES and APMS, it appears that APMS shows more promise to bring the silica particles into a higher stability range of zeta potential than untreated silica, because it is capable of much larger shifts.

However, even though APMS is able to shift the zeta potential so much more than APES, it is still not at a very stable regime at neutral pH compared with untreated silica. This could be potentially alleviated with a higher surface charge density by increasing the coverage of APMS. However, as stated above, the coverage achieved in sample APMS-6 is close to the maximum possible with this method of

SCA addition without causing aggregation. If the number of SCA molecules per unit of area of silica particle cannot be appreciably increased, another way to increase the surface charge density is to increase the charge per molecule of SCA. This is done by using TMPE instead of APMS or APES, since it has two amine groups that can be protonated to provide additional positive charge.

4.4 TMPE Dilute Addition

TMPE was diluted in pure ethanol to the concentration shown in Table 3 and was added dropwise over roughly 15-20 minutes to untreated silica in varying quantities to the concentrations listed in Table 8.

Table 8: Concentrations and Percent Coverage of TMPE Dilute Additions

Sample Descriptor	Concentration (mM)	Percent Coverage
TMPE-1	2.77	2.96
TMPE-2	5.45	5.92
TMPE-3	10.58	11.84
TMPE-4	15.42	17.75
TMPE-5	28.40	35.51
TMPE-6	39.49	53.26

Figure 20 shows the size of each of the above TMPE samples after addition of the TMPE. All the sizes were measured 24 hours after addition of TMPE, with the dotted line indicating the initial size before TMPE addition.

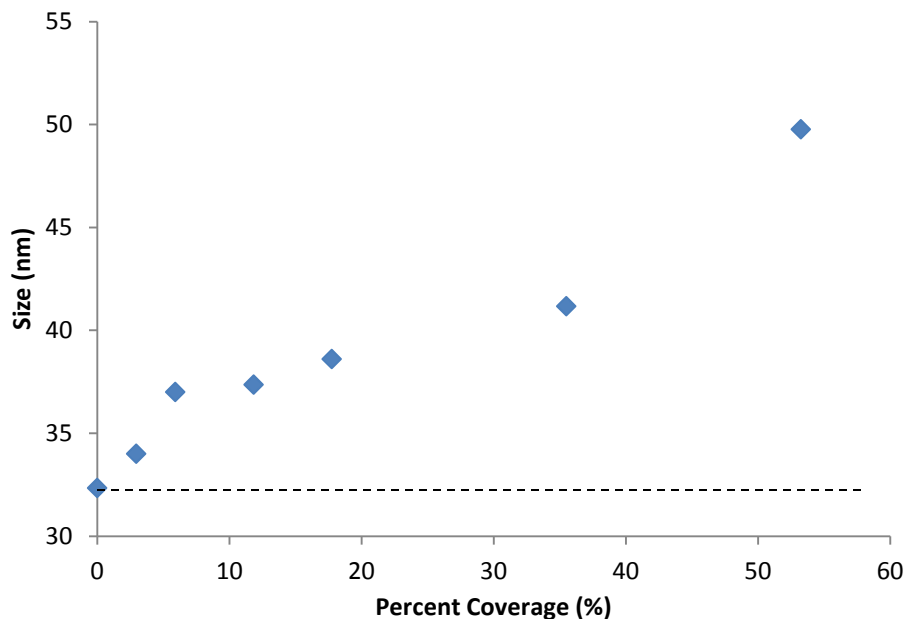


Figure 20: Size of TMPE Dilution Treated Samples

The TMPE treatments were stopped at TMPE-6 because the initial size after TMPE addition for the last sample had increased so much past untreated silica. By comparing Table 7 with Table 8, it can be seen that more TMPE can be added to untreated silica than APMS without causing irreversible aggregation, both in terms of concentration and percent coverage. This is very surprising given that TMPE has three hydrolyzable groups and thus should be expected to be more similar to APES and cause aggregation at a low percent coverage rather than allow for a higher coverage than APMS with only one hydrolyzable group. There is not currently a satisfactory explanation to make clear why this phenomenon occurs. One possible explanation is that the longer carbon backbone chain present in TMPE provides enough steric hindrance to prevent the particle bridging that is typical in APES-coated silica. Another explanation could be that the extra amine group provides additional surface charging that prevents the particles approaching close enough to cause bridging, but this is unlikely considering the zeta potential results for the TMPE samples shown in Figure 21.

