

PREDICTING ZETA POTENTIAL AND ADSORPTION BEHAVIOR
IN THE $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{TiO}_2 - \text{ZrO}_2$ - SURFACTANT SYSTEM

BY
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Abstract

The adsorption characteristics of four common oxide powders with a proprietary polyacrylate-type surfactant have been determined. Zeta potential measurements were used to characterize the charge on the oxide particles in suspension across a wide processing range. Unadsorbed surfactant levels were detected using potentiometric titrations. It was determined that α -Al₂O₃, TiO₂, and ZrO₂, exhibit strong adsorption of the surfactant. Crystalline SiO₂ displayed a weak interaction with the surfactant.

Individual oxide adsorption data was then compiled and combined in an attempt to predict the adsorption behavior of mixed oxide suspensions. Zeta potential and unadsorbed surfactant predictions provided reasonable estimates for the actual measured values of the mixed oxide suspensions.

1 Introduction

Metal oxide powders are key ingredients in numerous finished ceramic materials. For most industrial applications, these oxide powders are mixed and consolidated in what is known as a slip. A slip is a suspension of ceramic particles in a liquid that is usually water.¹ Additional additives such as deflocculants, binders, and pH modifiers make up the remainder of a ceramic suspension. Additional ingredients in the slip are typically added to aid in suspension stability and/or final processing of consolidated powder.

1.1 Suspension Stability

Suspension stability is one of the most important aspects of processing ceramic slips. The success of operations such as slip or tape casting relies on well-dispersed solid particles to produce high final products. Well-dispersed slips produce finished ceramic bodies with uniform densities and high strength. When referring to the stability of a ceramic suspension, kinetic stability is usually inferred. Kinetic stability is achieved when the particles in suspension resist the desire to coalesce and aggregate with neighboring particles. Coalescence occurs when two or more particles fuse together to form a larger particle. Aggregation is when two or more particles form a cluster of particles that will act like one large particle in suspension.² In order to have particles that resist coalescence and aggregation, the particles in suspension must experience a repulsive force from neighboring particles in suspension. Figure 1 demonstrates the nature of interactions between particles and the possible volume fraction of particles in suspension as a function of the interactive potential between them.

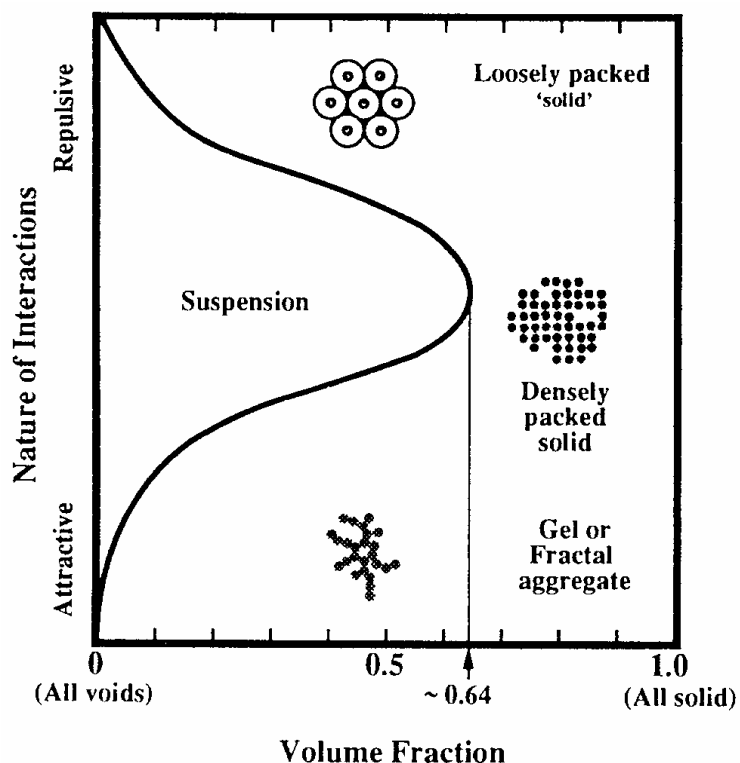
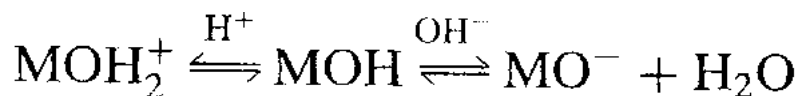


Figure 1. Plot demonstrating the relationship between the particle-particle interactions and the possible solids loading that one can get into a suspension.²

An optimized suspension is shown in Figure one where the black line moves farthest to the right. This condition illustrates the maximum possible solids loading in a suspension with minimum aggregation. A maximum in solids loading occurs when the interparticle forces are slightly repulsive. Overly repulsive interactions reduce the packing efficiency while highly attractive forces lead to aggregate structures and inefficient packing. In order to control particles in suspension and create such forces, an understanding of how and why these interactions come about is required.

1.2 Charged Particle Surfaces

Metal oxides hydrolyze in the presence of water to form hydroxide layers. Hydroxide layers will react with protons (H^+ ions) in the surrounding medium to create a charge on the particle surfaces according to the following reaction:³



At every pH across the range there exists a large number of positive, negative, and neutral surface sites due to these reactions.³ As the pH of the suspension is changed, the number of positive and negative surface sites will change accordingly. If the suspension is made to be very acidic, a higher concentration of positive surface sites will develop. If the pH is made to be basic (> a pH of 7), then negative surface sites will develop. The charges created by this type of reaction determine suspension properties like rheology, aging, and stability.

Charged surfaces will attract ions in suspension of opposite charge. These ions are called *counter-ions*. Conversely, ions of the same charge as the charged surface are called *co-ions*. Counter-ions will preferentially adsorb onto the oppositely charged particle surfaces. The magnitude of counter ion adsorption onto a charged particle surface is a function of the charge on the particle and the valence state of the counter ions. The counter ions in solution will compress the charge surrounding a charged particle and cause these particles to come closer together. A high enough counter-ion concentration will cause particles to coagulate and reduce the quality of the slip. The concentration of counter ions necessary to cause coagulation in the suspensions varies according to the Schulze-Hardy rule:²

$$C \propto Z^6 \quad (1)$$

Where C is the concentration necessary to produce coagulation and Z is the valence state of the counter ions. No additional ions were added to the suspensions in this study because of this effect.

The region associated with a high counter-ion concentration near the surface of the charged particles is known as the *Stern layer*. The charge will decrease as the distance increases away from the charged particle in what is known as the *diffuse double layer*. The thickness of the double layer is typically described by the Debye-Hückel parameter, κ^{-1} , which is a measure of the distance over which the potential decreases by a factor of $1/e$.² The adsorbed ions will move with the particle in suspension, effectively increasing its sphere of influence with neighboring particles. The point at which the adsorbed ions stop moving with the charged particle in suspension is known as the *shear plane*. The electrical potential associated with the shear plane is known as the *zeta potential* and is a common parameter used to define the charge on a particle surface. The

pH at which the zeta potential is neutral, or zero, is called the *iso-electric point* (IEP).

Figure 2 shows a schematic representation of a positively charged particle surface and the arrangement of counter and co-ions as the distance from the particle increases. At a distance of a few tens of nanometers from the particle surface the charge balance is neutral once again.

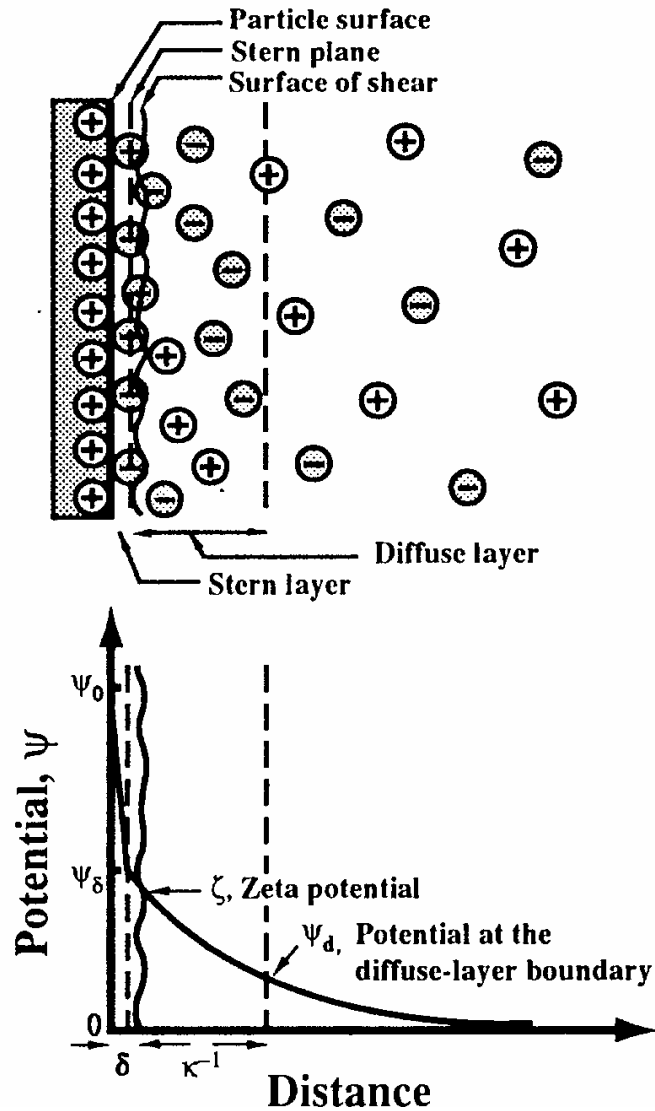


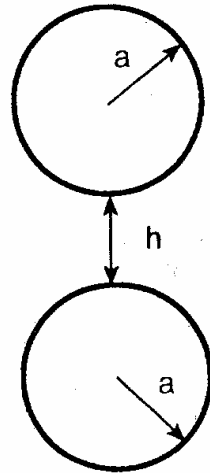
Figure 2. Schematic representation of a positively charged particle surface with counter and co-ions and the potential associated with that particle surface.²

1.3 Van der Waals Forces

In order to control the interactions between the particles in a highly loaded suspension, the forces at work between the particles must be understood. The forces that act between particles ultimately determine the behavior of the suspension.⁴ The van der Waals attractive potential is one force that is always present between two particles in suspension. Van der Waals forces originate from the interactions between electrical dipoles on the surface of the particles in suspension and the medium in which they are dispersed.⁵ The following interactions between charged surfaces sum to produce the van der Waals attractive forces:

- Debye forces (permanent/induced dipole interactions)
- Keesom forces (permanent/permanent dipole interactions)
- London forces (induced/induced dipole interactions)

The van der Waals attractive potential, V_A , between two spheres of radius, a , with separation, h , can be calculated from the following formula:⁶


$$V_A = \frac{Aa}{(12h)} \quad (2)$$

$(h \ll a)$

A represents a term known as the Hamaker constant. The Hamaker constant is a materials constant that corresponds to the nature of the attraction of two particles separated by a medium.⁵ Hamaker constants typically lie on the order of 10^{-19} to 10^{-20} Joule.² The Hamaker constant will be investigated into greater detail later.

As the distance between particles in suspension, h , increases, the attractive potential will decrease. At small distances ($<1 \mu\text{m}$) the attractive potential can however be quite strong. If the van der Waals attractive potential becomes large enough, two

neighboring particles will coalesce or aggregate. Both phenomena can lead to segregation due to size and increases in suspension viscosity. These poor suspension properties will typically lead to undesirable properties in the final product due to microstructural inhomogeneities.⁷ Figure 3 represents the interaction energy between two particles as a function of their separation distance.

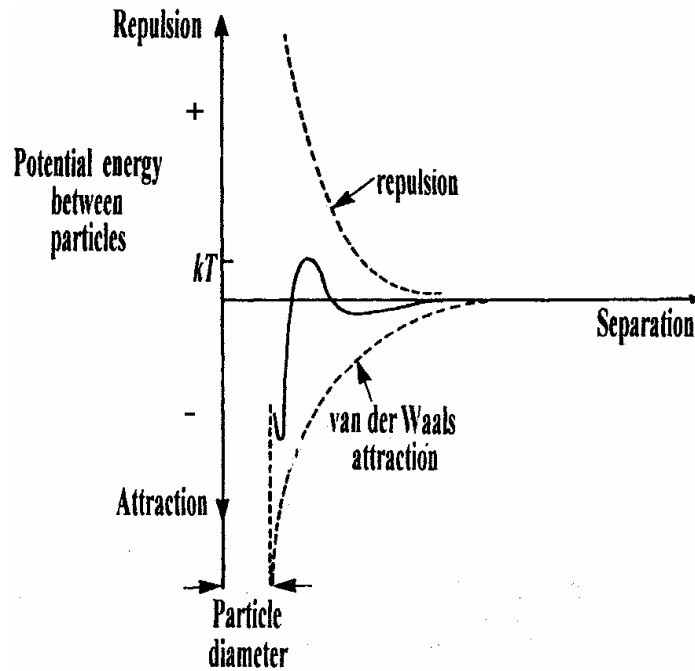


Figure 3. Interaction energy between two spherical particles as a function of separation distance. At a small separation distance the particles experience strong van der Waals attractive forces that lead to agglomeration. Image taken from Rahaman⁷ with permission.

The curve shown in Figure 3 is a representation of the forces acting on two particles in suspension. Once the separation between two particles gets small enough, the van der Waals attractive forces dominate and cause the particles to aggregate. This is shown by the deep attractive well associated with separation distances on the order of the particle diameter. The energy barrier typically associated with the separation of agglomerated particles is shown on the plot as, kT , or thermal energy. If the energy applied to an agglomeration is greater than the energy holding them together (kT), then they will most likely separate.

1.4 Stabilization Methods

It should not be inferred that large separation distances are necessary to produce stable suspensions. In fact, many highly loaded, stable suspensions have small separation distances between particles. The separation distance between the particles is a function of the solids loading in suspension and the repulsive forces between the particles. The magnitude of the repulsion between the particles therefore plays a very big role in inducing stability. Many different methods exist for inducing stability in suspension. These include electrostatic stabilization, steric stabilization, and electrosteric stabilization. Electrostatic stabilization utilizes the adsorption of counter ions and the repulsive interaction between neighboring diffuse layers to stabilize the particles. Steric stabilization involves the adsorption of polymeric molecules to mask the charge of the particles. This method produces more of a physical repulsive barrier between neighboring particles rather than a chemical barrier as seen with electrostatic stabilization methods. The focus of this work will be electrosteric stabilization, which is a combination of the two previously mentioned methods. Electrosteric stabilization involves the adsorption of charged polymers, or polyelectrolytes, onto the particle surfaces. Adsorption of a negatively charged polyelectrolyte onto a positively charged particle surface is demonstrated in Figure 4.

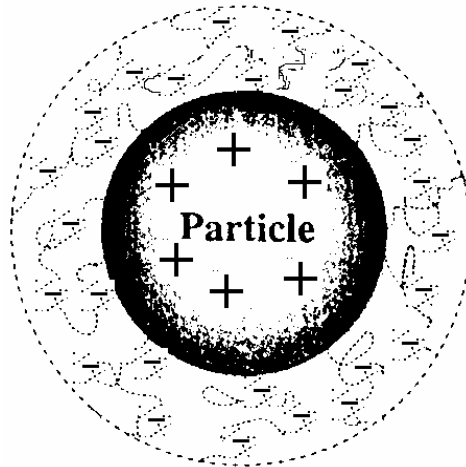


Figure 4. Schematic representation of a negatively charged polyelectrolyte adsorbing on the surface of a positively charged particle.²

1.5 Measurement of Stability

Suspension stability has long been characterized using viscosity measurements.⁸⁻¹² A minimum in viscosity is typically viewed as a maximum in stability. Although this technique virtually guarantees results for single-oxide or even evenly distributed multi-oxide suspensions, it does not guarantee the stability of all phases in a non-evenly mixed suspension. Intuitive thinking suggests that a system with 90% one material and 10% another material will have a viscosity that mimics to the stability of the 90% phase while the stability of the minor phase might be overshadowed.

In order to take into account the stability of each phase of a multi-component suspension, a measurement technique that represents the properties of each particle in suspension rather than the suspension as a whole should be employed. The zeta potential was chosen for this work as the determining factor for suspension stability in a mixed oxide suspension. Repulsion between neighboring particles should be quite easy to achieve if the zeta potential can be made to be the same sign for all particles in suspension with sufficient magnitude to overcome the van der Waals attraction.

The objective of this work was to characterize the adsorption behavior of four commonly used commercial ceramic oxide powders using a proprietary ammonium polyacrylate type surfactant. The zeta potential of the particles in suspension was also monitored for each adsorption condition for each powder. Single-oxide suspension data was then combined in an attempt to predict the zeta potential and adsorption behavior of mixed oxide suspensions.

2 Literature Survey

With the evolution of high tech ceramic materials comes the need for a better understanding of the phenomena that occur in ceramic oxide suspension. The colloidal domain, which describes particles with some linear dimension between 1 nanometer (10^{-9} m) and 1 micrometer (10^{-6} m), encompasses nearly all powders used in the production of modern ceramic products.² Colloidal particles have such small dimensions that the thermal motion in suspension, known as Brownian motion, will be enough to dissuade the forces of gravity so that the particles resist settling. A complete investigation and explanation of the forces experienced by colloidal particles and the methods by which they are processed is provided by Lewis.⁴

The studies cited in this work focus on electrosterically stabilized ceramic processes. One theme common between many studies is that the amount of surfactant adsorbed onto the powder surface in the suspension must be quantified in order to characterize the nature of any adsorption. The most common method of determining this amount is to measure the amount of surfactant that has *not* adsorbed. This can be a difficult task at times, but many novel methods have been discovered for measuring dilute concentrations of polymer in solution. For all studies, a supernatant solution was created via centrifugation of the initial suspension. The supernatant is then analyzed using different chemical or spectroscopic methods for the amount of surfactant remaining in solution.

One popular method by which the supernatant solutions were analyzed was by potentiometric titration. This method was first outlined by Arnold and Overbeek¹³ in 1950 by titrating dilute solutions of poly(methacrylic acid) in water and has been used extensively since then. The titration method was used successfully by Gebhardt and Fuerstenau¹⁴ in 1983 to quantify the amount of unadsorbed poly(acrylic acid) in TiO_2 and Fe_2O_3 suspensions. Cesarano et al.⁹ studied the adsorption of sodium poly(methacrylic acid) onto $\alpha\text{-Al}_2\text{O}_3$ and its effect on suspension stability using titrations and viscosity measurements. Several other research groups have since employed the titration method in order to quantify residual surfactant.^{3,10,11,15-19}

Many other novel methods have been used to quantify the amount of unadsorbed surfactant in solution. These include ultraviolet-visible spectroscopy (UV-Vis),^{10,20-22}

thermo-gravimetric analysis (TGA),^{23,24} ellipsometry,²⁵ carbon analysis,²⁶ Auger electron spectroscopy (AES),¹¹ and the decolorization method of specific salts.²⁷

Still other studies concerned their efforts to investigate the method by which certain surfactants adsorb onto powder surfaces. Various types of infrared spectroscopy were typically used to look at the types of adsorption witnessed at a polymer/particle interface. Surfactants adsorb in a number of different conformations depending on the structure and molecular weight of the polymer. A study performed by McCluskey et al.²⁸ gives a nice overview of the various functional groups and their infrared absorption behavior at various processing conditions. Tang²⁹ and Wang³⁰ each show how the properties of nanometer-sized ZrO₂ powder changes as a function of adsorbed surfactant levels using Fourier transform infrared spectroscopy (FTIR). Attenuated total reflectance (ATR)-FTIR was employed as a method of monitoring the changing properties of adsorbing surfactants and the powder surfaces during the adsorption.^{31,32} Conformation of adsorbed surfactants onto Al₂O₃ surfaces was studied by Vermöhlen³³ using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Pan et al.³⁴ used fluorescence and electron spin resonance (ESR) to determine the structure of poly(acrylic acid) adsorbed on Al₂O₃ particles.

Few adsorption studies were found that involved multiple oxides in the same study. Of the research investigated on multiple oxide systems, very experimental work has been performed using the properties of single oxide systems to predict the behavior of mixed oxide systems. Pettersson et al.³ studied the adsorption behavior of a variety of surfactants onto α -Al₂O₃, ZrO₂, and 3Y-ZrO₂ powders. Zaman et al.²⁶ explored the adsorption of low molecular weight poly(acrylic acid) onto α -Al₂O₃, SiO₂, and kaolin particles. Numerous studies have been conducted on α -Al₂O₃ simply because it is one of the most widely used ingredient in commercial ceramics. Individual oxide powder studies were readily available for the oxides of Al₂O₃,^{8-10,16,34,35} SiO₂,³⁶ TiO₂,¹⁹ and ZrO₂.^{12,21,22,29,30}

The data from the studies cited above was used extensively for experimental procedure development and data comparison.

3 Raw Materials

The powders under investigation in this work are common metal oxide powders used in traditional and high tech ceramic processes and were chosen for this study based on the broad range of iso-electric points that could be expected from them.

The four oxides chosen were Baikowski CR6 α -Al₂O₃, US Silica Min-U-Sil 5 crystalline SiO₂, Ishihara Sangyo Kaisha CR-EL TiO₂, and Tosoh TZ-0 ZrO₂. The broad pH range of the iso-electric points makes this study a nice model for nearly all ceramic processes. Table I shows the expected iso-electric points for the oxides chosen based on reported values.³⁷

Table I. Expected Iso-electric Points for Oxide Powders Used.³⁷

Powder	Expected iso-electric point (pH)
α -Al ₂ O ₃	7-9.5
SiO ₂	3-4
TiO ₂	4-6
ZrO ₂	4-5

α -Al₂O₃ is one of the most widely used inorganic material for ceramics.³⁷ It is primarily used when applications require thermal and electrical insulation, structural integrity, high temperature refractoriness, and mechanical abrasion or wear resistance.³⁸ Crystalline SiO₂ is used extensively in the paint and sealant industry as a filler and extender.³⁹ TiO₂ is a common grain boundary dopant material for many electronic ceramics like lead zirconate titanate (PZT) and as a pigment for paint and paper products.⁴⁰ Finally, ZrO₂ is used as a thermal barrier in heating applications and as a coating for many cutting tools due to its high strength and toughness.³⁸

The powders were chosen on the basis of the particle size, particle size distribution, and specific surface areas reported by their suppliers. These properties were reported as being similar for each oxide, making it a relatively true comparative study.

The particle size distributions and specific surface area of the oxides had to be known in order to properly characterize any adsorption onto the particle surfaces.

Density of the powders was obtained from supplier. Dielectric constants were known values from previously reported work.⁴¹ These values are listed in table II and are essential for effective measurements of zeta potential using the methods employed in this work.

Table II. Density and Dielectric Constants for the Oxides Used.

Powder	Density (g/cm³)*	Dielectric Constant**
Baikowski CR6 Al ₂ O ₃	3.96	10
Min-U-Sil 5 SiO ₂	2.65	4.45
Ishihara Sangyo Kaisha CR-EL TiO ₂	4.10	127
Toso TZ-0 ZrO ₂	6.05	12.5

* Density as reported by suppliers

**⁴¹

The surfactant chosen for this study has an NH₄-polyacrylate type structure similar to that shown in Figure 5. Polyacrylate surfactants are generally negatively charged. As the pH of its solution is made to be more acidic, the polymer will appear more neutrally charged, higher pH values will increase its negativity. The surfactant was received as a yellowish liquid with a density of 1.17 g/cm³ as reported by the supplier. It had 45% solids content and a pH of approximately 2.5. Its solubility is reported as being infinite in water. The surfactant was originally thought to be quite similar to the commercially popular Darvan 821A, the ammonium salt of poly(acrylic acid) due to supplier suggestions. Since the surfactant was proprietary, further investigation was necessary to determine the validity of comparing its adsorption behavior to previously reported adsorption behavior of other surfactants. After further examination, some differences were shown to exist. Amine groups were found to be present in the structure, something that Darvan 821A does not have. Infrared spectroscopy was employed to investigate the surfactant and will be discussed later.

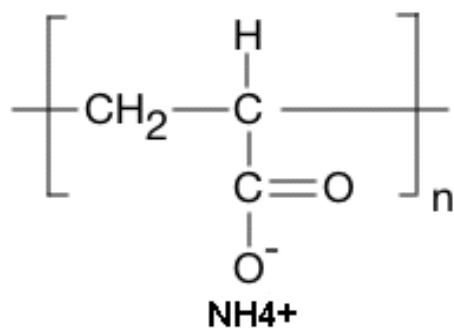


Figure 5. Structure of NH_4 -PAA with n repeating groups depending on the molecular weight of the polymer in question. The molecular weight of the surfactant used in this study is 4500 g/mole.

4 Experimental Procedure(s)

4.1 Particle Size Analysis

All powders used in the study were analyzed using scanning electron microscopy (SEM) and light scattering in order to determine average particle sizes and particle size distributions. SEM samples were prepared by placing a small amount of powder on a 1/2-inch conductive aluminum SEM stub. One drop of ethanol was then dropped onto the powder using a pipette. The ethanol rapidly dispersed the powder across the stub and then evaporated leaving nicely distributed agglomerates of the powder on the stub. Samples were then analyzed with a Philips 515 SEM in secondary electron mode with an accelerating voltage of 25 keV. SEM micrographs of the four powders can be seen in Figure 8.

The powders were also analyzed for particle size and distribution using a Microtrac FRA (Leeds & Northrup, Largo, Florida). The Microtrac FRA measures the intensity and angle of scattered light from particles that are well dispersed in a medium, which is usually water. Approximately two grams of powder was added to 50 mL of deionized water with a resistivity $>17 \text{ M}\Omega\text{-cm}$. The sample was then dispersed using an ultrasonication probe (Vibra-Cell, Sonics & Materials, Newtown, Connecticut) at 500 watts for eight minutes, and employing a duty cycle at 50%. The dispersion was then loaded into a reservoir and pumped into the sample cell for analysis. The difference in refractive index between the particles and dispersing medium (water) was considered to be large enough for each powder, such that the particles would be non-transparent to incident light. A more in depth description of the theory behind light scattering particle size measurements can be found in Seitz (1999).⁴² Studies done by Malghan et al.⁴³ show that light scattering particle size measurements become more repeatable as the particle sizes measured decreases. Table IV shows the measured particle sizes via SEM and light scattering techniques along with the repeatability of the techniques as reported by Malghan et al.⁴³

4.2 Surface Area Measurements

Surface area measurements were performed using BET multi-point nitrogen adsorption with an ASAP 2010 C sorptometer (Micromeritics, Norcross, Georgia). Glass sample tubes were first weighed followed by the addition of approximately four grams of powder was added to the sample tube. The sample was then outgassed at 150°C under vacuum. After outgassing, the sample was re-weighed to determine the exact mass of the powder being measured. The instrument then applies equations from the BET (Brunauer, Emmett, and Teller) Theory, which is based on multi-layer adsorption, to calculate the specific surface area of the powder. Physical adsorption of nitrogen molecules onto the powder surfaces at relative pressures from 0.05 to 0.3 was measured. High-purity nitrogen gas (99.999%) was used to introduce nitrogen molecules as the adsorbing species. Further explanation of the theory can be found in Seitz (1999).⁴² Studies done by Malghan et al.⁴³ show that BET multipoint surface area measurements are repeatable to $\pm 0.1 \text{ m}^2/\text{g}$. The surface area values determined from the BET measurements can be found in table V.

