

AN INVESTIGATION INTO THE STABILITIES OF CRUDE OIL EMULSIONS
AND COLLOIDAL SILICA SYSTEMS

A Thesis

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Master of Science

by

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ABSTRACT

The effectiveness of enhanced oil recovery techniques depends strongly on the stability of the crude oil emulsions. The ionic nature of the aqueous phase influences emulsion stability and can vary between oil wells. To better understand the influence specific ion effects may have on these systems, the stability was measured using the bottle test for crude oil emulsions in various monovalent and divalent electrolytic solutions. Specific ion effects were not found to have a significant influence on emulsion stability, and restabilization at higher ionic strengths was not observed.

Owing to its natural abundance, biocompatibility, and surface modification performance, silica is widely used in industrial applications ranging from surface treatments to medicine and, more recently, to the stabilization of crude oil emulsions. Silica's effectiveness in these roles is similarly dependent on its colloidal stability characteristics. The aggregation kinetics of bare and sulfonated silica nanoparticles were studied via absorbance measurements. Specific ion effects significantly influenced the colloidal stability of both particles. Restabilization was only observed for the sulfonated silica nanoparticles.

BIOGRAPHICAL SKETCH

Bryan Calloway was born December 1, 1992 in Maryville Tennessee to Kellie and Marty Calloway. He attended college at Virginia Tech where he graduated with Bachelor of Science degrees in physics, mathematics, and aerospace engineering. In 2016, Bryan was admitted to the Department of Applied and Engineering Physics at Cornell University to pursue a Master of Science degree. While studying at Cornell, Bryan joined the Giannelis Research Group where he had the privilege of working alongside and learning from numerous talented scientists.

For Mom, Dad, Ammom, Anna, & Matthew

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CHAPTER 1

INTRODUCTION

This chapter briefly introduces various terms referred to in this thesis.

1.1 Stability of Emulsions and Colloids

Emulsions and colloids tend to phase separate over time to reach energetically favorable configurations. In emulsions, droplets coalesce or flocculate. If the disperse and continuous phases have different densities creaming or sedimentation will occur, contributing to phase separation¹. In colloids, phase separation occurs through aggregation of suspended particles². Emulsions and colloids which phase separate more rapidly are termed less stable. Phase separation is impeded by the formation of repulsive forces between droplets or particles thereby increasing stability¹. These interactions can be supported by a variety of mechanisms. The two primary mechanisms are electrostatic repulsion and hydration forces.

1.1.1 Electric Double Layer and Zeta Potentials

In aqueous solution solid and liquid interfaces can develop a net charge through the dissociation of surface groups or adsorption of ions or molecules². This net charge causes electrostatic repulsion between particles or droplets stabilizing the system. However, any ions in solution will migrate in response to an electric field. Migration of ions screens the electric charge reducing the electrostatic repulsion and promoting phase separation. Similarly charged ions will be depleted near the surface while oppositely charged ions are concentrated^{1,2}. Competition between diffusive and

electrostatic forces acting on the ions establishes an equilibrium. The resulting structure is referred to as the electric double layer.

The precise structure of the electric double layer is still debated but is universally considered to consist of a Stern (inner) layer and a diffuse (outer) layer. Under the Stern-Gouy-Chapman (SGC) model³, the Stern layer is seen as a single layer of specifically adsorbed ions followed by a single layer of non-specifically adsorbed (fully solvated) ions. The diffuse layer is composed of ions free to move around but which are largely pulled with the particle as it moves through the fluid. The diffuse layer is bounded by the slipping plane and the remaining unscreened electric potential at this point is termed the zeta (electrokinetic) potential. Increasing ionic strength screens more of the surface charge, weakening electrostatic repulsions.

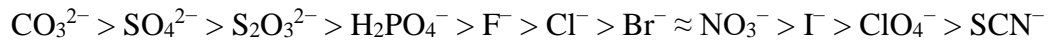
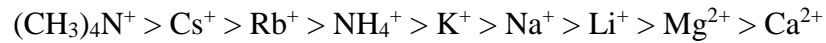
1.1.2 Hydration Forces

Hydration forces can form between sufficiently hydrophilic surfaces due to the energy necessary to dehydrate approaching surfaces². Hydration forces are net repulsive forces and are limited to a range of about 6nm. For sufficiently rigid and smooth surfaces the hydration force has been shown to oscillate with separation distance with a periodicity of 0.25nm suggesting molecular layering of adjacent water molecules⁴.

1.2 Specific Ion Effects

The specific ion effect refers to the phenomenon wherein two different ions of the same valency may behave differently in solution. Specific ion effects are often significant in situations involving the screening of electric charge such as in electric double layers. The relative effects of different ions generally follow a consistent ordering referred to as the Hofmeister series. This consistent ordering was first

described by Franz Hofmeister through his studies on the solubility of proteins in response to various cations and anions^{5,6}. For a variety of cations and anions the Hofmeister series is given as follows⁷:



For sufficiently hydrophilic interfaces the Hofmeister series is reversed⁸. The mechanisms behind specific ion effects are not fully understood but are believed to include effects on bulk water structure, surface-water interactions, and ion-surface interactions⁹.

Recent research measured the surface potential of colloidal silica in electrolyte solutions using x-ray photoelectron spectroscopy. The results supported the theory that the stern layer for silica nanoparticles is composed of a single layer of water molecules followed by a hydrated cation^{10,11}. Similarly, a study on the colloidal stability of both positively and negatively charged polystyrene latex nanoparticles also suggested that the specific ion effects observed in these systems were largely due to influences on the surface charge¹².

