

Copyright
by
Cigdem Metin
2012

**The Dissertation Committee for Cigdem Metin Certifies that this is the approved
version of the following dissertation:**

**Characterization of Nanoparticle Transport in Flow Through
Permeable Media**

Committee:

Quoc P. Nguyen, Supervisor

Jimmie R. Baran Jr.

Roger T. Bonnecaze

Steven L. Bryant

Chun Huh

Larry W. Lake

Caetano R. Miranda

**Characterization of Nanoparticle Transport in Flow Through
Permeable Media**

by

Cigdem Metin, B.S.;M.S.

Dissertation

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

**The University of Texas at Austin
May 2012**

Dedication

To my family.

Acknowledgements

I would like to thank Dr. Quoc Nguyen for his valuable support and guidance throughout my PhD. I am privileged to have had chance to work under his supervision. His keen observations, fascinating ideas and vast knowledge guided me through this work. None of the achievements in this dissertation would be possible without his guidance and encouragement.

I would like to express my gratitude to my committee members, Dr. Roger Bonnacaze, Dr. Larry Lake, Dr. Jimmie Baran, Dr. Steven Bryant, Dr. Chun Huh and Dr. Caetano Miranda for their time, valuable comments and support. I have learned a lot from their profound insight and vast knowledge.

Special thanks to Dr. Sujeewa Palayangoda, Wenjun Liu, Monet Motiee, Tianyu Li, Alex Trinh, Akshay Agrawal, Markos Freeman for their contributions to the experiments and scientific discussions. I also appreciate great help from Dr. Do Hoon Kim, Chris Britton, Vincent Lynch, Glen Baum, Gary Miscoe, Dori Coy, Roger Terzian and Frankie Hart throughout my PhD.

I am also thankful that my friends Kelli Rankin, Nazan Izmirlier, Gina Choo, Louis diStefano, Holly Green, Rachel Showstack, Genevieve Smith, Selin Atliman Eren, Sevtac Bulbul, Sujeewa Palayangoda, Naveed Arsalan, Nhut Nguyen and Yasar Mehmani were very supportive and understanding.

I would like to thank Advanced Energy Consortium (AEC) for their financial support of this project.

Finally my special and sincere thanks go to my family for their endless love and support.

Characterization of Nanoparticle Transport in Flow Through Permeable Media

Cigdem Metin, PhD

The University of Texas at Austin, 2012

Supervisor: Quoc P. Nguyen

An aqueous nanoparticle dispersion is a complex fluid whose mobility in porous media is controlled by four key factors: the conditions necessary for the stability of nanoparticle dispersions, the kinetics of nanoparticle aggregation in an unstable suspension, the rheology of stable or unstable suspensions, and the interactions between the nanoparticles and oil/water interface and mineral surfaces. The challenges in controlling nanoparticle transport come from the variations of pH and ionic strength of brine, the presence of stationary and mobile phases (minerals, oil, water and gas), the geochemical complexity of reservoir rocks, and pore-network.

The overall objective of this work is to achieve a better understanding of nanoparticle transport in porous media based on a systematic experimental and theoretical study of above factors. For this purpose, the critical conditions for the aqueous stability of nanoparticles are identified and fit by a theoretical model, which describes the interaction energy between silica nanoparticles. Above critical conditions nanoparticle aggregation becomes significant. A model for the aggregation kinetics is developed and validated by experiments.

A mechanistic model for predicting the viscosity of stable and unstable silica nanoparticle dispersions over a wide range of solid volume fraction is developed. This model is based on the concept of effective maximum packing fraction.

Adsorption experiments with silica nanoparticles onto quartz, calcite and clay surfaces and interfacial tension measurements provide insightful information on the interaction of the nanoparticles with minerals and decane/water interface. The extent of nanoparticle adsorption on mineral/water and decane/water interfaces is evaluated based on DLVO theory and Gibbs' equation. Visual observations and analytical methods are used to understand the interaction of nanoparticles with clay.

The characterization of nanoparticle behavior in bulk phases is built into an understanding of nanoparticle transport in porous media. In particular, the rheology of nanoparticle dispersions flowing through permeable media is compared with those determined using a rheometer. In the presence of residual oil, the retention of silica nanoparticles at water/oil interface during steady flow is investigated. The results from batch experiments of nanoparticle adsorption are used to explain the flow behavior of these nanoparticles in a glass bead pack at residual oil saturation.

Table of Contents

List of Tables	xii
List of Figures	xiii
List of Figures	xiii
Chapter 1: Introduction	1
1.1 PROBLEM STATEMENT	1
1.2 OBJECTIVE	4
1.3 RESEARCH APPROACH	5
1.4 OUTLINE OF THE DISSERTATION	7
Chapter 2: Stability of Aqueous Silica Nanoparticle Dispersions	11
2.1 INTRODUCTION	11
2.2 MATERIALS AND METHODS	13
2.3 RESULTS AND DISCUSSION	15
2.3.1 The Effect of pH on Aqueous Stability of Silica Nanoparticle Dispersion	15
2.3.2 Phase Behavior of Silica Nanoparticle Dispersions in Presence of Electrolytes	21
2.3.3 Effect of Divalent Cations on Critical Salt Concentration (CSC)	25
2.3.4 Effect of Particle Size on CSC	34
2.3.5 Effect of Surface Modification on CSC	37
2.3.6 Effect of Temperature on Critical Salt Concentration	43
2.4 CONCLUSIONS	48
2.5 REFERENCES	49
Chapter 3: Shear Rheology of Silica Nanoparticle Dispersions	52
3.1 INTRODUCTION	52
3.2 MATERIAL AND METHODS	56
3.3 RESULTS AND DISCUSSION	57
3.3.1 The Effect of Temperature on the Viscosity of Silica Nanoparticle Dispersions	61

3.3.2 The Effect of Particle Size on the Viscosity of Silica Nanoparticle Dispersions	62
3.3.3 The Effect of Surface Modification on the Viscosity of Silica Nanoparticle Dispersions	64
3.3.4 The Unified Model.....	66
3.4 CONCLUSIONS.....	73
3.5 REFERENCES	74
Chapter 4: Aggregation Kinetics and Shear Rheology of Aqueous Silica Suspensions	78
4.1 INTRODUCTION	78
4.2 MATERIAL AND METHODS	81
4.3 RESULTS AND DISCUSSION	82
4.3.1 Aggregation Kinetics	82
4.3.2 Shear Rheology of Silica Suspensions.....	100
4.4 CONCLUSIONS.....	106
4.5 REFERENCES	107
Chapter 5: Phase Behavior and Rheological Characterization of Silica Nanoparticle Gel.....	110
5.1 INTRODUCTION	110
5.2 MATERIALS AND METHODS.....	111
5.3 RESULTS AND DISCUSSION	112
5.3.1 Phase Behavior.....	112
5.3.2 Rheological Measurements.....	119
5.4 CONCLUSIONS.....	135
5.5 REFERENCES	136
Chapter 6: Adsorption of Surface Functionalized Silica Nanoparticles onto Mineral Surfaces and Decane/Water Interface	138
6.1 INTRODUCTION	139
6.2 MATERIALS AND METHODS.....	142
6.3 RESULTS AND DISCUSSION	145
6.3.1 Adsorption on Minerals	145

6.3.2 Interfacial Tension of Silica Nanoparticle Dispersion/Decane Interface	153
6.3.3 Contact Angle Measurements	159
6.4 CONCLUSIONS.....	169
6.5 REFERENCES	170
Chapter 7: Interaction of Nanoparticles with Clay Mineral.....	174
7.1 INTRODUCTION	174
7.2 MATERIALS AND METHODS.....	176
7.3 RESULTS AND DISCUSSION	177
7.4 CONCLUSIONS.....	194
7.5 REFERENCES	195
Chapter 8: Flow of Silica Nanoparticles in Permeable Media.....	197
8.1 INTRODUCTION	198
8.2 MATERIALS AND METHODS.....	200
8.3 RESULTS AND DISCUSSION	207
8.4 CONCLUSIONS.....	216
8.5 REFERENCES	217
Chapter 9: Retention of Nanoparticles at Oil/Water Interface.....	219
9.1 INTRODUCTION	219
9.2 MATERIALS AND METHODS.....	220
9.3 RESULTS AND DISCUSSION	222
9.4 CONCLUSIONS.....	241
9.5 REFERENCES	241
Chapter 10: Contributions and Recommendation.....	243
10.1 MAJOR CONTRIBUTIONS.....	243
10.2 RECOMMENDATIONS FOR FUTURE WORK	244

Appendix A: List of Acronyms.....	246
Appendix B: List of Equipment and Vendors.....	247
Bibliography	248

List of Tables

Table 3.1- Shear rates encountered in hydrocarbon recovery applications.....	58
Table 3.2- The existing viscosity models of colloidal dispersions evaluated in this study	60
Table 3.3- The summary of experimental systems studied	65
Table 6.1- Zeta potential of silica nanoparticles dispersed in water	144
Table 7.1- The peak assignments of the clay/nanoparticle mixture by ATR-FTIR.	185
Table 8.1- Properties of porous media studied.....	207

List of Figures

Figure 1.1- The stages of the nanoparticle transport from surface to reservoir. In (A), the figure shows a stable nanoparticle suspension, agglomeration of nanoparticles and the assembly of nanoparticles at fluid interface. The relationship between shear stress and shear rate relation is the top figure in (B). Figures in the middle and at the bottom in (B) show schematically viscosity as a function of nanoparticle concentration, shear rate and temperature. In (C), the figure illustrates the thin oil film stability and the formation of a contact angle because of nanoparticles. The effect of nanoparticles on contact line motion is presented in (D). Porous media -represented as a capillary flow and the displacement of oil by nanoparticle suspension are illustrated schematically in (E). ...3

Figure 2.1- The bright field scanning transmission electron microscopy (STEM) images of dried silica dispersions at (a) 350k magnification and (b) 700k magnification.14

Figure 2.2- ATR-FTIR transmission spectrum of dried silica powder, 25nm unmodified silica particle dispersion, and deionized water. Stretching and bending vibrations of water molecules show peaks at 3330 and 1629 cm^{-1} , respectively. The silica powder has the Si-O bond vibrations at 793.4 and 1055.3 cm^{-1} . Only the Si-O at 1100 cm^{-1} is detectable in case of the silica dispersion.17

Figure 2.3- The area under the Si-O peak at 1110 cm^{-1} as a function of pH for 0.5 and 1 wt% particle concentrations. The change in the slope of the peak area of the Si-O bond around pH=7 indicates a structural change of the silica nanoparticle surface.	18
Figure 2.4- Zeta potential of silica particle dispersions as a function of dispersion pH. The vertical error bars in the graph are the mean standard errors of the zeta potential measurements. The isoelectric point (IEP) is estimated as pH=3.4 by extrapolation of linear regression fit to points at pH=8 or smaller. The zeta potential measurements below pH=4 exceeded the conductance limit of the zeta potential analyzer therefore zeta potential measurements are not in this pH range.	19
Figure 2.5- (a) UV-Vis absorbance of 0.5 and 1 wt% silica particle dispersions at 400nm wave length as a function of pH, (b) The effect of pH on effective particle diameter for 0.5 and 1 wt% silica dispersions by DLS measurements.....	20
Figure 2.6- Photographs of sealed tubes that show the phase behavior of unmodified silica nanoparticle dispersions at various NaCl and nanoparticle concentrations at (a) 1 hour, (b) 10 days and (c) 41 days. Three distinct sequential stages of aggregation, i.e., single clear phase, a turbid single phase and two separate phases.	23
Figure 2.7- Effective particle diameter and UV-Vis absorption at 400nm wave length of 0.5 wt% unmodified silica dispersions in the presence of NaCl. A significant increase in effective diameter and absorbance occur initially at 2 wt% NaCl but this critical concentration shifts to an equilibrium value (CSC) of 1 wt% at 43 days.	24

Figure 2.8- UV-Vis light absorption of a 0.5 wt% unmodified silica particle dispersion with 3 wt% NaCl as a function of time.	25
Figure 2.9- Photographs of sealed tubes that illustrate the phase behavior of silica dispersions with MgCl ₂ at 1 hour, 1 day and 7 days at 25°C. Three distinct sequential stages of aggregation are observed at various MgCl ₂ and nanoparticle concentrations. The transition between a stable and an unstable dispersion (aggregation followed by sedimentation) occurs around 0.03 wt% MgCl ₂ for all three nanoparticle concentrations....	27
Figure 2.10- Photographs of sealed tubes that illustrate the phase behavior of silica dispersions with CaCl ₂ at 1 hour, 1 day and 7 days at 25°C. Three distinct subsequent stages of aggregation are observed at various CaCl ₂ and nanoparticle concentrations. The transition between a stable and an unstable dispersion (aggregation followed by sedimentation) occurs around 0.05 wt% CaCl ₂ for all three nanoparticle concentrations....	28
Figure 2.11- UV-Vis absorbance of a 1 wt% silica dispersion in the presence of different salts (NaCl, MgCl ₂ , CaCl ₂ and BaCl ₂) at 400nm wave length at 25°C. Mg ²⁺ exhibits the smallest CSC while the CSCs for Ca ²⁺ and Ba ²⁺ are both about 0.025 wt%.	29
Figure 2.12- Effective particle diameters for a 1 wt% silica dispersion as a function of NaCl, MgCl ₂ , CaCl ₂ and BaCl ₂ concentrations at 25°C. An increase in the effective diameter indicates aggregation of the silica particles. .	30
Figure 2.13- Two-particle interaction potential as a function of dimensionless separation distance according to DLVO theory for (a) NaCl concentrations. The secondary and primary minima are shown clearly in the (b) small scale range of the y-axis, a zoom-in of (a).....	32