4.3 Infrared Spectroscopy of Surfactant

Infrared spectroscopy was performed on the surfactant to determine what types of functional groups may be present on the polymer. ATR-FTIR, attenuated total reflectance – Fourier transform infrared spectroscopy, was chosen as the tool for the analysis of absorption bands. A Nicolet Nexus 670 FTIR spectrophotometer (Thermo Electron Corporation, Waltham, Massachusetts) equipped with a zinc selenide ATR crystal was used. An MCT/A detector cooled with liquid nitrogen with a resolution of 4 cm^{-1} was used with a potassium bromide beamsplitter. The chamber was purged for 30 minutes prior to any analysis using a zero-air generator. The zero-air generator effectively removes water and carbon dioxide, both major absorbers of infrared light. This creates a nitrogen-rich atmosphere in the chamber. A background spectrum was collected using the ATR crystal/purged atmosphere interface and subtracted from subsequent sample runs. Samples were acquired using 100 scans over a range of 4000 to 800 cm^{-1} . No dilution of the surfactant was required for testing. The spectra of the surfactant in question compared to that of Darvan 821A is shown in Figure 9.

4.4 Suspension Preparation

All suspensions were prepared on a twenty weight-percent powder and eighty weight-percent water/surfactant basis. Deionized water with a resistivity $>17 \text{ M}\Omega\text{-cm}$ from a NanoPure D4741 still (Barnstead, Dubuque, Iowa) was used as the dispersion medium for all suspensions. All surfactant additions were made on a dry weight basis of the powder added. The samples were prepared and processed on a random basis. Each powder was investigated at six surfactant levels, 0, 0.1, 0.3, 0.5, 1.0, and 1.5 weight percent. Surfactant additions were made on a dry weight percentage basis of the powder in the suspension. The 45-wt% surfactant solution was considered to be 100% surfactant for all additions in this study as to avoid confusion during processing. This range was chosen because historical data showed that the surface saturation of similar powders fell well within this range for similar surfactants.

Samples were prepared and processed in one-liter polypropylene bottles. 530 g of 5-millimeter diameter yttria-stabilized ZrO_2 media (YTZ grinding media, Tosoh Corporation, Tokyo, Japan) was added to achieve gentle mixing; no particle size reduction was intended. Any pH changes made to the suspensions were made using grade 0.5M HCl and 0.5M KOH solutions (Sigma-Aldrich, St. Louis, Missouri). Measurements of pH were made using a Metrohm 691 pH meter (Metrohm, Switzerland). Figure 6 represents the flow chart followed for all sample preparations and measurements.

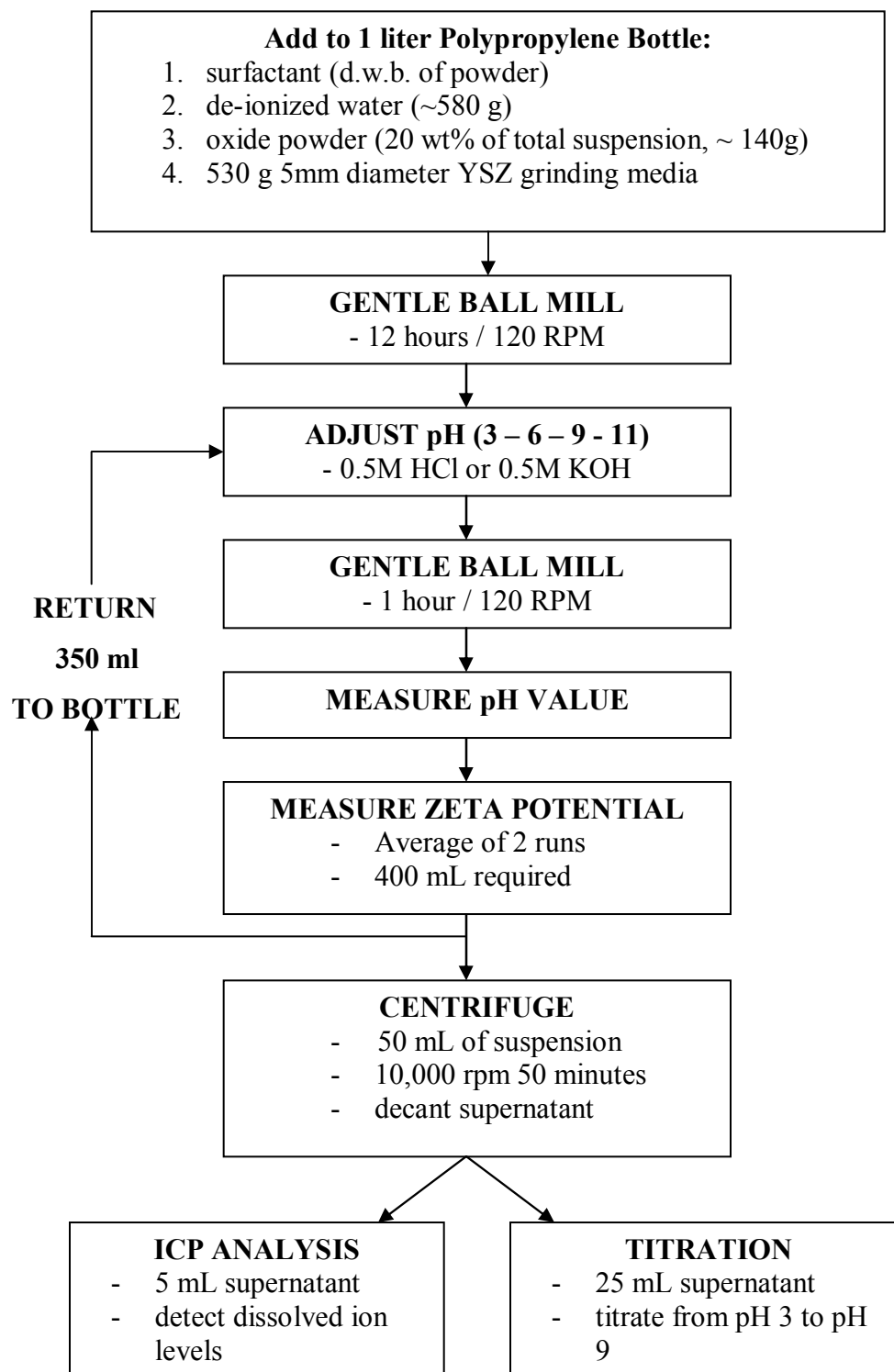


Figure 6. Flowchart of the suspension preparation procedure used for all suspensions in this work. Explanation about each action item in the flow chart is described in the following text.

Step 1 – mixing of the suspension in 1 liter polypropylene bottle

- Add calculated amount of surfactant
- Add calculated amount of deionized water
- Add calculated amount of dry oxide powder
- Add 530g of 5 mm diameter milling media

Step 2 – gentle ball milling

- The bottle was placed on a ball mill at 120 RPM for 12 hours.
- 120 RPM was not fast enough to produce cascading of grinding media

Step 3 – adjust pH of the suspension

- Add 0.5 M HCl in order to reduce pH to a low value (target pH 3)

Step 4 – gentle ball milling

- The bottle was placed on the ball mill for 1 hour at 120 RPM for further equilibration at the new pH value
- After 1 hour of milling the suspension was removed from the mill and the pH was measured.

Step 5 – Measure zeta potential

- 400 mL of suspension was removed from the bottle and placed in the AcoustoSizer for zeta potential analysis
- Sample allowed to equilibration to room temperature (25°C) prior to measurement.

Step 6 – Centrifugation

- Approximately 50 mL was extracted from the AcoustoSizer sample for centrifugation
- Samples were centrifuged at 10,000 RPM for 50 minutes in polypropylene copolymer vials

Step 7 – Repeat the process

- The remainder of the sample (~350mL) was returned to the 1 liter bottle
- The pH was adjusted to approximately 6 using 0.5 molar KOH
- The process returns to step 4 and repeats to step 7 for pH values of 6, 9, and 11

Step 8 – ICP analysis

- Approximately 5 mL was saved for ICP analysis in order to determine dissolved ion level in solution

Step 9 – Titration

- Supernatant from centrifuge was carefully decanted
- Supernatant titrated using Titrando 808 with KOH as titrant

Upon completion of a twelve-hour gentle ball milling cycle the pH of the suspension was adjusted using 0.5 M HCl. A pH of three was the target, but due to the solubility of some oxides, particularly Al_2O_3 , a value of pH 4.0 was typically accepted. After the pH adjustment, the sample was milled for an additional hour to allow the sample equilibrate at its new pH value. It was found that an additional hour was sufficient to achieve equilibration at the new, lower pH value. The pH was measured after mixing and considered to be the pH for any analysis at that point. Figure 7 shows the relationship of the pH of an Al_2O_3 suspension as a function of milling time.

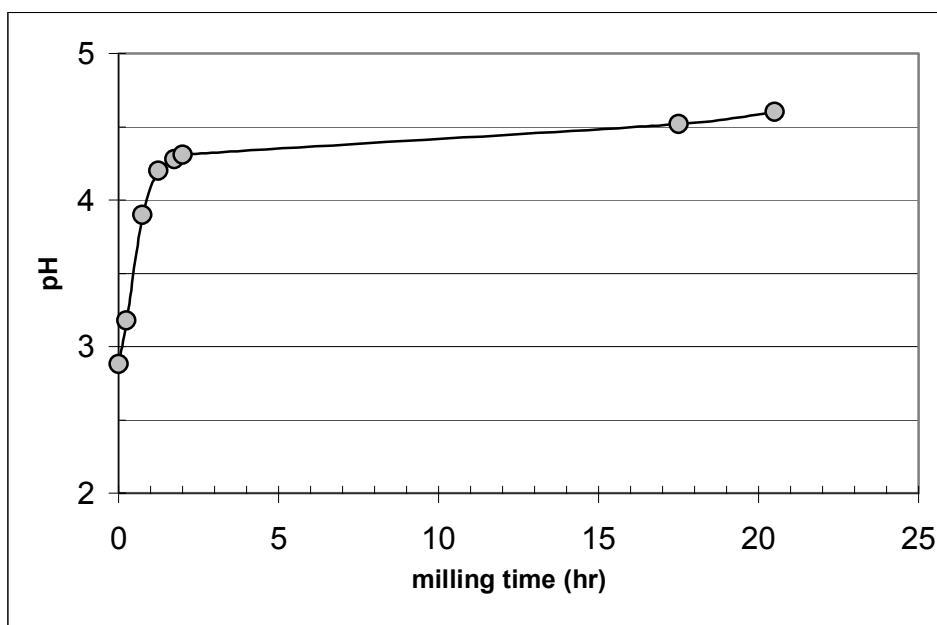


Figure 7. pH of a 20 wt% Al_2O_3 suspension with no surfactant as a function of milling time. The suspension was prepared and allowed to equilibrate for 12 hours to its natural pH, then reduced to approximately 3 with the addition of 0.5 M HCl.

Although Figure 7 seems to show that the pH of the Al_2O_3 suspension begins to level off after approximately 12 hours, this was just not a reasonable amount of time for additional milling of the sample. Since no particle size reduction was intended, additional milling was kept to a minimum. One additional hour was chosen decided to be adequate time for pH equilibration based upon the approximate results shown in Figure 7.

4.5 Zeta Potential Measurements

Traditionally, zeta potential is measured on dilute suspensions using electrophoretic mobility.^{3,9,19} Electrophoretic mobility, μ , is the measure of how fast a charged particle moves through a dispersing medium under the application of an electric field. The larger the charge is on the particle or the greater the applied field, the faster the particle will move.

Traditional methods require that very dilute samples be prepared to ensure that individual particles are being observed instead of agglomerates. These methods typically utilize light scattering or microscopic analysis techniques. The method employed in this work relies on a completely different principle.

Zeta potential measurements in this work were performed using an AcoustoSizer Plus (Matec Applied Sciences, Hopkington, Massachusetts). The AcoustoSizer measures the zeta potential of the particles in suspension by measuring an ESA (Electrokinetic Sonic Amplitude) signal. The ESA signal arises from the emanation of acoustic waves from moving particles in suspension. The particles are driven toward the oppositely charged electrodes causing a local compression of the material in that region.⁴⁴ The compression of the material will lead to movement and momentum of that material. The AcoustoSizer measures the ESA signal across a wide frequency range from 300 kHz to 11 MHz. The ESA signal is automatically converted into a frequency dependant electrophoretic mobility known as the *dynamic mobility*.

The ESA signal will be a function of the device geometry and the dynamic mobility. The dynamic mobility, μ_D , can be determined from the following equation:⁴⁵

$$\frac{ESA}{S_A - S_S} = B\phi \frac{\Delta\rho}{\rho} \langle \mu_D \rangle \quad (3)$$

Where S_A and S_S are the Fourier transform of the reflected signals on the transducer of air and the suspension respectively. B is an instrument factor based on the geometry of the cell, ϕ is the volume fraction of particles in suspension, $\Delta\rho$ is the density difference between the particles in suspension, ρ_p , and the dispersing medium, ρ .

As a charged particle moves through the suspension it creates a sound wave, a transducer records the magnitude of this wave. As the frequency of the applied electric

field is altered the AcoustoSizer can relate the magnitude of this “sound wave” to the charge on the particles and the particle size distribution in the suspension. Further explanation of the origin and analysis of the ESA and dynamic mobility can be found in a paper by O’Brien (1995).⁴⁵

No dilution is required for the zeta potential measurements because of the ability of the AcoustoSizer to measure highly concentrated suspensions (up to 50 volume %). This is extremely advantageous over those methods used in previous work where care had to be taken in order to ensure that consecutive zeta potential measurements were indeed measurements of the same suspensions.^{3,9,10,14,16,19}

The dynamic mobility was measured on suspensions at a constant temperature, 25°C. 400 mL of suspension was added to the AcoustoSizer cell and allowed to equilibrate to room temperature (25°C) with a Pelletier effect type heating/cooling element. The sample was stirred at a speed of 300 rpm during the course of measurement to maintain a homogeneous blend of particles in suspension. Once the temperature had equilibrated, two measurements of the zeta potential were made. The average of the two readings was reported as the zeta potential for the particles in suspension. The Smoluchowski zeta potential was reported for all suspensions because of the fact that a particle size distribution was not always possible to fit from the suspensions. The AcoustoSizer reports the Smoluchowski zeta potential by converting the dynamic mobility into a d.c. mobility. It does so by correcting for the inertia effect of the particles at the lowest measured frequency value (300 kHz). The inertia effect is quite pronounced in many systems and will affect the measurement considerably at high frequency where dense particles will lag behind the applied frequency considerably. Gibb and Hunter⁴⁶ give a wonderful explanation into the causes of this occurrence. The d.c mobility is then used in the Smoluchowski equation [3] to determine zeta potential.⁴⁵

$$\mu_E = \frac{\varepsilon \zeta}{\eta} \quad (4)$$

Where μ_E is the mobility of the particles in suspension, ε is the dielectric constant (permittivity) of the dispersing medium, ζ is the zeta potential of the particles, and η is the viscosity of the dispersing medium.

4.6 Centrifugation

After measuring the zeta potential of the particles in suspension, 50 mL was taken for centrifugation. The samples were centrifuged using a 2001-E rotor-type centrifuge system (Intertest Corporation, Fremont, California). Samples were centrifuged in 50 mL round Nalgene polypropylene copolymer centrifuge tubes for 50 minutes at 10,000 rpm, this is approximately equivalent to a g-force of 16000. The supernatant was carefully decanted using a pipette. Extra care was taken to ensure that no visible particles were included in the supernatant. Approximately 30 mL of supernatant was generated from each centrifugation. Five mL were saved for ICP analysis while 25 mL was used for titration.

4.7 Inductively Coupled Plasma

An Optima 3000 DV (Perkin-Elmer, Wellesley, Maryland) ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometer) equipped with ICP Winlab software was used to measure dissolved ion concentrations in supernatant solutions. Inductively coupled plasma works by injecting an atomized stream of solution into a plasma that can reach temperatures of 10,000K. The plasma will provide enough energy to excite any dissolved ions in the atomized solution to higher energy levels. The natural desire to decrease free energy forces the excited ions to return to ground state. When the ions fall back to their ground state they will radiate the energy corresponding to the energy difference between the excited and ground states. Each ion will give off specific radiation according to the energy states that it was excited to.

A higher concentration of dissolved ions will correlate to a higher intensity at a given wavelength. The instrument is calibrated against a set of known standards (Sigma-Aldrich, St. Louis, Missouri) for the suspected elements in the solution at known radiation wavelengths for each element. Calibration standards were prepared in 2 wt% HNO₃ at levels of 1, 10, and 50 ppm ($\mu\text{g metal/g solution}$). The wavelengths used for aluminum, silicon, titanium, and zirconium are shown in table III.

Table III. ICP Emission Wavenumbers Used for Al, Si, Ti, and Zr ions

Element	Wavelength (nm)
Al	396.15
Si	251.61
Ti	334.94
Zr	343.82

Samples were pumped into the plasma using a peristaltic pump at a rate of 1 mL per minute. A delay time of one minute was used between the commencement of pumping and the actual sample measurement to allow the sample to reach the plasma. Three repeat runs were done by the spectrometer and the average of the three readings was reported for the sample. The tubing and spectrometer were rinsed for 30 seconds between samples with de-ionized water to ensure that no contamination was experienced.

4.8 UV-Vis Spectroscopy

The first attempt to detect and quantify the amount of residual surfactant in solution was made using UV-Vis spectroscopy. A Cary UV-Vis spectrometer in dual beam mode was used for analysis. UV-Vis works very similar to infrared spectroscopy. The difference is the range of the electromagnetic spectrum that the instrument applies to the sample being analyzed. Incident light is applied to the sample in the low end of the ultraviolet (190 nm) and the visible region (400-700 nm) of the electromagnetic spectrum. Molecules and functional groups will bend, stretch, vibrate, or rotate when the incident light hits them. These reactions cause the material to absorb the incident light. Since light is absorbed, it will reduce the intensity of the light transmitted through the sample. Each molecule or functional group will absorb the incident light of a different wavelength based on the energy required for that absorption to take place. The intensity of the absorption can be related to the concentration of that certain molecule or functional group in solution. Standard solutions were prepared using de-ionized water and the surfactant in question from 0.00055 wt% to 22.5 wt%. Samples were placed in plastic

cuvettes and scanned from 190 nm to 900 nm in the ultraviolet and visible ranges. De-ionized water and air were subtracted as background solutions.

Experiments proved that UV-Vis spectroscopy would not be sensitive enough to detect very dilute surfactant levels in solution. Further explanation and rationalization is provided in section 5.4.

4.9 Potentiometric Titrations

Once the supernatant was collected from the centrifugation the amount of residual surfactant in solution had to be quantified. Potentiometric titrations were very common in the literature and were used in this work. A Titrand 808 with PC control software (Metrohm Instruments, Switzerland) was used to automatically titrate the supernatants generated. The supernatant mass was recorded and entered into the computer as the sample size. The pH was then measured and reduced to approximately 2.8 with the addition of 0.5 M HCl in order to ensure that the pH range 3 to 9 would be witnessed.

The titration was carried out with controlled additions of KOH at a dosing rate of 0.1 mL/minute from an initial pH of 2.8 up to a final pH of 10.5. A series of titrant solutions of KOH were prepared at 0.05M, 0.1M and 0.2M and used according to the suspected amount of residual surfactant in the solution. Stronger titrant solutions were used for supernatant solutions with larger amounts of residual surfactant so that no more than 5 mL of titrant was used for any one titration. Figure 10 shows typical titration data for three levels of surfactant in solution.

4.9.1 Water Correction

To create a calibration for the amount of surfactant in solution, the titration data must be corrected for the amount of KOH required to titrate anything other than residual surfactant. For the oxide suspensions, it was assumed that the only possible species other than surfactant that could be in solution were water and any dissolved ions from the oxide powder.

The correction for water was developed as a function of the mass of water in the solution. Samples of de-ionized water were weighed and recorded. The amount of 0.5M HCl to reduce the pH of the water to approximately 2.8 was also considered to be water

in the sample. The amount of KOH required to titrate the water from a pH of 2.8 to a pH of 9 was also considered. Figure 11 shows the relationship between the amounts of KOH (mmol) required to titrate a sample of de-ionized water from pH 3 to pH 9 as a function of the sample size.

After the water correction was developed, a series of standards containing known amounts of surfactant were titrated across the pH range 3 to 9. Standard solutions were prepared by adding a known amount of surfactant to an empty polypropylene container. De-ionized water was added to create solutions of known concentration of the surfactant. Standard solutions were allowed to equilibrate by shaking for approximately five minutes. The samples were allowed to remain stationary for 2 weeks for further equilibration before being titrated. After the water correction was made to the data, a calibration curve was plotted showing the amount of KOH necessary to titrate a given amount of surfactant from a pH of 3 to a pH of 9. This relationship is shown in Figure 12.

4.9.2 Dissolved Ion Correction

Upon commencement of suspension processing, titration data was leading to final unadsorbed surfactant levels that were higher than the initial concentration of surfactant added to the suspension. This is of course impossible. Since no visible particles were present in the supernatant solutions, the error in the titration results was attributed to dissolved ions from the oxide powders in the supernatant. The changing pH conditions created for each suspension could very easily dissolve the oxide powder and create a background electrolyte solution in suspension. This background electrolyte will affect the adsorption behavior of the surfactant and the zeta potential of the particles, it will also affect the titration of the supernatant solution, ultimately requiring more KOH for the same pH change.

To correct for the dissolved ions in solution, twenty weight-percent suspensions were prepared for each oxide in the absence of surfactant. The suspensions were prepared and equilibrated with gentle ball milling for 12 hours. The pH of the suspension was then reduced to approximately 3 with the addition of 0.5 M HCl and milled for an additional hour. A sample was then taken from the suspension for centrifugation. 50 mL

samples were centrifuged for 50 minutes at 10,000 rpm. The supernatant was carefully removed with a pipette and saved for a titration. The remainder of the suspension was changed to a higher pH value and milled for one hour. The process was repeated to obtain numerous pH values across the range until a suitable curve was developed that would correlate the amount of titrant required to titrate a solution from pH 3 to pH 9 for a given pH.

The amount of KOH required for the titration after the water correction had been made to the data was the amount of KOH attributed to the dissolved ions in solution at that particular pH value. Figures 13-19 represent the corrections used for the dissolved ions for each oxide at different pH values. This method does not however provide quantitative results for the actual dissolved ion levels in solution.

An alternative method to the one described for the dissolved ion correction was developed later in the study. ICP-OES (methods described in section 4.7) was used to detect the actual concentration of dissolved ions in the supernatant solutions. In order to calibrate the method, a series of standards were created at 0, 5, 10, and 25 ppm for aluminum, silicon, titanium, and zirconium ions. Surfactant was also added systematically to the samples at 0, 0.1, 0.3, and 0.5 wt% of the solution. The samples were analyzed using ICP for dissolved ion levels and then titrated. The amount of KOH required to complete the titration could then be correlated to the dissolved ion level in solution. Results are shown in section 5.6.

5 Results and Discussion

5.1 Particle Size Results

Figure 8 shows SEM images obtained for the four oxides studied. Particle sizes were determined from the images for the Al_2O_3 , SiO_2 , and TiO_2 using the intercept method as described by King.¹ The particle size seen in the micrograph of the ZrO_2 powder was simply too small for this method to work since the individual particles cannot be seen clearly. A simple estimate based on the 1-micrometer bar shown in the graph was used for the particle size of the ZrO_2 powder.

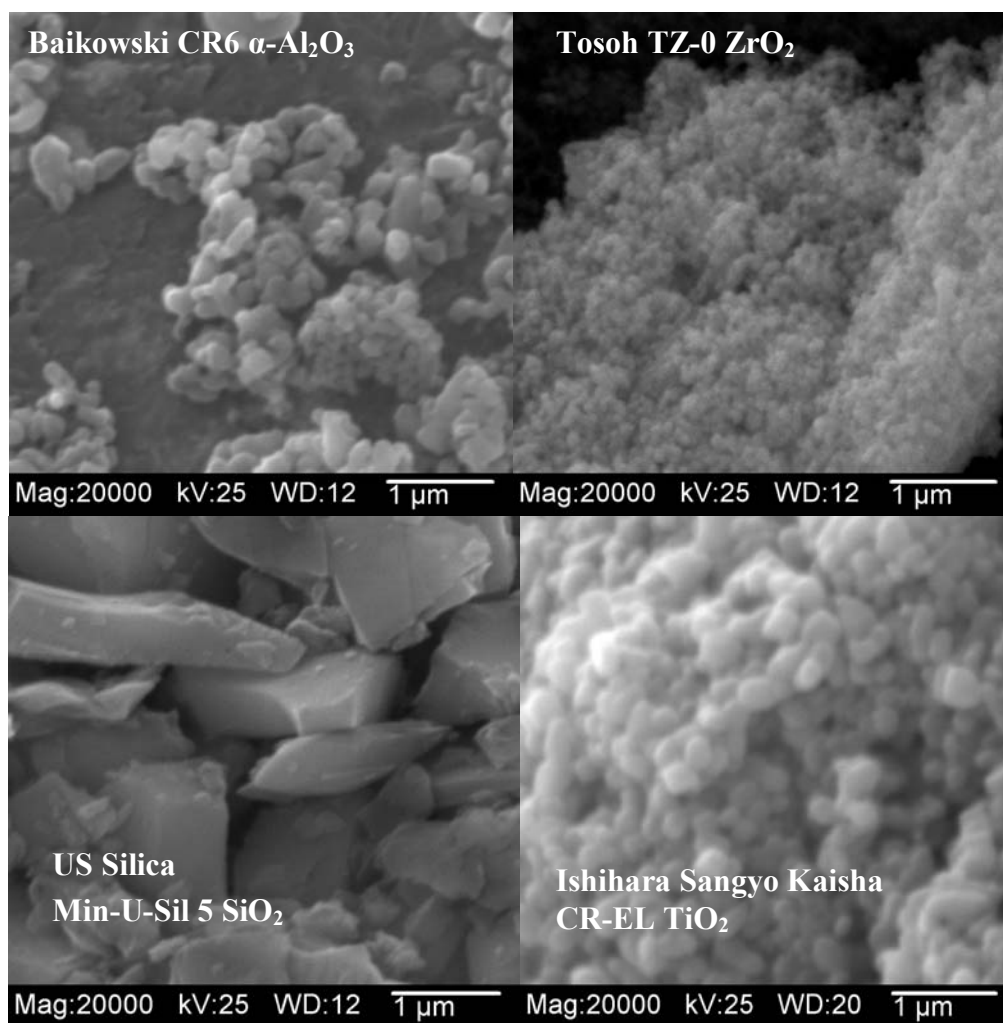


Figure 8. SEM images taken of the four oxide powders used in this study. Images were taken using a Philips 515 SEM in secondary electron mode with an accelerating voltage of 25 keV.