1.3 Enhanced Oil Recovery

Extraction of crude oil from underground reservoirs is a vital component to meeting global energy demands. However, in a typical oil well, primary recovery methods fail to extract more than approximately 1/3 of the total crude oil. The majority remains trapped underground due to viscous and capillary forces¹³. A variety of enhanced oil recovery methods have been developed to increase the recoverable percentage of oil

including chemical flooding. In chemical flooding, water, surfactants, and sometimes other chemicals are injected into the reservoir to reduce interfacial tension and drive the remaining oil towards a production well¹³. Optimizing these enhanced oil recovery techniques presents significant challenges due to the geological diversity and chemical complexity of oil reservoirs as well as environmental and economic considerations. For economic reasons, reservoirs are usually flooded with sea water, introducing additional salts which influence emulsion stability. Consequently, a more complete understanding of the stability of crude oil emulsions in electrolytic environments, as well as any potential specific ion effects or restabilization effects, is crucial to the optimization of enhanced oil recovery techniques.

1.4 Future Work

The results presented in this thesis suggest two productive directions for future research. The observed stability of sulfonated silica nanoparticles (reported here) prompts investigation into their ability to also act as surfactants in crude oil-in-water emulsions. Furthermore, any influence on a crude oil emulsion's tendency to form a Winsor type III emulsion, in the presence of sulfonated silica nanoparticles, as opposed to forming a less stable oil-in-water emulsion, would be of interest to enhanced oil recovery efforts.

Secondly, research into the influence of dissolved gases on the stability of crude oil emulsions is advisable. In prior research, a strong influence of dissolved gases on the stability of emulsions of hydrophobic liquids was reported. Samples emulsified after degassing exhibited dramatically increased stability and did not destabilize when gases were subsequently re-dissolved^{14,15}. Dissolved gases appear to impede droplet release

(and thereby emulsion formation)¹⁵. Although the lack of sufficient explanation for this effect motivates further research in its own right, the similarly strong influence of dissolved gases on specific ion effects¹⁶ suggests the possibility that research in this area may produce a significant breakthrough in oil emulsion stability.

CHAPTER 2

STABILITY OF CRUDE OIL EMULSIONS

2.1 Introduction

Control over the stability of crude oil emulsions is important in a variety of industrial applications including waste water treatment and enhanced oil recovery¹³. The surface of crude oil is chemically complex and highly variable. It can contain waxes, resins, asphaltenes, organic acids, and other surfactants which can stabilize or destabilize the system through steric or electrostatic interactions¹³. Specific ion effects have been reported in a variety of hydrocarbon systems^{17,18}. Restabilization has been well documented in systems such as proteins^{19,20}, which can contain both hydrophobic and hydrophilic parts. This work primarily focused on specific ion effects and restabilization in crude oil emulsions.

2.2 Sample Preparation and Emulsification

Samples were prepared in glass 20mL scintillation vials. Salt solutions of various concentrations were prepared using deionized water. In each glass vial 10mL of salt solution was added, followed by crude oil just prior to emulsification. Experiments were performed at a variety of oil/water ratios.

Samples were emulsified using a Branson 450 Digital Sonifier with a 3/16" sonic horn. The horn tip was positioned approximately 1mm below the sample surface. The emulsifications were performed following a duty cycle of 2 seconds of active sonication followed by a 4 second pause. Various sonication durations and intensities were tested. Sonication durations reported here refer to the total active sonication time and do not include the pause time. Magnetic stirring during sonication was found to

reduce experimental repeatability because the emulsification process was far more sensitive to the horn tip position and depth. However, sonication intensities above 15% ensured proper mixing, so magnetic stirring was not used for any results reported here.

The demulsification process was measured using the bottle test. Following emulsification, the samples were capped and photographed over time for comparison. Samples were placed inside of a homemade lightbox and photographed using a Speedlite 600EX-RT external flash with a flash diffuser to guarantee consistent exposure.

2.3 Results and Discussion

2.3.1 Emulsion Stability in Monovalent Ionic Solutions

Samples comprised of 1.0 g crude oil in 10 mL of 0.01-0.05M NaCl and KCl solutions were sonicated at 15% intensity for 30 seconds and the subsequent phase separation was followed. The results are presented in Table 1. The emulsions rapidly destabilize beyond 0.03M monovalent ions. The phase separating behavior in response to NaCl and KCl are nearly identical except at 0.01M and 0.04M. At those concentrations uncoalesced droplets were observed at the surface of the NaCl solution. At 0.04M the NaCl sample shows less turbidity than the KCl sample. These results seem contradictory. Resistance to coalescence of macroscopic droplets at the surface suggests increased stability, yet the 0.04M NaCl sample shows more phase separation. The formation of non-coalescing droplets at the surface was not reliably reproducible but did seem to occur in solutions of NaCl and CaCl₂ more frequently. A possible explanation for the stability of the macroscopic surface droplets to coalescence was

discovered through experiments performed by shaking samples by hand and photographing the droplet creaming and coalescence over time as shown in Figure 1. The droplets most resistant to coalescing with the surface have water droplets trapped inside them, forming a more complex oil-in-water-in-oil emulsion. It could be that the increased density slows the droplet's ascension to the surface, allowing it to grow larger which increases the concentration of surfactants at its surface. A similar phenomenon could be occurring in the case of the emulsion in 0.04M NaCl. If immediately following sonication, the oil droplets contained a sizable fraction of water their effective volume fraction would increase, causing more rapid creaming but less rapid coalescence upon reaching the surface. Additional evidence for this theory might come from comparing the surface coalescence behavior in emulsions of different depths.