Figure 2.14- Relationship between electrolyte concentration and the amount of energy (V_T / kT) required to bring two nanoparticles from infinity to a critical distance, x_c , for (a) NaCl and (b) CaCl_2 and MgCl_2 concentrations.	33
Figure 2.15- The effect of particle size and divalent cations on CSC of unmodified silica nanoparticle dispersions. The values on x-axis are the diameter of silica particles that were studied.	34
Figure 2.16- (a) The total interaction potential as a function of dimensionless distance according to DLVO for 5nm unmodified particles and NaCl (b) Relationship between electrolyte concentration and the amount of energy (V_T / kT) required to bring two nanoparticles from infinity to a critical distance, x_c , for NaCl.	36
Figure 2.17- The effect of particle size and divalent cations on CSC of sulfonate coated silica nanoparticle dispersions. The values on the x-axis are the diameter of silica particles studied.....	37
Figure 2.18- The effect of divalent cations and temperature on CSC for 5nm PEG modified silica nanoparticle dispersions.....	38
Figure 2.19- The effect of divalent cations, anions and temperature on CSC for 5nm alumina modified silica nanoparticle dispersions.....	42
Figure 2.20- The effect of pH on the CSC for NaCl for 5nm alumina modified silica nanoparticle dispersions.....	43
Figure 2.21- DLS measurements of 1 wt% silica dispersion in the presence of different salts (NaCl, CaCl_2 and MgCl_2) at 25°C and 70°C. DLS measurements are taken after 18 days.	44

Figure 2.22- Critical salt concentration (CSC) for 25 nm diameter unmodified silica nanoparticle dispersions. The effects of divalent cations and temperature are presented.	45
Figure 2.23- The effect of particle size and divalent cations on CSC of unmodified silica nanoparticle dispersions at 70°C. The values on x-axis are the diameter of silica particles that was studied.	46
Figure 2.24- The effect of divalent cations on CSC of unmodified and sulfonate modified silica nanoparticle dispersions at 70°C.	47
Figure 2.25- The effect of particle size and divalent cations on CSC of sulfonate coated silica nanoparticle dispersions at 70°C. The values on x-axis are the diameter of silica particles that we studied.	47
Figure 3.1- Viscosity of 25 nm unmodified silica particle dispersions as a function of shear rate at different particle concentrations. Shear rate-independent viscosity indicates a Newtonian behavior of the dispersions.....	58
Figure 3.2- Comparison of the fit of viscosity models present in the literature to the experimental data of 25 nm unmodified silica dispersions.....	59
Figure 3.3- Relative viscosity, the ratio of the viscosity of silica dispersion to the viscosity of water, is plotted as a function of nanoparticle volume fractions at three different temperatures: 25, 50 and 80°C. The relative viscosity of 25 nm unmodified silica particles is independent of temperature.	62

- Figure 3.4-** The viscosity of unmodified silica dispersions is plotted as a function of particle volume fraction for various particle diameters of 5, 8, 25 and 75 nm. The viscosity decreases as particle size increases at a given volume fraction of nanoparticles. The lines represent the modified Chong *et al.* model by fitting the effective maximum packing fraction to experimental data. The estimated $\phi_{\max}^{\text{eff}}$ values are presented in Table 3.3.....64
- Figure 3.5-** The dispersions of silica nanoparticles with surface modification by sulfonate group attached to a short chain of hydrocarbon, exhibit smaller viscosities compared to unmodified silica dispersions value at a given volume fraction.66
- Figure 3.6-** Schematic view of the proposed model of effective maximum packing fraction for (a) unmodified and (b) surface modified silica particles.68
- Figure 3.7-** Viscosity ratio as a function of volume fraction of silica nanoparticles of various sizes (5, 8, 25 and 75 nm) and two different surface types (unmodified and sulfonate coated). Data from Thwala *et al.* (2008) for much larger particles are also shown. The volume fractions are normalized to the corresponding effective maximum packing fraction. All the data collapse onto a single curve that is well represented by our unified model.69
- Figure 3.8-** The parameters A (for unmodified silica nanoparticles) and l (for modified silica nanoparticles) of the proposed model (Equations 3.10 and 3.11) as a function of particle radius.71

- Figure 3.9-** The normalized effective maximum packing fraction with respect to maximum packing fraction, $\phi_{\max}^{\text{eff}}/\phi_{\max}$, as a function of dimensionless parameter l/a for modified surface and $A\kappa^{-1}/a$ for unmodified surface. The solid line is constructed using Equations 3.10 and 3.11.72
- Figure 3.10-** Viscosity ratio as a function of volume fraction of alumina nanoparticles in dispersed in water (Das *et al.* 2003; Wang *et al.* 1999; Mackay *et al.* 2003) and MEG coated silica nanoparticle dispersions (Thwala *et al.* 2008). The effective maximum volume fractions are determined by Equations 3.9-3.11. All the data collapse onto a single curve that is well represented by our unified model.73
- Figure 4.1-** Effect of NaCl concentration on the rate of aggregation expressed as diameter growth. The samples are at 25°C and contain 1wt% of 25 nm diameter primary silica nanoparticles. The solid lines correspond to the model proposed in Equation 4.7 and the dashed lines correspond to the exponential model in Equation 4.8.83
- Figure 4.2-** Effective particle diameter as a function of time as measured by DLS for 25 nm diameter primary particles at early aggregation times. Lines correspond to a linear fit to experimental data.....85
- Figure 4.3-** Comparison of the slow aggregation rate constant, k_s , in Equation 4.1 and experimental results for 25 nm unmodified nanoparticles.....86
- Figure 4.4-** Effect of silica concentration on the kinetics of aggregation. The samples are at 25°C and contain 3wt% NaCl. The primary particle diameter is 25 nm. The lines are from the model proposed in Equation 4.7.....88
- Figure 4.5-** The slow aggregation rate constant, k_s , as a function of initial silica particle concentration. The solid line corresponds to Equation 4.2. .89

Figure 4.6- Schematic for the growth of an aggregate of diameter D in a cell of volume β .	90
Figure 4.7- The model parameter, k_2 , in Equation 4.7 as a function of NaCl and silica concentration for 25 nm diameter primary particles.	92
Figure 4.8- The equilibrium diameter and comparison between the rate constant, $s = \frac{k_2 D_{eq}^2}{2}$, in Equation 4.7 and c the exponent of the slow aggregation regime in Equation 4.8, as a function of NaCl concentration at 1 wt% silica particles of 25 nm primary diameter.	95
Figure 4.9- The equilibrium diameter and comparison between the rate constant, $s = \frac{k_2 D_{eq}^2}{2}$, in Equation 4.7 and the constant c in Equation 4.8 as a function of silica concentration at 3 wt% NaCl. The primary silica particles are of 25 nm in diameter.	96
Figure 4.10- The comparison of parameter β obtained by Equations 4.11-4.12 with Equation 4.13 as a function of silica concentration at 3 wt% NaCl. The primary silica particles are 25 nm in diameter.	98
Figure 4.11- Effect of particle size on the kinetics of aggregation at 25°C. The samples contain 4wt% NaCl for the samples with the primary particle diameter of 5 and 25 nm and 5wt% NaCl for those with 25 and 75nm diameter. The change in aggregate diameter, measured by DLS in time is presented. The lines are from the model in Equation 4.7.	99
Figure 4.12- Scaling of the aggregation data by Equation 4.14. The samples are at 25°C and contain primary silica particles of 5, 25 and 75 nm diameters.	100

Figure 4.13- Viscosity of 1 wt% unmodified silica nanoparticle with 3 wt% NaCl at different aggregation stages as presented by the effective diameter of the aggregate in Figure 4.1.	101
Figure 4.14- Evolution of average viscosity over the range of shear rates from 1-300 s ⁻¹ of 1 wt% unmodified silica nanoparticle with 3 wt% NaCl in time. The line is from Equation 4.16 combined with Equations 4.7 and 4.15.	102
Figure 4.15- Test tubes containing 3 wt% NaCl and 0.5-3 wt% silica nanoparticles of 25 nm diameter. As silica concentration increases the sediment height also increases.	104
Figure 4.16- The determination of the aggregate volume fraction by the proposed equilibrium approach. The slope of the line corresponds to the aggregate volume fraction, $\phi_{\max}^{eff}=0.68$	105
Figure 4.17- Comparison of the proposed model with experimental data of relative viscosity of silica nanoparticle dispersions.	106
Figure 5.1- Phase behavior diagram of 5 nm unmodified silica nanoparticles at 25 °C.	113
Figure 5.2- Phase behavior diagram of 25 nm unmodified silica nanoparticles at 25 °C.	113
Figure 5.3- Schematic presentation of sedimentation and gel behavior of aggregates as proposed by Senis and Allain (1997).	114
Figure 5.4- The volume fraction of sediment, C_{sed} , vs. particle volume fraction for 25 nm unmodified silica nanoparticle dispersions. The lines correspond to Eq. 5.2.	116

Figure 5.5- The map of the volume fraction of sediment as a function of NaCl and silica concentration for 25 nm unmodified silica nanoparticles. The points on the map correspond to Φ^{**} as a function of NaCl.....	118
Figure 5.6- The map of the volume fraction of sediment as a function of NaCl and silica concentration for 5 nm unmodified silica nanoparticles.	119
Figure 5.7- Schematic presentation of the samples studied during rheology experiments.....	121
Figure 5.8- Dynamic time sweep test and UV-Vis absorbance of 4 wt% silica and 5 wt% NaCl.....	121
Figure 5.9- Gelation time as a function of silica concentration at 25 °C as measured using a rheometer.....	123
Figure 5.10- Gelation time as a function of salinity for 4 wt% silica suspensions at 25 °C as measured using a rheometer.	124
Figure 5.11- Gelation time as a function of temperature for 3 wt% silica suspensions with 3 wt% NaCl as measured using a rheometer. The lines correspond to Equation 5.4.....	125
Figure 5.12- Storage modulus G' as a function of silica concentration at 25 °C.	126
Figure 5.13- Loss modulus G'' as a function of silica concentration at 25 °C....	127
Figure 5.14- Storage modulus G' as a function of NaCl concentration at 25 °C.	128
Figure 5.15- Loss modulus G'' as a function of NaCl concentration at 25 °C....	128
Figure 5.17- Loss modulus G'' as a function of NaCl concentration at 25 °C....	131
Figure 5.18- Scaling the storage modulus G' as a function of strain at varying silica nanoparticle concentrations 25 °C.	132
Figure 5.19- Scaling the storage modulus G' as a function of strain at varying NaCl nanoparticle concentrations at 25 °C.....	133

Figure 5.20- Viscosity profile for 3M nanoparticle gels at varying nanoparticle and NaCl concentration. The solid line is power law model and the dashed line corresponds to the Carreau model fit for 3 wt% silica, 3 wt% NaCl sample.	135
Figure 6.1- UV-Vis spectra of 0.04, 0.2 and 1wt% 5-nm unmodified silica nanoparticle dispersion with and without NaCl before and after contact with quartz sand or calcite grains.....	146
Figure 6.2- UV-Vis spectra of 0.2 wt% 25-nm unmodified silica nanoparticle dispersion with or without NaCl before and after contact with quartz sand or calcite grains.....	147
Figure 6.3- UV-Vis spectra of 0.04 and 0.2 wt% 5-nm sulfonate or PEG modified silica nanoparticle dispersion after contact with quartz sand or calcite grains.....	148
Figure 6.4- Total interaction energy between calcite plate and 25 nm diameter silica nanoparticles as a function of NaCl concentration (Equations 6.3 and 6.5).	152
Figure 6.5- Total interaction energy between 420 micron diameter quartz grain and 25 nm diameter silica nanoparticles as a function of NaCl concentration (Equations 6.2 and 6.4).	153
Figure 6.6- IFT of decane/water in presence of 5 nm silica unmodified or surface modified nanoparticles.....	155
Figure 6.7- IFT of decane/water in presence of nanoparticles. The effect of nanoparticle size and concentration is shown.....	156
Figure 6.8- The effect of 5 wt% 5nm nanoparticles on IFT of water/decane.	157

Figure 6.9- Schematic presentation of adsorption of PEG to water/decane interface (a) in the absence of silica nanoparticle and (b) attached to silica nanoparticle.....	157
Figure 6.10- Adsorption of PEG or PEG modified silica nanoparticles on decane/water interface. The line corresponds to Langmuir isotherm.	159
Figure 6.11- Schematic of an oil droplet on a solid substrate (mineral) immersed in water.....	160
Figure 6.12- Decane droplet on quartz plate immersed in (a) water and (b) 5nm unmodified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 59° and (b) 46°.....	161
Figure 6.13- Decane droplet on quartz plate immersed in (a) water and (b) 25nm unmodified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 60° and (b) 52°.....	161
Figure 6.14- Decane droplet on quartz plate immersed in (a) water and (b) 75nm unmodified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 56° and (b) 52°. The color in (b) is digitally altered to more easily see the droplet.	162
Figure 6.15- The change in contact angle in the presence of 1wt% silica nanoparticles	163
Figure 6.16- Decane droplet on quartz plate immersed in (a) water and (b) 5nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 34° and (b) 20°.....	164
Figure 6.17- Decane droplet on quartz plate immersed in (a) water and (b) 25nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 51° and (b) 38°.....	164