Particle size measurements performed using the Microtrac FRA light scattering device produced values similar to those obtained using SEM techniques. The values for both techniques are reported in Table IV.

Table IV. Particle Sizes and Distributions for Oxides Used

Powder	Particle Size (μm) SEM	Particle Size (μm) light scattering ($\pm \mu\text{m}$)		
		D10 ± 0.1	D50 ± 0.25	D90 ± 0.5
Baikowski CR6 $\alpha\text{-Al}_2\text{O}_3$	0.1	0.36	0.66	2.14
Min-U-Sil 5 SiO_2	5.0	0.50	1.85	4.60
Ishihara Sangyo Kaisha CR-EL TiO_2	0.1	0.29	0.41	0.69
Tosoh TZ-0 ZrO_2	0.05	0.28	0.49	1.48

The repeatability of the light scattering technique was determined by Malghan et al.⁴³ and is shown in Table IV on the right hand side for each particle size distribution.

5.2 Surface Area Results

Surface area measurements were performed using BET multi-point nitrogen adsorption methods on a Micromeritics ASAP 2010 C sorptometer. Measured values are reported in Table V along with the repeatability of the surface area measurement technique as reported by Malghan et al.⁴³ The values obtained were important in determining the adsorption characteristics of each individual powder.

Table V. Surface Area Values Determined for Oxides Used

Powder	BET surface area (m^2/g) ($\pm 0.1 \text{ m}^2/\text{g}$)
Baikowski CR6 Al_2O_3	6.5
Min-U-Sil 5 SiO_2	4.5
Ishihara Sangyo Kaisha CR-EL TiO_2	7.0
Tosoh TZ-0 ZrO_2	15.1

5.3 Infrared Spectroscopy of Surfactant

The ATR-FTIR analysis of the surfactant proved to be quite telling of the structure. When compared to that of Darvan 821A ($\text{NH}_4 - \text{PAA}$), several additional absorption bands are witnessed. As shown in Figure 9 the absorption spectra of the two surfactants are compared and seem quite similar at first glance. Further investigation shows additional bands near 1660 , 1200 , and 1050 cm^{-1} .

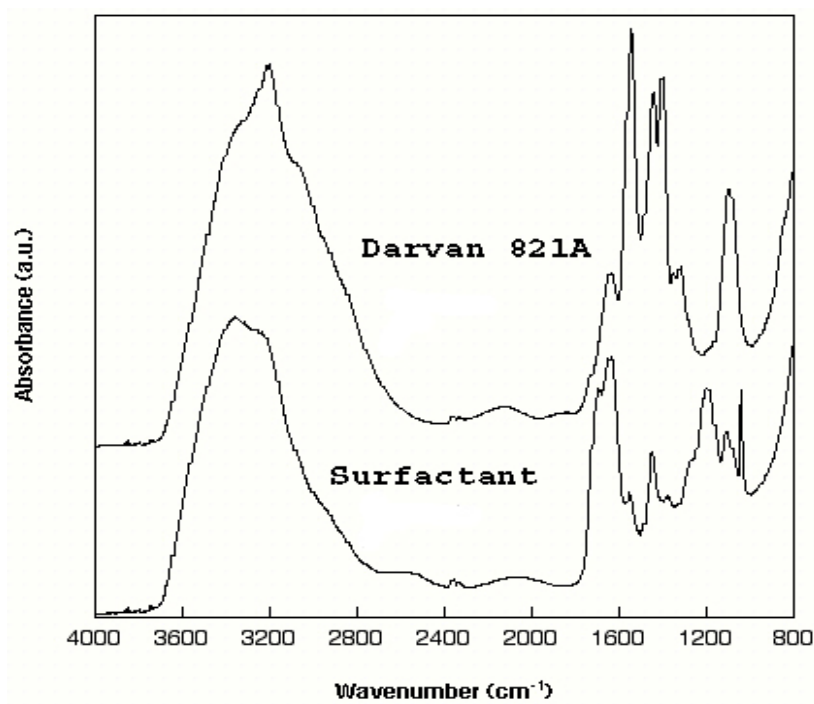


Figure 9. ATR-FTIR spectra comparing the proprietary surfactant with Darvan 821A. Analysis courtesy of Dr. Matthew Hall, Alfred University.

The absorption bands witnessed with the two surfactants are listed in Table VI along with a probable functional group and vibration modes associated with that specific wavenumber.

Table VI. FTIR Absorption Bands and Possible Vibration Modes.

Wavenumber range (cm ⁻¹)	Functional Groups	Vibration Mode
3600-2800	H ₂ O	All modes
2350	CO ₂	Stretching
1680-1620	Alkenes	Multiple bond stretching
1610-1550	Carboxylate anion	Stretching
1470-1430	Alkane -CH ₃	Bending
1220-1020	Aliphatic C - N	Vibrations

* Absorption spectra analyzed using Silverstein and Webster⁴⁷

The most broad absorption band witnessed for the two surfactants exists between the wavenumbers of approximately 3600 and 2800 cm⁻¹. This band is widely recognized as the absorption band for water, specifically the O-H stretch. The small band observed just above 2400 cm⁻¹ is due to the absorption by a small amount of CO₂ in the FTIR chamber atmosphere. There are two bands witnessed for the proprietary surfactant in the range of 1680 – 1620 cm⁻¹. The first is relatively minor and the second is somewhat larger and seems to be shared with Darvan 821A. These peaks are due to the absorption by Alkene groups in many different stretching modes. The bands witnessed between 1610 and 1430 cm⁻¹ were common to both polymers and were expected to be found in the structure. The absorption of energy by the carboxylate and methane (CH₃) groups was a sign that these surfactants were in fact somewhat similar. The final absorption witnessed for the proprietary surfactant was the most telling evidence that it was in fact different than Darvan 821A. The absorptions witnessed between 1220 and 1020 cm⁻¹ were evidence of amine groups without aromatic groups, hence the term aliphatic. This is definitely a feature not found in Darvan 821A.

5.4 UV-Vis Results

UV-Vis spectroscopy was used as a first attempt to quantify the concentration of surfactant in a solution. The surfactant studied showed a strong absorption band at 289 nm, but a good correlation between concentration and peak height or area could not be established. The UV-Vis absorption spectra is shown in Figure 10, the attempted calibration curve is shown in Figure 11.

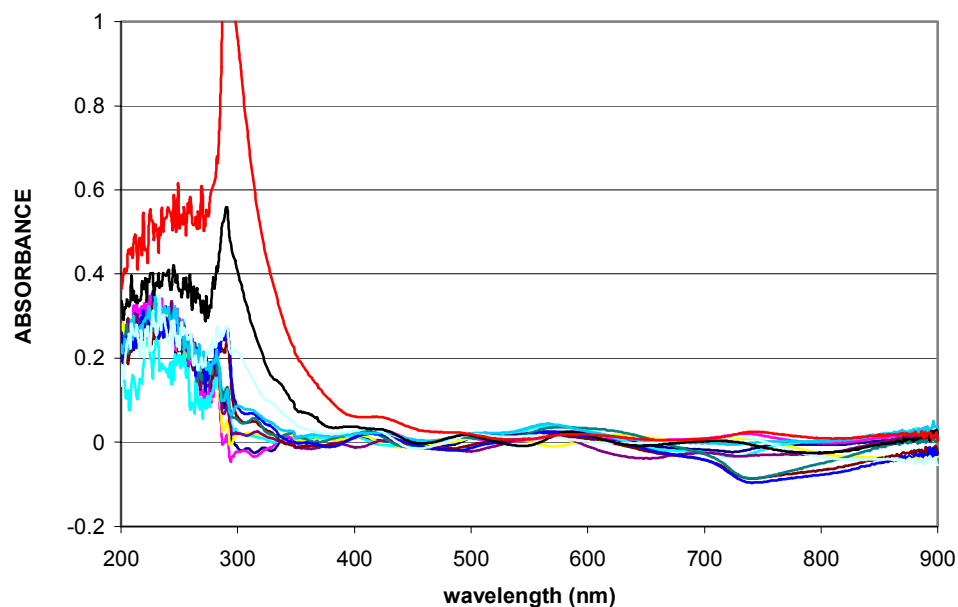


Figure 10. UV-Vis spectra of the surfactant used in this study. Concentrations from 0.09 mg polymer/g solution to 225 mg polymer/g solution were tested. The most concentrated solutions show the largest absorption band at 289 nm.

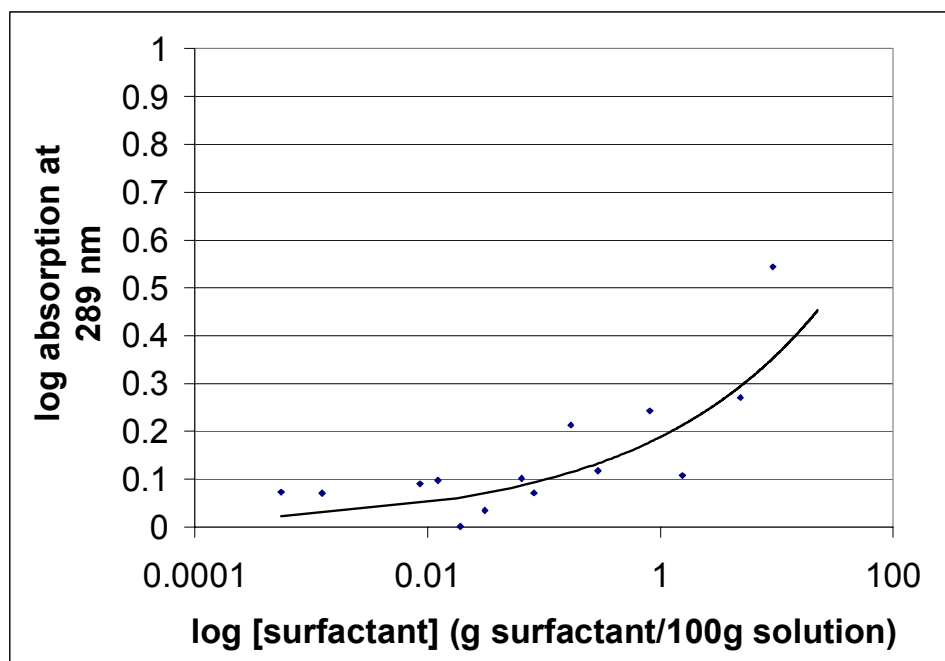


Figure 11. Calibration curve developed from UV-Vis analysis of the surfactant. The absorption band at 289 nm was used and the calibration curve was made using the peak height at that wavelength.

The calibration curve shown in Figure 11 was not considered to be sufficient for determining the concentration of surfactant in solution. Other methods were then explored.

5.5 Surfactant Titration Results

The pH range of the titration shown in Figure 10 was considered sufficient and was shown to encompass three major equivalence points for the surfactant in question. Volumes of titrant were converted into molar equivalents of titrant used from a pH of 3 to a pH of 9 so that all titrant volumes were normalized when comparing samples. This value was then used to describe the amount of residual polymer in the supernatant solution. Figure 12 shows typical titration curves developed for three standard solutions of increasing surfactant concentration.

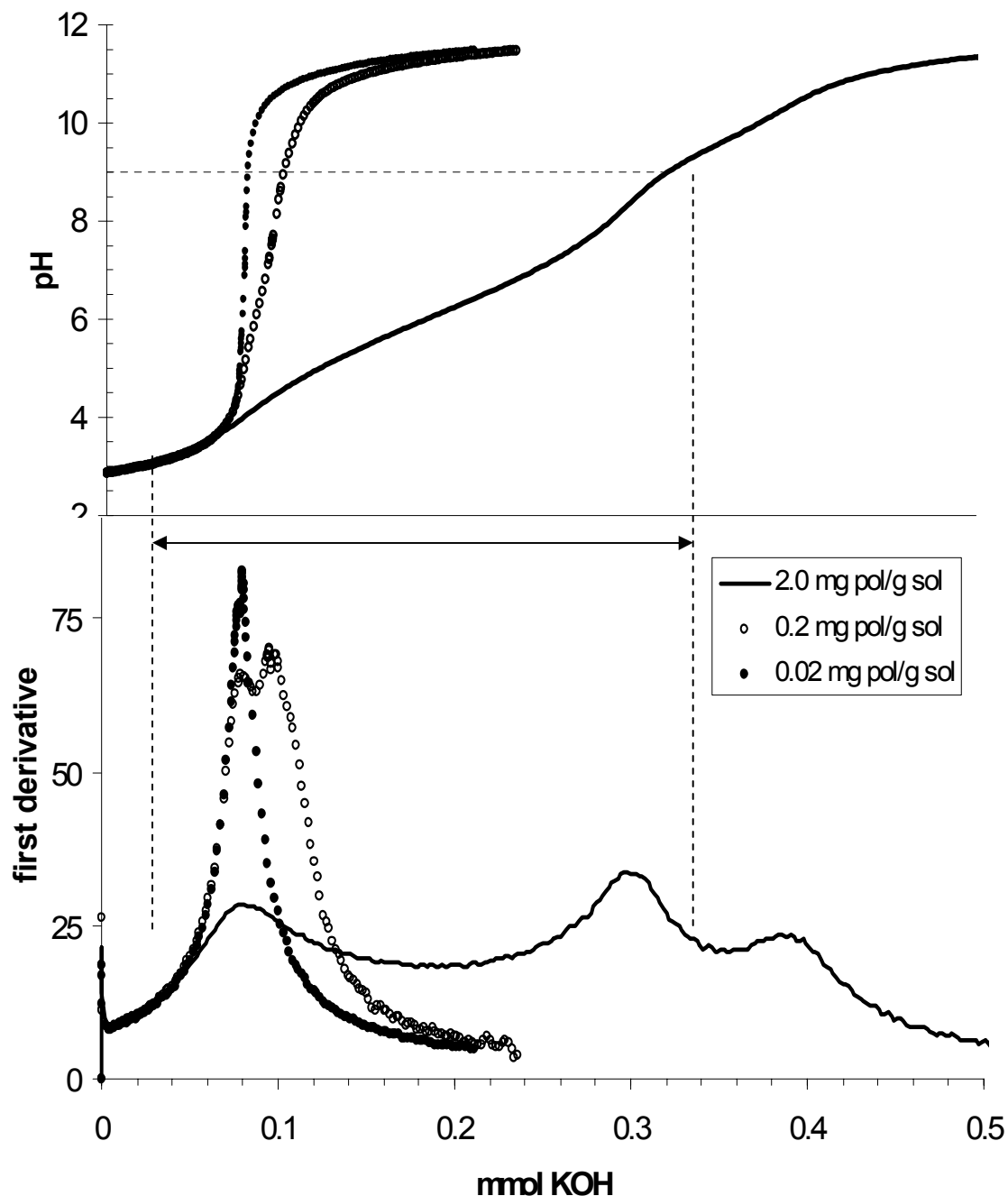


Figure 12. Titration curves for increasing levels of surfactant in question. The x-axis represents the mmol KOH used during the course of the titration. The y-axis in the top plot represents the pH of the solution. The y-axis in the bottom plot represents the first derivative of the pH curve as a function of the KOH addition.

The curves shown in Figure 12 show that as the level of surfactant in solution increases, the amount of KOH required to complete the titration will increase. Three surfactant levels were tested, 0.2 wt%, 0.02 wt%, and 0.002 wt%, these values are shown

in Figure 10 as 2.0, 0.2, and 0.02 mg polymer/g solution respectively. Solutions were prepared with the surfactant and de-ionized water. The surfactant was measured on a weight percentage basis of the entire solution.

At high concentration (0.2 wt%) the distances between the first derivative peaks are quite considerable. However, it can be discerned that as the surfactant level decreases in solution, the distance between the peaks reduces until there is no distinguishable difference. For this reason, the distance between first derivative peaks was not used to calibrate the concentration of surfactant in solution. Instead, the amount of KOH required to titrate the sample from a pH of 3 to a pH of 9 was used. This region was chosen because two major equivalence peaks for the surfactant fall within this region.

5.5.1 Water Correction

The water correction described in section 4.9.1 for the titration method is shown in Figure 13.

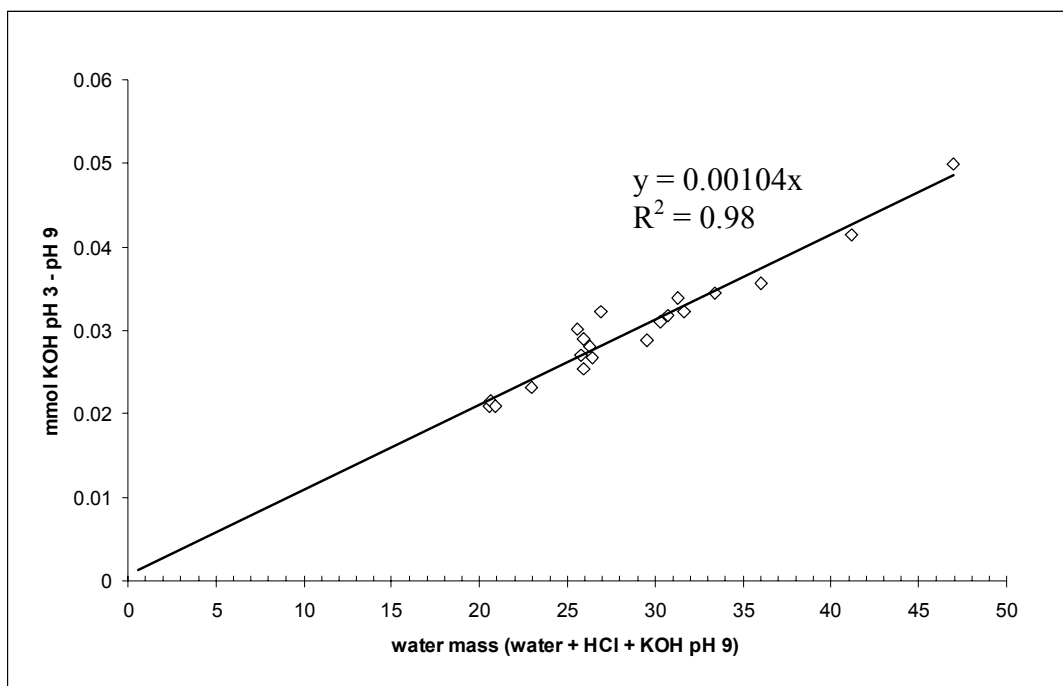


Figure 13. Calibration curve developed to create a subtraction for the amount of water titrated in a supernatant sample

The linear approximation through the measured data points in Figure 11 was forced through zero for obvious reasons. A titration of zero water should require zero KOH. The equation for the line is:

$$y = 0.00104x$$

Where y is the mmol KOH required to titrate the sample from pH 3 to pH 9 and x is the mass of water in the sample. The slope of the line shows that 0.00104 mmol of KOH is required to titrate 1 gram of water from a pH of 3 to 9. The theoretical value for this water correction would be 0.00101 mmol KOH for one gram of water. The 3% difference between the theoretical value and the actual measured value may be attributed to a number of factors. These factors may include impurities in the de-ionized water, an error in the assumed concentration of the KOH used for the titration, or an error in the pH measurement.

5.5.2 Surfactant Calibration Curve

The calibration curve developed by titrating the standard surfactant solutions is shown in Figure 14. The data shown has already been corrected for the amount of water in solution using the equation shown previously in Section 5.5.1. Unknown supernatant solutions were compared to this plot according to the amount of KOH required to titrate from a pH of 3 to 9. The concentration of surfactant in the supernatant was calculated from the linear approximation in Figure 14.

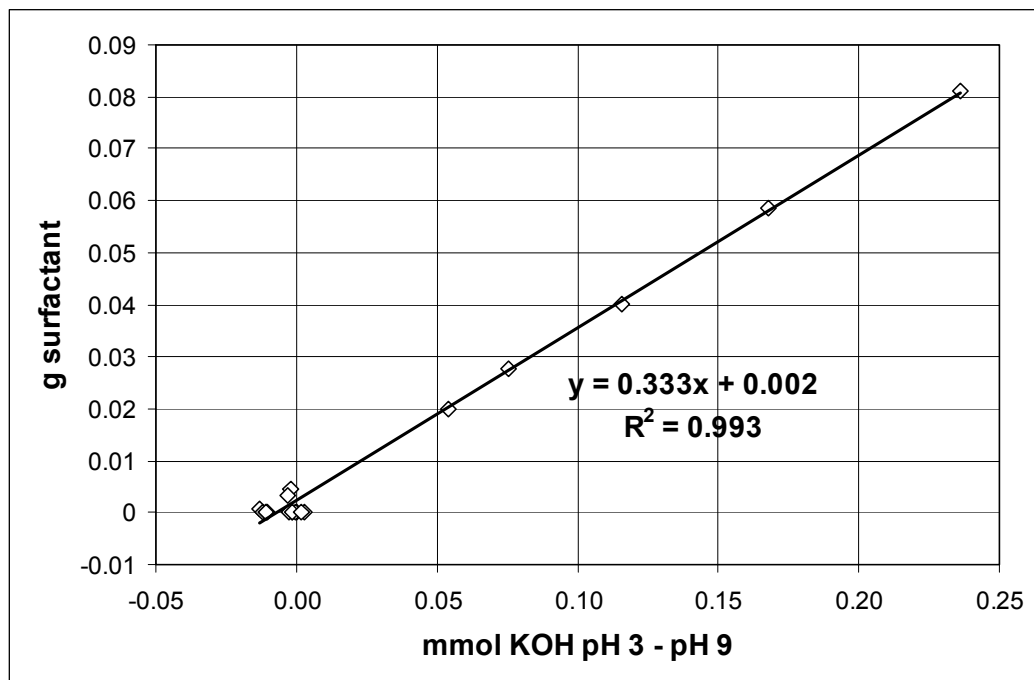


Figure 14. Calibration curve developed to calculate the amount of residual surfactant in solution. The scatter in the data around zero represents the error in the titration technique for determining extremely dilute levels of polymer in solution.

5.5.3 Dissolved Ion Corrections

The dissolved ion corrections can be compared to the typical background electrolyte corrections made in many studies that use a standard background electrolyte such as 0.001 M KCl. Figures 15-22 show solubility plots found in the literature⁴⁸ and the dissolved ion correction curves developed in this work.

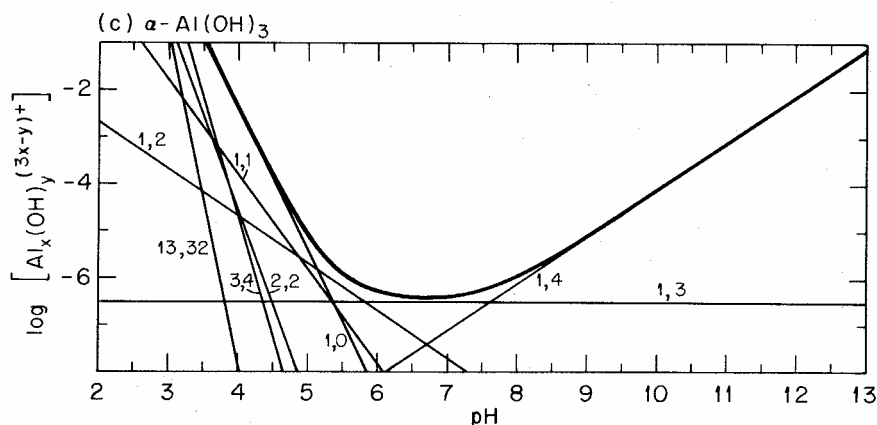


Figure 15. Solubility plot for Al_2O_3 across the pH range. The solubility product of Al_2O_3 is a hydroxide, its concentration is shown on the y-axis as a function of pH.⁴⁸

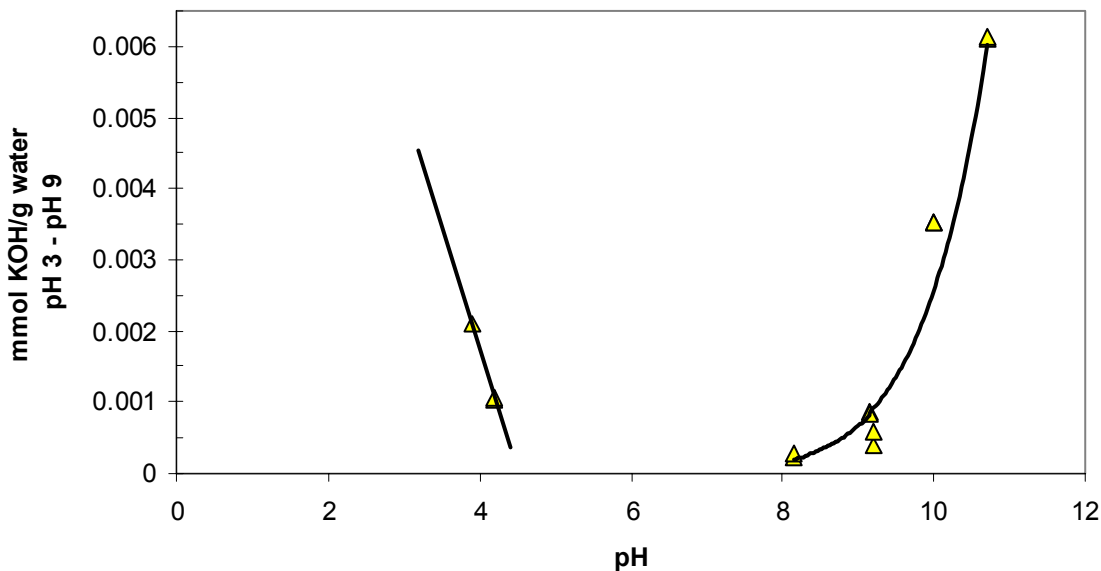


Figure 16. Dissolved ion correction made for Al_2O_3 suspensions across the pH range. Data points were created from supernatant solutions from 20 wt% suspensions at various pH values.

The shape of the curves shown in Figures 15 and 16 are quite similar. Although the concentration of dissolved ions is not given in Figure 16, the shape of the curve is convincing and can be used as a rough approximation to the solubility plot for Al_2O_3 shown in Figure 15.