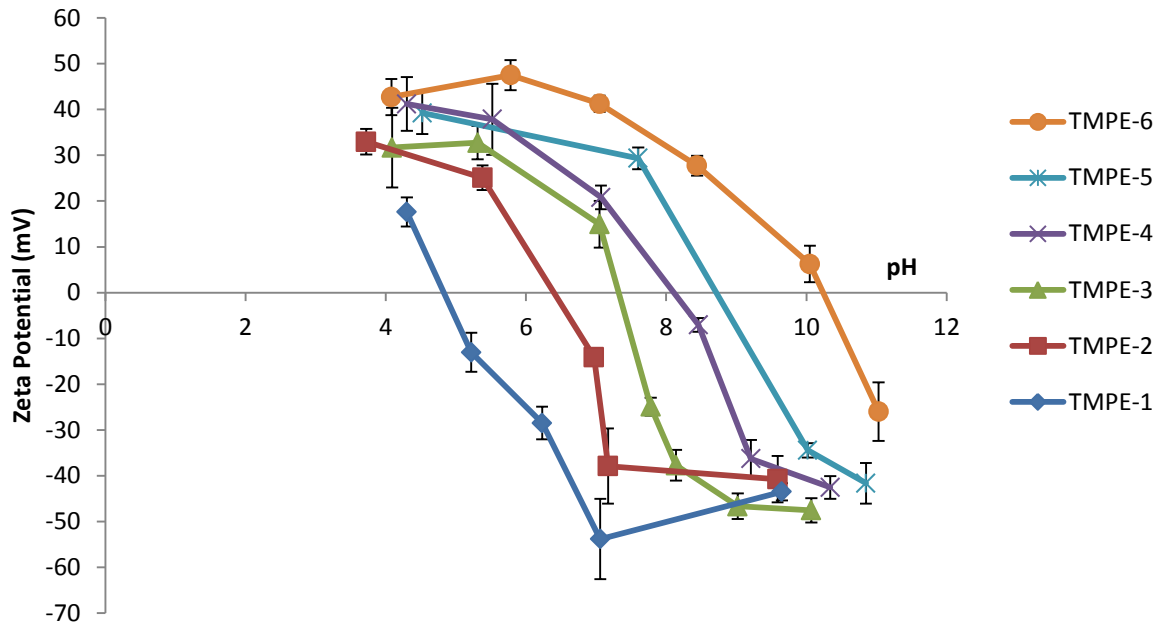


Figure 21: Zeta Potential Results for Dilute TMPE Addition

The reason that increased surface charge from the additional amine in TMPE is not a satisfactory explanation for the greatly increased surface coverages that can be achieved compared with APES is that all coating is done at the native pH of solution, and it can be seen comparing Figure 21 with Figure 17 that the zeta potential of TMPE at native pH is smaller in magnitude than APES, so additional stability at this pH is not expected based on electrostatics alone. Even though the mechanism that allows for much higher surface coverages of TMPE compared with APES is not completely known, it is a very important result that could suggest further study into the use of TMPE as an SCA.

It is clear from the zeta potential results for dilute addition of APMS and TMPE that much larger changes in the surface charging of silica is possible compared with APES, which can be explained by the higher surface coverages achieved with APMS and TMPE. However, even with the maximum amounts added of APMS and TMPE before aggregation occurred, complete coverage of the silica has not been reached, since the zeta potential at native pH still shows a negative value, indicating there are terminal

hydroxyls left from uncoated parts of the silica particles, which charge negatively in water at this pH compared with the amine terminated SCAs which would be positive or neutral. To attempt to approach closer to the maximum coverage, one series of experiments were done with a staged addition of diluted TMPE, which is described in the next section.