- Figure 6.18-** Decane droplet on quartz plate immersed in (a) water and (b) 75nm sulfonate modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 55° and (b) 43°. The color in (b) is digitally altered to see the droplet clearly since the light transmittance of nanoparticle dispersion is low because of particle size.165
- Figure 6.19-** Decane droplet on quartz plate immersed in (a) water and (b) 5nm quat/PEG (50:50) modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 91° and (b) 14°.165
- Figure 6.20-** Decane droplet on quartz plate immersed in (a) water and (b) 25nm quat/PEG (50:50) modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 30° and (b) 20°.166
- Figure 6.21-** Decane droplet on quartz plate immersed in (a) water and (b) 75nm quat/PEG (50:50) modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 35° and (b) 26°.166
- Figure 6.21-** Decane droplet on quartz plate immersed in (a) water and (b) 5nm PEG modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 20° and (b) 14°. The quartz plate in (a) is not tilted.167
- Figure 6.23-** Decane droplet on quartz plate immersed in (a) water and (b) 25nm PEG modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 56° and (b) 51°.167
- Figure 6.24-** Decane droplet on quartz plate immersed in (a) water and (b) 75nm PEG modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 52° and (b) 49°. The color in (b) is digitally altered to see the droplet clearly since the light transmittance of nanoparticle dispersion is low because of particle size.167

Figure 6.25- Decane droplet on quartz plate immersed in (a) water at 80°C and (b) 5nm PEG modified silica nanoparticle dispersion of 1wt% at 80°C. The contact angle is (a) 59° (b) 45°.....	168
Figure 6.26- Decane droplet on calcite plate immersed in (a) water and (b) 5nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 32° and (b) 24°.....	168
Figure 6.27- Decane droplet on calcite plate immersed in (a) water and (b) 25nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 21° and (b) 18°.....	169
Figure 6.28- Decane droplet on calcite plate immersed in (a) water and (b) 75nm sulfonate modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 38° and (b) 36°.....	169
Figure 7.1– Pictures of 10 g solution with 0, 0.5, 0.75, 1, 1.25, 1.5 and 1.75 wt% NaCl with 0.2 g clay.	179
Figure 7.2– Pictures of 10 g solution with 0.5, 1, 1.5, 1.75, 2 wt% KCl with 0.2 g clay.....	180
Figure 7.3 – Picture of 10 g solution of DI water, 1 wt% 5 nm unmodified, 1 and 5 wt% sulfonate modified, 1 and 5 wt% PEG modified and 1 and 5 wt% quat/PEG modified silica nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.	180
Figure 7.4 – Picture of 10 g solution of DI water, 1 and 10 wt% 5 nm unmodified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.	181

Figure 7.5 – Picture of 10 g solution of DI water, 1, 5 and 10 wt% 5 nm sulfonate modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.	181
Figure 7.6 – Picture of 10 g solution of DI water, 1, 5, and 10 wt% 5 nm PEG modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.	182
Figure 7.7 – Picture of 10 g solution of DI water, 1, 5, 7.5 and 10 wt% 5 nm quat/PEG modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.	182
Figure 7.8 – Picture of 10 g solution of 5 wt% 5 nm particles of unmodified and 0.5 wt% NaCl, quat/PEG modified and 0.5 wt% NaCl and 0.5 wt% KCl, sulfonate modified and 0.5 wt% NaCl and 0.5 wt% KCl, PEG modified and 0.5 wt% NaCl and 0.5 wt% KCl. Each sample contains 0.2 g clay. The picture was taken 4 months after preparation of samples.	183
Figure 7.9 – ATR-FTIR spectra of dried clay/nanoparticle dispersion mixture.	184
Figure 7.10 – X-ray diffraction of clay/nanoparticle dispersion mixture in glass capillary.	187
Figure 7.11 - Picture of 5g solution of 1.5wt% NaCl with 0.05g clay without nanoparticles and with 5 nm PEG modified nanoparticles at 0.04, 0.06, 0.1, 0.4, 0.6 and 1wt% concentration in dispersion.	188
Figure 7.12 - Calibration curve for 5 and 25nm diameter PEG modified nanoparticle dispersions by UV-Vis spectrophotometer.	190

Figure 7.13- UV-Vis spectra for 5 nm PEG modified silica nanoparticle dispersions before and after in contact with clay.....	191
Figure 7.14- Adsorption of PEG modified silica nanoparticles on clay at 1.5wt% NaCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.....	192
Figure 7.15- Adsorption of PEG or quat/PEG modified silica nanoparticles on clay at 1.5wt% NaCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.....	193
Figure 7.16- Adsorption of PEG modified silica nanoparticles on clay at 1.5wt% NaCl and 1.5 wt% KCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.....	194
Figure 8.1- Schematic presentation of the experimental setup for determination of viscosity of nanoparticle dispersions in porous media.	204
Figure 8.2- Picture of the flow loop with glass beads packed in a glass column of 2.5 cm diameter and 18 cm long.....	204
Figure 8.3- Picture of sand pack flow loop.....	205
Figure 8.4- Picture of epoxy coated Berea sandstone core.....	205
Figure 8.5– Calibration curve for NaCl concentration using a conductivity probe.....	206
Figure 8.6– Normalized concentration of the tracer vs. cumulative injection through sand pack. The line connecting the data points is for visual purpose.....	206
Figure 8.7- Pressure drop across the glass bead pack.....	208
Figure 8.8- Normalized concentration vs. cumulative injection in terms of pore volume (PV) for tracer (NaCl) and nanoparticle dispersion in flow through glass bead pack.....	209

Figure 8.9- Pressure drop across the glass bead pack vs. flow rate for 5nm and 25nm unmodified nanoparticle dispersions.	210
Figure 8.10- Pressure drop across the sand pack vs. flow rate for 5nm and 25nm unmodified nanoparticle dispersions	211
Figure 8.11- Pressure drop as a function of flow rate for 1 wt% 5 nm unmodified nanoparticle dispersion and for water.	212
Figure 8.12- Pressure drop profile in time for a tracer (0.05 wt% NaCl) and 1 wt% 5 nm unmodified nanoparticle dispersion flowing through sandstone core.	215
Figure 8.13- Viscosity ratio as a function of volume fraction of silica nanoparticles of various sizes (5, 8, 25 and 75 nm) and two different surface types (unmodified and sulfonate coated). The volume fractions are normalized to the corresponding effective maximum packing fraction. All the data collapsed onto a single curve that is well represented by the unified model. The results obtained from glass bead, sand pack and limestone follow the same curve as the bulk rheology data.	216
Figure 9.1– Calibration curve for 5nm PEG coated nanoparticle dispersions by a using conductivity probe and a UV-Vis spectrophotometer.	222
Figure 9.2– Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 7 and there is no background electrolyte. Picture of an oil drop at the tip of the J-needle immersed into water or silica nanoparticle dispersion is shown for different nanoparticle concentrations.	224
Figure 9.3– The change in IFT of crude oil/water as a function of 5 nm PEG modified nanoparticles at pH 7 and 9.	224

Figure 9.4 – The adsorption of nanoparticles at the crude oil/water interface. The equivalent molecules of PEG concentration at the interface as a function of bulk nanoparticle concentration at pH 7 and 9	225
Figure 9.5 – The change in IFT of crude oil/water with time in the presence of 5 nm PEG modified nanoparticles at pH 7 and 9.....	228
Figure 9.7 – The change in IFT of crude oil/water and volume of oil drop used in the measurements in time for 5 nm PEG modified nanoparticles at pH 9.	230
Figure 9.8 – Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5. The initial pH of aqueous phase is 7.....	231
Figure 9.9 – Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The initial pH of aqueous phase is 7 and the concentration of 5 nm PEG-modified nanoparticles is 5 wt% in aqueous phase.	232
Figure 9.10 – Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The initial pH of aqueous phase is 9.	232
Figure 9.11 – Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The initial pH of aqueous phase is 9 and the concentration of 5 nm PEG modified nanoparticles is 5 wt% in aqueous phase.	233

Figure 9.12 – Volume of middle phase as a function of NaCl concentration. The initial pH of aqueous phase is 9 and the concentration of 5 nm PEG modified nanoparticles is 5 wt% in aqueous phase.	233
Figure 9.13 – Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 9 and there is no background electrolyte.	235
Figure 9.14 – Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 9 and there is no background electrolyte.	236
Figure 9.15 –Picture of the glass bead pack at residual oil saturation.	238
Figure 9.16 –The effect of residual oil on the retention of PEG coated silica nanoparticles in glass bead pack.	239

Chapter 1: Introduction

1.1 PROBLEM STATEMENT

A nanoparticle is an aggregate of atoms bonded together with a size between 1 and 100 nm. Emerging nanotechnology is bringing new ideas to the application of nanoparticles in the petroleum industry as subsurface applications of nanotechnology appear especially promising in the alteration of reservoir rock and fluid properties, such as, the wettability and interfacial tension, or monitoring reservoir properties, and removing subsurface hydrocarbon contaminants.

A better understanding of reservoir rock and fluid properties is essential to accurately characterize the reservoir, design enhanced oil recovery processes, and improve risk evaluation. Nanoparticles can offer a way of controlling oil recovery processes that is unmatched by current or previous technology. Nanoparticles can be functionalized to perform as sensors. They can collect spatial distribution of pressure, temperature, and fluid saturation when injected into a reservoir. In-situ mapping of modified nanoparticles can also provide important information on the rock heterogeneity. In addition, they offer a means of interrogating small-scale physics.

Although recent advances in nanotechnology show potential applications in hydrocarbon formation characterization and enhanced oil recovery, the behavior of nanoparticles in porous media and governing factors have not been well understood. The stability of nanoparticles in the aqueous phase (Figure 1.1-A) can be influenced by a significant variation of harsh environmental conditions, i.e., temperature, pressure, salinity and pH, during their transport from the surface facility into a reservoir. The rheological behavior, i.e., stress-strain rate relationship of a nanoparticle suspension (Figure 1.1-B), may vary in time due to a possible change in the nanoparticle

concentration (due to phase separation or deposition of nanoparticles) or the effective particle size (due to aggregation). Another factor that can cause a change in particle concentration is the partitioning of nanoparticles onto fluid-solid and fluid-fluid interfaces. In the former process, the presence of nanoparticles may destabilize the thin oil film coating on the rock surface and hence alter the wettability (Figure 1.1-C). The adsorption of nanoparticles on a rock surface and their structural ordering at the three-phase region, may contribute to an enhanced motion of the contact line (Figure 1.1-D). The latter process may change the interfacial tension between an aqueous phase and an oleic phase. Therefore, the presence of nanoparticles would have a direct effect on the displacement of the oleic phase in a porous media through modifying capillary and viscous forces (Figure 1.1-E).

The success of nanoparticles in such applications depends on the ability to place them in the right location in a reservoir. Therefore a systematic study, with both elements of modeling and experiments, will provide a better understanding of the dynamics of nanoparticles in porous media. The results of this research bring new insight to the characterization of the stability of nanoparticles in the aqueous phase, the adsorption at fluid/fluid and fluid/mineral interface and the characterization of nanoparticle transport. The findings of this research help enable new possibilities to apply nanoparticles for improved oil recovery.