Table 1 Phase separation of crude oil emulsions over time following sonication in low concentration NaCl and KCl solutions.






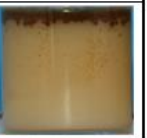

















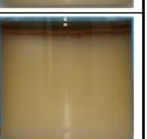






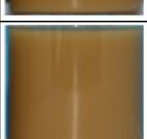






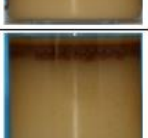

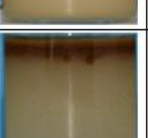









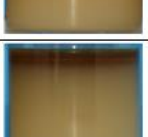



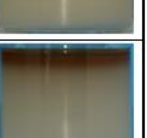

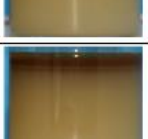
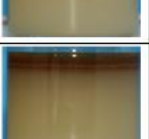
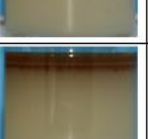






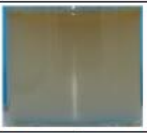























































			Time (minutes)					
			0	6	15	30	45	60
Salt Concentration (M)	0.01	NaCl						
		KCl						
	0.02	NaCl						
		KCl						
	0.03	NaCl						
		KCl						
	0.04	NaCl						
		KCl						
	0.05	NaCl						
		KCl						



Figure 1 Photographs showing coalescence of crude oil droplets at the surface of NaCl solution shortly (top) after shaking the sample vigorously by hand and approximately 1 minute later (bottom).

To search for restabilization behavior at higher ionic strengths, samples comprised of 0.1 g crude oil in 10mL of 0.1-0.9M NaCl and KCl solutions were sonicated at 20% intensity for 30 seconds and the subsequent phase separation was observed. The results are presented in Table 2. Emulsion stability is independent of ionic strength in this region, suggesting that the emulsion has become maximally unstable by 0.1M solutions of monovalent ions. Restabilization was not observed. K^+ and Na^+ ions were found to destabilize equally at these concentrations.






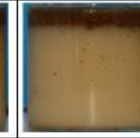






















































Table 2 Phase separation of crude oil emulsions over time following sonication in high concentration NaCl and KCl solutions.

		Time (minutes)						
		0	6	15	30	45	60	
Salt Concentration (M)	0.1	NaCl						
		KCl						
	0.3	NaCl						
		KCl						
	0.5	NaCl						
		KCl						
	0.7	NaCl						
		KCl						
	0.9	NaCl						
		KCl						

2.3.2 Emulsion Stability in Divalent Ionic Solutions

To compare the destabilizing effects of monovalent and divalent ions, samples were prepared comprised of 1.0 g crude oil in 10 mL of 0.01-0.05M NaCl and CaCl₂ solutions. The samples were sonicated at 15% intensity for 2 minutes and the subsequent phase separation was observed. The results are displayed in Table 3. As expected, Ca²⁺ destabilized the emulsions at lower concentrations than monovalent ions. Restabilization was not observed to occur for divalent ions. Similar experiments at higher concentrations revealed that crude oil emulsions maximally destabilized by divalent cations show the same phase separation behavior as those maximally destabilized by monovalent cations, the only difference being the concentrations necessary to reach maximum destabilization.












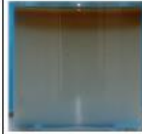





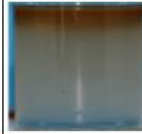





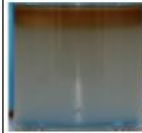




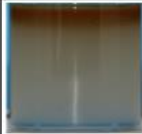












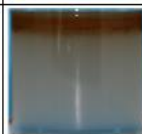















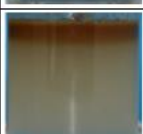
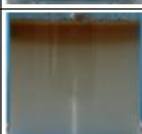
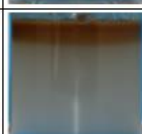
Table 3 Phase separation of crude oil emulsions following sonication in low concentration NaCl and CaCl₂ solutions.

			Time (minutes)					
			0	6	15	30	45	60
Salt Concentration (M)	0.01	NaCl						
		CaCl ₂						
	0.02	NaCl						
		CaCl ₂						
	0.03	NaCl						
		CaCl ₂						
	0.04	NaCl						
		CaCl ₂						
	0.05	NaCl						
		CaCl ₂						

2.3.3 Chemical Stability of the Interface in Ionic Solutions

To investigate the interactions between ions and organic acids at the oil-water interface, samples were prepared which were emulsified, and then re-emulsified 2 days later. The samples were capped and left undisturbed at room temperature between emulsifications. The samples were composed of 1.0 g crude oil in 10mL 0.04-0.08M NaCl solutions and sonicated for 30 seconds at 15% intensity. Table 4 compares the phase separation behavior and shows that no measurable change occurred.


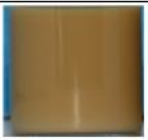






































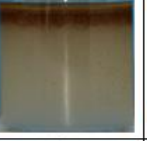
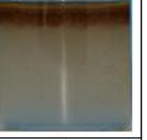







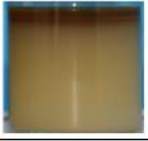

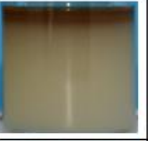








Table 4 Phase separation of crude oil emulsions over time following sonication in NaCl solutions compared with the same samples re-emulsified 2 days later.