4.5 TMPE Staged, Dilute Addition

In order to potentially allow for larger amounts of TMPE to be added, as well as to investigate the effect of timing of SCA addition, the diluted TMPE was added over a period of several days instead of 15-20 minutes as before. Specifically, TMPE was diluted in pure ethanol to the concentration indicated in Table 3. Then, this diluted TMPE was added to untreated silica using the method of dilute addition until a concentration of 30.83 mM was reached. After this, the diluted TMPE was added in small quantities with between 6 and 12 hours in between each addition, or stage. The size of the particles was monitored after each subsequent addition, and the additions were stopped once the size started increasing or showing aggregation. This resulted in 4 total additions past 30.83 mM, with the concentration and theoretical percent coverage after each addition shown in Table 9.

Table 9: Concentrations and Percent Coverages in Staged TMPE addition

Stage Number	Concentration (mM)	Percent Coverage	Size (nm)
1	39.98	47.35	37.0
2	48.62	59.18	36.5
3	56.81	71.02	37.75
4	64.57	82.86	38.7

The additions were stopped at the fourth step because even though the size was measured as 38.7 nm right after the addition, the size had increased to over 100 nm within one day of the addition. It

is clear that this method of addition leads to higher coverage and amounts of TMPE that can be added compared with the dilute method of addition of TMPE over a shorter time period of 15-20 minutes that was shown in Table 8 with an increase of theoretical percent coverage of $\frac{82.86\%}{53.26\%} = 155\%$. To confirm that higher coverage is actually achieved, the zeta potential after each addition at the native pH was measured versus the theoretical percent coverage achieved by that point, with these results shown in Figure 22.

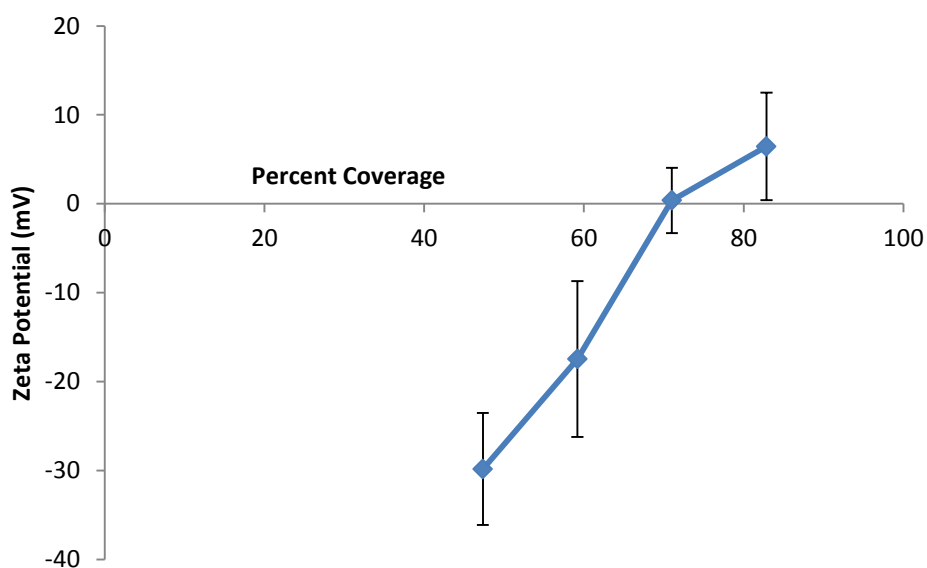


Figure 22: Zeta Potential at native pH versus Percent Coverage of TMPE

The most important feature of the graph in Figure 22 is that the zeta potential is positive at native pH with the highest amount of TMPE used. This is the first time in our research with these SCAs, that enough SCA could be added before aggregation occurred such that the zeta potential could be brought into a positive regime at native pH, indicating that this is the highest surface coverage achieved at this point. It also shows that the silica particles have least 50% actual coverage of TMPE, since the positive and neutral charges at the surface must outnumber the negatively charged, uncoated

hydroxyls. To get a better idea of the stability of the sample with the maximum TMPE added, the zeta potential was measured as a function of pH of the sample after the 4th stage of addition with 82.86 percent coverage, with these results shown in Figure 23.