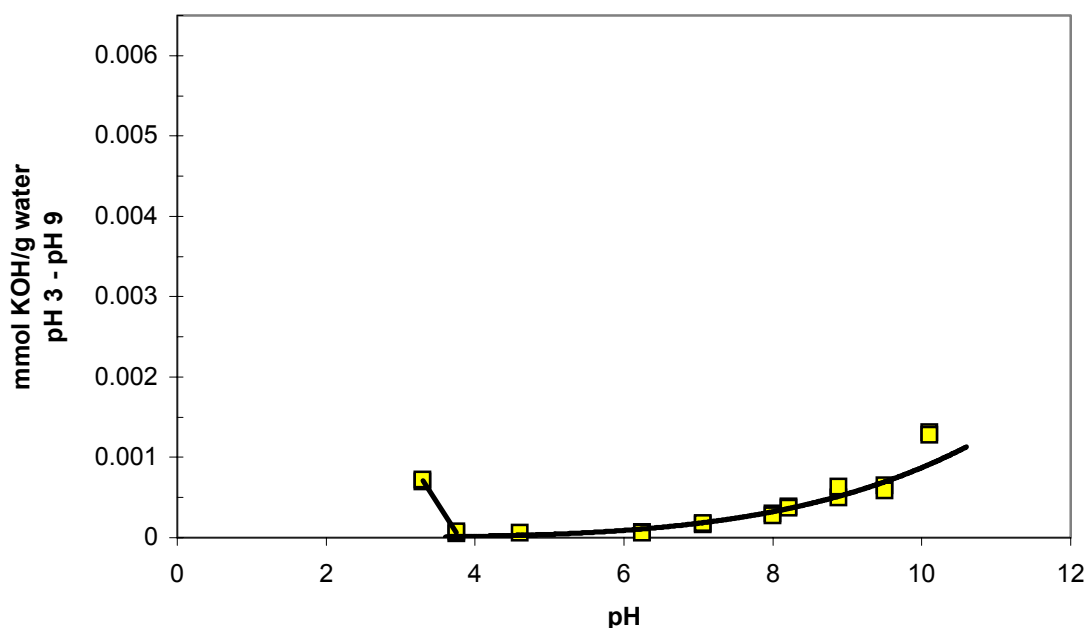


Figure 17. Dissolved ion correction made for SiO_2 suspensions across the pH range. Data points were created from supernatant solutions from 20 wt% suspensions at various pH values.

A solubility plot for SiO_2 was not found in the literature for comparison to the data generated in Figure 17.

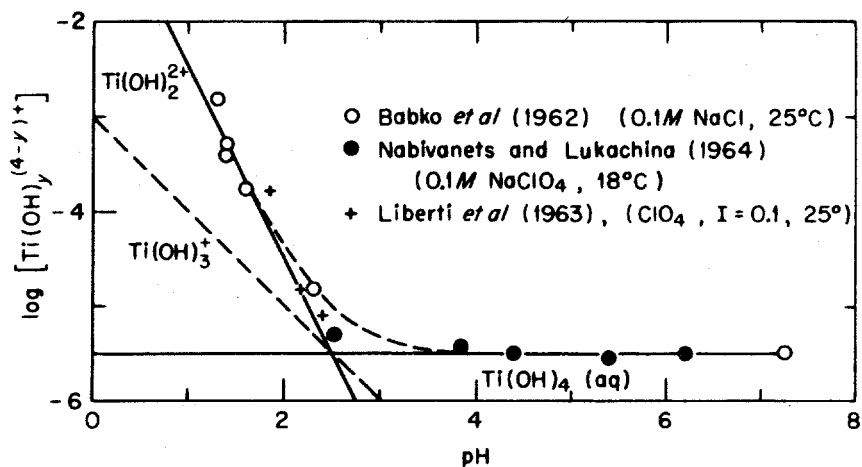


Figure 18. Solubility plot for TiO_2 across the pH range. The solubility product of TiO_2 is a hydroxide, its concentration is shown on the y-axis as a function of pH.⁴⁸

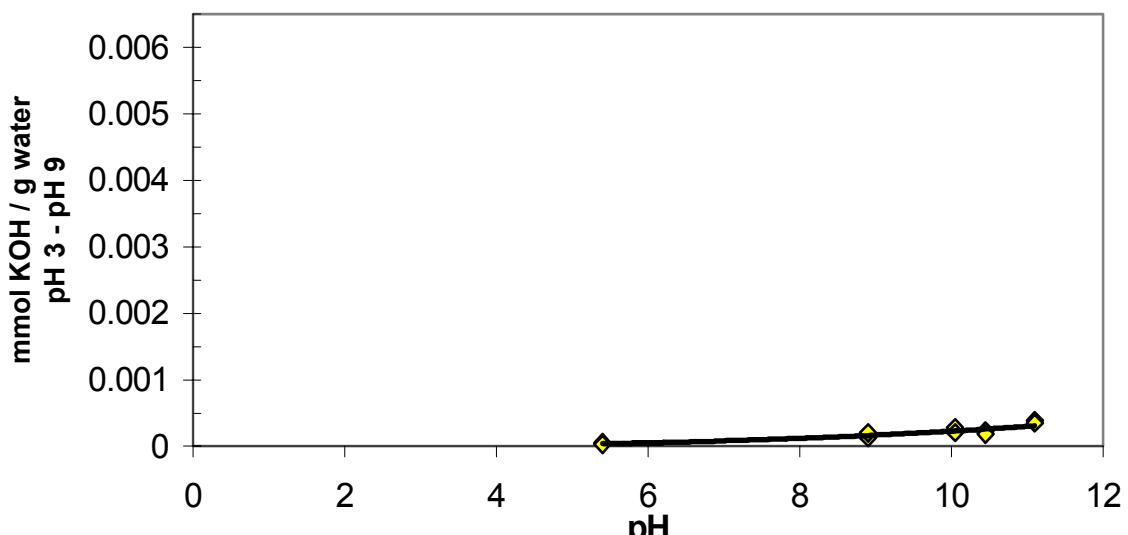


Figure 19. Dissolved ion correction made for TiO_2 suspensions across the pH range. Data points were created from supernatant solutions from 20 wt% suspensions at various pH values.

The data shown in Figure 19 agrees somewhat with the plot in Figure 18. The pH range witnessed in Figure 18 goes much lower than the range tested in Figure 19. No correction was made to TiO_2 supernatant solutions with a pH less than 5.0.

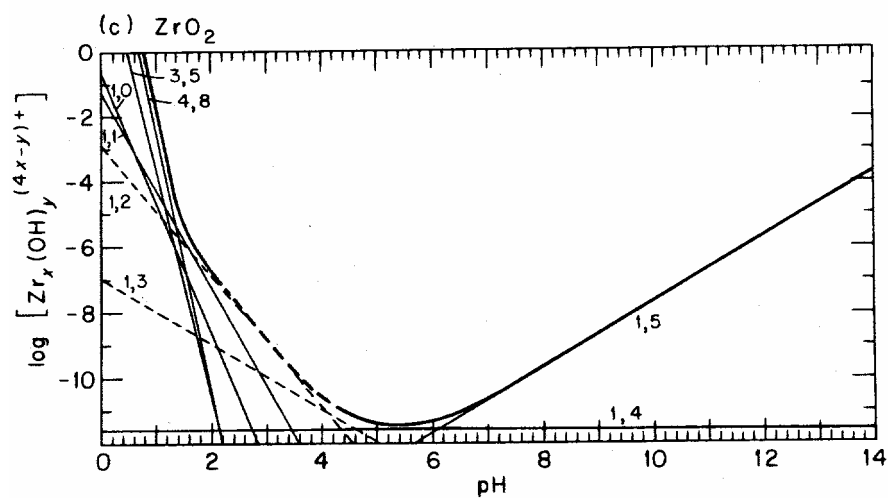


Figure 20. Solubility plot for ZrO_2 across the pH range. The solubility product of ZrO_2 is a hydroxide, its concentration is shown on the y-axis as a function of pH.⁴⁸

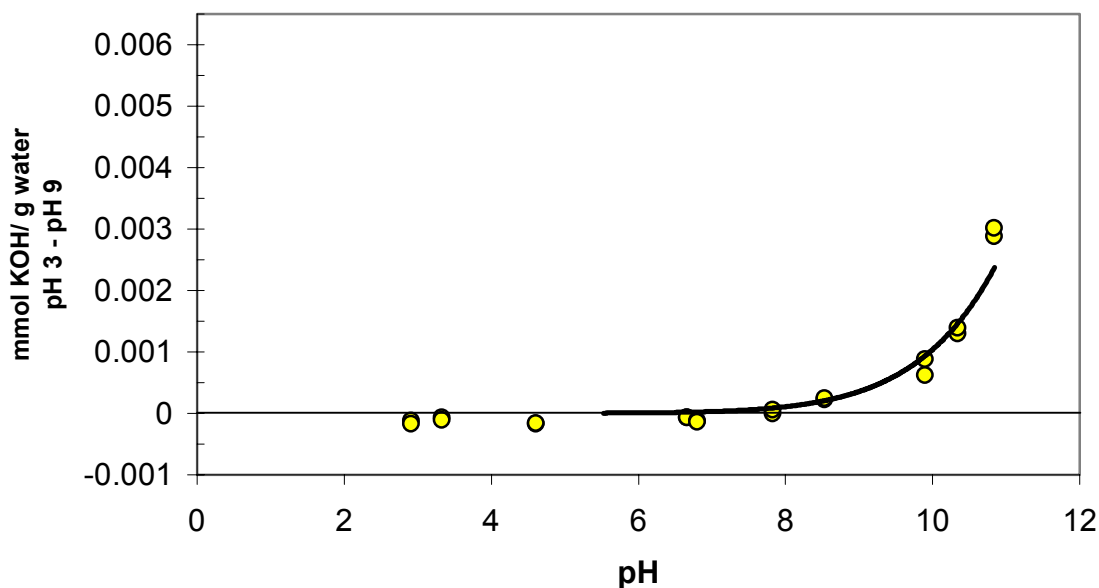


Figure 21. Dissolved ion correction made for ZrO_2 suspensions across the pH range. Data points were created from supernatant solutions from 20 wt% suspensions at various pH values.

After constructing Figures 16-21 it became evident that the assumption that dissolved ions having no effect on the titration was incorrect. There is a significant contribution to the volume of titrant necessary for altering the pH of a solution that contains a large amount of dissolved metal ions. It should be pointed out that the dissolved ion subtractions for Al_2O_3 and ZrO_2 are about ten times greater than the subtractions used for the SiO_2 and TiO_2 suspensions. All plots are shown on the same scale for the sake of easy comparison.

5.6 ICP Correction

Adsorption data was generated using the water correction in Figure 13 and the dissolved ion corrections from Figures 16-21. Negative adsorption characteristics were witnessed some times. This was believed to be due to an over correction to the titration data.

The water correction seemed reasonable and was assumed to be correct, but the dissolved ion correction was drawn into question because of the fact that no surfactant was present in the suspensions used to create the dissolved ion correction data. In other

words, it was assumed that the surfactant had no effect on the amount of dissolved ions present in a given suspension at a given pH value.

The only way to validate this assumption was to employ a method that would measure the actual dissolved ion concentration in solution. The method used was ICP-OES (inductively coupled plasma-optical emission spectroscopy) and found to be a common method for the determination of background electrolyte concentrations in the literature.¹⁵ Other methods for detecting dissolved ion levels include conductivity¹² and ion chromatography.¹² Samples were prepared using ICP standards (Sigma Aldrich, St. Louis, Missouri) for aluminum, silicon, and titanium ions. Zirconium ions were added by dissolving Zirconyl nitrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) powder in de-ionized water. Dissolved ion levels added to the solutions ranged from 0, 5, 10, and 25 ppm (μg metal/g solution) additions. The surfactant level was added across the range of 0, 0.1, 0.3, and 0.5 weight percent of the total solution. Solutions were prepared as 30 mL samples so that there was enough material for ICP and a titration to be run. The resulting ICP analysis and titration data are shown in Figures 22-25.

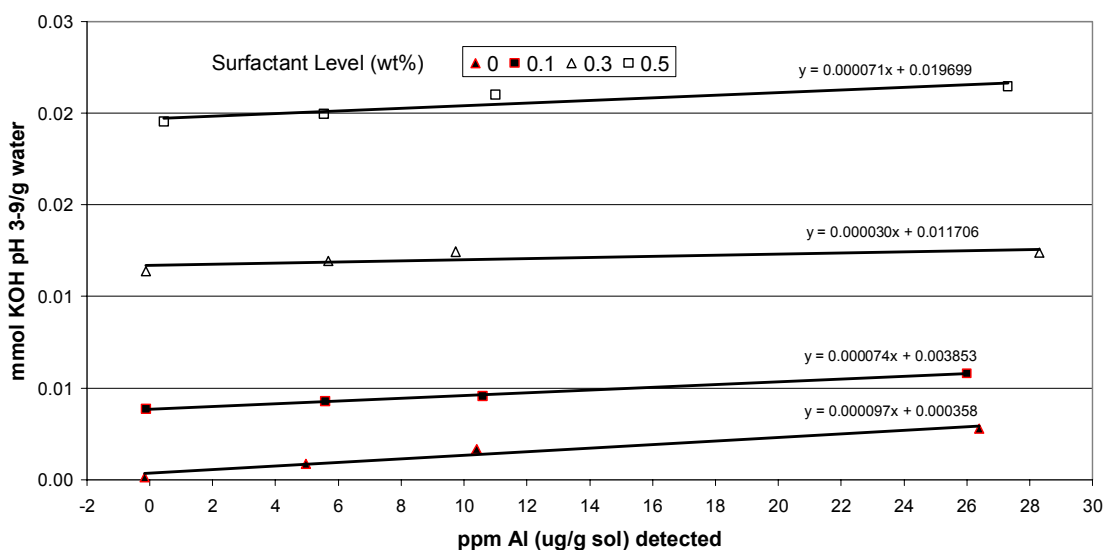


Figure 22. Comparison of ICP and titration results for aluminum standard solutions prepared at 0, 5, 10, and 25 ppm Al as a function of surfactant level. The average slope of correlates to 0.0000675 mmol KOH/g water for every one ppm Al ion in solution.

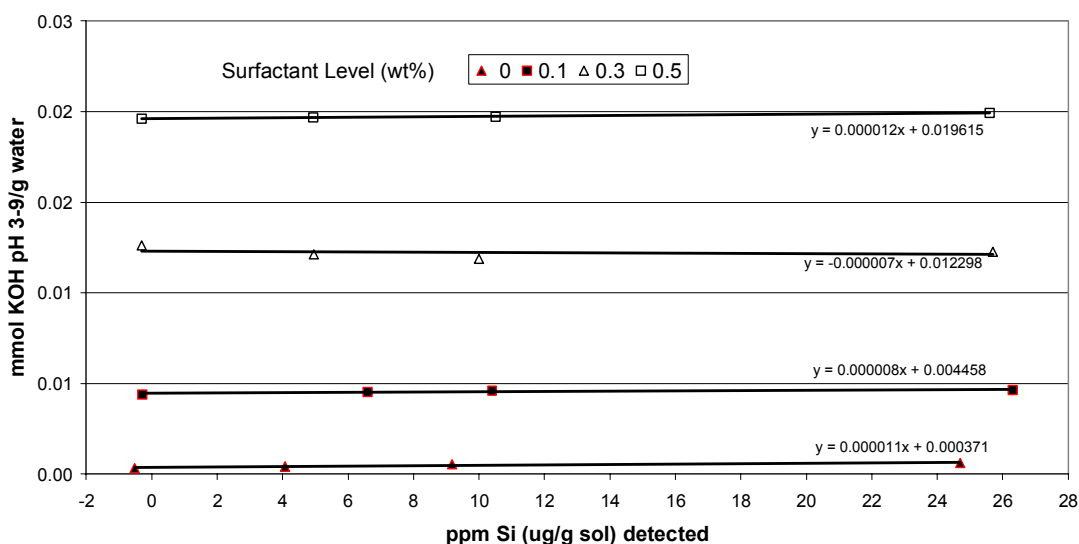


Figure 23. Comparison of ICP and titration results for silicon standard solutions prepared at 0, 5, 10, and 25 ppm Si as a function of surfactant level. The average slope of correlates to 0.00001 mmol KOH/g water for every one ppm Si ion in solution.

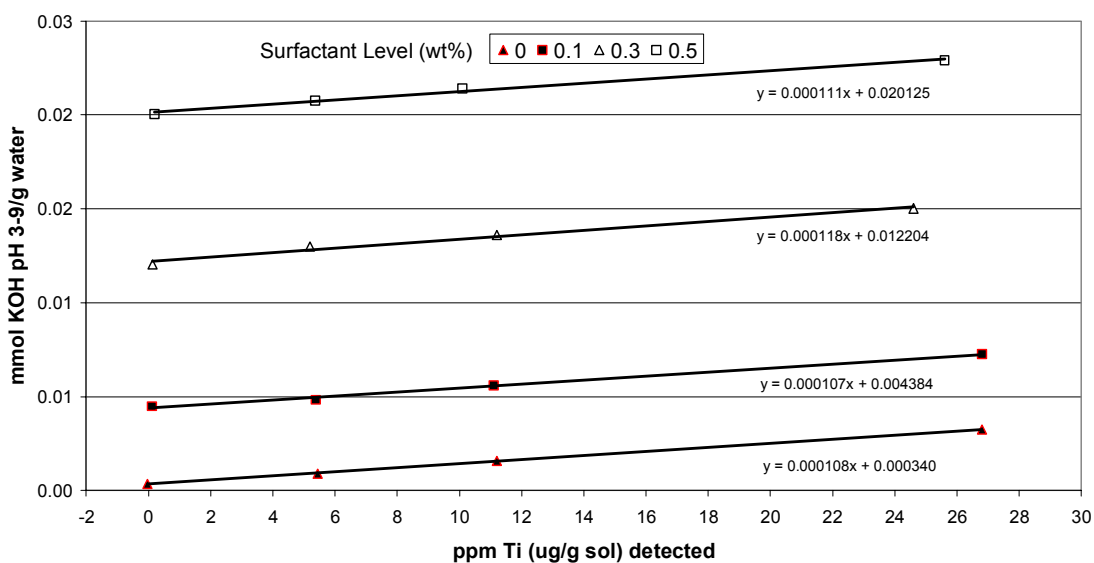


Figure 24. Comparison of ICP and titration results for titanium standard solutions prepared at 0, 5, 10, and 25 ppm Ti as a function of surfactant level. The average slope correlates to 0.0001 mmol KOH/g water for every one ppm Ti ion in solution.

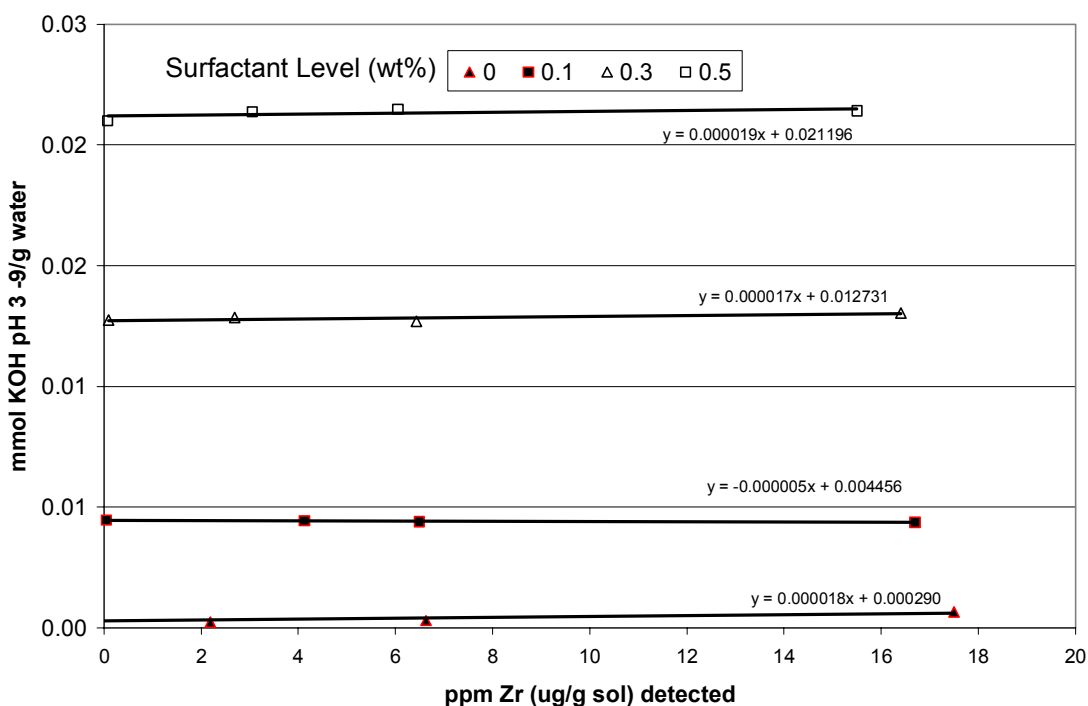


Figure 25. Comparison of ICP and titration results for zirconium standard solutions prepared at 0, 5, 10, and 25 ppm Zr as a function of surfactant level. An average slope correlates to 0.0000125 mmol KOH/g water for every one ppm Zr ion in solution.

The data in Figures 23 and 25 show relatively flat lines for the contribution of dissolved ions in SiO_2 and ZrO_2 suspensions. The behavior witnessed in Figure 23 shows that increasing levels of surfactant effectively decreased the contribution of dissolved ions to the titration. It should also be noted that the detected amount of Zr ions in solution is quite different than the 0, 5, 10, and 25 ppm thought to be added initially. This difference was attributed to the use of zirconyl nitrate as the Zr source rather than the standard solutions. The water content of the zirconyl nitrate most likely was quite high, which in fact reduced the concentration of Zr in the sample.

The data shown in Figures 22-25 show relatively parallel lines for each surfactant level for each type of ion added to solution. This holds the assumption true that the surfactant plays no role in changing the dissolved ion content of the solution. The upward slope of the lines hints that higher levels of dissolved ions in solution will increase the need for KOH in order to change the pH of the solution from pH 3 to pH 9. As shown earlier in Figure 10 the amount of KOH required to titrate a sample containing the surfactant will increase with increasing surfactant levels.

Using the data from Figures 22-25, a new dissolved ion correction was developed. The average slope for each metal was used as a correction factor for the amount of KOH required to titrate the amount of dissolved ions in solution. Table VII below shows the calculated amount of residual surfactant for the same sample using the two dissolved ion corrections described above.

Table VII. Dissolved Ion Corrections Used Throughout the Study.

Metal	Old Correction (y=mmol KOH/g water) (x = pH)	Applicable pH range	New Correction $\left(\frac{\text{mmolKOH} / \text{gH}_2\text{O}}{\text{ppm}_{\text{metal}}} \right)$
Aluminum	y = -0.0035x + 0.0157 y = $6.1130 \times 10^{-16} x^{12.6230}$	pH < 5 pH > 7	0.0000675
Silicon	y = -0.0014x + 0.0054 y = $3.028 \times 10^{-8} x^{4.459}$	pH < 4 pH > 4	0.0000100
Titanium	y = $3.2611 \times 10^{-7} x^{2.8471}$	all values	0.0001000
Zirconium	y = $6.2534 \times 10^{-14} x^{10.22}$	all values	0.0000125

The old dissolved ion corrections shown in Figures 16-21 were corrections made based on the pH of the suspension. Fit functions were developed for each oxide and used to make subtractions to the titration data based on the amount of supernatant titrated (g H₂O). The new dissolved ion corrections are taken from the averages slopes of the lines in Figures 22-25. Corrections were made using the actual dissolved ion levels detected in the supernatant solution. The numbers show in table VII represent the amount of KOH (mmol) required to titrate one gram of supernatant with one part per million metal dissolved. Table VIII shows four suspensions measured for each oxide on which both dissolved ion corrections have been performed. The final columns to the right of the table represent the amount of unadsorbed surfactant detected in the supernatant solution after the respective dissolved ion correction had been performed.

Table VIII. Dissolved Ion Correction Comparison

Sample	Process Conditions		Titration*		ICP Results (ppm)				Ion correction mmol KOH/g H ₂ O		g pol/gH ₂ O in solution	
	pH	Init. Pol. gpol/gH ₂ O	g H ₂ O	mmol KOH	Al	Si	Ti	Zr	Old	New	Old	New
KG 156-159 Al ₂ O ₃	3.98	0.00075	29.684	0.0612	3.47	0.50	-0.093	0.60	0.00183	0.00025	-0.0002	0.00032
	7.69	0.00075	27.759	0.0424	0.25	12.9	-0.129	0.09	0.00009	0.00015	0.00020	0.00018
	8.39	0.00075	29.604	0.0596	0.93	2.15	-0.128	0.08	0.00028	0.00009	0.00029	0.00036
	9.86	0.00075	27.732	0.1327	35.0	5.39	-0.120	2.83	0.00210	0.00250	0.00058	0.00048
KG 176-179 SiO ₂	2.70	0.00075	28.695	0.1485	11.9	15.3	-0.121	0.63	0.00157	0.00096	0.00091	0.00110
	4.93	0.00075	28.475	0.1393	8.28	32.0	-0.114	1.15	0.00003	0.00088	0.00132	0.00103
	7.69	0.00075	28.575	0.1281	0.003	31.2	-0.107	1.07	0.00027	0.00033	0.00110	0.00108
	9.40	0.00075	29.727	0.1413	0.093	49.8	-0.118	1.20	0.00066	0.00052	0.00106	0.00111
KG 148-151 TiO ₂	2.99	0.00025	32.394	0.0498	-0.08	0.624	-0.100	0.09	0.000007	0.000007	0.00022	0.00022
	5.32	0.00025	32.600	0.0476	-0.16	0.101	-0.137	0.06	0.000038	0.000001	0.00018	0.00020
	8.48	0.00025	29.708	0.0606	-0.14	-0.28	16.70	0.63	0.000143	0.00168	0.00034	-0.0002
	10.68	0.00025	36.605	0.1085	-0.22	-0.14	23.90	1.31	0.000277	0.00241	0.00059	-0.0001
KG 189-192 ZrO ₂	2.88	0.00251	29.188	0.0491	-0.20	-0.51	-0.144	0.05	0.000000	0.0000007	0.00028	0.00028
	4.85	0.00251	29.135	0.0465	-0.36	-0.58	-0.133	0.09	0.000001	0.0000012	0.00025	0.00025
	7.50	0.00251	28.905	0.0462	-0.25	-0.56	-0.124	9.01	0.000055	0.000112	0.00023	0.00021
	8.50	0.00251	28.190	0.0607	-0.24	-0.57	-0.120	12.7	0.000197	0.000159	0.00038	0.00039

* - mmol KOH required for titration of all water in the supernatant has been subtracted using the fit function from Figure 13.