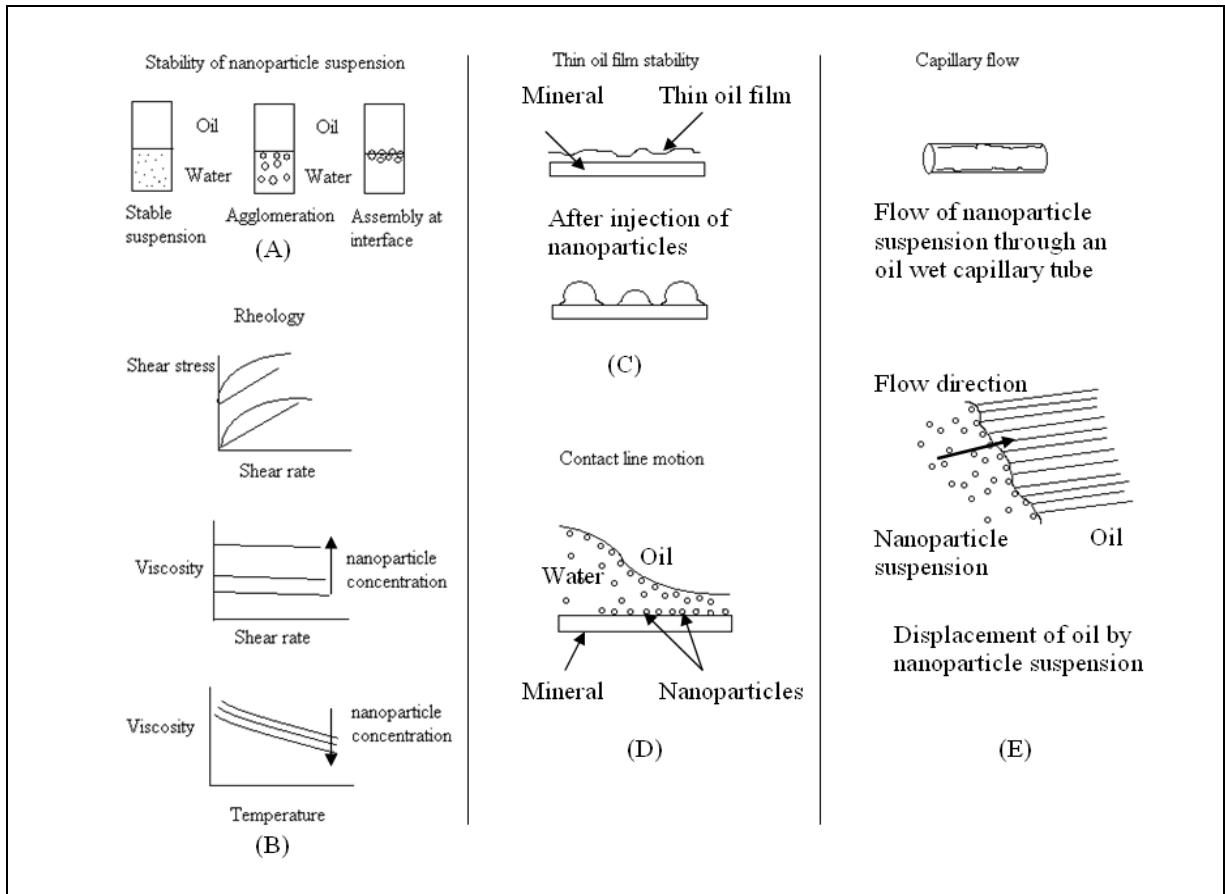


Figure 1.1- The stages of the nanoparticle transport from surface to reservoir. In (A), the figure shows a stable nanoparticle suspension, agglomeration of nanoparticles and the assembly of nanoparticles at fluid interface. The relationship between shear stress and shear rate relation is the top figure in (B). Figures in the middle and at the bottom in (B) show schematically viscosity as a function of nanoparticle concentration, shear rate and temperature. In (C), the figure illustrates the thin oil film stability and the formation of a contact angle because of nanoparticles. The effect of nanoparticles on contact line motion is presented in (D). Porous media - represented as a capillary flow and the displacement of oil by nanoparticle suspension are illustrated schematically in (E).

1.2 OBJECTIVE

The overall objective of this dissertation is to characterize and demonstrate control the mobility of nanoparticles in porous media based by a thorough understanding of the conditions necessary for the stability of nanoparticle dispersions, the aggregation kinetics for unstable suspensions, the rheology of stable or unstable suspensions as a function of particle size, volume fraction and surface type, and the interactions between the nanoparticles and oil/water interface and mineral surfaces, Figure 1.2. This understanding is extended to the challenges facing the control of nanoparticle transport such as the variations of pH, ionic strength of the brine, presence of crude oil, variety of minerals present in the reservoir rocks and the pore-network structures, and a possible alteration of mineral surface wetting and spreading due to nanoparticle adsorption.

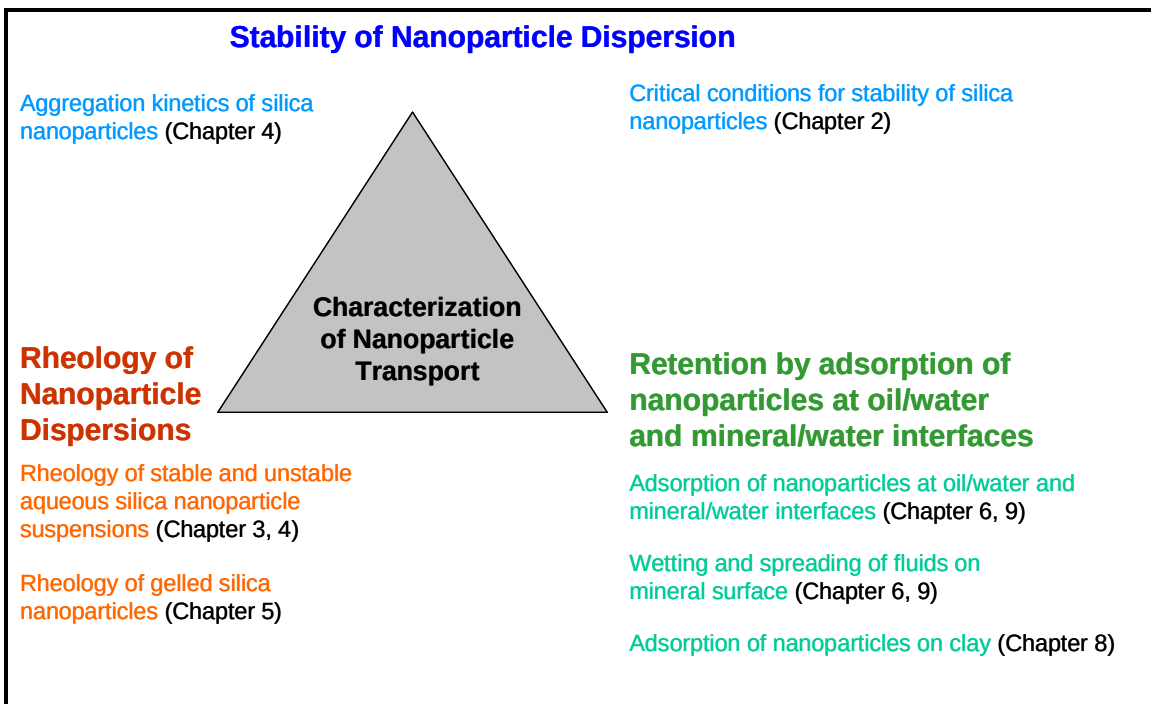


Figure 1.2- The objectives of this research include the determination of the stability of silica nanoparticle dispersions, their rheology and the interaction of nanoparticles with minerals and oil/water interface to characterize the transport of nanoparticle dispersions through a permeable media.

1.3 RESEARCH APPROACH

The research objective was carried out through a systematic approach with both elements of experiments and modeling. The aqueous stability of nanoparticle dispersions was evaluated by visual observations and quantitative methods using non-intrusive analytical techniques: attenuated total reflectance, Fourier transform infrared (ATR-FTIR) spectroscopy, an ultraviolet-visible (UV-Vis) spectrophotometer, zeta potential analyses, and dynamic light scattering (DLS). These techniques were used to study the effects of pH, temperature and electrolytes on colloidal stability. Dynamic light scattering (DLS) gave the size distribution of nanoparticles in the suspension. Any change in the size and shape of nanoparticles was detected by DLS and UV-Vis as the intrinsic

nanoparticle size, pH and temperature of the suspension change. The aggregation kinetics was determined by measuring the change, over time, in the effective size of an aggregate using DLS. Zeta potential measurements were used to characterize the surface charge of nanoparticles. Experimental observations were validated by DLVO theory. The results were also compared with molecular dynamics (MD) simulations to better understand the details in the underlying mechanisms. The local structure of solvents near the nanoparticles in the presence of electrolytes was obtained through MD simulations which shed light on the understanding and modeling of critical conditions for colloidal stability.

Rheological characterization of nanoparticle dispersions first involved experimental studies. Rheology data gave the relation between the shear rate and shear stress of stable nanoparticle dispersions. The effects of particle size, surface type and temperature on this relationship were quantified. These effects were incorporated into a scaled Newtonian viscosity model that was validated against the experiments.

A phase behavior study was carried out for unstable silica nanoparticle dispersions as a function of electrolyte concentration. The samples in the phase region of gelation were studied experimentally and existing non-Newtonian models were used to explain the viscosity-shear rate relation observed.

The adsorption of silica nanoparticles onto representative mineral surfaces (quartz and calcite) was studied experimentally by measuring the concentration of nanoparticles in dispersion using a UV-Vis spectrophotometer. The adsorption of nanoparticles at the decane/water interface was evaluated by interfacial tension (IFT) measurements. The effects of particle size, concentration and surface type on the adsorption were studied in detail. The results of adsorption experiments were validated with Gibbs equation of adsorption and DLVO theory. Inverse gas chromatography was used to measure the surface energy of mineral powders. Then contact angle measurements of a decane droplet

on quartz or calcite plate immersed in water (or aqueous nanoparticle dispersion) were carried out using a goniometer to investigate the influence nanoparticles exert to change the original wetting of mineral surfaces.

Flow experiments of nanoparticle dispersions through an unconsolidated medium incorporated all the knowledge acquired with the understanding and modeling of the thermodynamics, i.e., stability and transport, i.e., rheology properties of nanoparticles and their interactions with minerals and fluid/fluid interface.

1.4 OUTLINE OF THE DISSERTATION

The outline of this dissertation follows the research approach explained above. The methods used to identify and evaluate the stability of aqueous nanoparticle dispersions are introduced in chapter 2. The effects of pH, electrolyte concentration and type, nanoparticle size, concentration and surface type on the colloidal stability are presented. The effect of temperature on stability is also discussed. DLVO theory for the interaction energy between particles is applied in this chapter to nanoparticle dispersion. The match of the theory with experimental data and the limiting factors in DLVO theory which may be better addressed through MD simulations are also discussed.

In chapter 3, systematic study on the characterization of the shear rheology of silica nanoparticle dispersions is presented. The effects of particle size, concentration, and surface type and temperature on the viscosity of silica nanoparticle dispersions are quantified. A methodology for predicting viscosity of silica nanoparticle dispersions at a given solid volume fraction based on the concept of effective maximum packing fraction is introduced. This concept is used to scale all the measured viscosity data.

The aggregation behavior of colloidally unstable nanoparticle suspensions is discussed in chapter 4. A systematic study of the aggregation of silica nanoparticle dispersions and their rheological behavior under the pH and NaCl conditions that can occur in hydrocarbon reservoirs is discussed. The effect of the size of the primary silica nanoparticles, NaCl and particle concentration on the aggregation kinetics of silica is determined by measuring the change in aggregate size as a function of time. A new model to describe the aggregation kinetics is proposed and experimental data or theory is used to determine the model parameters. The proposed model provides the framework to collapse all of the data onto a single curve by using dimensionless numbers. The rheology of unstable silica suspensions is also modeled using the effective maximum packing fraction concept coupled with effective aggregate volume fraction.

Chapter 5 covers the study of the equilibrium phase behavior of silica nanoparticle solutions in the presence of sodium chloride (NaCl). The experiments of the rheology of solutions in the gel region are presented. This chapter focuses on the determination of the onset of gelation as a function of silica and NaCl concentration and temperature. The rheological parameters such as storage/loss modulus and viscosity of these silica nanoparticle gels are obtained experimentally and used to understand the structure of nanoparticle networks and their behavior under applied strain and shear rate. The viscosity results are matched with existing non-Newtonian models.

Chapter 6 presents the study on the interaction of unmodified and surface modified silica nanoparticles with mineral surfaces and decane/water interface. Adsorption experiments with the silica nanoparticles onto quartz and calcite surfaces are presented. Interfacial tension (IFT) measurements are also given to provide insightful information on the interaction of silica nanoparticles with decane/water interface. The effects of particle size, concentration and surface type of silica nanoparticles are studied

in detail. This chapter highlights the importance of surface modifiers on silica nanoparticles and the design of experiments when studying the adsorption of nanoparticles with minerals or water/hydrocarbon interface. Modeling of the adsorption of nanoparticles on minerals is done by using DLVO theory and Gibbs equation is used for the determination of the adsorption of nanoparticles at decane/water interface from IFT results. The restrictions in DLVO theory are discussed. Contact angle measurements are also presented to confirm the findings from nanoparticle dispersion/mineral and nanoparticle dispersion/decane interactions.

Chapter 7 presents the adsorption of nanoparticles on clay minerals. The swelling behavior of clays in the presence of nanoparticles is discussed. Visual observations and analytical methods such as ATR-FTIR and x-ray diffraction (XRD) are used to understand the interaction of nanoparticles with clay minerals. The adsorption of nanoparticles on clay surface is studied experimentally using a UV-Vis spectrophotometer as discussed in chapter 6. Adsorption isotherms are built based on the experimental results.

In chapter 8, the behavior of nanoparticle dispersions during flow through an unconsolidated medium are discussed. The model developed for the bulk rheology of silica nanoparticle dispersions is applied to flow through glass bead or sand packs. The rheological behaviors of the dispersions are compared with those determined using a rheometer. A correlation between the nanoparticle concentration and dispersion viscosity in porous media for various nanoparticle sizes is presented. The effects of pore structure and shear rate are also studied.

In chapter 9, the retention of silica nanoparticles at water/crude oil interface is investigated. Similar methodology, as stated in chapter 6, is applied. Interfacial tension (IFT) measurements are used to investigate the adsorption of silica nanoparticles at the

crude oil/water interface. The effects of nanoparticle surface type and concentration and dispersion pH on the IFT are presented. The adsorption isotherms are obtained using Gibbs equation. The effect of nanoparticles on the phase behavior of water and crude oil is discussed. Contact angle measurements show the ability of the nanoparticles to change the wettability of a mineral surface. The results from batch experiments are used to explain the flow behavior of these nanoparticles in glass bead pack at residual oil saturation.

In chapter 10, the possible areas of future research are discussed based on the findings presented in this dissertation. Recommendations based on both experimental and theoretical study are presented. I believe that the fundamental understanding of the stability of nanoparticle dispersions, interactions of nanoparticles with minerals and oil/water interface and the rheology of these dispersions acquired, as a result of the systematic research approach presented in this work, will contribute to the development of applications of nanotechnology in oil and gas industry as well as bring a new perspective to future research.