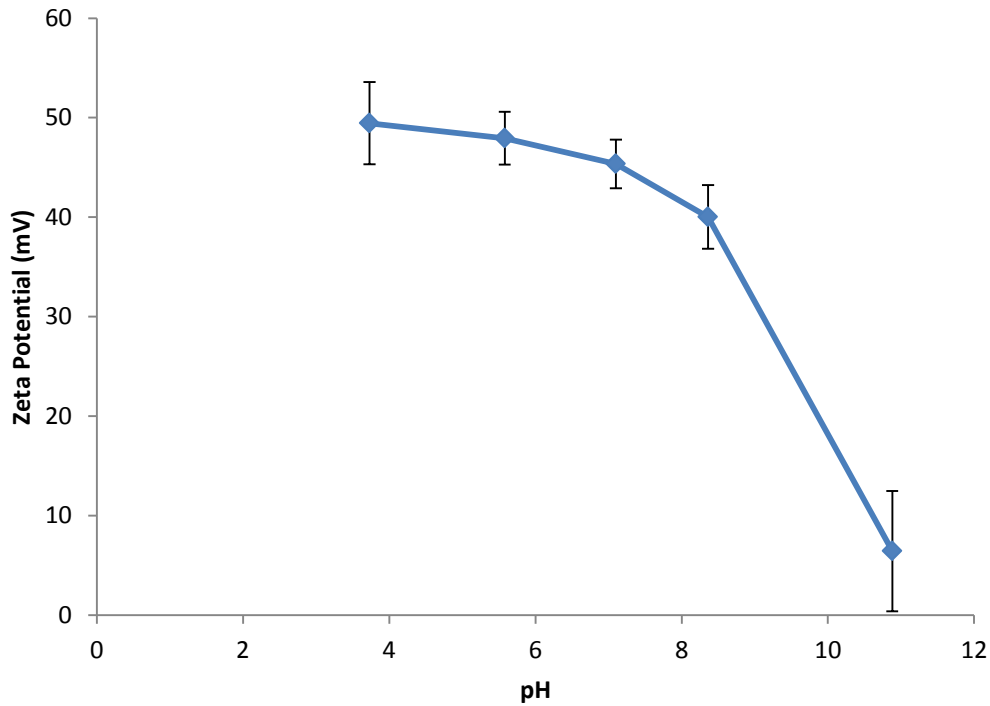


Figure 23: Zeta Potential vs. pH for Max TMPE Staged Addition

The zeta potential in Figure 23 starts positive as explained earlier, and quickly rises to a zeta potential value of 40 mV and higher values at neutral and acidic pH. These are the highest positive zeta potential values that have been achieved for coated silica and make this a promising treatment to increase the stability of untreated silica by coating with SCA. In addition, this experiment shows that a slower addition of SCA can allow for larger amounts to be added and a higher surface coverage to be achieved. Thus the rate of addition of any SCA is an important factor that can be utilized to achieve more complete coverage.

Chapter 5: Conclusions

In this thesis, the surface of colloidal silica in aqueous solution was coated with three silane coupling agents: APES, APMS and TMPE. There were two methods of adding the SCA to the particles that were tested. The first, direct addition involved adding pure SCA to the aqueous silica solution and stirring for 24 hours. The second, dilute addition involved first diluting the SCA in ethanol and then adding it dropwise over 15-20 minutes. In addition, there was one experiment performed which used dilute addition, but added the SCA over several days to investigate the effect of timing of addition on surface coverage of SCA.

For all three SCAs tested, the dilute method of addition allowed for increased amounts to be added without causing complete aggregation of the silica particles, when compared with direct addition. The primary reason for this is that all the SCAs hydrolyze in the presence of water, which can cause them to polymerize or bond with each other, preventing their attachment to the particle surface. However, this polymerization is a kinetic process and its rate will be dependent on the concentration of SCA present in the water, so adding it in dilute form over a longer time should allow for more to be added and effectively coat the particles. Our results show that this is indeed true, since more is able to be added without causing irreversible aggregation, and since we get much larger changes in the zeta potential with dilute addition than with direct addition, indicating more complete coverage.