5.7 Unadsorbed Surfactant Results

Once samples of each surfactant level and each pH level were created for the four oxides, the adsorption behaviors could be characterized. Figures 26-29 show the amount of unadsorbed surfactant detected by titration in solution versus the pH of the suspensions. Data for five different surfactant levels is reported for each oxide. The amount of surfactant detected by the titration was converted using the following steps:

1. mmol KOH $\rightarrow$ g surfactant using Figure 14
2. gram surfactant divided by g supernatant to obtain concentration of surfactant in supernatant
3. concentration in supernatant converted into concentration in entire sample by multiplying by (g total water/g supernatant) ratio.

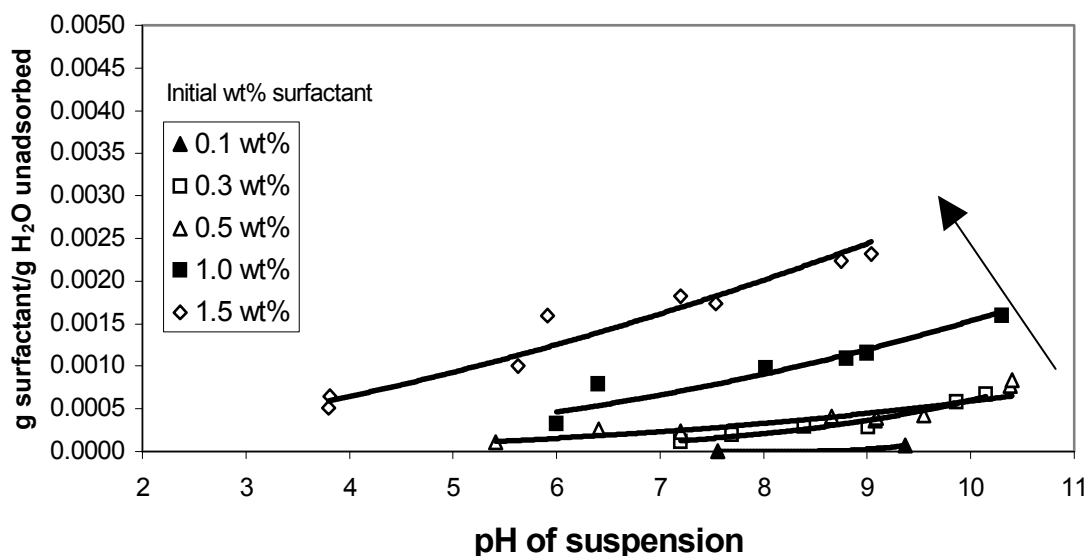


Figure 26. Plot of residual surfactant detected for different initial surfactant levels as a function of pH for the Al₂O₃ / surfactant system. The direction of increasing initial surfactant level is shown with the arrow. A relative degree of the scatter in the data is shown in the 1.5 wt% series.

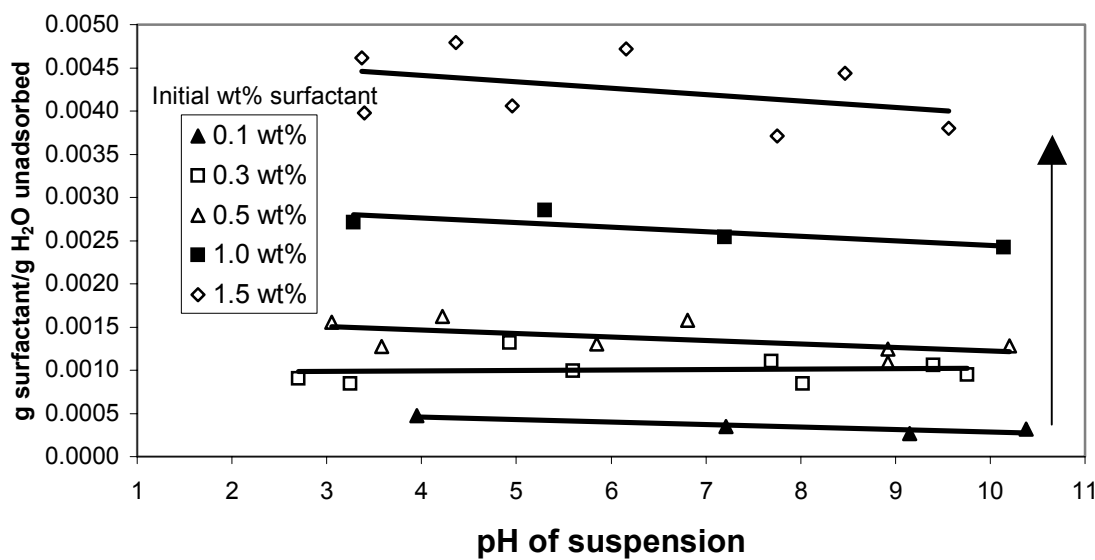


Figure 27. Plot of residual surfactant detected for different initial surfactant levels as a function of pH for the SiO_2 / surfactant system. The direction of increasing initial surfactant level is shown with the arrow. A relative degree of the scatter of the data is shown in the 1.5 wt% series.

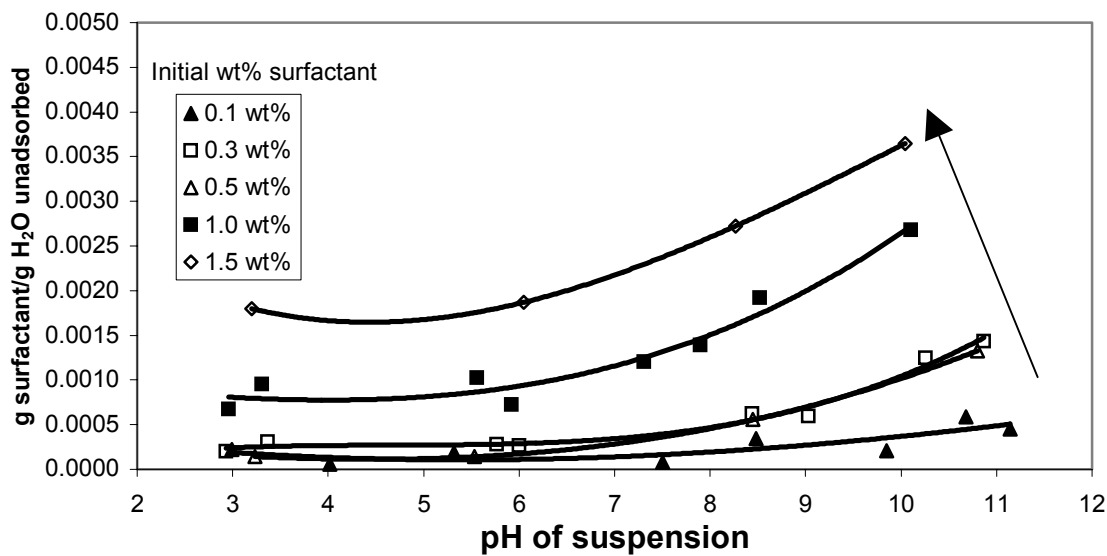


Figure 28. Plot of residual surfactant detected for different initial surfactant levels as a function of pH for the TiO_2 / surfactant system. The direction of increasing initial surfactant level is shown with the arrow.

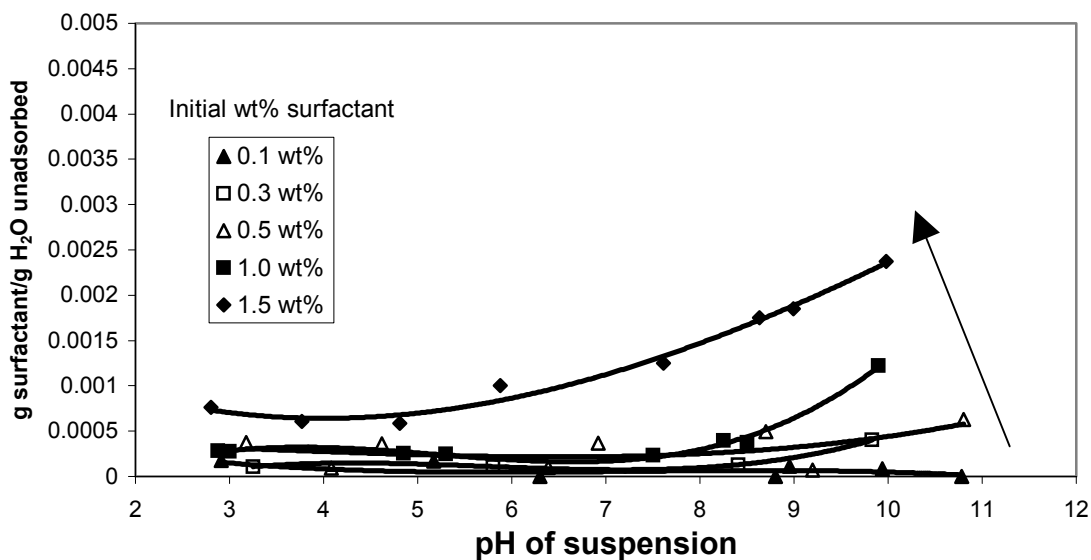


Figure 29. Plot of residual surfactant detected for different surfactant levels as a function of pH for the ZrO_2 / surfactant system. The direction of increasing initial surfactant level is shown with the arrow.

From Figures 26-29 it was possible to create a more descriptive way of illustrating adsorption onto the powder surfaces. Adsorption isotherms describe the amount of surfactant adsorbed on the particle surfaces as a function of the amount added. All samples are reported for a temperature of 25°C . Figures 30-33 show adsorption isotherms created for the single oxide systems. The solid black line represents the condition where 100% of the added surfactant is adsorbed onto the particle surfaces in suspension. The adsorption is plotted as a function of initial added surfactant level for pH values from a pH of 4 to a pH of 10. The point at which the lines begin to plateau is commonly described as the monolayer adsorption capacity. This type of adsorption can also be described as Langmuir type adsorption and assumes that the surfactant will not adsorb in multiple layers on the particle surfaces. Once the monolayer capacity is reached, any additional surfactant added to the suspensions will remain in solution.

The data in Figures 25-29 was converted into data for the adsorption isotherms using the following steps:

1. concentration of unadsorbed surfactant in solution taken from Figures 25-29
2. concentration of unadsorbed surfactant in solution converted into a concentration based on the powder by multiplying the concentration by 4 (80% water / 20% powder)
3. concentration based on powder remaining in solution subtracted from the initial amount added to the suspension (d.w.b. = g surfactant / g powder) to obtain the concentration of surfactant adsorbed onto the powder surfaces
4. concentration adsorbed onto powder surfaces converted into g surfactant adsorbed / m² surface area by dividing the concentration by the surface area of the powder (m²/g)

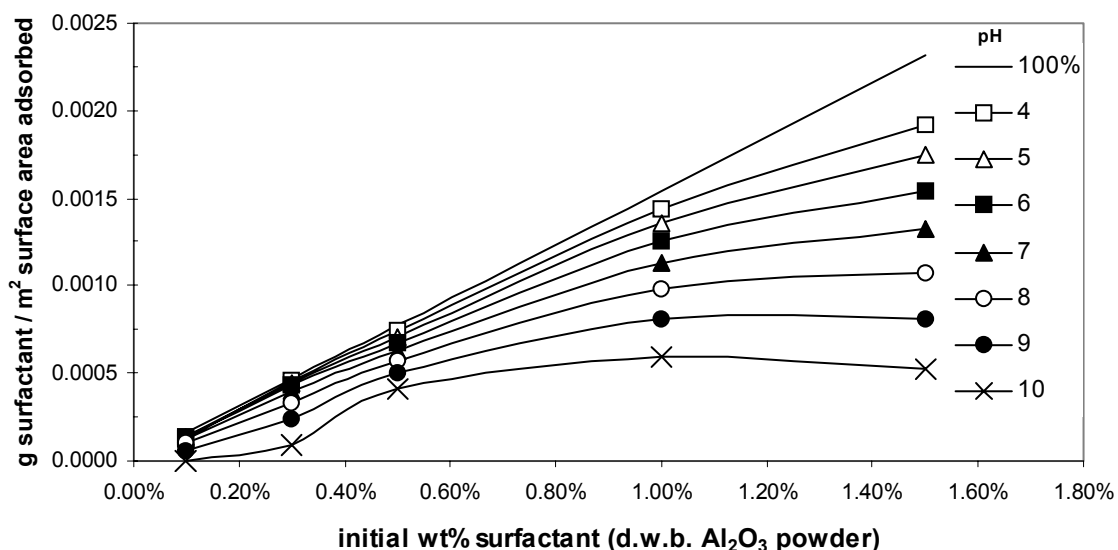


Figure 30. Adsorption isotherm for the Al₂O₃ / surfactant system. Data created from the measured points in Figure 26.

The Al₂O₃ adsorption data agrees well with historical data for Al₂O₃ / PAA-type suspensions. Cesarano et al.⁹ show that Al₂O₃ will completely adsorb Na-poly(methacrylic acid) up to approximately 0.4 initial wt% (d.w.b.) surfactant at a pH of 5.8. Davies and Binner¹⁶ report that the Al₂O₃ surfaces become completely covered by NH₄-PAA at an initial polymer level of 2.7 ± 0.2 mg/g for a suspensions at a pH of 9.5. This value corresponds to an initial surfactant concentration between 0.25 wt% and 0.29 wt% (d.w.b.). Due to the fact that the data is limited in Figure 24 in terms of initial wt% surfactant values, a true monolayer adsorption capacity is difficult to discern from the

data. The deviation from the 100% adsorption line appears to take place between initial surfactant levels of 0.3 and 0.5 wt% for most pH values. This range can be considered believable due to the data furnished by Cesarano⁹ and Davies and Binner.¹⁶

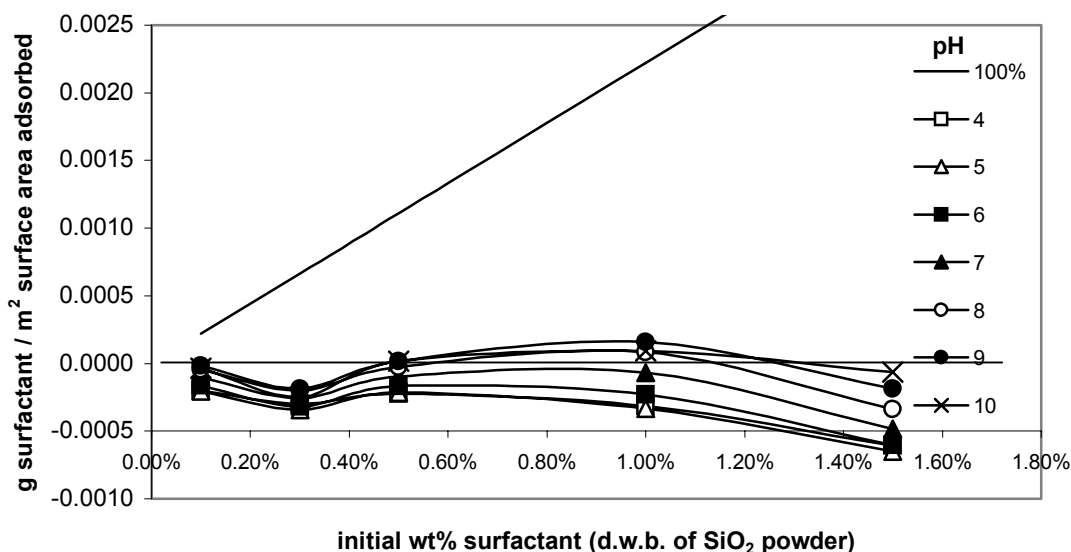


Figure 31. Adsorption isotherms created for the SiO₂ / surfactant system from measured data in Figure 27.

As seen in Figure 31, the adsorption of the surfactant is negligible for all pH values on SiO₂ particles. Due to the fact that the dissolved ion corrections shown in table xx produce approximately the same numbers for SiO₂ suspensions, the dissolved ion correction was assumed to be reasonable and not an overcorrection in this case. The negative values illustrated in Figure 29 are most likely a function of the error of the titration technique. The adsorption behavior shown here is in good accordance with the data of Gebhardt and Fuerstenau,¹⁴ who found that PAA does not adsorb onto SiO₂ surfaces. Their explanation was that electrostatic repulsion between the surfaces and the polyelectrolyte prohibited adsorption of the polymer.

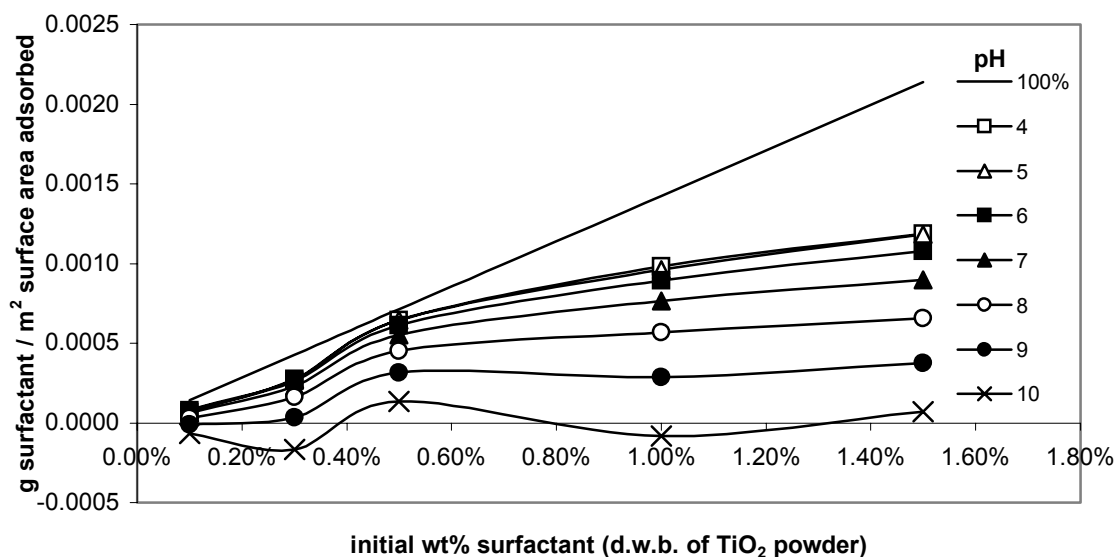


Figure 32. Adsorption isotherms created for the TiO_2 / surfactant system from the measured data in Figure 28.

The data in Figure 32 shows strong adsorption behavior of the surfactant for TiO_2 particles up to approximately 0.5 wt% surfactant added for low pH values. The negative values seen for the pH 10 line can be attributed to the error of the titration technique or to an over correction of the data due to the dissolved ion correction. Strauss et al.¹⁹ show that TiO_2 will adsorb PAA quite strongly up to 0.5 wt% (d.w.b.) at low pH values. This is approximately equivalent to 0.6 mg/m^2 surface area available. It should be noted that the surfactant used in their study was somewhat different than that used for this study. The molecular weight of their surfactant was 10,000 grams per mole in a 50 wt% solution whereas the surfactant used in this study was only 4500 grams per mole in a 45 wt% solution. The molecular weight should not change the adsorption levels considerably when the adsorption is characterized on a weight percent basis, but this does provide a possible solution to small variations between the two studies.

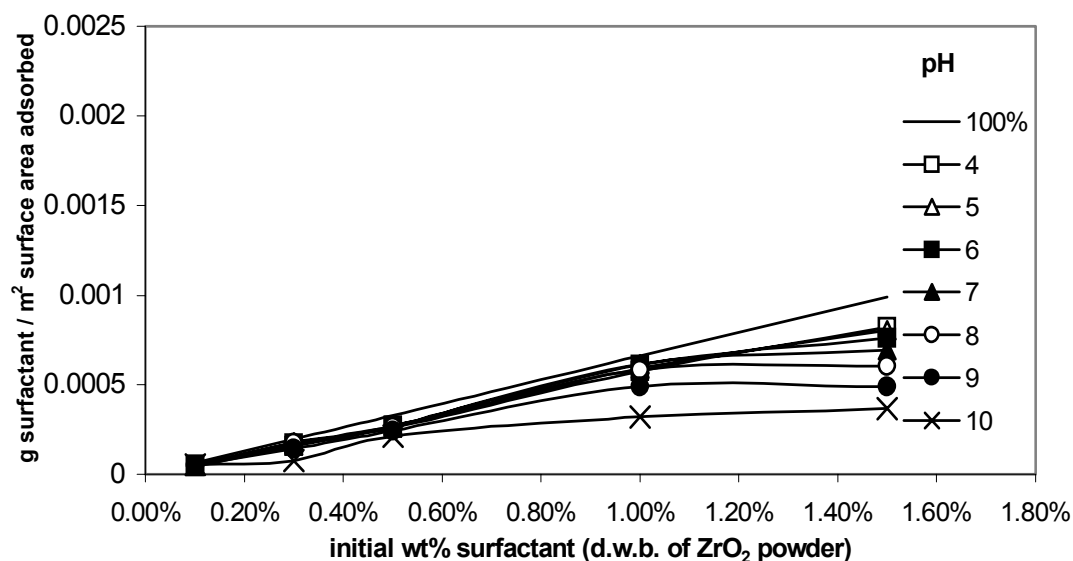


Figure 33. Adsorption isotherms created for the ZrO_2 / surfactant system from measured data in Figure 29.

ZrO_2 shows very strong adsorption behavior for pH values 9 and lower. Sun et al.²¹ report that the initial pH of the suspension did not influence that adsorption of NH_4 - PAA onto nanometer sized ZrO_2 powder. Only for pH values >10 does the data above deviate significantly from the 100% adsorption line.

It is evident from each of the above plots that the Al_2O_3 , TiO_2 , and ZrO_2 powders will readily adsorb the surfactant at low pH values. This may be attributed to the highly positive surface charges created in an acidic solution and the assumed conformation of the surfactant at these pH values. As the pH of the suspension increases the surfaces of the particles become more negatively charged. At the same time, the negatively charged polymer will become increasingly negative as the pH of the suspension is increased. Both of these factors will contribute to the lack of adsorption at high pH values.

Adsorption data generated for the individual oxides obtained in this study agree nicely with the individual adsorption studies done by Pettersson et al.³ Cesarano III et al.,⁹ and Strauss et al.¹⁹ ZrO_2 has a very specific adsorption for polyacrylate-type surfactants which is why the work reported here is in good accordance with the data supplied by Pettersson et al.,³ Sun,²¹ and Tang.²⁹

5.8 Zeta Potential Results

The Smoluchowski zeta potential was reported for each suspension at four pH values. Calculating the properties of the particles in a suspension requires that the properties for the dispersing medium be put into the AcoustoSizer. The values used for zeta potential measurements in the AcoustoSizer for the dispersing medium (water) were a dielectric constant of 78.8, a viscosity of 0.997 centipoise, and a density of 0.997 g/cm³.

The data shown in Figures 34-37 show how the addition of the surfactant and the pH of the suspension affect the zeta potential of the particles. The reported zeta potential for each pH value is an average of two runs made consecutively over the course of approximately 30 minutes. A variance of ± 0.5 mV was witnessed between the two runs making the error of the technique approximately 1% for consecutive runs on the same day.

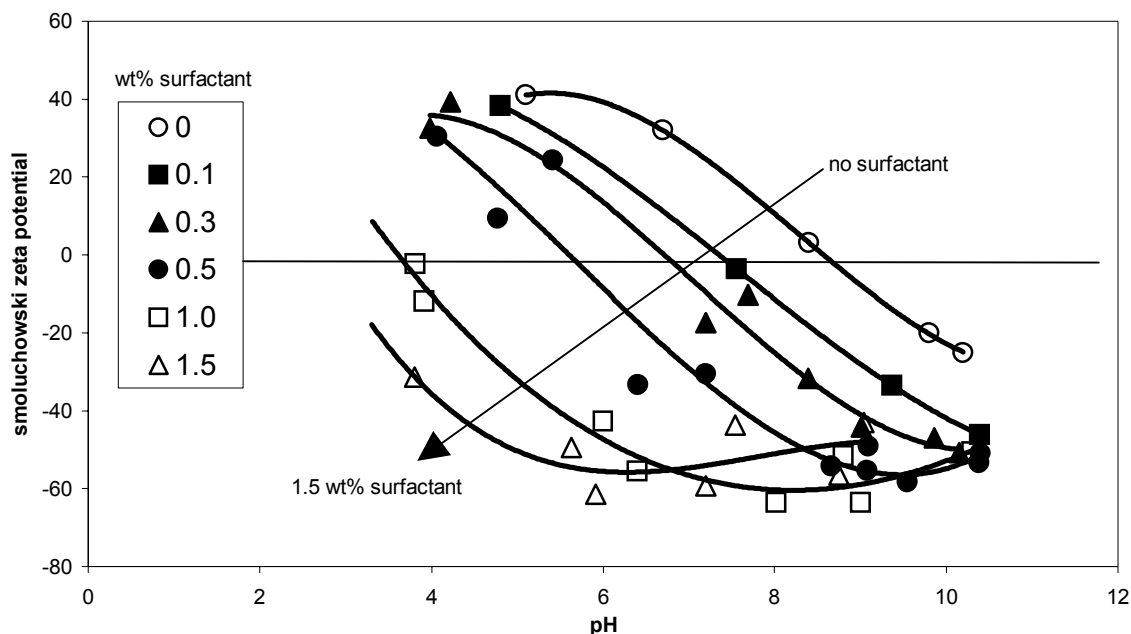


Figure 34. Measured zeta potential values for 20 wt% Al₂O₃ suspensions as a function of the initial surfactant level and pH.