Chapter 2: Stability of Aqueous Silica Nanoparticle Dispersions

In this chapter, I present quantitative methods for nanoparticle stability analysis using non-intrusive analytical techniques: attenuated total reflectance, Fourier transform infrared (ATR-FTIR) spectroscopy, ultraviolet-visible (UV-Vis) spectrophotometer, zeta potential analyses, and dynamic light scattering (DLS). These techniques are used to study the stability of silica nanoparticle dispersions and the effects of pH, temperature and electrolytes that would be encountered in brines in oil field reservoirs.

Spectral analysis of the Si-O bond at wavenumber of 1110 cm^{-1} with the ATR-FTIR indicates a structural change on the surface of silica particles as the dispersion pH changes, which agrees with zeta potential measurements. A critical salt concentration (CSC) is defined for different salts, NaCl, CaCl_2 , BaCl_2 and MgCl_2 , above which the silica dispersion becomes unstable. Three distinct stages of aggregation occur in the presence of salt: clear dispersed, turbid and separated phases. Divalent cations Mg^{2+} , Ca^{2+} and Ba^{2+} are more effective in destabilizing silica nanoparticle dispersions than the monovalent cation Na^+ . The CSC for Na^+ is about 100 times more than for Ca^{2+} , Ba^{2+} and Mg^{2+} . Among the divalent cations studied, Mg^{2+} is the most effective at destabilizing the silica particles. The CSC is independent of silica concentration, and lowers at high temperature. Surface modification by sulfonate or polyethylene glycol (PEG) improves stability for monovalent and divalent cations. However, PEG gives much larger CSC than sulfonate modified nanoparticles at relatively low temperature, 25°C .

2.1 INTRODUCTION

In the recent years, nanotechnology has drawn the attention of many researchers to develop innovative solutions to satisfy the growing demand for hydrocarbons. The potential application of nanoparticle dispersions has significantly advanced into the

upstream oil and gas industry, from drilling, formation characterization, to improved hydrocarbon and geothermal heat recovery (Mokhatab 2006). The success of all of the petroleum engineering applications rests on the transport of nanoparticles in wellbores and in hydrocarbon formations. The mobility of nanoparticles in natural formations is strongly influenced by the dispersion stability of nanoparticles in a continuous phase. Typical subsurface conditions such as temperature, pH, and electrolyte concentration vary over wide ranges. It is thus difficult to control the stability of nanoparticle dispersion particularly at high salinity and high temperature.

Silica, SiO_2 , dispersions have been of interest in colloidal science because of their many applications and because their anomalous behavior of aggregation may not be predicted by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948) (Healy 2006). An aqueous nanoparticle dispersion is defined to be stable when the number of particles in a unit volume is constant with respect to time (Kissa 1999). The stability of silica dispersions depends on the structure of the silica surfaces and associated water molecules that define the characteristics of the near surface region (Hofmann et al. 1934; Zhuravlev 1987; Yalamanchili et al. 1996; Asay and Kim 2005; Hair 2006). The presence of silanol groups (Si-OH) on a silica surface was postulated by Hofmann in 1934. These hydrophilic silanol groups on a silica surface act as binding sites (H^+ bonds) for water. From experimental observations with silica gels, aerogels, and porous glasses, Zhuravlev (1987) concluded that a silanol group was the most probable compound on the surface of amorphous, fully hydroxylated silica, and that one OH group corresponded to one surface Si atom. The protonation and deprotonation of these silanol groups determines the surface charge of silica nanoparticles and the extent of the repulsive energy to keep them dispersed in the solution. For a given surface charge, the aggregation of silica

nanoparticles occurs because of the presence of electrolytes. The increasing rate of aggregation of silica nanoparticles with concentration of electrolytes is known but not well understood (Roberts 2006). The interparticle interactions of two silica nanoparticles have been recently investigated through molecular simulations to understand the stability of dispersion (Jenkins et al. 2007, 2008; Lane et al. 2009). Jenkins et al. (2007, 2008) have shown that the electrical surface charge of silica nanoparticle in the presence of background sodium, Na^+ , concentration affects the ordering of water molecules around the silica surface and the particle-water interactions (oscillatory interparticle forces). Lane et al. (2009) studied the forces acting on surface coated silica nanoparticles and concluded that surface coating suppressed the force oscillations. The study of the effects of pH, temperature, cation type and electrolyte concentration on the stability of silica nanoparticle dispersions is yet to be explored.

In this chapter, a systematic study of the stability of silica nanoparticle dispersions is presented. The effect of pH on the colloidal stability of silica is determined by different analytical methods. A critical salt concentration (CSC) is identified for monovalent (NaCl) and divalent cations (CaCl_2 , MgCl_2 and BaCl_2) above which silica nanoparticle dispersion becomes unstable. Development of quantitative methods for determining the CSC is discussed. The effect of temperature on the CSC is also investigated.

2.2 MATERIALS AND METHODS

The material under study is an aqueous dispersion of silica particles as provided by 3M, Co (St. Paul, MN, USA). The mean diameters of primary particles are 5, 8 and 25 nm, which have an unmodified (bare) surface or a modified surface with sulfonate covalently attached to a short alkyl chain or covalently bond polyethylene glycol (PEG). The shape and size of silica particles were examined by a scanning transmission electron

microscope (STEM). A droplet of the unmodified silica nanoparticle dispersion was dried on a commercial copper transmission electron microscope (TEM) grid with carbon film support. The images of silica nanoparticles are in Figure 2.1 at two magnifications. The result from dynamic light scattering (DLS) measurements also shows a mean diameter of 25nm with a polydispersity index of 0.077 indicating a narrow size distribution. Iler (1979) argued that the capillary forces during drying do not affect the shape of particles. Van Blaaderen (2006) and Vrij (2006) observed that drying does not influence the radius of particles determined with TEM measurements and that the shape of silica particles depends mainly on the method of synthesis.

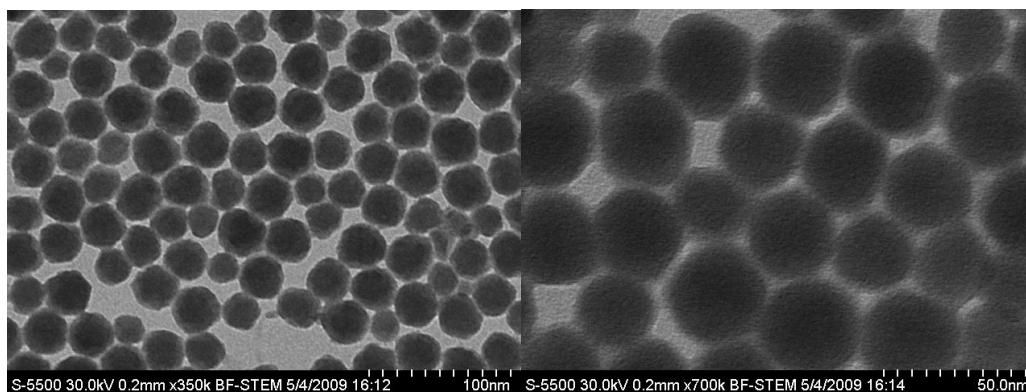


Figure 2.1- The bright field scanning transmission electron microscopy (STEM) images of dried silica dispersions at (a) 350k magnification and (b) 700k magnification.

A stock solution containing 41.13% by weight silica nanoparticles was diluted with deionized water to the desired silica concentration. Then, the pH of the silica dispersion samples was adjusted by adding a dilute hydrochloric acid (HCl) solution. NaCl, MgCl₂, BaCl₂ and CaCl₂ were the inorganic salts used in the experiments to determine the effects of electrolytes on aqueous dispersion stability. All chemicals were

of analytical grade quality. The stock solutions of the inorganic salts and the silica dispersion samples were mixed to reach the desired electrolyte concentrations. Typical ranges of salinity and hardness from natural hydrocarbon reservoir brines were used in our experiments.

A spectrum 100 FTIR spectrometer was used to identify chemical functional groups present in the silica nanoparticles and their dispersions. Samples were positioned in direct contact with an attenuated total reflectance (ATR-FTIR) diamond crystal. The ATR-FTIR spectra were then recorded from 4000 to 600 cm^{-1} at a resolution of 2 cm^{-1} . A baseline correction was applied to ATR-FTIR spectra before each measurement.

We also used an ultraviolet-visible spectrophotometer (UV-Vis) of to analyze optical absorbance of silica dispersions. The absorbance-time relationship provided a means to study the aggregation of silica dispersions.

A zeta potential analyzer was also used with a dynamic light scattering option to determine the zeta potential and effective particle diameter of silica nanoparticle dispersions.

2.3 RESULTS AND DISCUSSION

In this section, I present the results on the effect of pH on aqueous stability of silica nanoparticle dispersion, phase behavior of silica nanoparticle dispersions in presence of electrolytes, the effect of divalent cations, particle size and surface modification on critical salt concentration (CSC) and the effect of temperature on CSC.

2.3.1 The Effect of pH on Aqueous Stability of Silica Nanoparticle Dispersion

Figure 2.2 shows the respective ATR-FTIR transmittance spectra of deionized water, a dry silica sample, and a silica dispersion sample with a pH of 9.65 after dilution of stock solution to 1wt% silica. The dry silica sample was prepared by evaporating water

from the silica dispersion at 120°C for 12 hours. Deionized water shows a broad peak at 3330 cm^{-1} and a sharp peak at 1629 cm^{-1} because of the stretching and bending vibrations of the O-H bonds in the water molecules. Comparing the spectra of deionized water and the silica dispersion reveals the presence of silica nanoparticles by a characteristic Si-O peak at 1100 cm^{-1} . The deionized water curve coincided with the silica dispersion at the peaks corresponding to vibrations of O-H bonds. In the spectrum of the silica powder, two peaks corresponding to Si-O bond vibration occur at 793.4 and 1055.3 cm^{-1} . Morrow and Molapo (2006) also observed similar peaks at 1100 and 800 cm^{-1} for a silica thin film. A small and broad peak at 3300 cm^{-1} and a small peak at 1650 cm^{-1} in the spectrum of the silica powder indicate the presence of adsorbed water that remains after drying. The transmittance corresponding to the Si-O peak at 1100 cm^{-1} in the silica dispersion is large compared to silica powder because of the small concentration of silica nanoparticles (1 wt%) in the dispersion. For a given nanoparticle concentration, the area of the Si-O peak varies with the degree of hydroxylation of silica nanoparticle surface as pH changes. Moreover, the Si-O peak at 793.4 cm^{-1} observed with powder silica particles is suppressed by water in silica dispersions (Figure 2.2). Therefore, only the Si-O peak at 1100 cm^{-1} is used to evaluate the effect of pH on the aqueous stability of a silica nanoparticle dispersion.

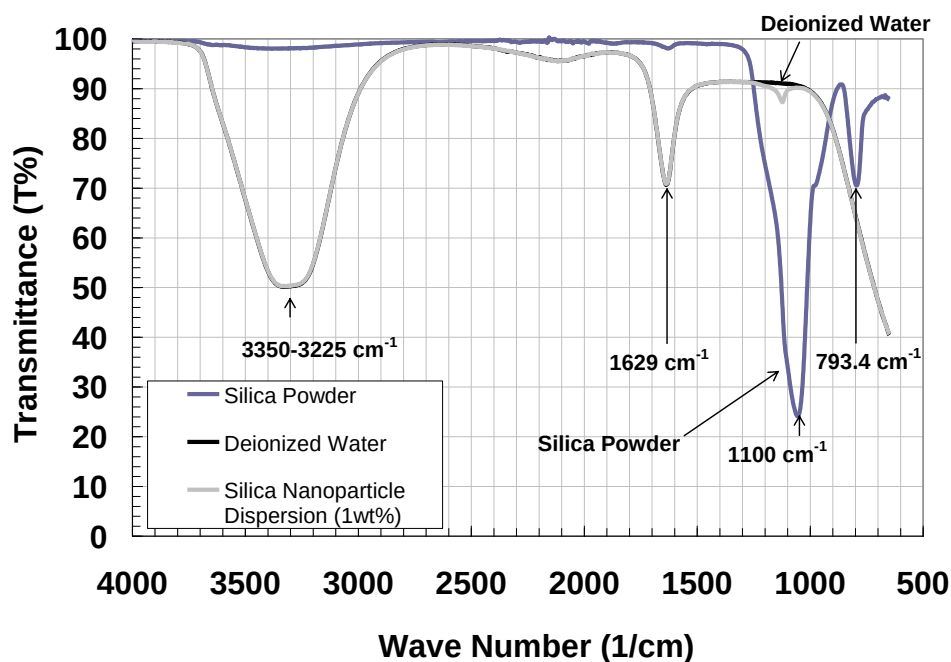


Figure 2.2- ATR-FTIR transmission spectrum of dried silica powder, 25nm unmodified silica particle dispersion, and deionized water. Stretching and bending vibrations of water molecules show peaks at 3330 and 1629 cm⁻¹, respectively. The silica powder has the Si-O bond vibrations at 793.4 and 1055.3 cm⁻¹. Only the Si-O at 1100 cm⁻¹ is detectable in case of the silica dispersion.