		Time (minutes)						
		0	6	15	30	45	60	
Salt Concentration (M)	0.04	NaCl Day 0						
		NaCl Day 2						
	0.05	NaCl Day 0						
		NaCl Day 2						
	0.06	NaCl Day 0						
		NaCl Day 2						
	0.07	NaCl Day 0						
		NaCl Day 2						
	0.08	NaCl Day 0						
		NaCl Day 2						

2.3.4 Influences of Oil/Water Ratio

The oil/water ratio can influence emulsion stability due to concentration of surfactants at interfaces. Samples were prepared containing either 1.0g or 0.2g crude oil in 10mL of 0.01-0.05M NaCl solution. Samples were sonicated at 15% intensity for 30 seconds. The results are displayed in Table 5. Although the samples containing more crude oil are slightly more turbid, this appears to be due to the greater mass of oil rather than greater stability. Both samples appear to become highly unstable between 0.03 and 0.04M NaCl.

Table 5 Phase separation behavior of crude oil emulsions having 1.0g or 0.2g oil in 10mL of NaCl solution.

		Time (minutes)						
		0	6	15	30	45	60	
Salt Concentration (M)	0.01	1.0						
		0.2						
	0.02	1.0						
		0.2						
	0.03	1.0						
		0.2						
	0.04	1.0						
		0.2						
	0.05	1.0						
		0.2						

2.4 Conclusions

The stability of crude oil-in-water emulsions was studied using the bottle test. The results showed no signs of restabilization behavior. The results generally did not show signs of specific ion effects with the possible exception of Na^+ increasing the susceptibility of the crude oil to form non-coalescing macroscopic droplets on the surface during phase separation. It is possible that specific ion effects are being suppressed by the chemical heterogeneity of the interface.

CHAPTER 3

STABILITY OF COLLOIDAL SILICA

3.1 Introduction

Many industrial applications involve silica because of its natural abundance, susceptibility to surface modification^{21,22} and biocompatibility²³. Functionalized silica nanoparticles have also recently been used to stabilize oil-in-water emulsions²⁴, suggesting applications in enhanced oil recovery. Understanding and controlling the stability of silica nanoparticles is important to the development of new applications. The colloidal stability of bare and sulfonated silica nanoparticles was studied through absorbance measurements. Specific ion effects were observed to affect stability in both systems. Restabilization was found to occur for the sulfonated silica nanoparticles.

3.2 Stability of Non-Functionalized Silica Nanoparticles

3.2.1 Sample Preparation and Procedure

The stability of non-functionalized colloidal silica in various ionic environments was studied by measuring absorbance over time. LUDOX SM colloidal silica was used as the source of silica nanoparticles. Manufacturer specifications list it as 30 wt% SiO₂ and having monodisperse particles with an average diameter of 7nm, a specific surface area of 350 m²/g SiO₂, and a pH of 10. Colloidal silica solutions of the appropriate concentrations were prepared by dilution with deionized water. The dilutions were performed immediately prior to measurement as this was observed to be necessary for experimental consistency. Salt solutions of various ionic species and concentrations

were prepared using deionized water. Samples were mixed in 96 well Falcon Clear microplates. 200 μ L of salt solution were added to each of the microplate wells. 100 μ L of the diluted silica solution was added to each well immediately prior to measurement. The reported salt and silica concentrations are those of the resulting 2:1 salt solution to colloidal silica solution mixtures. The absorbance of each sample was measured on a SpectraMax M2 microplate reader. The absorbance was measured at 400nm as this wavelength was long enough not to be susceptible to scattering from non-aggregated particles yet short enough to be sensitive to aggregation of fewer particles.

3.2.2 Definition and Interpretation of the Stability Factor

Figure 2 shows a typical kinetic-absorbance plot, in this case for 2.5 wt% colloidal silica in NH_4Cl solutions of varying concentrations. As expected, the rate of aggregation increases with ionic strength. Over time, the absorbance of a sample increases asymptotically towards a final steady state value.