Of the three SCAs tested with dilute addition, TMPE allowed for the highest amounts to be added as well as showed the most pronounced changes in zeta potential from untreated silica. It is surprising that much more TMPE was able to be added than APES under the same experimental conditions, because both have three hydrolyzable groups that can cause self-polymerization. It is possible that the longer backbone chain in TMPE provides some additional stabilization through steric effects, but this is unlikely to fully explain the effect given the relatively short chains in both APES and

TMPE. Thus, future work in this area could attempt to explain the mechanism whereby so much more TMPE can be added than APES.

As explained before, we expect a larger amount of SCA addition to be possible with a slower rate of addition. This was tested in the case of TMPE, by adding diluted TMPE in stages over several days instead of all at once over 15-20 minutes. This resulted in a higher percent coverage by a factor of 155% and larger changes in zeta potential than the quick addition of diluted TMPE. This shows that the rate of addition of SCA is an important controlling factor that can be used to achieve more complete coverage.

Below is a list of future work that can be done in this area to further this research.

1. The stability tests that were done in Chapter 4.1 on the silica treated by direct addition were not done with any samples treated by dilute addition, due to time constraints. These are important tests that should be done, since the dilute addition samples (particularly staged TMPE), showed more promise than direct addition.
2. Further work should be done to determine the mechanism whereby so much more TMPE can be added than APES despite both having three hydrolyzable groups. The hypothesis that steric hindrance is responsible could potentially be tested by finding an SCA with three hydrolyzable groups and longer backbone chain than TMPE, and testing the amount that can be added before aggregation.
3. It is surprising that APMS samples aggregate after a lot of APMS is added, since only having one hydrolyzable group makes it impossible to form a polymer network as in APES or TMPE. Work should be done to elucidate the mechanism whereby this aggregation occurs.
4. Silica was used as model colloidal system in this thesis because it is well understood. However, these coating techniques could potentially be applied to other nanoparticles, such as

copper oxide, titania or aluminum oxide, which may be better suited in a heat exchanger medium due to a higher thermal conductivity. Thus, these systems should be studied and coating methods applied to them to increase particle stability.

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EDUCATION

The Pennsylvania State University

Schreyer Honors College

Bachelor of Science in Chemical Engineering

Bachelor of Science in Mathematics

Expected Graduation: May 2011

University Park, PA

RESEARCH EXPERIENCE

Penn State Department of Chemical Engineering

Research Assistant

- Develop methods to keep nanoparticles stable using practical applications of colloid science and surface chemistry
- Synthesize different types of nanoparticles to be used in heat exchangers as a method to increase energy efficiency
- Trained a new graduate student in techniques and laboratory procedures specific to this research
- Worked with an industry sponsor to obtain funding for the project
- Completed an undergraduate thesis on this research

University Park, PA

January 2010 - Present

Penn State Department of Biology

Research Assistant

- Developed original software in several programming languages to model species competition
- Employed novel theoretical and modeling approaches to determine how fires and other disturbances affect species diversity
- Submitted a paper on this research as the lead author to the journal *Population Ecology*

May 2010 - August 2010

TEACHING EXPERIENCE

Penn State Department of Chemical Engineering

Teaching Assistant

- Worked closely with a professor to assist in the teaching of an honor's course in chemical engineering thermodynamics
- Developed homework problems and taught several lectures without supervision
- Held weekly office hours to help students in the course

August 2010 - December 2010

PUBLICATIONS

- Reilly, D., Miller, A., Shea, K. "Interactions between Frequency and Size of Disturbance Affect Competitive Outcomes" (Under review at *Population Ecology*)

AWARDS AND HONORS

Summer Research Fellowship in Biomolecular Engineering
Schreyer Honors College Scholarship
A.P. Scholar with Distinction
Steamfitters Local 420 Scholarship

ACTIVITIES

Treasurer of Omega Chi Epsilon (Chemical Engineering Honor Society)
Member of Tau Beta Pi (Engineering Honor Society)
Captain of High School Mathletes and Hi-Q teams

SKILLS

Proficient in C++, Matlab, Mathematica, and Microsoft Office