We measured the infrared light (IR) transmittance of two respective series of 0.5 and 1 wt% silica particle dispersions, whose pH varied over a wide range from 2.5 to 10. All of these samples exhibit a stable clear phase, indicating an indiscernible effect of pH on the stability of silica nanoparticle dispersion. However, a plot of Si-O peak area, which is the area under the peak at 1100 cm⁻¹, versus pH, as shown in Figure 2.3, suggests a significant variation of silica nanoparticle surface structure with pH. The peak area first decreases sharply as pH increases, and then levels off at around a pH=7, regardless of particle concentration. A small increase in the peak area at a given pH is because of an increase in particle concentration.

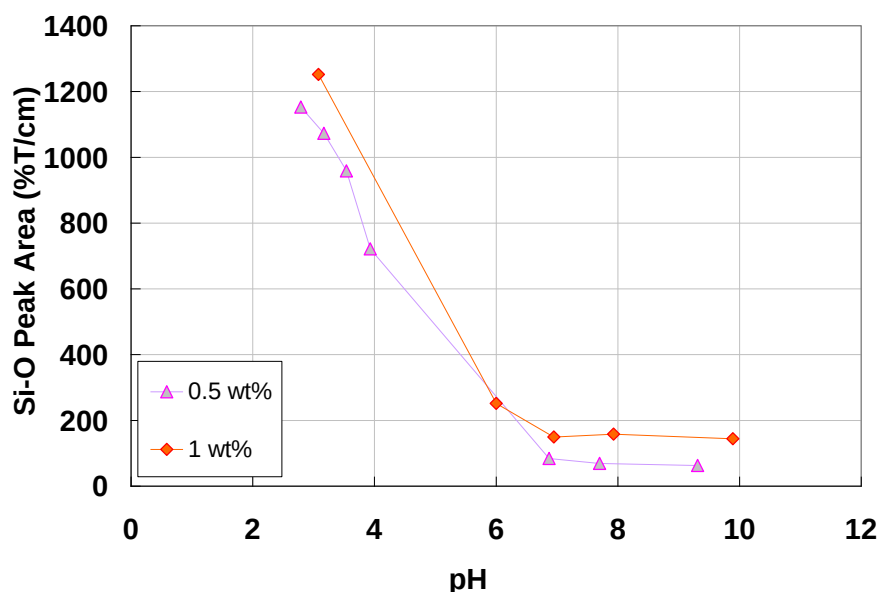


Figure 2.3- The area under the Si-O peak at 1110 cm^{-1} as a function of pH for 0.5 and 1 wt% particle concentrations. The change in the slope of the peak area of the Si-O bond around pH=7 indicates a structural change of the silica nanoparticle surface.

The surface charge of metal-oxide particles in water may vary from positive to negative as pH increases because of surface deprotonation (Hunter 2001). The isoelectric point is defined as the pH at which the surface is neutrally charged. The measured zeta potential, which represents the potential at the shear plane (Hunter 2001) of the silica nanoparticles, is plotted versus pH as shown in Fig. 2.4. It is around -45mV as pH decreases from 10 to 6, but sharply increases with further decrease in pH. This trend is observed for both 0.5 and 1 wt% particle concentrations, which is consistent with the relationship between IR transmittance and pH (see Figure 2.3). Furthermore, extrapolating the potential curve to the smaller pH range in Figure 2.4 suggests that the silica surface approaches the isoelectric point at a pH around 3.4.

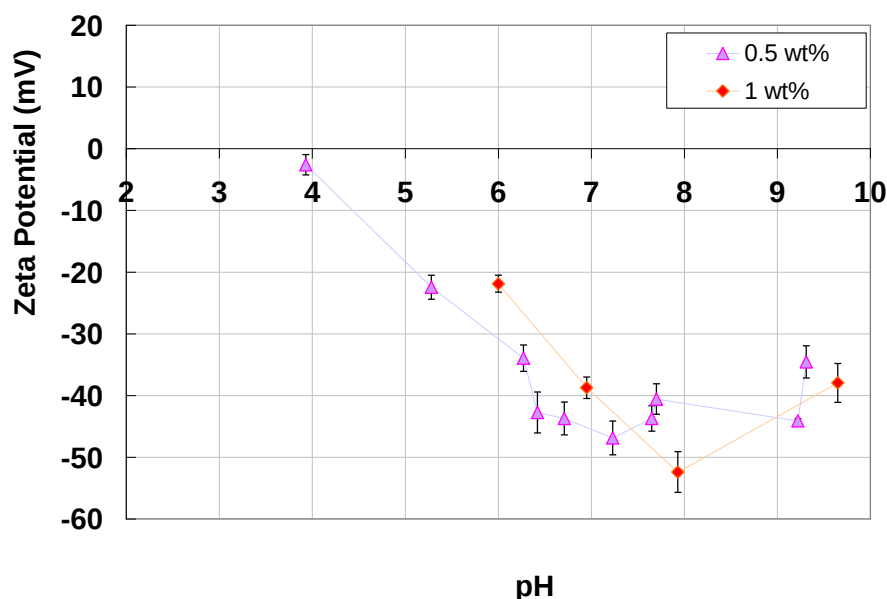


Figure 2.4- Zeta potential of silica particle dispersions as a function of dispersion pH. The vertical error bars in the graph are the mean standard errors of the zeta potential measurements. The isoelectric point (IEP) is estimated as pH=3.4 by extrapolation of linear regression fit to points at pH=8 or smaller. The zeta potential measurements below pH=4 exceeded the conductance limit of the zeta potential analyzer therefore zeta potential measurements are not in this pH range.

The pH-induced aggregation of silica particles is not seen by visual observation because of the possible nanometer-sizes of aggregates. Another way to identify the presence of nanoparticle aggregation is through ultraviolet-visible spectroscopy (UV-Vis) and dynamic light scattering (DLS). Figure 2.5a shows the light absorbance of silica dispersions as a function of pH for two different particle concentrations at 400 nm. The variation of absorbance with pH could be clearly observed at this wavelength. From this figure the absorbance does not significantly change with pH. This suggests the absence of particle aggregation, which is confirmed by the results from the DLS measurements in

Figure 2.5b. The effective particle diameter increases by a factor of 1.36 as pH decreases from 10 to 2. Therefore, particle aggregation is not responsible for the observed slight change of the effective particle diameter with pH despite of the significant pH-induced reduction of particle surface charge (see Figure 2.4). The effective diameter determined by DLS is the diameter of the nanoparticle plus the thickness of a layer of water and ions that are bound, with varying degrees of strength, to the particle. The latter is partially determined by the surface potential of particles, which is in turn influenced by pH as shown in Figure 2.4. This most likely explains the relationship between the effective particle diameter and pH shown in Figure 2.5b.

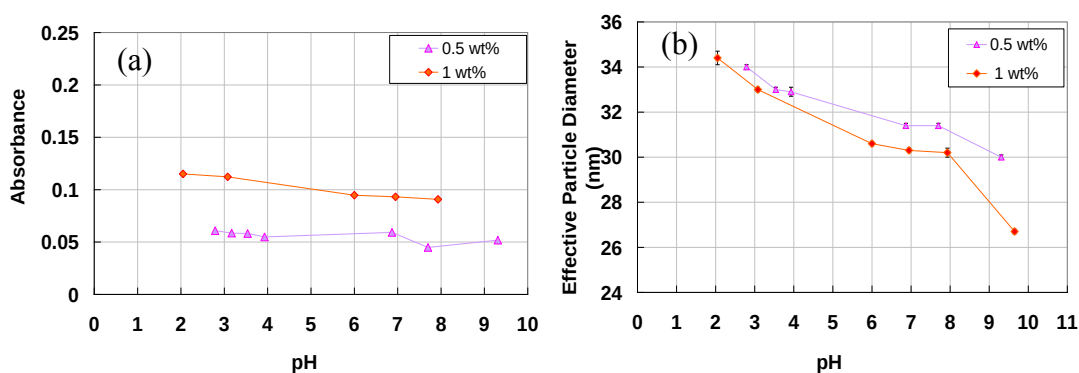


Figure 2.5- (a) UV-Vis absorbance of 0.5 and 1 wt% silica particle dispersions at 400nm wave length as a function of pH, (b) The effect of pH on effective particle diameter for 0.5 and 1 wt% silica dispersions by DLS measurements.

The silica nanoparticles used in the experiments on the effect of pH made a stable clear phase with water. The effective particle diameter was close to the actual diameter of nanoparticles (Figure 2.5b). These clear dispersions had an absolute zeta potentials much smaller than 40mV, which indicates the degree of the stability of a dispersion (ASTM

Standard 1985). When the extent of the repulsive energy is smaller compared to the van der Waals attraction energy the dispersion becomes unstable giving rise to the aggregation of particles. As discussed above, the silica nanoparticles exhibit a stable dispersion in the pH range studied. Kitchener (1971) drew attention to this anomalous stability of silica dispersions, in contradiction with DLVO theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948), around pH 2-3 where their zeta potential is minimal. Kitchener (1971) discussed that the existence of polysilicic acid filaments on the silica surface formed in situ, could be the reason for this extraordinary stability around the isoelectric point.

These thin silica hairs on the surface (Iler 1979) could push the double layer repulsion out to extend further than van der Waals attraction and also generate an additional short-range steric repulsion (Israelachivili et al. 1996).

2.3.2 Phase Behavior of Silica Nanoparticle Dispersions in Presence of Electrolytes

Electrolytes could also destabilize particle dispersions by compressing the electrical double layer. As the electrolyte concentration increases, the energy barrier is lowered to an extent that kinetic energy of particles dictates the kinetics of particle aggregation (Derjaguin and Landau 1941; Verwey and Overbeek 1948). In this section, the effect of NaCl as an indifferent electrolyte on the stability of silica nanoparticle dispersions is evaluated. The NaCl is indifferent because it does not adsorb on the particles.

Figure 2.6 shows the phase behavior of silica dispersions that are different in NaCl and particle concentrations. For small particle concentration (e.g. 0.5 wt% particle in Figure 2.6), the addition of NaCl up to around 1.5 wt% does not destabilize the aqueous dispersion of silica nanoparticles. However, a further increase in NaCl

concentration leads to a phase transition. This phase behavior suggests that 1.5 wt% NaCl represents a critical salt concentration (CSC) above which particle aggregation and sedimentation visually occurs. When the NaCl concentration is increased above its CSC, three distinct subsequent stages of particle aggregation could be observed: (1) an early-time stage characterized with a single clear phase (e.g. vials shown in Figure 2.6 with 0.5 wt% particle concentration and 3 wt% NaCl at 1 hour), (2) a precipitation stage with a single turbid phase (e.g. same vials 10 days later), and (3) a sedimentation stage with two separate phases (e.g. the same vials after 41 days). The subsequent occurrence of the precipitation and sedimentation stages is accelerated by either increasing NaCl or particle concentration. For example, Figure 2.6 shows that for 2 wt% NaCl concentration the particle dispersion with 2 wt% particle concentration approaches the end of the precipitation stage after 10 days while the dispersion with 0.5 wt% particle concentration is still in the early-time stage. However, these two factors were found not to significantly influence the CSC for NaCl.

Particle aggregation occurs during the early-time stage when the electrolyte concentration is above its CSC. However, the formation of nanometer-sized aggregates may not be visually observed. In addition, a CSC could be determined accurately through DLS measurements of effective particle diameter. It is important to determine the light absorption characteristic of silica particle aggregates in the UV-Vis range as the UV-Vis spectrophotometer provides a convenient technique for studying aggregation kinetics. For the above purposes, DLS and UV-Vis measurements were conducted on a series of particle dispersions with different electrolyte concentrations. The results are in Figure 2.7.

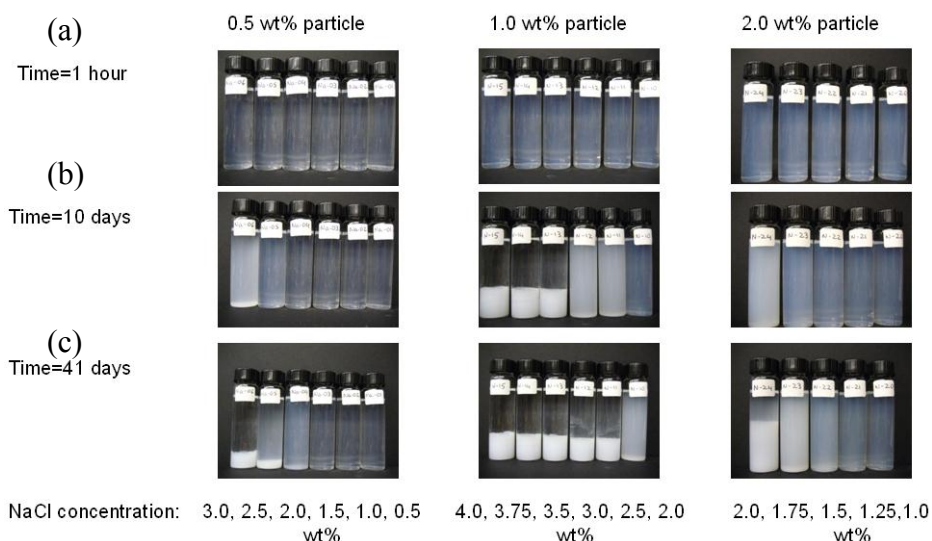


Figure 2.6- Photographs of sealed tubes that show the phase behavior of unmodified silica nanoparticle dispersions at various NaCl and nanoparticle concentrations at (a) 1 hour, (b) 10 days and (c) 41 days. Three distinct sequential stages of aggregation, i.e., single clear phase, a turbid single phase and two separate phases.