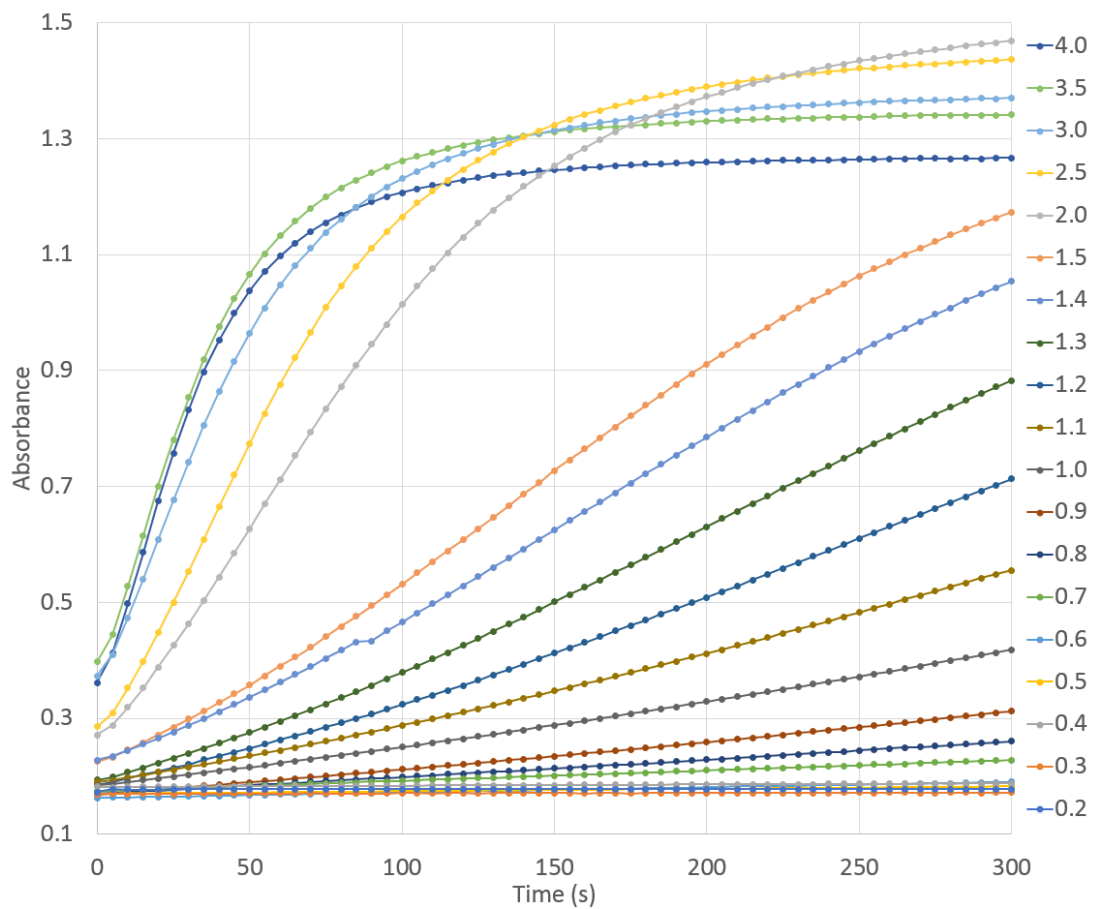


Figure 2 Kinetic absorbance ($\lambda = 400 \text{ nm}$) response of 2.5 wt% silica nanoparticles to various concentrations of NH_4Cl .

Note that for high ionic strength solutions the steady state absorbance decreases with increasing ionic strength. This should not be considered evidence of restabilization. The absorbance of a sample depends on the aggregate morphology in addition to its size. The aggregate morphology is known to depend on whether the aggregate was formed from a diffusion limited process or a reaction limited process²⁵. Diffusion limited colloidal aggregation tends to form less compact aggregates. Therefore, the absorbance as time goes to infinity is not a measure of colloidal stability.

3.2.3 Stability Factor W

While figure 2 represents the raw output from an aggregation experiment, it is not a convenient way of comparing the colloidal stability of multiple different systems. Instead, the colloidal stability in various electrolytic environment can be expressed in terms of a single value referred to as the stability factor W. The kinetics-aggregation constant k can be calculated from measurement of the time rate of change of the absorbance (dAbs/dt)²⁶. The stability factor W is defined as the ratio of kinetics-aggregation constants according to the following equation²⁷.

$$W = \frac{k_f}{k_s} = \frac{\left(\frac{dAbs}{dt}\right)_f}{\left(\frac{dAbs}{dt}\right)_s}$$

Here f (fast) refers to the system with the fastest aggregation rate while s (slow) refers to the system for which W is calculated. The stability factor can therefore be interpreted as related to the average number of times a pair of particles will collide before aggregating²⁷. Higher W values imply greater stability while W = 1 is maximally unstable.

3.2.4 Results and Discussion

Figure 3 gives the stability factors for 1.33 wt% colloidal silica solutions in various ionic environments. In all cases colloidal stability decreases monotonically with increasing ionic strength. Restabilization is not observed for any of these systems which is consistent with a particle surface insufficiently hydrophilic to support hydration forces. Furthermore, the ordering of the Li^+ , Na^+ , and K^+ ions is in agreement with the Hofmeister series. A small anion dependence is illustrated by comparing the NaCl and NaI curves.