The adsorption of the surfactant appears to reduce the zeta potential of the Al₂O₃ particles. This is most likely due to the negative charge created by the adsorption of the surfactant. The measurements for the raw powder in suspension show an IEP for Al₂O₃ of 8.5. This value readily agrees with reported values.^{37,49}

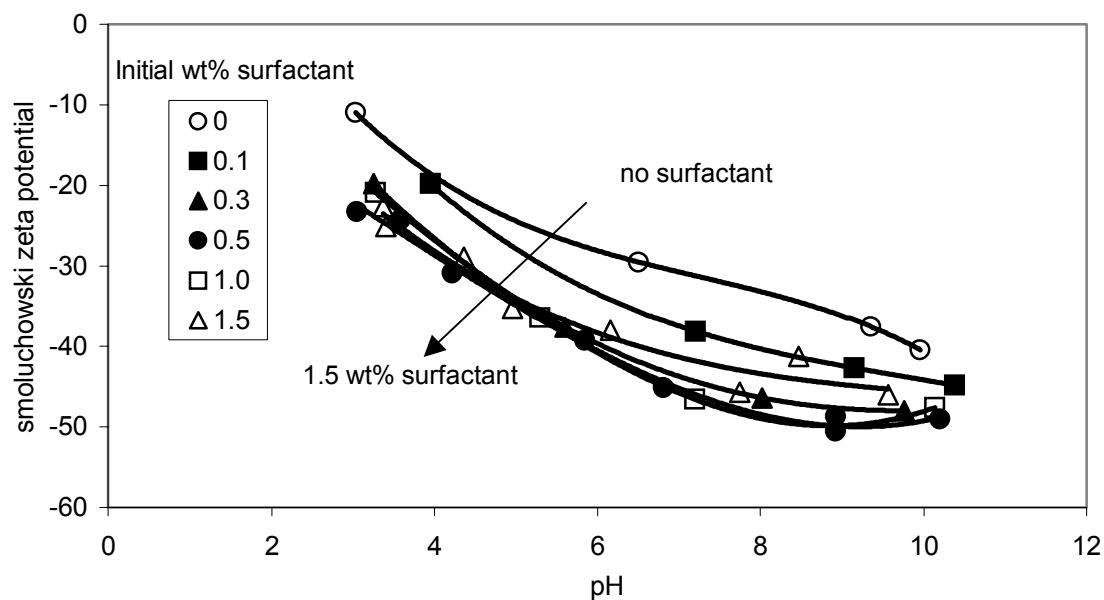


Figure 35. Measured zeta potential for 20 wt% SiO₂ suspensions as a function of the initial surfactant level and pH.

Extrapolation of the 0 wt% surfactant line leads to an IEP for SiO₂ of 2.2, which is within the range of previously reported values.³⁷ Due to the adsorption behavior witnessed in Figures 27 and 31, SiO₂ will not adsorb the surfactant. The low adsorption of the surfactant provides a simple explanation as to why the zeta potential of SiO₂ suspensions does not readily decrease with increasing surfactant levels.

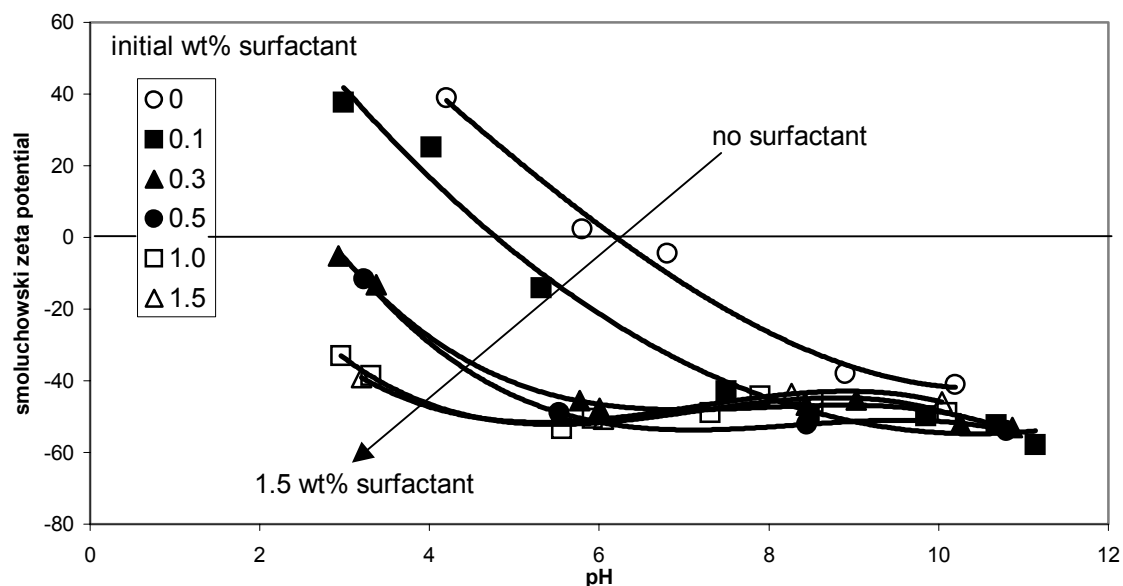


Figure 36. Measured zeta potential values for 20 wt% TiO_2 suspensions as a function of the initial surfactant level and pH.

The IEP for TiO_2 was found to be at a pH of 6.5. This agrees with previously reported data.^{37,49} The zeta potential of the TiO_2 particles in suspension appear unaffected by the surfactant at pH values above 6 for initial surfactant levels of 0.3 wt% and higher.

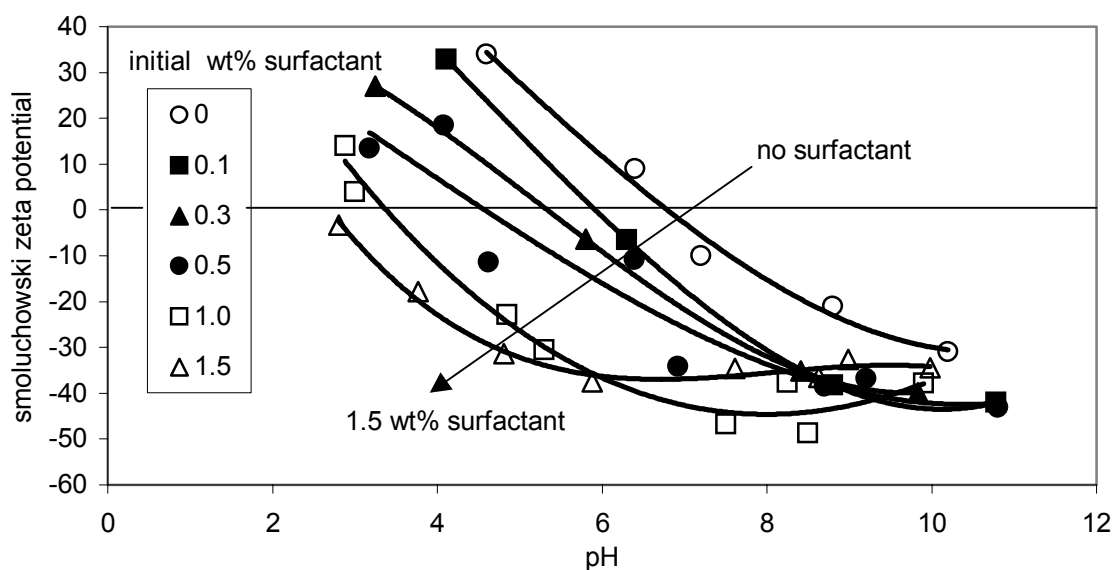


Figure 37. Zeta potential for ZrO_2 suspensions across the pH range 3-11 as a function of the initial surfactant level.

The IEP of the ZrO_2 was found to be at a pH of 6.8. This agrees with previously reported data for pure ZrO_2 particles.^{37,49} As the pH was increased to a value greater than 8, the zeta potential of the particles seemed to be unaffected. The consistency of more negative surfaces being created by the adsorption of the surfactant follows true for the ZrO_2 suspensions. The iso-electric points measured for the four oxides are reported and compared to the values previously reported in Table I from the literature in Table IX.

Table IX. Measured Iso-electric Points for Oxides Used

Powder	Iso-electric point (pH) (from Reed) ³⁷	Measured Iso-electric point (from AcoustoSizer)
$\alpha\text{-Al}_2\text{O}_3$	7-9.5	8.5
SiO_2	3-4	2.2
TiO_2	4-6	6.5
ZrO_2	4-5	6.8

5.9 Repeatability of Data

The matrix of twenty suspensions was completed during the course of an approximate two month period, in the summer of 2003. Random suspensions were selected for repeat measurements in the spring of 2004 in order to test the repeatability of the measurement techniques. Table X shows the measured zeta potential and unadsorbed surfactant levels detected on similar samples measured approximately seven months apart.

Table X. Repeatability of Measurements

Date	Time (months)	Sample	ID	pH	zeta potential ($\pm 0.5\text{mV}$)	difference (mV)	Unads. Surf. (g surf. / g H ₂ O)	difference
7/24/2003	5.50	Al ₂ O ₃	KG91	9.01	-44.20	4.85	0.00029	0.00004
1/5/2004		0.3 wt% surfactant	KG159	9.13	-39.35		0.00025	
8/6/2003	7.50	Al ₂ O ₃	KG122	3.80	-31.35	7.40	0.00051	0.00013
3/31/2004		1.5 wt% surfactant	KG226	3.81	-38.75		0.00064	
5/28/2003	8.00	SiO ₂	KG15	3.82	-50.55	1.85	0.00109	0.00016
1/20/2004		0.5 wt% surfactant	KG188	3.82	-48.70		0.00125	
8/7/2003	7.50	SiO ₂	KG127	8.66	-46.00	4.75	0.00380	0.00060
3/25/2004		1.5 wt% surfactant	KG223	8.47	-41.25		0.00440	
6/27/2003	6.00	TiO ₂	KG40	11.14	-57.85	5.60	0.00044	0.00014
12/17/2004		0.1 wt% surfactant	KG151	10.68	-52.25		0.00058	
7/3/2003	8.50	TiO ₂	KG48	5.92	-50.50	2.85	0.00072	0.00030
3/24/2004		1.0 wt% surfactant	KG211	5.56	-53.35		0.00102	
5/28/2003	10.00	ZrO ₂	KG14	9.20	-36.85	1.60	0.00007	0.00042
3/23/2004		0.5 wt% surfactant	KG216	8.70	-38.45		0.00049	
8/11/2003	7.50	ZrO ₂	KG135	9.00	-35.99	3.39	0.00190	0.00080
3/25/2004		1.5 wt% surfactant	KG224	8.99	-32.60		0.00110	
					AVERAGE	4.04		0.00029

The data shown in Table X shows that the zeta potential measurements varied by an average of 4.04 mV over the seven-month time span between samples. The unadsorbed surfactant amounts can be considered repeatable to 0.29 mg surfactant/g H₂O in the supernatant. This data should not be confused with the repeatability of two consecutive zeta potential measurements. As previously reported, the zeta potential values for suspensions were an average of two consecutive runs over the course of approximately 30 minutes. These two runs were considered repeatable to within ± 0.5 mV. The repeatability of the same value for the zeta potential on a similar suspension seven months later was determined to be ± 4.04 mV.

5.10 Predicting Zeta Potential and Unadsorbed Surfactant Levels

Once the raw data for each oxide system was compiled the adsorption isotherms were created. The measured zeta potentials values reported in Figures 32-35 were then melded with the adsorption data in Figures 24-31 to produce zeta potential values as a function of initial surfactant level at various pH values. A typical plot showing the zeta potential values for two oxide suspensions at a specific pH value can be seen in Figure 38.

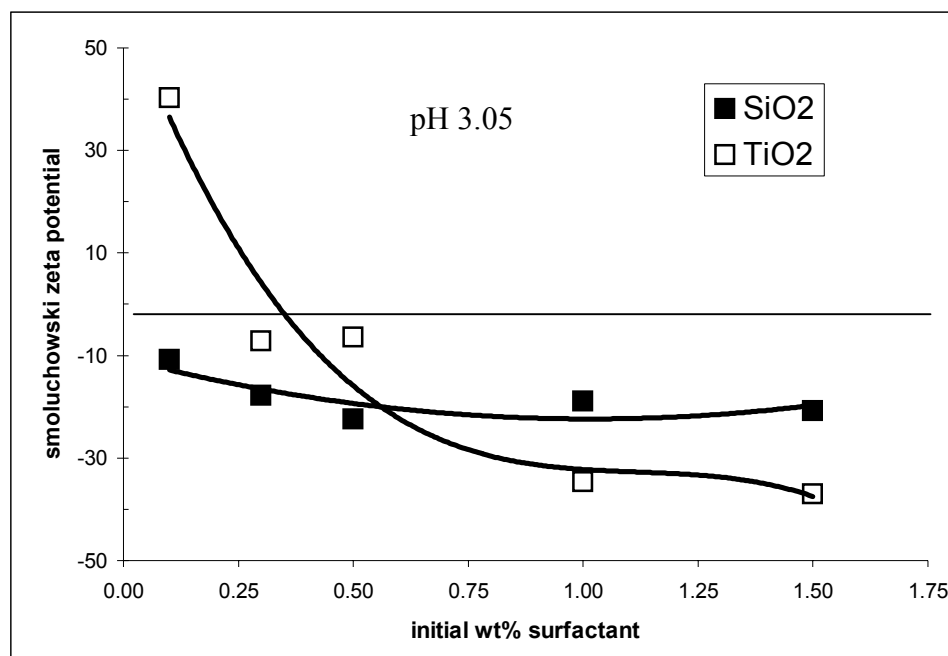


Figure 38. Combined zeta potential values for TiO₂ and SiO₂ suspensions as a function of initial surfactant level. Data shown above is for suspensions at a pH of 3.05.

The goal of combining the data from two individual oxide suspensions was to predict what would happen if they were mixed together. Mixed oxide systems were prepared in a manner consistent with the single oxide systems according to the flow chart in Figure 6. Total powder additions were always twenty weight-percent of the total suspension. Typically two oxides were blended at ten weight-percent each oxide. Eighty weight-percent was considered to be de-ionized water and surfactant. Surfactant additions were again based on the dry weight of the total powder added to the suspension.

Zeta potential measurements were made on the AcoustoSizer using average values for the density and dielectric constants of the powders in the suspension. Dissolved ion subtractions were made using the full subtraction curve assuming that enough powder existed to produce the equilibrium dissolved concentration of ions at the given pH.

Once the suspension properties and titrations had been completed, the simulation procedure began. The data created from the single oxide adsorption study was used to predict the zeta potential and adsorption behavior of the mixed oxide suspensions at the pH values measured. The process was not performed in the reverse manner due to the changing pH conditions after milling and the difficulty of creating suspensions at specific pH values.

Figure 39 is an account for all surfactant added to a $\text{TiO}_2\text{:SiO}_2$ suspension. The amount of surfactant adsorbed on each oxide is shown by the solid black lines while light gray line on the top of the plot shows the amount of surfactant adsorbed onto each powder plus the amount detected via titration.

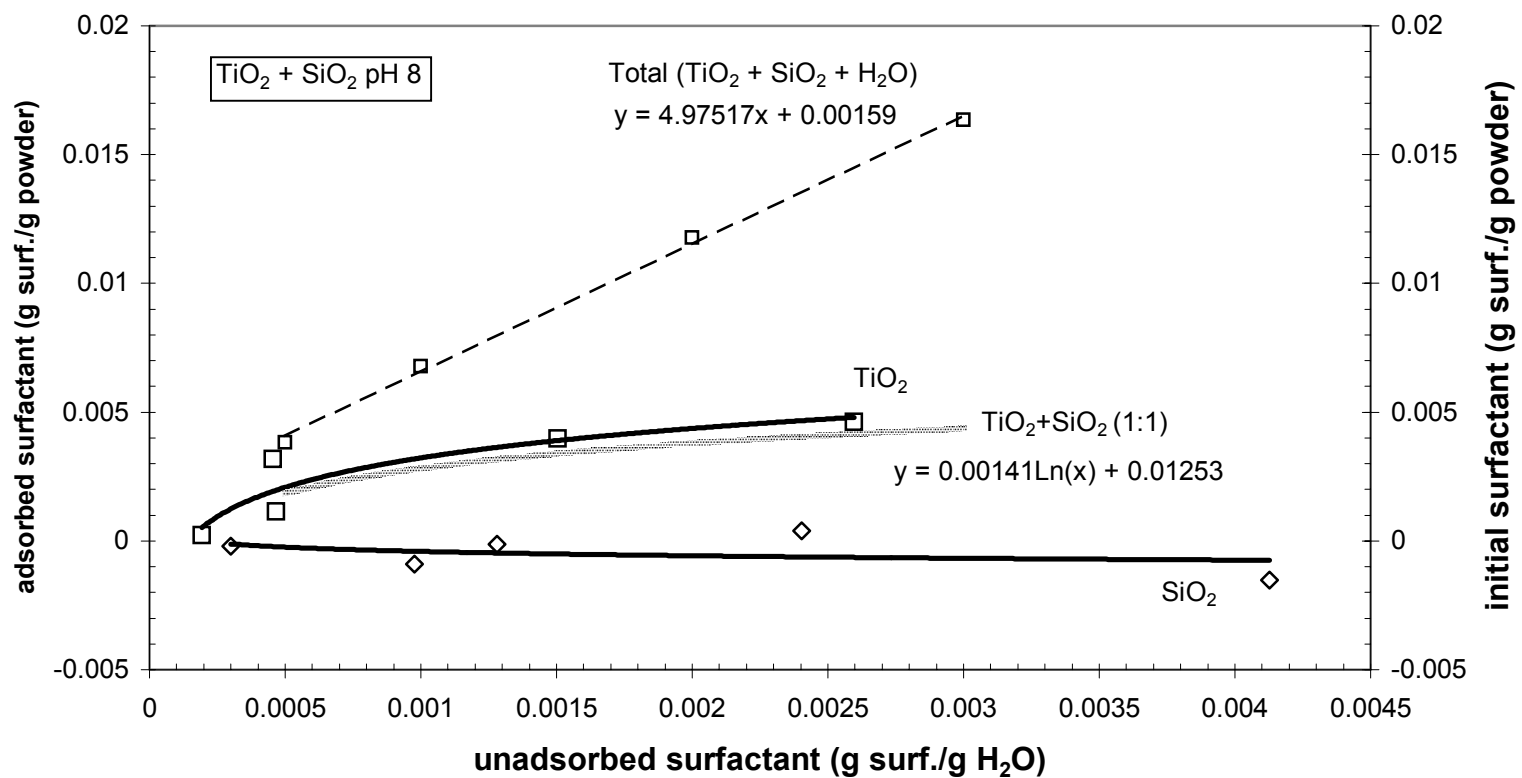


Figure 39. Plot used for the prediction of the unadsorbed surfactant levels to be found in the supernatant solutions of mixed oxide systems. This model is for the $\text{TiO}_2/\text{SiO}_2$ system with a pH of 8.0. Instructions for using the plot above are given in the text on the pages following.

Notice that Figure 39 is constructed from the two individual adsorption studies using TiO_2 and SiO_2 . The data was taken from Figures 28 and 32 for the TiO_2 and Figures 27 and 31 for SiO_2 at pH values of 8.0. The right hand y-axis in Figure 39 shows the initial amount of surfactant added on a weight basis to the powder. The left hand y-axis shows the amount of surfactant adsorbed on the powder surfaces on a weight basis to the powder. The x-axis shows the amount of surfactant unadsorbed in solution.

The lines shown on the plot are important to the prediction process. The two solid lines represent the individual adsorption behavior for TiO_2 and SiO_2 at a pH of 8.0. The shaded line corresponds to the addition of half of each solid line. The addition of half of each line is because mixed oxide suspensions are on a 1:1 weight basis. All suspensions are 20 wt% powder, so each oxide actually represents 10 wt% of the suspension. The three previous lines should be analyzed using the left hand y-axis. The dashed line accounts for the total amount of surfactant that should be found in the suspension, including adsorbed and unadsorbed surfactant. If the initial surfactant level is plugged into the fit function for the dashed line, the predicted level of unadsorbed surfactant will result.

Plots similar to the one shown in Figure 39 were created for multiple mixed oxide suspensions. Similar plots for $\text{Al}_2\text{O}_3\text{:SiO}_2$, $\text{Al}_2\text{O}_3\text{:ZrO}_2$, $\text{TiO}_2\text{:SiO}_2$, and $\text{TiO}_2\text{:ZrO}_2$ suspensions are shown in the Appendix. Table XI gives a representation of the accuracy of the predictions for measured zeta potential of the mixed oxide suspensions and the measured residual surfactant levels for the same suspensions.

Table XI. Predicted vs. Measured Zeta Potential and Unadsorbed Surfactant Levels

Powders	pH	Initial Surfactant	Surfactant		Zeta Potential	
			Predicted	Measured	Predicted	Measured
Units →		wt %	mg surf. / g H ₂ O	mg surf. / g H ₂ O	mV	mV
Al ₂ O ₃ :SiO ₂	3.85	0.5	0.57	-0.26	-12.5	-10.4
Al ₂ O ₃ :SiO ₂	5.60	0.7	0.30	0.47	-31.9	-32.6
Al ₂ O ₃ :SiO ₂	7.90	0.5	0.23	0.48	-44.4	-53.4
Al ₂ O ₃ :ZrO ₂	5.90	0.5	0.64	0.24	2.1	-20.8
Al ₂ O ₃ :ZrO ₂	8.75	0.5	0.21	0.22	-40.2	-41.1
TiO ₂ :SiO ₂	3.05	0.5	0.24	0.33	-18.7	-21.9
TiO ₂ :SiO ₂	8.00	0.5	0.69	1.29	-44.0	-43.7
TiO ₂ :ZrO ₂	6.52	0.7	0.16	0.14	-38.0	-35.9
TiO ₂ :ZrO ₂	10.49	0.7	1.27	1.03	-44.6	-37.4
Al ₂ O ₃ :TiO ₂ :ZrO ₂	3.65	1.0	0.11	0.00	19.7	-10.0
Al ₂ O ₃ :TiO ₂ :ZrO ₂	6.0	1.0	0.13	0.62	-47.9	-47.7

The predicted values seem somewhat accurate for some of the mixed oxide systems. As shown above, the predicted values for the residual surfactant level to be found in solution are consistently deviated from the actual measured value, and are not considered to be good predictions for the unadsorbed surfactant levels. The zeta potential values seem relatively close to the predicted values for most systems.

6 Summary and Conclusions

The methods employed in this work to characterize the degree of adsorption of common industrial oxides with a NH_4 -polyacrylate type surfactant were very similar to those used in past work examined. Although the surfactant studied was somewhat different to those studied in the past, it proved to show very similar adsorption behavior to other NH_4 -polyacrylate surfactants on the same oxides. The adsorption behavior of the proprietary surfactant has been duly characterized for four common industrial oxides and this work should provide sufficient aid in the processing of such oxides with similar surfactants.

The process of using single oxide adsorption and zeta potential data to predict the properties of mixed oxide suspensions is a novel concept and proved to be accurate to some degree. The prediction process does appear to be in need of refinement due to the fact that several predicted values were somewhat different than the measured values for zeta potential. The zeta potential predictions were even oppositely charged when compared to the actual measured values at times. Perhaps the averaging of the zeta potential values from the single oxides is somewhat of a raw method, but seemed to be a decent method for an initial study. The methods shown in Figure 39 for predicting the level of unadsorbed surfactant did not produce sufficient accuracy. The averaging of the adsorption levels for suspensions containing SiO_2 was most likely a key problem in the prediction process. Any suspension with SiO_2 will have effectively twice the surfactant available for the other oxides in the suspensions. The idea of merging single oxide adsorption data in an attempt to predict the results for a mixed suspension was novel and showed some degree of success. Further modification of the prediction process is indeed necessary for this method to prove its merit however.

7 Future Work

There are many avenues that may be explored which may yield improvement to this work. The adsorption data produced for the single oxide suspensions agrees readily with historical work and has been shown to be repeatable. The prediction process seems to be in need of some refinement.

In order to properly correct for the dissolved ions in solution, ICP should be employed as the sole method for correcting for their contribution to the titration. Data shown in Figures 22-25 shows good correlation between the dissolved ion concentration and the KOH requirement in the titration. With exact dissolved ion levels, this correction has the potential to become very accurate.

The prediction process will also benefit from the improved dissolved ion correction. Each specific ion in solution will have a different affect on the titration, with the determination of exact amounts for mixed oxide suspensions; multiple dissolved ion corrections would be elementary and would most likely produce data that gives a better representation of the unadsorbed surfactant levels in solution.

7.1 Hamaker Constant Evaluation

The basis of a study such as the one performed here should be quite evident to the reader. The need for the determination of processing conditions that will create optimal stability in oxide suspensions is necessary for all industrial ceramic arenas. Such conditions cannot be properly distinguished for mixed oxide suspensions without considering the nature of the interactions between the particles in suspension.

The surface forces between two bodies in close proximity play an important role in area such as adhesion, wetting, adsorption, flocculation, and rheology.⁵ There are many surface forces that can be acting between two particles in suspension, but the one force that always exists is the van der Waals attractive potential. The Hamaker constant is an easy way to represent the magnitude of the van der Waals attractive forces for different materials. The van der Waals attractive potential was given in Equation [1] for two spheres at a small separation distance. The spheres can be taken as a rough approximation to the oxide particles in a ceramic suspension. The methods by which the Hamaker constant can be calculated are somewhat laborious and were investigated fully

by Bergstrom.⁵ Full Lifshitz theory was used to calculate the Hamaker constants using water as the dispersing medium between neighboring particles. Table XI shows the calculated Hamaker constants for the materials used in this study.

Table XII. Hamaker Constants for Oxides Used with Water as the Dispersion Medium

Material	Hamaker Constant (10^{-20} Joule)*
α -Al ₂ O ₃	3.67
SiO ₂ (quartz)	1.02
TiO ₂	5.35
3Y-ZrO ₂	7.23

*5

The different values for Hamaker constants can be quite significant when it comes to determining the stability of a colloidal system. The Hamaker constant is related to the attraction that two like particles will have for one another. A larger Hamaker constant is evidence of a greater attraction between the like particles. In order to effectively stabilize particles with a large attraction for one another, one must induce an even larger repulsive force. Table VI shows that TiO₂ has approximately five times the interaction with a neighboring TiO₂ particle than two similar SiO₂ particles in suspension. The same repulsive force will lead to much different stability in the two systems. This draws a question as to the validity of the statement posed by Colloidal Dynamics, “If one is relying on the electric charge alone to keep the system in a disperse state then the zeta potential will usually need to be kept above 25 mV.”⁵⁰ It is evident that a zeta potential of 25 mV will provide different stability to suspensions of different oxides based on the Hamaker constant values shown in Table XII.

If an adsorbed surfactant can mask the Hamaker constant between two particles, then one zeta potential will be sufficient to ensure the stability of equally sized particles in suspension at the same separation. Due to the fact that SiO₂ adsorbs the surfactant in a much different manner than the other three oxides in this study, its Hamaker constant will most likely be affected much differently than the other oxides at the same surfactant level. This may mean that two SiO₂ particles would require less of a repulsive force (zeta potential) than two Al₂O₃ particles of the same size and same separation to induce stability.

The answer to this problem must be established if a threshold value for zeta potential is to be determined. Without the knowledge of how adsorbed surfactant layers will affect the interactive potentials between two like surfaces, an accurate prediction of a necessary repulsive force for stability cannot be made.

Figure 40 gives a representation of the adsorbed layers of Na-PMAA onto mica surfaces. These adsorbed layer thicknesses were measured by Cesarano⁵¹ at pH values of 3.3 and 9.3 under different background electrolyte conditions.