Figure 2.7 shows that the absorbance profile for 0.5 wt% particle concentration at 400nm wavelength is characterized by a transition from a uniform to a sharp increase as NaCl increases above a critical value. This critical value does change with time (i.e. from 2 wt% at 1 hour to 1 wt% after 43 days) and eventually reaches an approximate value of 1 wt%, which defines the equilibrium CSC for NaCl. The variations of effective particle diameter in time and with NaCl concentration are in Figure 2.7. The effective particle size increases sharply from 25 nm to 200 nm with NaCl concentration above CSC. The effective particle diameter profiles are very close to the UV-Vis light absorbance profiles. Both techniques give almost the same CSC. Therefore, the UV-Vis spectrometry is also used in determining the kinetics of particle aggregation.

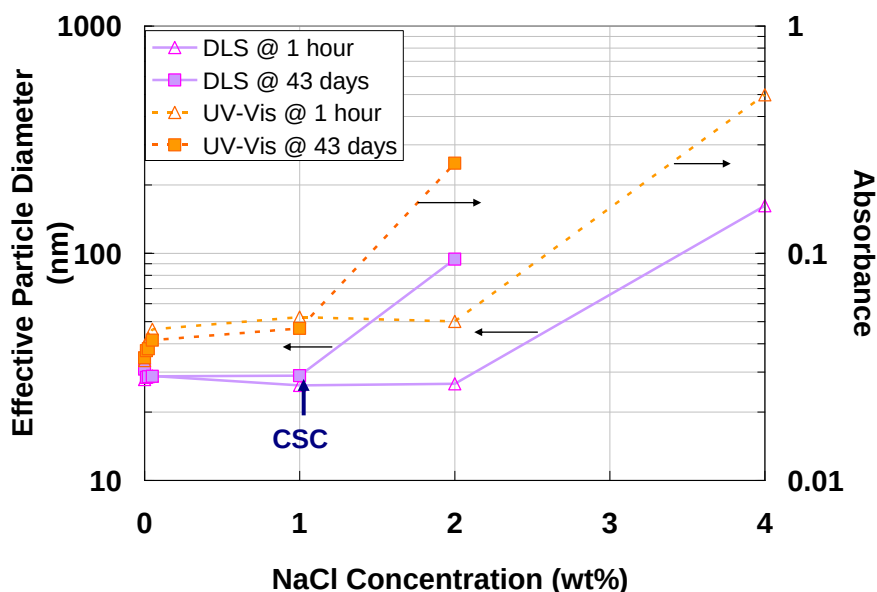


Figure 2.7- Effective particle diameter and UV-Vis absorption at 400nm wave length of 0.5 wt% unmodified silica dispersions in the presence of NaCl. A significant increase in effective diameter and absorbance occur initially at 2 wt% NaCl but this critical concentration shifts to an equilibrium value (CSC) of 1 wt% at 43 days.

Figure 2.8 shows the light absorbance for a 0.5 wt% particle dispersion in the presence of 3 wt% NaCl (above the NaCl CSC). The rate of increase in absorbance reflects the kinetics of particle precipitation. In the sedimentation stage, the gravitational potential overcomes the dispersive interparticle and particle-solvent interactions. The sedimentation of nanoparticles was clearly observed after around 190 hours. Plaza et al. (2002) carried out stability experiments with hematite/yttrium oxide core-shell particles by measuring their optical absorbance. They suggested that the slope of an absorbance curve carries the most significant information about particle-particle aggregation. A positive slope indicates a doublet of particles that has larger extinction cross section than two individual particles sufficiently far apart. In our experiments with 1, 2 and 3 wt% NaCl at 0.5 wt% silica concentration, we observed a negative slope during the early-time

stage (i.e. first one hour) which may indicate that a doublet of silica particles has a smaller extinction cross section than two individual particles far apart in the dispersion (Plaza et al. 2002). This negative slope is not visible in Figure 2.8 because of the large time scale.

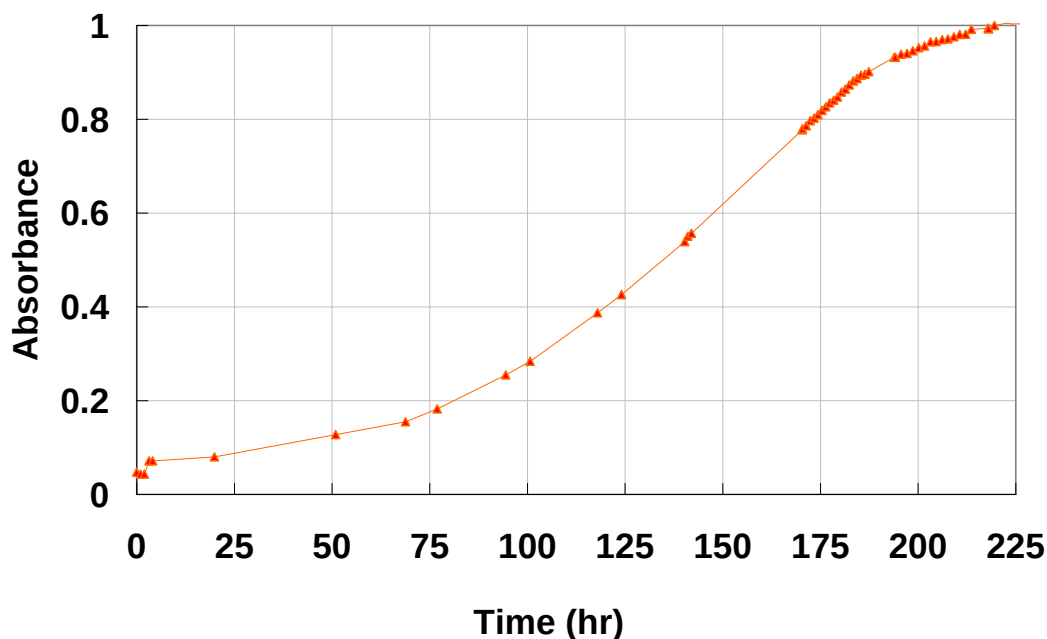


Figure 2.8- UV-Vis light absorption of a 0.5 wt% unmodified silica particle dispersion with 3 wt% NaCl as a function of time.

2.3.3 Effect of Divalent Cations on Critical Salt Concentration (CSC)

Figures 2.9 and 2.10 show phase behavior images of silica particle dispersions in the presence of MgCl_2 and CaCl_2 , respectively. There was no background NaCl in these experiments. For both Mg^{2+} and Ca^{2+} , an increase in concentration above a critical value gives rise to particle aggregation, consistent with the phase behavior observed for NaCl (see Figure 2.6). A silica particle dispersion exhibits an equilibrium clear phase for

divalent cation concentration lower than 0.02 wt%, which is one hundred times lower than that for the monovalent cation (CSC for NaCl is 1 wt%). For a divalent cation concentration above 0.04 wt%, the particle aggregation is so effective that the early-time stage is almost absent; sedimentation begins only after 1 day. Among these cations, Mg^{2+} exhibits the greatest effect on particle dispersion destabilization. Furthermore, comparing phase transitions of Mg^{2+} (Figure 2.9) and Ca^{2+} (Figure 2.10) at a given electrolyte and particle concentrations reveals that an increase in particle concentration accelerates aggregation for divalent cations. An increase in nanoparticle concentration shortens the average distance travelled by a particle between collisions, resulting in an increase in aggregation rate for a salt concentration above CSC. However, the particle concentration does not influence the CSCs for these cations. Elimelech (1998) argues that particle concentration should not affect critical coagulation concentration if the electrolyte is indifferent. In other words, if there is not any specific adsorption of counterions onto the surface of a particle, the extent of the repulsive energy is not changed and hence the concentration of particles does not affect critical salt concentration.

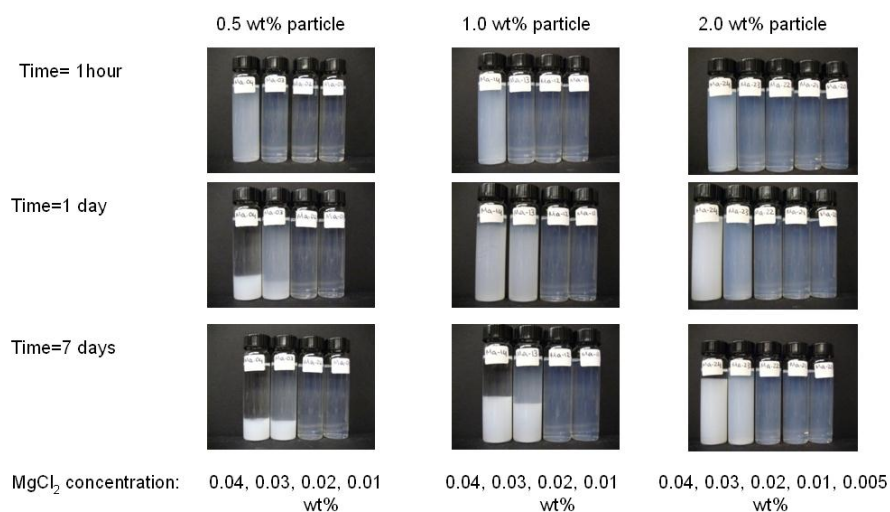


Figure 2.9- Photographs of sealed tubes that illustrate the phase behavior of silica dispersions with MgCl_2 at 1 hour, 1 day and 7 days at 25°C . Three distinct sequential stages of aggregation are observed at various MgCl_2 and nanoparticle concentrations. The transition between a stable and an unstable dispersion (aggregation followed by sedimentation) occurs around 0.03 wt% MgCl_2 for all three nanoparticle concentrations.

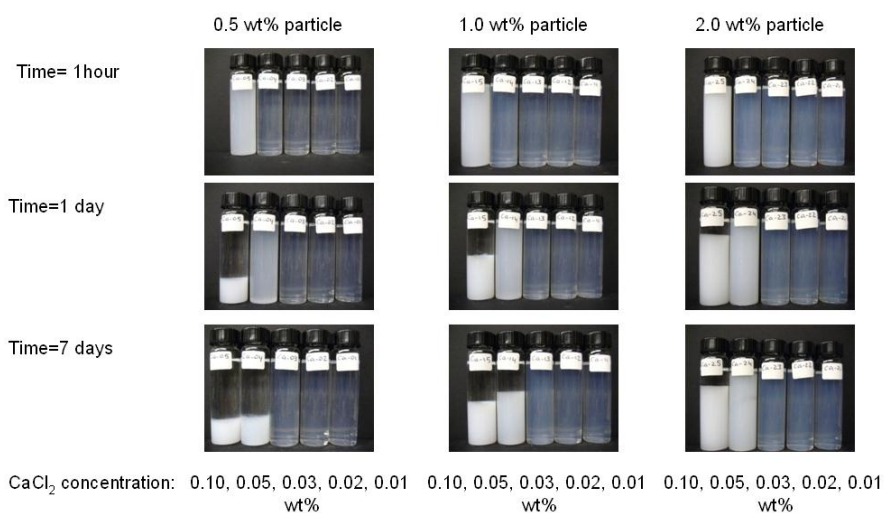


Figure 2.10- Photographs of sealed tubes that illustrate the phase behavior of silica dispersions with CaCl_2 at 1 hour, 1 day and 7 days at 25°C . Three distinct subsequent stages of aggregation are observed at various CaCl_2 and nanoparticle concentrations. The transition between a stable and an unstable dispersion (aggregation followed by sedimentation) occurs around 0.05 wt% CaCl_2 for all three nanoparticle concentrations.

Figure 2.11 shows the absorbance at 400 nm wave length as a function of concentration of the chloride salts for Mg^{2+} , Ca^{2+} , and Ba^{2+} for 1 wt% particle concentration. The CSCs, determined at a point of sharp change in the UV-Vis absorbance profiles in Fig. 11, are 0.0125 wt% for MgCl_2 and 0.025 wt% for both CaCl_2 and BaCl_2 . These values are confirmed by the measured effective particle diameter as a function of salt concentration as in Figure 2.12. From this figure the aggregate size is much more sensitive to the addition of divalent than monovalent cations.

Colic et al. (1998) studied the influence of monovalent cation size (Li^+ , Na^+ , K^+ , Cs^+) on short range repulsive forces in silica slurries at large salt concentrations. The authors argued that the layer of structured water molecules around the silica particle's surface favors the accommodation of small ions that prefer to be surrounded by organized

water at pH greater than isoelectric point (IEP). Hence, smaller cations can penetrate deep into the water layer at the particle surface resulting in less repulsive force compared to larger ions that reside outside the hydration layer (Torrie et al. 1989). The mechanism for the short-range repulsion would be the collapse of the counterion cloud. Our observations on the stability of silica dispersions with divalent cations Mg^{2+} , Ca^{2+} and Ba^{2+} agree with this theory. Mg^{+2} being the smallest cation with highest affinity to water induces the smallest repulsive force and, hence, exhibits the least CSC compared to Ca^{2+} and Ba^{2+} .