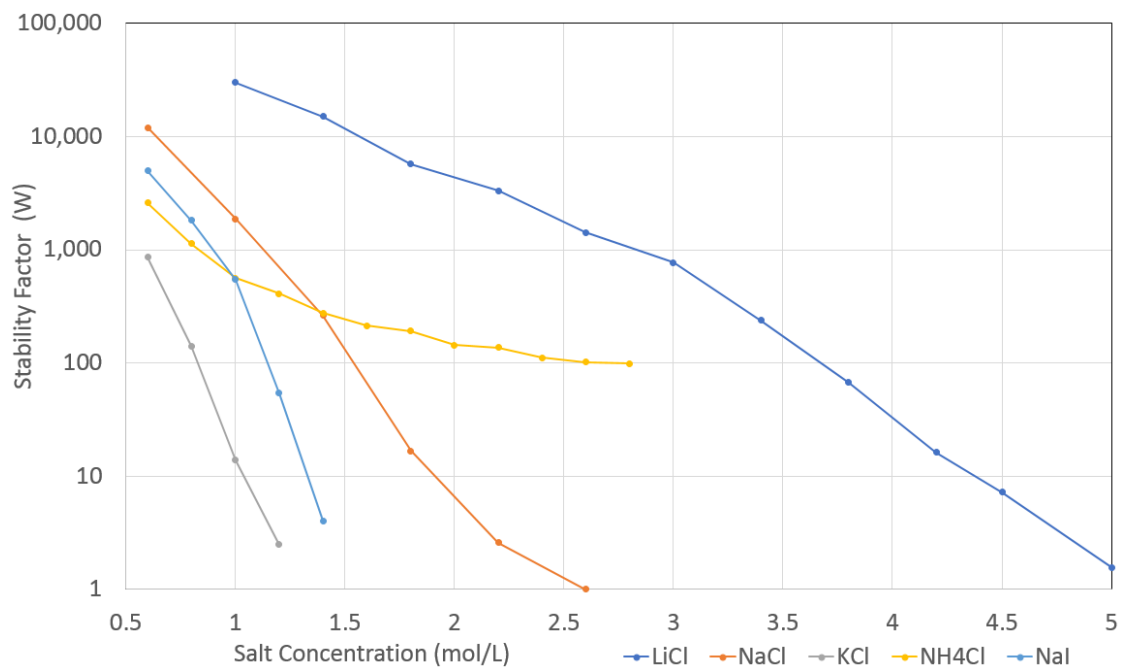


Figure 3 Stability factor curves for 1.33 wt% silica nanoparticles in various electrolyte solutions.

The stability curves for colloidal silica in LiCl, NaCl, KCl, and NaI all show similar linear behavior, consistent with already published work⁸. However, the stability curve for NH₄Cl solutions does not follow the same linear trend. Instead, it appears to gradually approach a point of maximum instability beyond which stability is independent of ionic strength.

3.2.5 Stability in Response to Divalent Cations

An attempt was made to measure the stability factors for colloidal silica in the presence of divalent cations. Figure 5 shows the absorbance over time for colloidal silica in solutions of CaCl₂ of various strengths. As expected, divalent ions induced aggregation at far lower concentrations than monovalent ions. The stability factors could not be calculated from the absorbance curves because aggregation is observed to occur either too fast or too slow to measure with the available instruments. In contrast to the monovalent cations which cause gradually increasing aggregation rates with increasing concentration, divalent cations switch from highly stable to highly unstable over a narrow range of concentrations. Such narrow ranges of ionic strengths prevent repeatable experiments because the samples must be prepared by injecting the colloidal silica into the salt solutions (thereby reducing the ionic strength while mixing occurs and causing the results to be overly sensitive to the injection process). The author speculates that this strong switching behavior is due to cationic saturation of the Stern layer being sufficient to fully screen the surface charge.

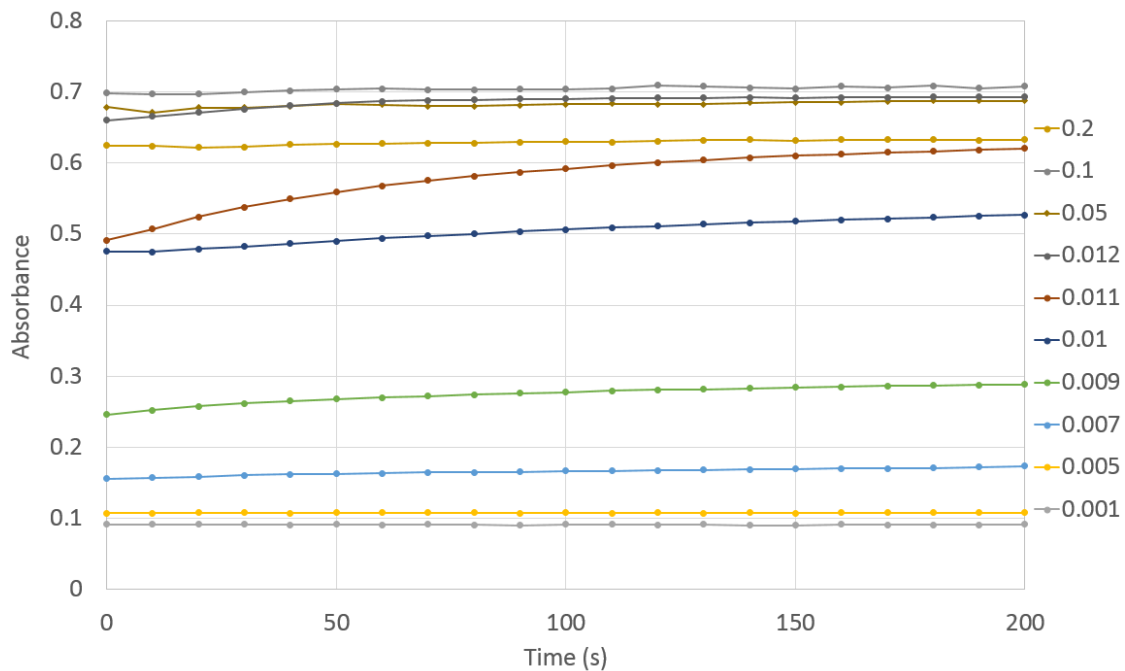


Figure 4 Kinetic absorbance ($\lambda = 400$ nm) response of 1.0 wt% silica nanoparticles to various concentrations of CaCl₂.

3.3 Colloidal Stability of Sulfonated Silica Nanoparticles

Experiments were performed to study the stability of sulfonated silica in response to salt solutions of varying ionic strength.