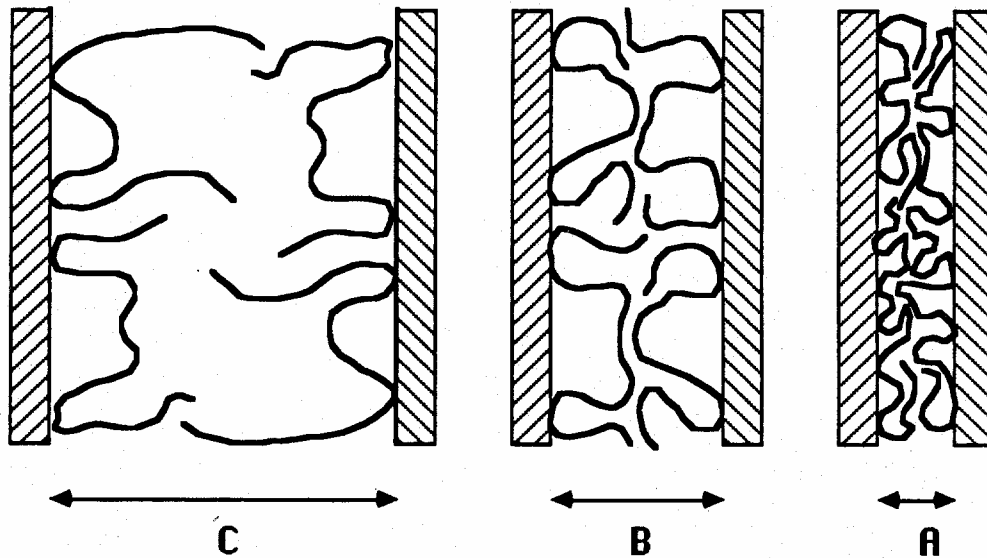


Figure 40. Schematic of adsorbed PMAA layers overlapping as particles approach one another in suspension. Image taken from Cesarano⁵¹ with permission. The terms are described below.

- A represents twice the collapsed layer thickness
- B is twice the loop thickness
 - B/2 is a relative measure of the overall average adsorbed thickness
- C is twice the maximum tail length to loop thickness.

Using the adsorbed layer thicknesses and the equations used to calculate Hamaker constants, Cesarano⁵¹ calculated the repulsive forces generated by adsorbed Na-PMAA on approaching Mica surfaces in different background electrolyte solutions. The data generated is shown in Table XIII.

Table XIII. Measured Adsorption Layer Thickness and Surface Forces for PMAA on Mica⁵¹

pH	[NaCl] M	A (Å)	B (Å)/(μN/m)	C (Å)/(μN/m)
3.3	0.003	58	90 / 1600	280 / 60
	0.05	54	85 / 1100	275 / 20
	0.1	47	81 / 830	235 / 30
	0.2	52	83 / 750	210 / 15
9.3	0.003	41	79 / 2600	260 / 125
	0.05	29	55 / 2800	240 / 100
	0.1	14	30 / 3300	220 / 90
	0.2	17	27 / 4100	180 / 60 *

Values for column B can be used as estimates for the adsorbed layer thicknesses and repulsive forces for common oxide suspensions. For calculations of Hamaker constants and the adsorbed layer affect on this value, the numbers in column B should be used. The separation distance given in column B is twice the average adsorbed layer thickness. The average thickness for adsorbed Na-PMAA in 0.003 M NaCl background electrolyte is 42.25 angstroms (4.225×10^{-9} m) should be used for any calculations of this parameter.

References

1. A.G. King, *Ceramic Technology and Processing*. Noyes Publications/William Andrew Publishing, Norwich, NY, 2002.
2. P.C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, 3rd ed. Marcel Dekker, New York, 1997.
3. A. Pettersson, G. Marino, A. Pursiheimo, and J.B. Rosenholm, "Electrosteric Stabilization of Al_2O_3 , ZrO_2 , and 3Y- ZrO_2 Suspensions; Effect of Dissociation and Type of Polyelectrolyte," *J. Colloid Interface Sci.*, **228** [1] 73-81 (2000).
4. J.A. Lewis, "Colloidal Processing of Ceramics," *J. Am. Ceram. Soc.*, **83** [10] 2341-2359 (2000).
5. L. Bergstrom, "Hamaker Constants of Inorganic Materials," *Adv. Colloid Interface Sci.*, **70**, 125-169 (1997).
6. D.H. Napper, *Polymeric Stabilization of Colloidal Dispersions*; Ch.1. Academic Press, London, 1983.
7. M.N. Rahaman, *Ceramic Processing and Sintering*; Ch. 4. Marcel Dekker, New York, 1995.
8. J. Cesarano III and I.A. Aksay, "Processing of Highly Concentrated Aqueous alpha-Alumina Suspensions Stabilized with Polyelectrolytes," *J. Am. Ceram. Soc.*, **71** [12] 1062-1067 (1988).
9. J. Cesarano III and I.A. Aksay, "Stability of Aqueous alpha- Al_2O_3 Suspensions with Poly(methacrylic acid) Polyelectrolyte," *J. Am. Ceram. Soc.*, **71** [4] 250-255 (1988).
10. B.J. Briscoe, A.U. Khan, and P.F. Luckham, "Optimising the Dispersion on an Alumina Suspension Using Commercial Polyvalent Electrolyte Dispersants," *J. Eur. Ceram. Soc.*, **18** [14] 2141-2147 (1998).
11. Y. Liu and L. Gao, "Dispersion of Aqueous Alumina Suspensions Using Copolymers with Synergistic Functional Groups," *Mater. Chem. Phys.*, **82** [2] 362-369 (2003).
12. Z. Xie, J. Ma, Q. Xu, Y. Huang, and Y.-B. Cheng, "Effects of Dispersants and Soluble Counter-Ions on Aqueous Dispersability of Nano-Sized Zirconia Powder," *Ceram. Int.*, **30** [2] 219-224 (2004).
13. R. Arnold and J.T.G. Overbeek, "The Dissociation and Specific Viscosity of Polymethacrylic Acid," *Rec. Trav. Chim. Pays-Bas.*, **69**, 192-206 (1950).

14. J.E. Gebhardt and D.W. Fuerstenau, "Adsorption of Polyacrylic Acid at Oxide/Water Interfaces," *Colloids Surf.*, **7** [3] 221-231 (1983).
15. J.-P. Boisvert, J. Persello, A. Foissy, J.-C. Castaing, and B. Cabane, "Effect of Surface Charge on the Adsorption Mode of Sodium Poly(acrylate) on Alumina-Coated TiO₂ Used as Coating Pigment," *Colloids Surf., A*, **168** [3] 287-296 (2000).
16. J. Davies and J.G.P. Binner, "The Role of Ammonium Polyacrylate in Dispersing Concentrated Alumina Suspensions," *J. Eur. Ceram. Soc.*, **20** [10] 1539-1553 (2000).
17. P.C. Hidber, T.J. Graule, and L.J. Gauckler, "Competitive Adsorption of Citric Acid and Poly(vinyl alcohol) onto Alumina and Its Influence on the Binder Migration during Drying," *J. Am. Ceram. Soc.*, **78** [7] 1775-1780 (1995).
18. J.-H. Jean and H.-R. Wang, "Dispersion of Aqueous Barium Titanate Suspensions with Ammonium Salt of Poly(methacrylic acid)," *J. Am. Ceram. Soc.*, **81** [6] 1589-1599 (1998).
19. H. Strauss, H. Heegn, and I. Strienitz, "Effect of PAA Adsorption on Stability and Rheology of TiO₂ Dispersions," *Chem. Eng. Sci.*, **48** [2] 323-332 (1993).
20. Y. Liu, L. Gao, and J. Guo, "Comparative Study on the Stabilizing Effect of 2-phosphonobutane-1,2,4-tricarboxylic Acid and Citric Acid for Alumina Suspensions," *Colloids Surf., A*, **193** [1-3] 187-195 (2001).
21. J. Sun, L. Gao, and J. Guo, "Influence of the Initial pH on the Adsorption Behaviour of Dispersant on Nano Zirconia Powder," *J. Eur. Ceram. Soc.*, **19** [9] 1725-1730 (1999).
22. J. Wang and L. Gao, "Adsorption of Polyethylenimine on Nanosized Zirconia Particles in Aqueous Suspensions," *J. Colloid Interface Sci.*, **216** [2] 436-439 (1999).
23. M.P. Albano, L.B. Garrido, and A.B. Garcia, "Surface Modification and Ammonium Polyacrylate Adsorption on Si₃N₄ Powders" (1999) Centro de Tecnologia de Recursos Minerales y Ceramica. Accessed on: January 8, 2004. Available at <www.ceramicabrasil.com/biblioteca/documentos/459.doc>
24. A.K. Berry, L.E. Bogan, and S.E. Agostine, "Adsorption of Organic Additives on Powder Surfaces," *Ceram. Trans.*, **62**, 125-132 (1996).
25. L. Luciani and R. Denoyel, "Adsorption of Polydisperse Surfactants on Solid Surfaces: An Ellipsometric Study," *J. Colloid Interface Sci.*, **188** [1] 75-80 (1997).

26. A.A. Zaman, R. Tsuchiya, and B.M. Moudgil, "Adsorption of a Low-Molecular-Weight Polyacrylic Acid on Silica, Alumina, and Kaolin," *J. Colloid Interface Sci.*, **256** [1] 73-78 (2002).
27. Y. Liu and L. Gao, "Effect of 2-Phosonobutane-1,2,4-tricarboxylic Acid Adsorption on the Stability and Rheological Properties of Aqueous Nanosized 3-mol%-Yttria-Stabilized Tetragonal-Zirconia Polycrystal Suspensions," *J. Am. Ceram. Soc.*, **86** [7] 1106-1113 (2003).
28. P.H. McCluskey, R.L. Snyder, and S. R.A. Condrate, "Infrared Spectral Studies of Various Metal Polyacrylates," *J. Solid State Chem.*, **83** [2] 332-339 (1989).
29. F. Tang, X. Huang, L. Wang, and J. Guo, "Infrared Spectral Studies of Ammonium Polyacrylate Adsorbed on Nano-Zirconia Powder Surfaces," *Nanostruct. Mater.*, **11** [7] 861-866 (1999).
30. J. Wang and L. Gao, "Surface Properties of Polymer Adsorbed Zirconia Nanoparticles," *Nanostruct. Mater.*, **11** [4] 451-457 (1999).
31. J. Billingham, C. Breen, and J. Yarwood, "Adsorption of Polyamine, Polyacrylic Acid and Polyethylene Glycol on Montmorillonite: An in Situ Study Using ATR-FTIR," *Vib. Spectrosc.*, **14** [1] 19-34 (1997).
32. M. Muller, M. Brissova, T. Rieser, A.C. Powers, and K. Lunkwitz, "Deposition and Properties of Polyelectrolyte Multilayers Studied by ATR-FTIR Spectroscopy," *Mater. Sci. Eng., C*, **8-9**, 163-169 (1999).
33. K. Vermöhlen, H. Lewandowski, H.-D. Narres, and E. Koglin, "Adsorption of Polyacrylic Acid on Aluminum Oxide: DRIFT Spectroscopy and Ab Initio Calculations," *Colloids Surf., A*, **170** [2-3] 181-189 (2000).
34. Z. Pan, A. Campbell, and P. Somasundaran, "Polyacrylic Acid Adsorption and Conformation in Concentrated Alumina Suspensions," *Colloids Surf., A*, **191** [1-2] 71-78 (2001).
35. A. Fan, P. Somasundaran, and N.J. Turro, "Role of Sequential Adsorption of Polymer/Surfactant Mixtures and Their Conformation in Dispersion/Flocculation of Alumina," *Colloids Surf., A*, **146** [1-3] 397-403 (1999).
36. T. Reihls, M. Muller, and K. Lunkwitz, "Deposition of Polyelectrolyte Complex Nano-Particles at Silica Surfaces Characterized by ATR-FTIR and SEM," *Colloids Surf., A*, **212** [1] 79-95 (2003).
37. J.S. Reed, *Principles of Ceramic Processing*, 2nd ed.; p. 152. John Wiley & Sons, New York, 1995.

38. G.B. Kenne and H.K. Bowen, "High-Tech Ceramics in Japan: Current and Future Markets," *Am. Ceram. Soc. Bull.*, **62** [5] 590-596 (1982).
39. (2004) US-Silica. Accessed on: May 5, 2004. Available at <<http://www.u-s-silica.com/mus.htm>>
40. (2004) Ishihara Sangyo Kaisha. Accessed on: May 4, 2004. Available at <http://web.inetba.com/ishiharacorpusa/high_purity.html>
41. *Handbook of Chemistry and Physics*, 73rd ed. Edited by D. R. Lide. CRC Press, Boca Raton, 1992.
42. K.W. Seitz, "Oxygen Reduction in Direct Nitrided Aluminum Nitride"; Master's Thesis. Alfred University, Alfred, NY, 1999.
43. S.G. Malghan, H. Hausner, R. Pompe, J. Tsubaki, and S.M. Hsu, "Development and Testing of Procedures for Characterization of Ceramic Powders," Oak Ridge National Laboratory, September, 1993.
44. R.W. O'Brien, "Electro-acoustic Effects in a Dilute Suspension of Spherical Particles," *J. Fluid Mech.*, **190**, 71-86 (1988).
45. R.W. O'Brien, D.W. Cannon, and W.N. Rowlands, "Electroacoustic Determination of Particle Size and Zeta Potential," *J. Colloid Interface Sci.*, **173** [2] 406-418 (1995).
46. S.E. Gibb and R.J. Hunter, "Dynamic Mobility of Colloidal Particles with Thick Double Layers," *J. Colloid Interface Sci.*, **224** [1] 99-111 (2000).
47. R.M. Silverstein and F.X. Webster, *Spectrometric Identification of Organic Compounds*, 6th ed.; Ch. 3, John Wiley & Sons, New York, 1998.
48. C.F. Baes, *The Hydrolysis of Cations*. Wiley, New York, 1976.
49. G.A. Parks, "The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems," *Chem. Rev.*, **65** [2] 177-198 (1965).
50. "Electroacoustics Tutorials" (1999) Colloidal Dynamics. Accessed on: April 29, 2004. Available at <www.colloidal-dynamics.com>
51. J. Cesarano III, "Polyelectrolyte Stabilization and Polysaccharide Gelation of Aqueous Alumina Suspensions"; PhD Thesis. University of Washington, Seattle, WA, 1989.

Appendix

Figures 41-50 represent the prediction plots for unadsorbed surfactant levels of mixed oxide suspensions reported in table XI.

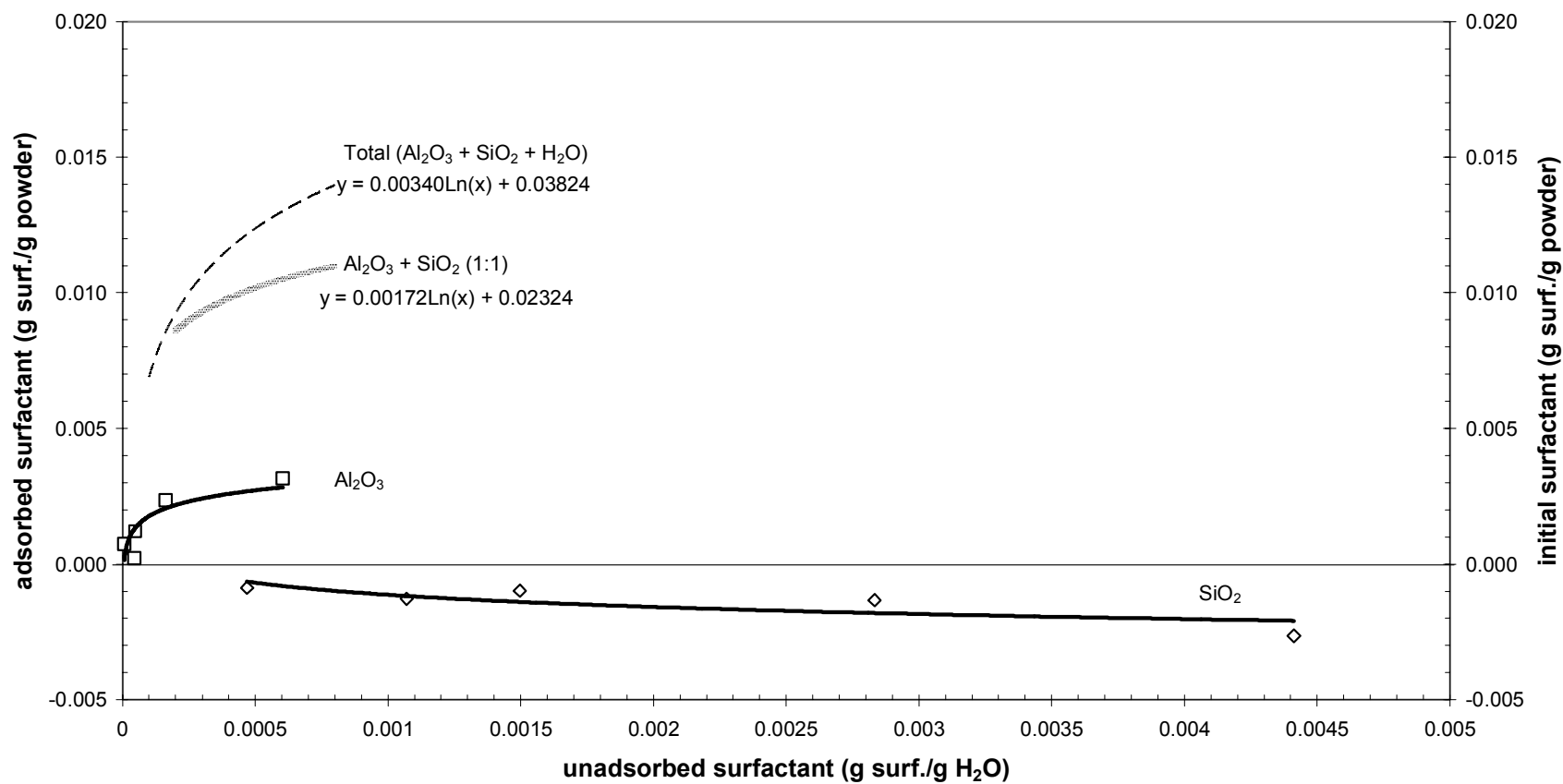


Figure 41. Unadsorbed surfactant prediction plot for an $\text{Al}_2\text{O}_3 / \text{SiO}_2$ suspension at a pH of 3.85.

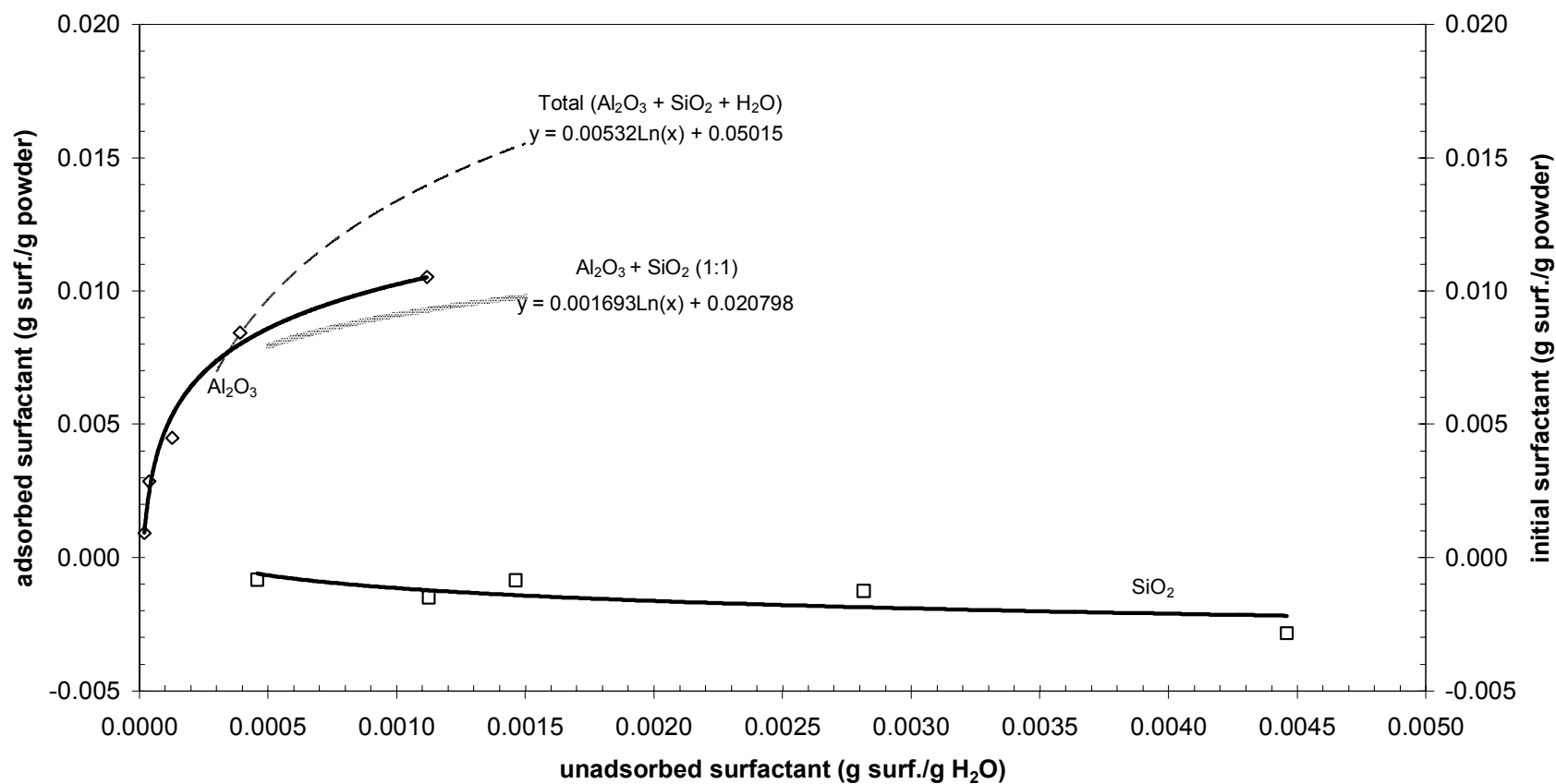


Figure 42. Unadsorbed surfactant prediction plot for an Al₂O₃ / SiO₂ suspension at a pH of 5.60.

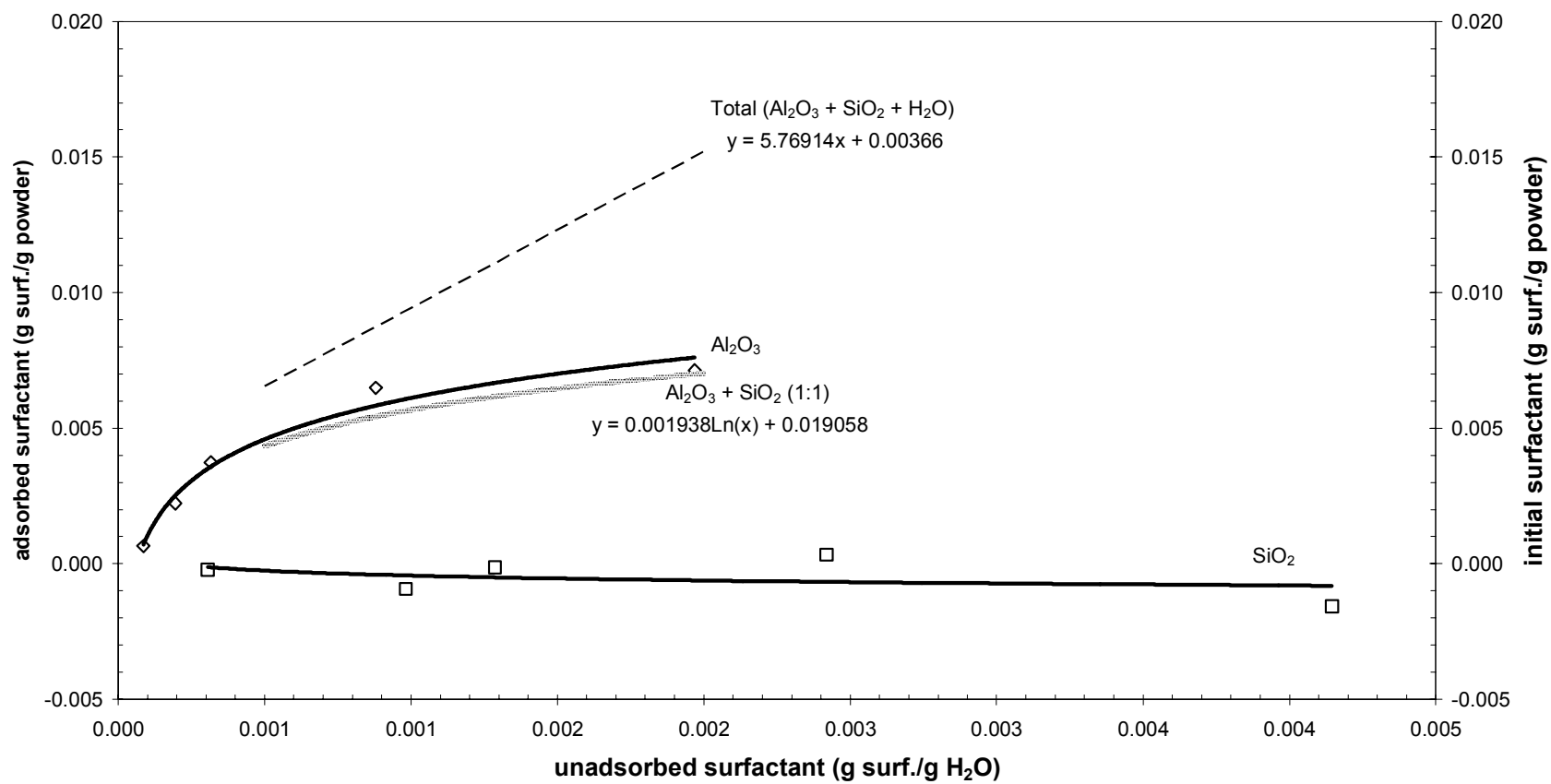


Figure 43. Unadsorbed surfactant prediction plot for an Al₂O₃ / SiO₂ suspension at a pH of 7.90.