3.3.1 Sulfonation Procedure

Silica nanoparticles were sulfonated to improve stability and increase surface hydrophilicity. LUDOX TMA colloidal silica purchased from Aldrich Chemical Company was used as the source of silica nanoparticles. Manufacturer specifications list it as 34 wt% SiO₂ and having monodisperse particles with an average diameter of 22nm, a specific surface area of 140 m²/g SiO₂. As shipped, it is pH stabilized with a pH from 4-7. LUDOX TMA colloidal silica was chosen for its surface modification performance and because the sulfonation process occurs in an acidic environment.

The particle size distributions were measured via dynamic light scattering on a Malvern Instruments Zetasizer Nano ZS90. The TMA colloidal silica was diluted to 0.1 wt% with Milli-Q deionized water. Particle diameter distributions were peaked at 22nm and 62nm comprising 52.4% and 47.6% volume respectively. The polydispersity index was 0.212.

The sulfonation process was performed as follows. 9g of the TMA colloidal silica was diluted in 110g deionized water followed by 2 minutes sonication in a sonic bath.

Solution of 3-(trihydroxysilyl) – 1 propanesulfonic acid 30-35% in water was purchased from Gelest Inc. 9.9g of the propanesulfonic acid solution was diluted in 48mL deionized water. NaOH was added to raise the pH to 4.0 to minimize self-condensation. The solutions were combined and heated in an oil bath at 80°C for 12 hours. The sample was then transferred to 10K MWCO SnakeSkin Dialysis Tubing

and dialyzed in 2L of water. The water was replaced 6 times in approximately 8 hour intervals.

3.3.2 Sample Preparation

Samples were prepared in glass 20mm scintillation vials. Solutions of varying concentrations of CaCl_2 and MgCl_2 were prepared in glass 20mm scintillation vials. Sulfonated silica solution was then added to each vial so as to make up 25% by volume of the resulting solution. Each vial was then mixed well by shaking twice. 1.5mL of each sample were then transferred to headspace vials and sealed with crimp caps to prevent evaporation during heating.

Each sample was then superglued to the bottom of a metal plate and suspended in a 94°C oil bath that was vigorously stirred with a magnetic stirring rod. Suspending the samples from above was necessary due to uneven heating that resulted when the vials were rested on the bottom of the oil bath. The superglue was necessary to immobilize the vials because when affixed to metal plate with tape the vials would wiggle in response to the magnetic stirring rod. The wiggles induced hydrodynamic forces causing inconsistent aggregation rates. After the samples had been heated, they were removed from the oil bath and the superglue affixing them to the metal place could be dissolved with acetone. Each sample was transferred to a disposable polystyrene cuvette and the absorbance was measured in a SpectraMax M2 molecular devices plate reader at 400nm.

3.3.3 Results and Discussion

The results for the aggregation of sulfonated silica in CaCl_2 and MgCl_2 are presented in figures 5 and 6 respectively. Ca^{2+} causes more rapid aggregation than Mg^{2+} at

equivalent concentrations. Such ordering is a reversal of the Hofmeister series and suggests a more highly hydrophilic surface. Restabilization is observed for this system and is also suggestive of a highly hydrophilic surface. In CaCl_2 colloidal stability is minimized at 0.1M and gradually restabilizes thereafter.

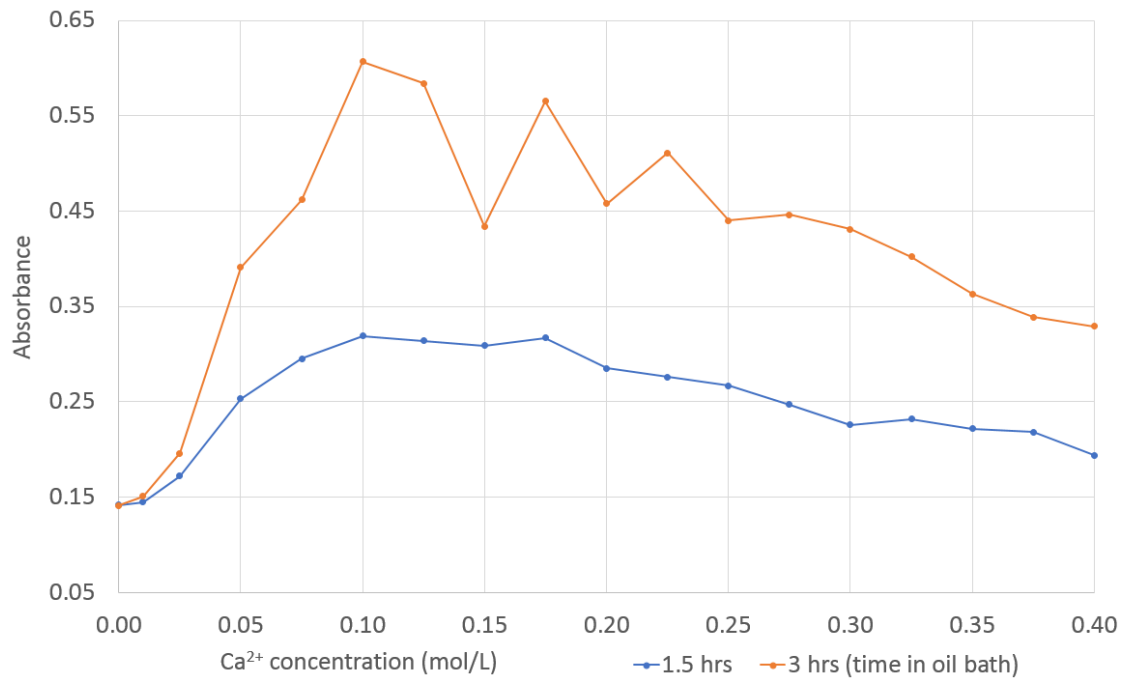


Figure 5 Absorbance ($\lambda = 400$ nm) of silica nanoparticles in CaCl₂ solutions following heating in 94°C oil bath.

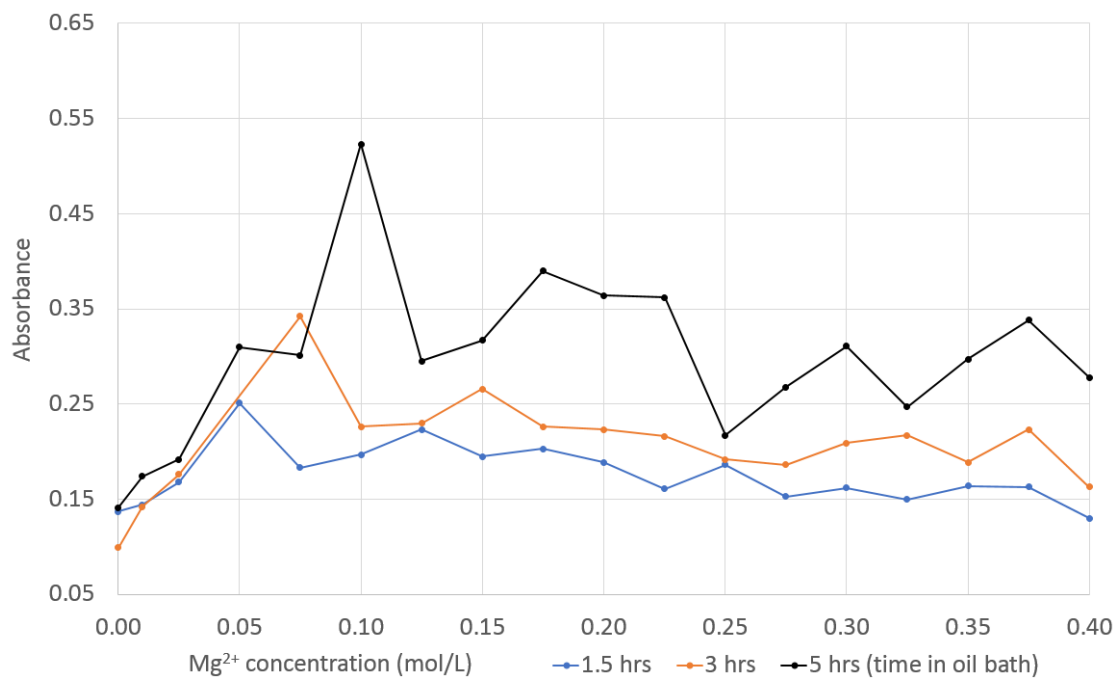


Figure 6 Absorbance ($\lambda = 400 \text{ nm}$) of silica nanoparticles in MgCl_2 solutions following heating in 94°C oil bath.

The stability response of sulfonated silica to Mg^{2+} is more unusual. The critical coagulation concentration appears to increase with time suggesting that absorbance is not increasing linearly with time. This non-constant rate of change of absorbance can also be seen for concentrations below the critical coagulation concentration. At 0.01M and 0.025M aggregation appears to stop between 1.5 and 3 hours and progresses only slightly by 5 hours. One possible explanation is that Mg^{2+} is either strongly adsorbed or chemically bonded to the particle surface or otherwise immobilized upon aggregation. In either case, one would expect to observe incomplete aggregation for small concentrations of Mg^{2+} . This would also explain the apparent time dependence of the critical coagulation concentration since the concentration of free Mg^{2+} would decrease as aggregation progresses.

In response to Ca^{2+} the sulfonated silica nanoparticles appear to exhibit a broad stability minimum. The critical stability concentration is about 0.175M, beyond which restabilization occurs gradually. In contrast, the stability minimum for Mg^{2+} is too narrow to estimate from the data and is followed by a sharp restabilization.

The measured absorbance fluctuates rapidly for concentrations greater than the critical coagulation concentration after 3 hours and 5 hours in the oil bath for Ca^{2+} and Mg^{2+} respectively. The measured absorbance exhibits narrow local minima but should not be taken as evidence that less aggregation has occurred. Instead, it is likely due to sedimentation. Through the process of refining the experimental procedure it was observed that settling was triggered in a seemingly stochastic manner after aggregation progressed beyond a certain point. On multiple occasions samples were observed to begin settling rapidly upon removal from the oil bath. On two occasions samples

appeared never to aggregate in the oil bath, but closer inspection revealed that the silica had aggregated at the meniscus and formed a ring inside the vial.

Following aggregation some samples were subjected to sonication to examine their redispersibility. Neither the sonic bath nor the Branson Sonifier at 30% intensity was able to redisperse the particles.

3.4 Conclusions

The colloidal stability of sulfonated and non-sulfonated silica nanoparticles was characterized through absorbance measurements. The non-sulfonated silica nanoparticles exhibited strong specific ion effects following the ordering given by the Hofmeister series and did not show any signs of restabilization.

Sulfonated silica nanoparticles were synthesized to increase colloidal stability and surface hydrophilicity. The sulfonated particles were shown to be highly stable at room temperature and to exhibit restabilization and Hofmeister series inversion, both of which are indicative of a strongly hydrophilic particle surface.

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