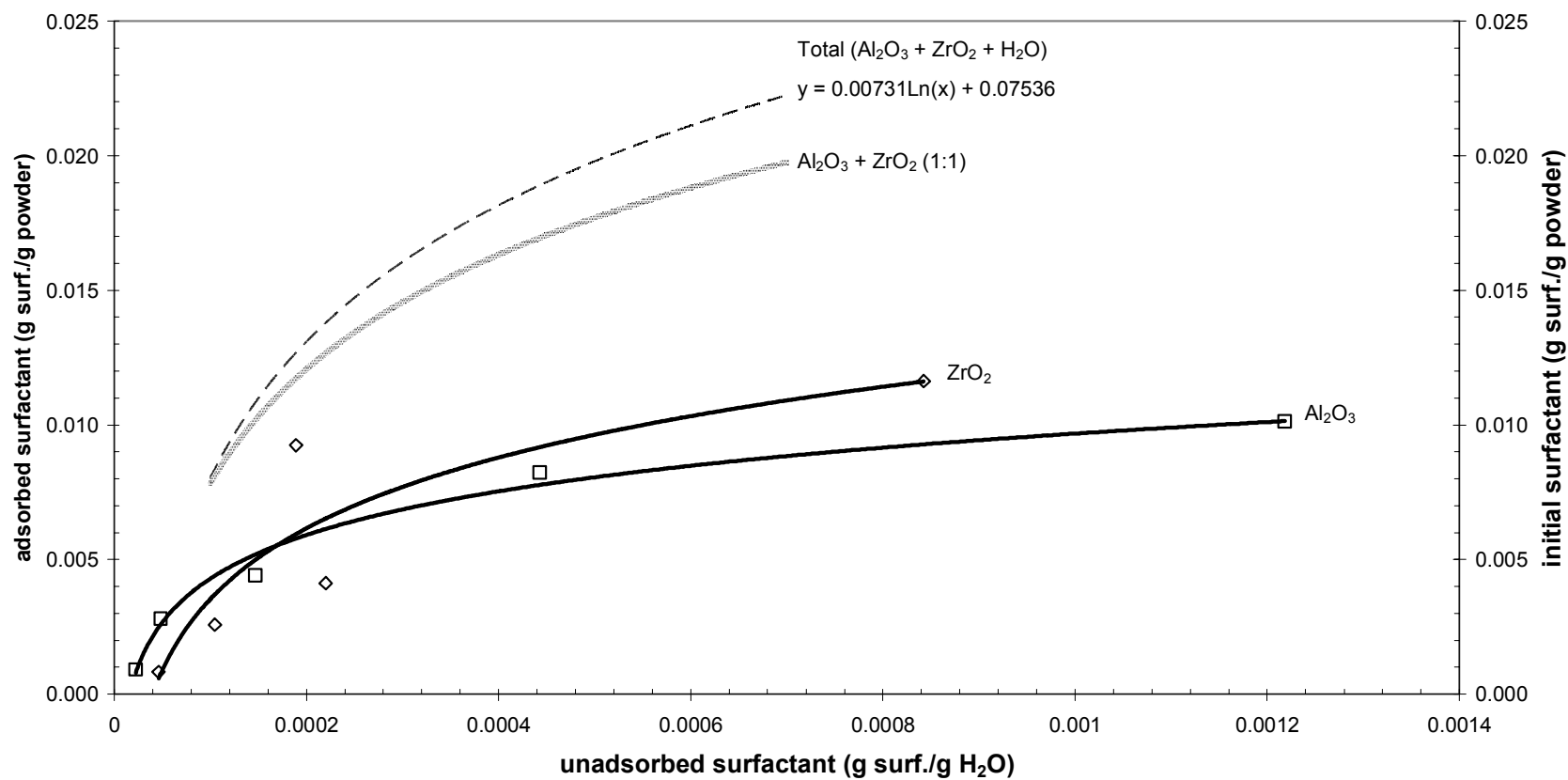


Figure 44. Unadsorbed surfactant prediction plot for an Al₂O₃ / ZrO₂ suspension at a pH of 5.90.

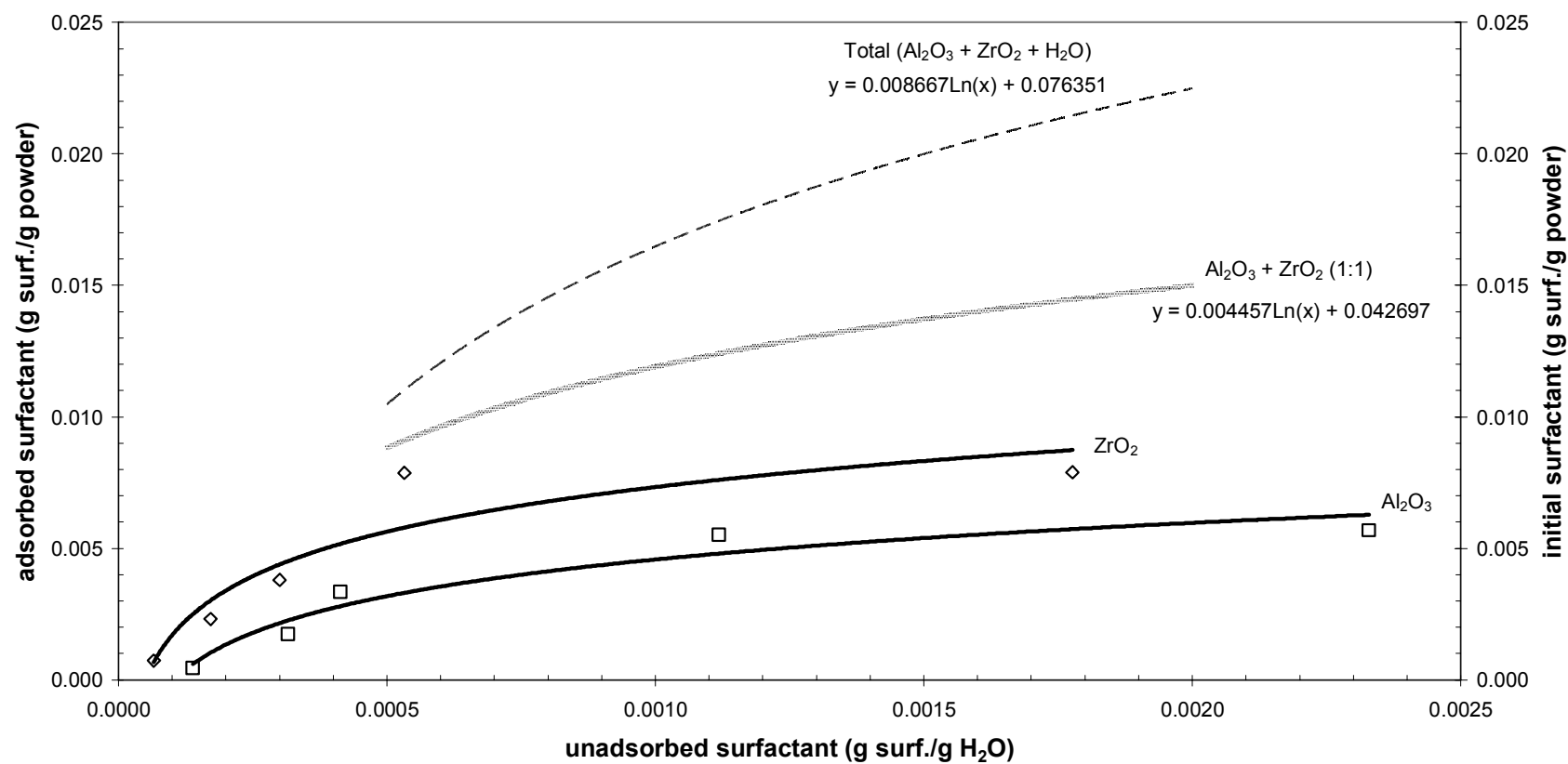


Figure 45. Unadsorbed surfactant prediction plot for an Al₂O₃ / ZrO₂ suspension at a pH of 8.75.

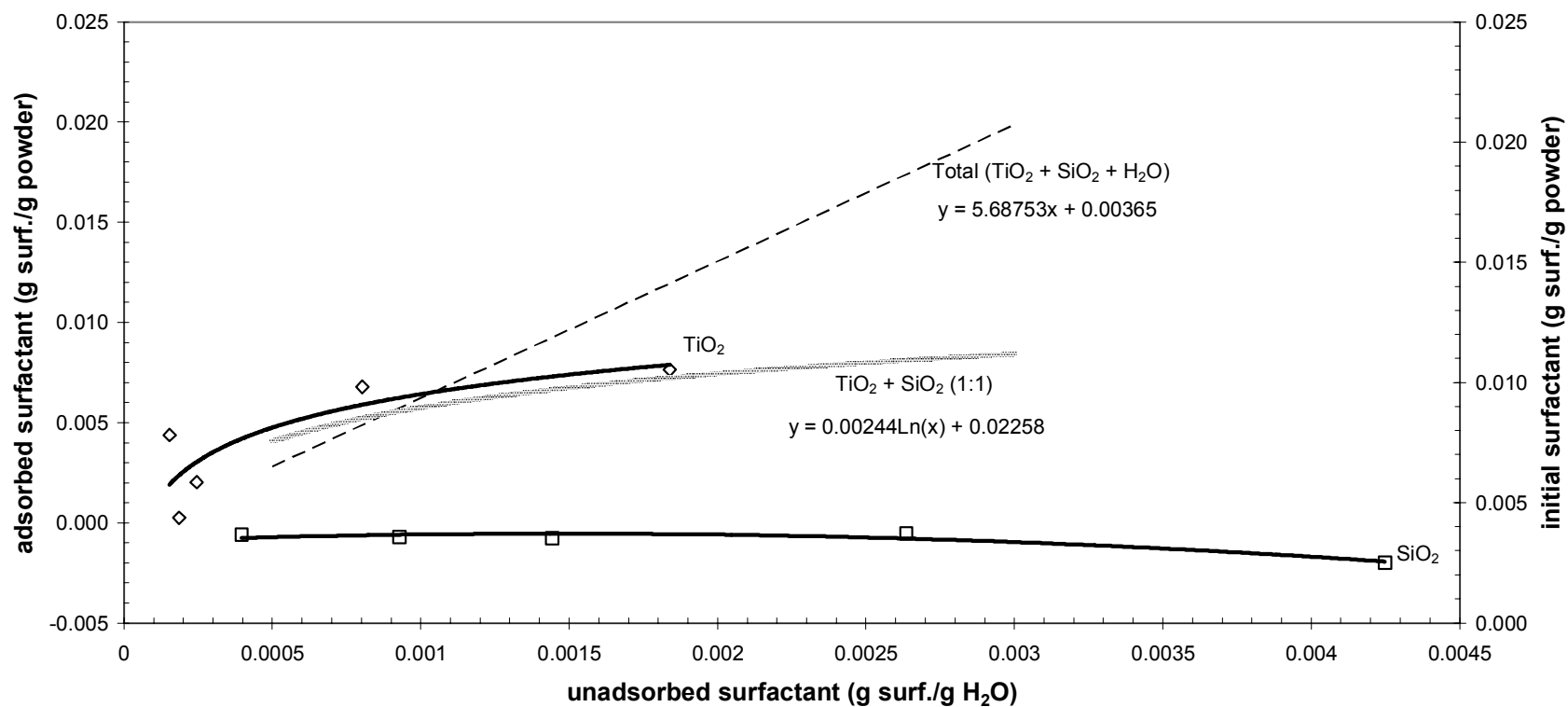


Figure 46. Unadsorbed surfactant prediction plot for an TiO_2 / SiO_2 suspension at a pH of 3.05.

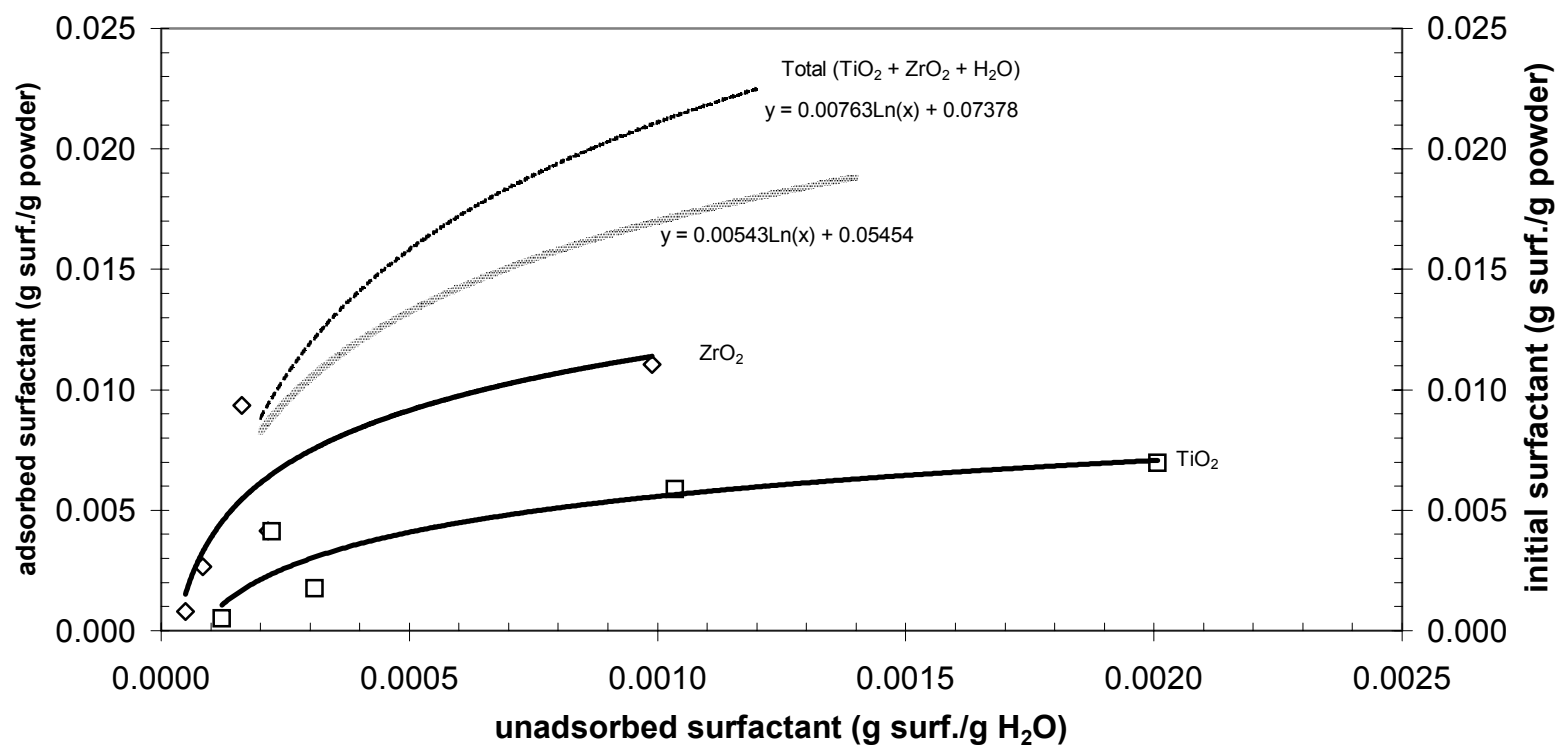


Figure 47. Unadsorbed surfactant prediction plot for an TiO₂ / ZrO₂ suspension at a pH of 6.52.

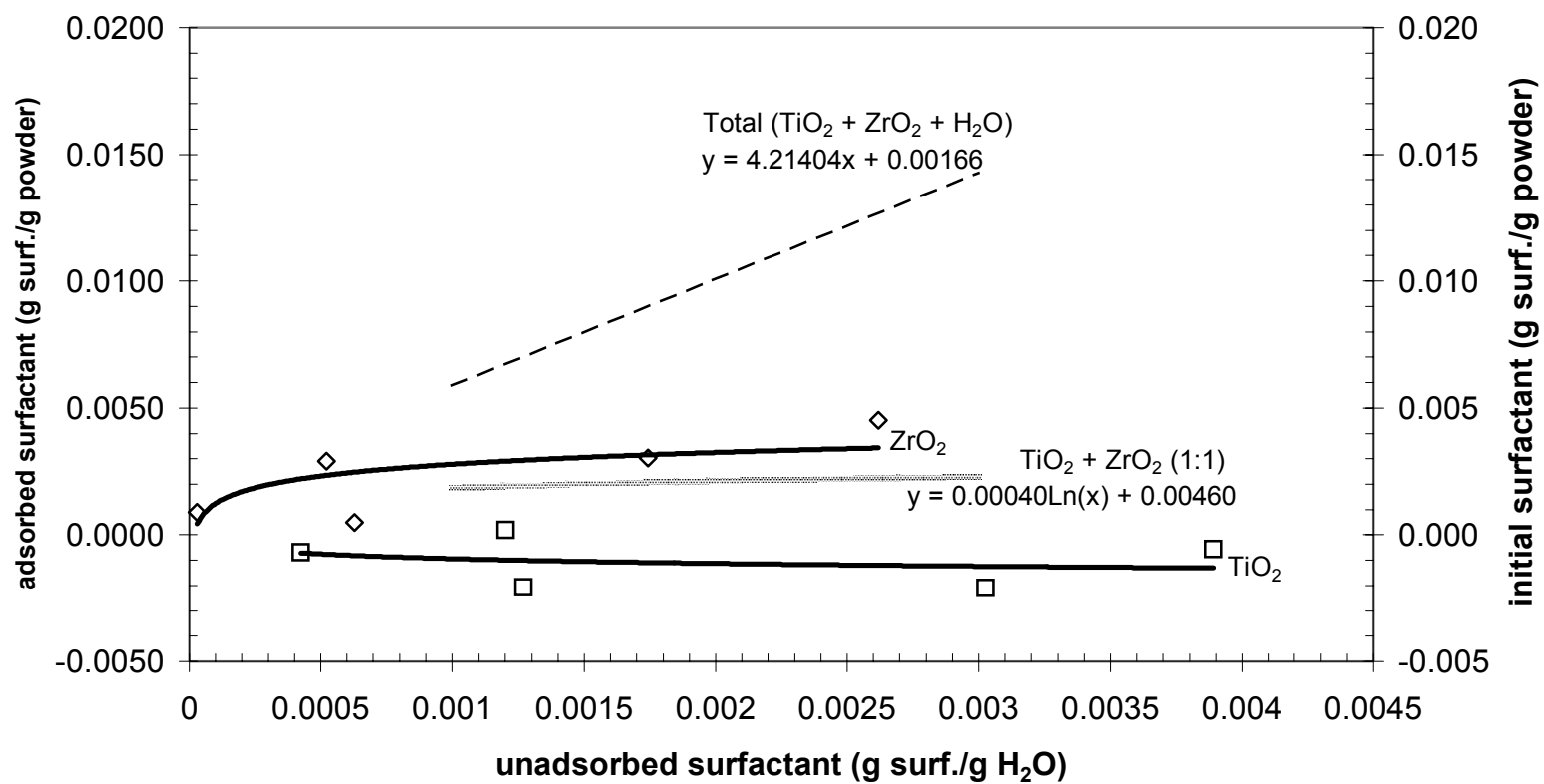


Figure 48. Unadsorbed surfactant prediction plot for a $\text{TiO}_2 / \text{ZrO}_2$ suspension at a pH of 10.49.

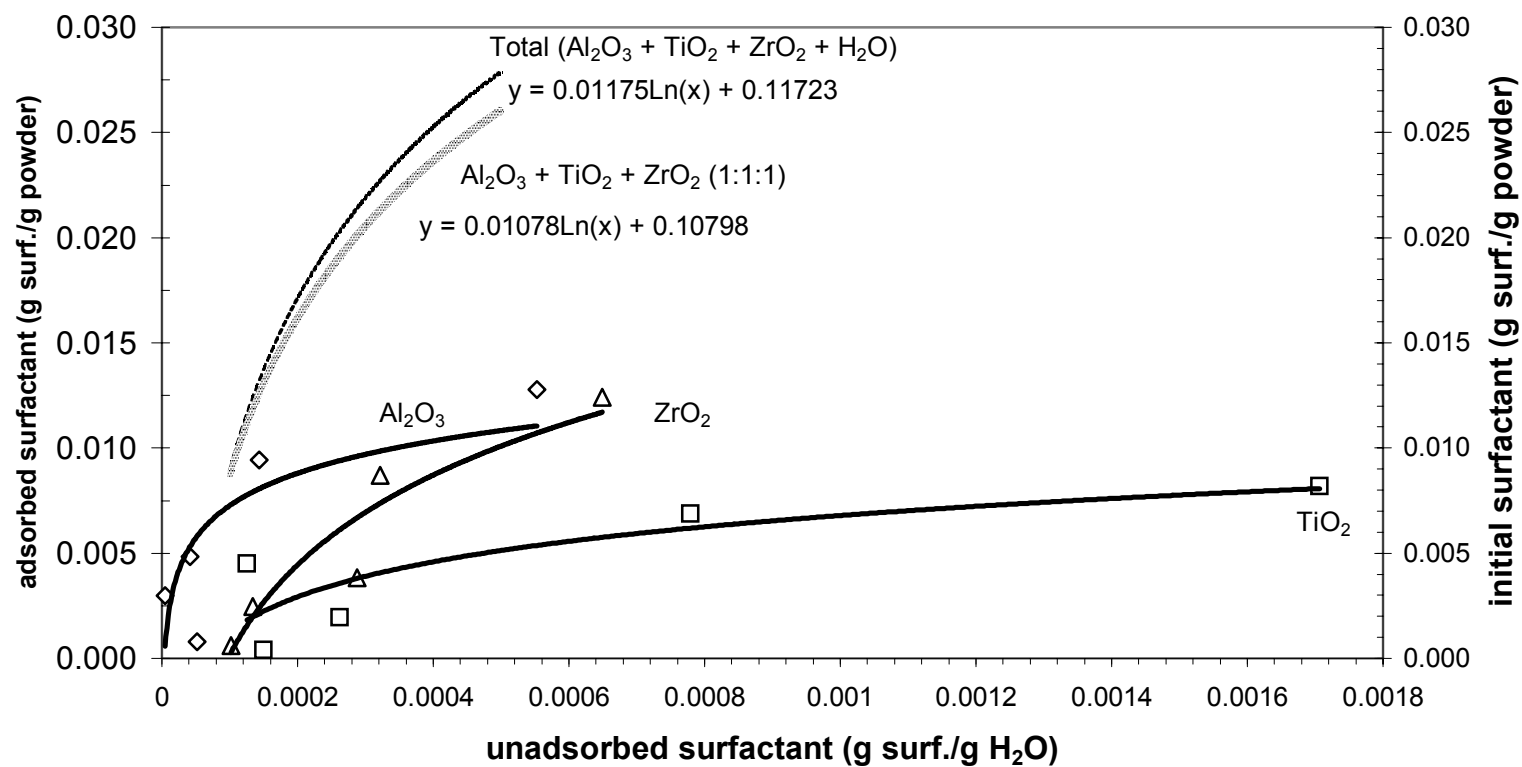


Figure 49. Unadsorbed surfactant prediction plot for an Al₂O₃/TiO₂/ ZrO₂ suspension at a pH of 3.65.

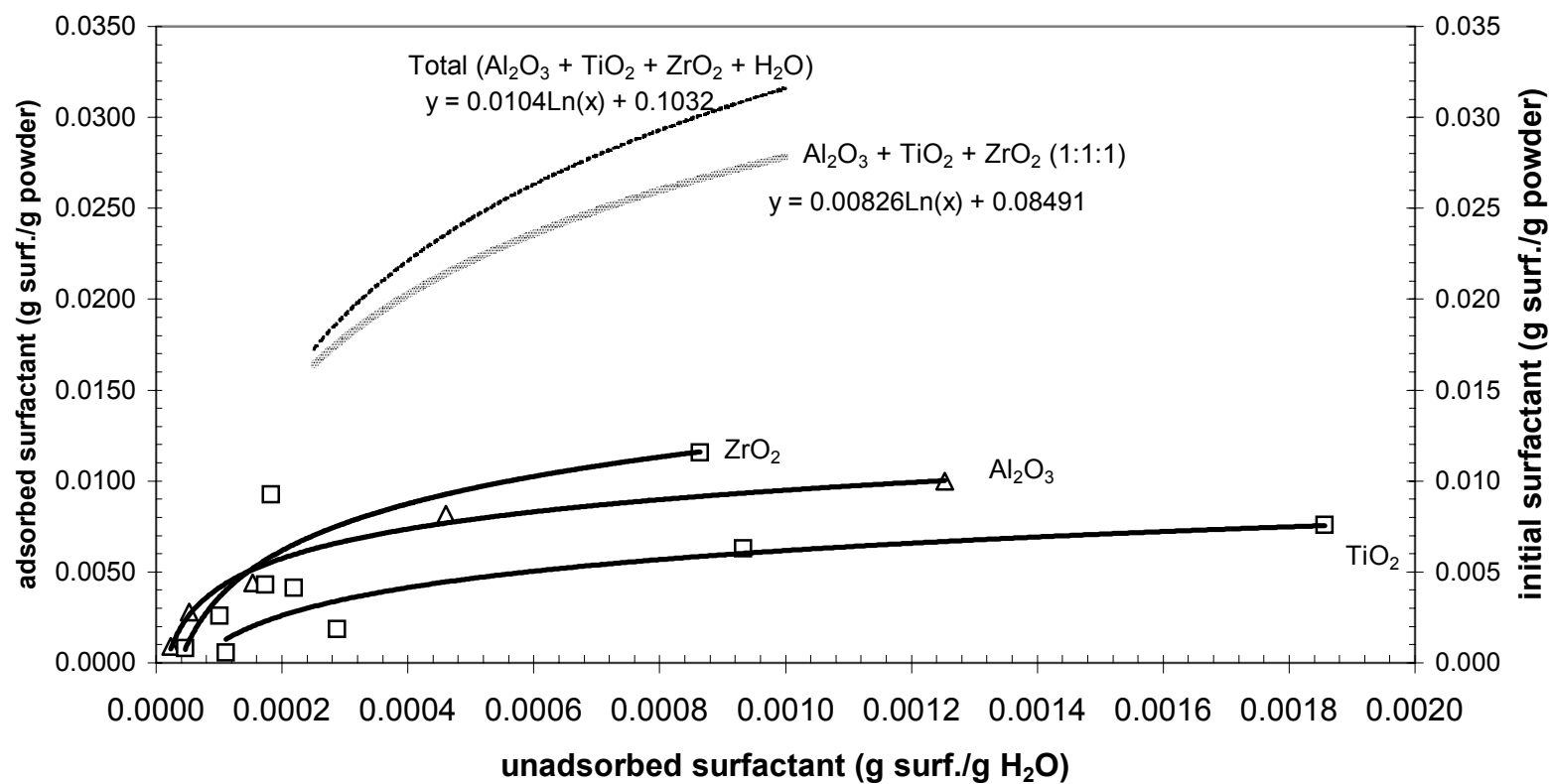


Figure 50. Unadsorbed surfactant prediction plot for an $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{ZrO}_2$ suspension at a pH of 6.