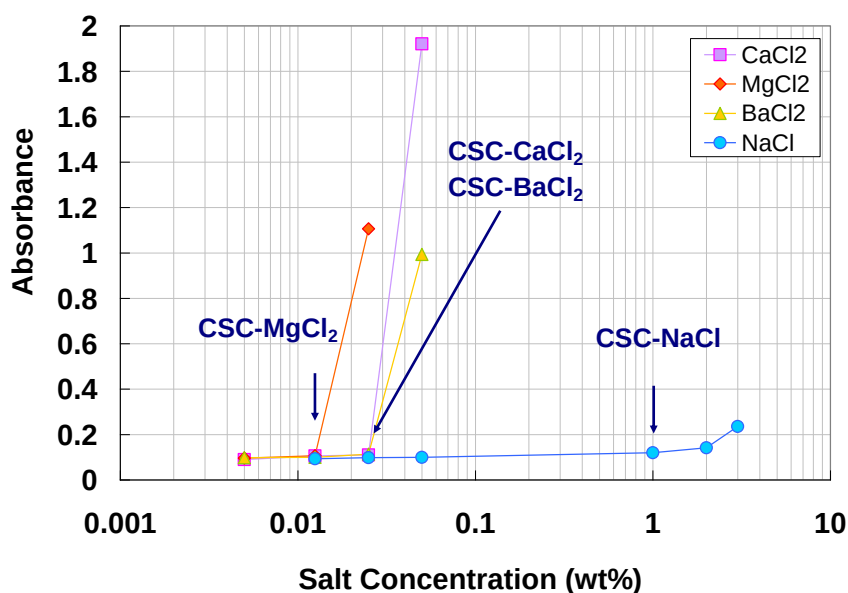


Figure 2.11- UV-Vis absorbance of a 1 wt% silica dispersion in the presence of different salts (NaCl, MgCl_2 , CaCl_2 and BaCl_2) at 400nm wave length at 25°C. Mg^{2+} exhibits the smallest CSC while the CSCs for Ca^{2+} and Ba^{2+} are both about 0.025 wt%.

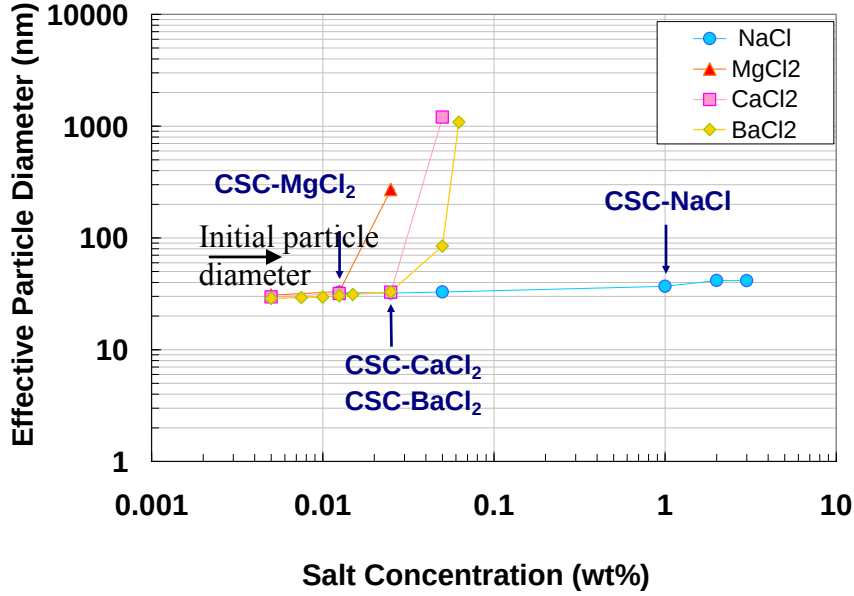


Figure 2.12- Effective particle diameters for a 1 wt% silica dispersion as a function of NaCl, MgCl₂, CaCl₂ and BaCl₂ concentrations at 25°C. An increase in the effective diameter indicates aggregation of the silica particles.

The significant difference in CSC between the monovalent and divalent cations could be further explained by the DLVO theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948). The interaction potential between two spherical nanoparticles includes the attraction (V_A) and repulsion energies (V_R) as described by Equations. 2.1 and 2.2, respectively

$$V_A = -\frac{A}{12} \left(\frac{1}{x^2 - 1} + \frac{1}{x^2} + 2 \ln \left(1 - \frac{1}{x^2} \right) \right) \quad (2.1)$$

$$V_R = 2\pi\epsilon_o\epsilon_r a\zeta^2 \ln \left[1 + \exp(-2\kappa a(x-1)) \right] \quad (2.2)$$

$$V_T = V_A + V_R \quad (2.3)$$

where x is the ratio of the center-to-center distance of spheres, r , to the diameter of the sphere, $2a$; κ is the inverse of Debye length; $\varepsilon_o\varepsilon_r$ is the dielectric permittivity; and A is the Hamaker constant. For silica dispersion the calculated value of A is 6.02×10^{-21} J in agreement with previously proposed constants for silica (Franks 2002; Dumont 2006). The diffuse layer potential, ζ , is obtained from zeta potential measurements. Equation 2.2 shows that the magnitude of the repulsive energy depends on the Debye length, which decreases with increasing electrolyte concentration. In Equation 2.3, V_T is the total interaction energy.

Figure 2.13 presents the normalized interaction energy (V_T / kT) between two identical spheres as a function of dimensionless distance x . Here, k is the Boltzmann constant, and T the temperature. A secondary minimum in energy occurs at NaCl concentrations greater than 1 wt% (Figure 2.13b). In Figure 2.14, we present the area under the DLVO curve as a function of electrolyte concentration. This figure also shows the relationship between electrolyte concentration and the amount of energy (V_T / kT) required to bring two nanoparticles from infinity to a critical distance, x_c , that is shorter than that at which particle aggregation is highly promoted because of the increasing attraction energy as x decreases. The gradient of the interaction potential with respect to x becomes positive for x which is smaller than x_c . The integration term, the area under the DLVO curve, decreases first sharply then much more gradually as electrolyte concentration increases, Figures 2.14a and 14b. This gradually decreasing slope, in the region between 0.5 and 1.5 wt% NaCl in Figure 2.14a, is the region where the transition of a stable dispersion into an unstable state occurs. The range of electrolyte concentration

for this transition region is significantly reduced as the cation's valence increases and is consistent with the measured CSCs for Na^+ , Ca^{2+} , and Mg^{2+} .

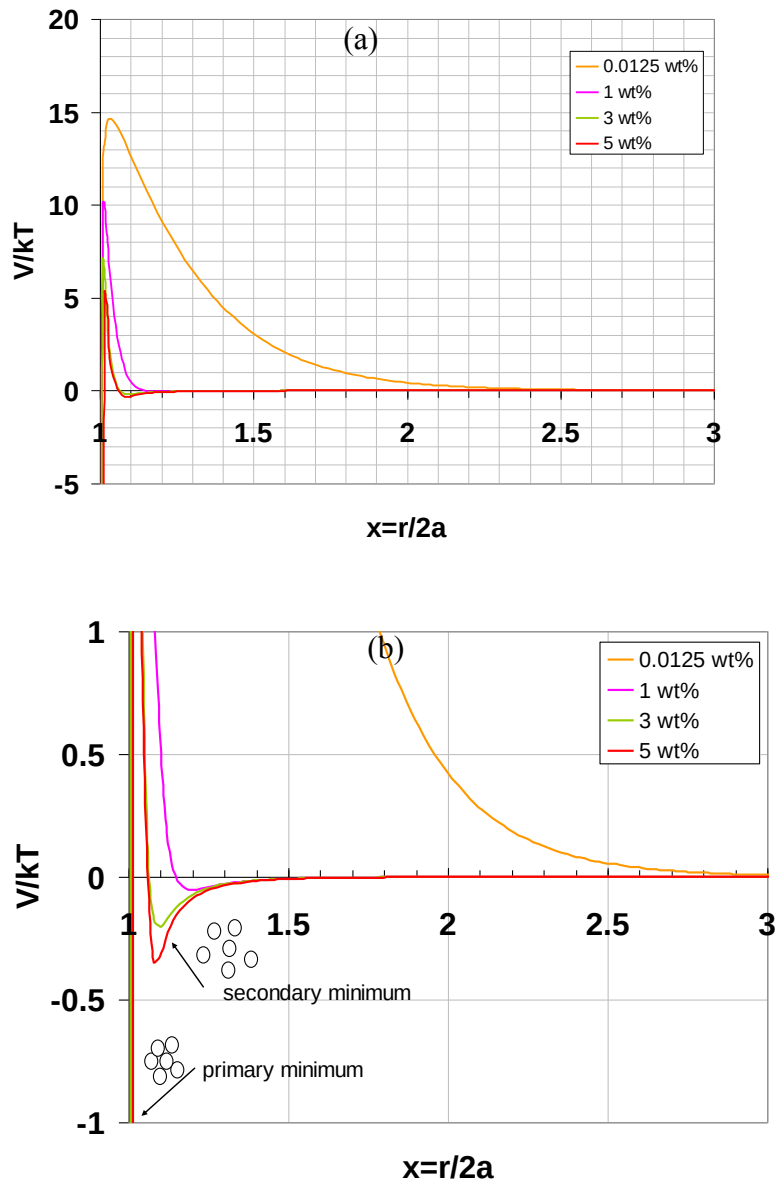


Figure 2.13- Two-particle interaction potential as a function of dimensionless separation distance according to DLVO theory for (a) NaCl concentrations. The secondary and primary minima are shown clearly in the (b) small scale range of the y-axis, a zoom-in of (a).

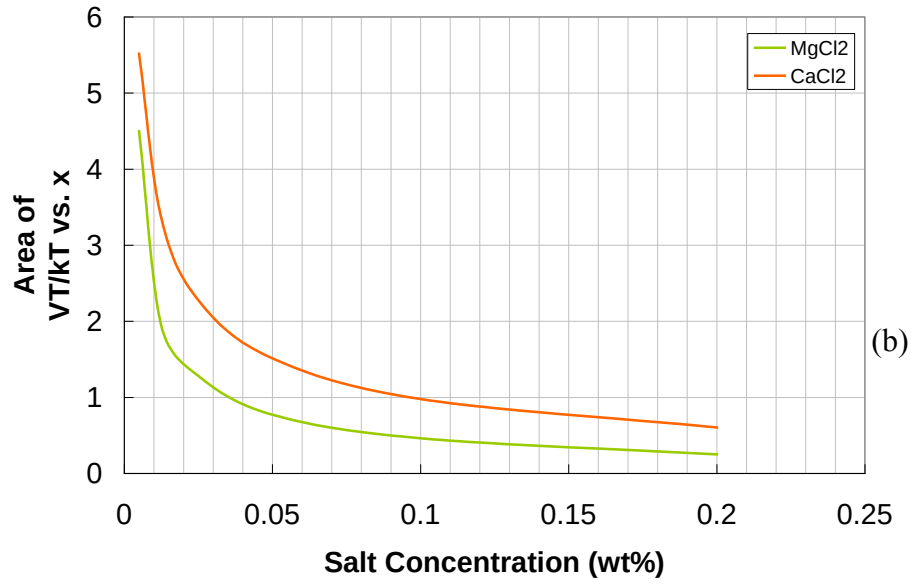
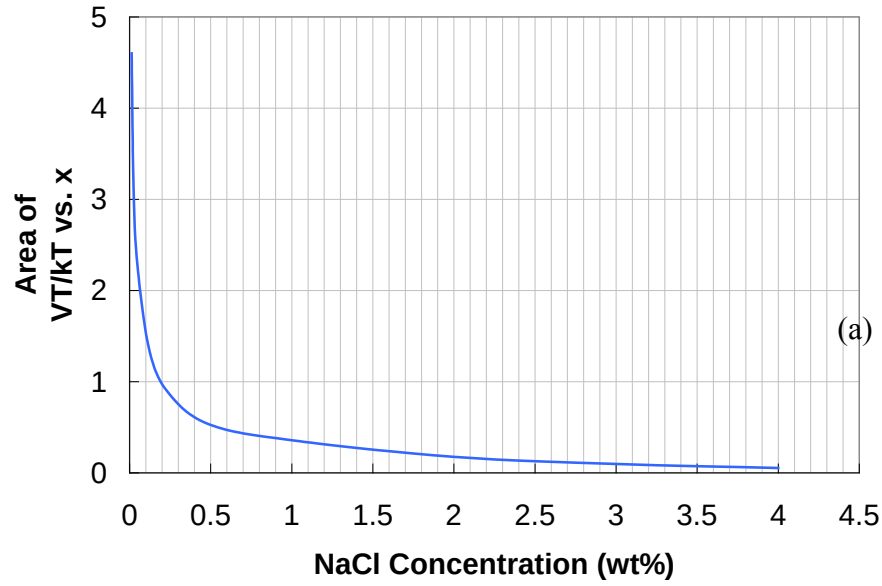


Figure 2.14- Relationship between electrolyte concentration and the amount of energy (V_T / kT) required to bring two nanoparticles from infinity to a critical distance, x_c , for (a) NaCl and (b) $CaCl_2$ and $MgCl_2$ concentrations.

2.3.4 Effect of Particle Size on CSC

The effect of particle size on the stability of aqueous silica nanoparticle dispersions is also studied. As shown in Figure 2.15, the effect of divalent cations in lowering CSC is still present at small particles diameters such as 5 and 8 nm. However, the effect of particle size on CSC is not significant when the results of CSC of a given electrolyte are compared in Figure 2.15 for 5, 8 and 25 nm unmodified particles.

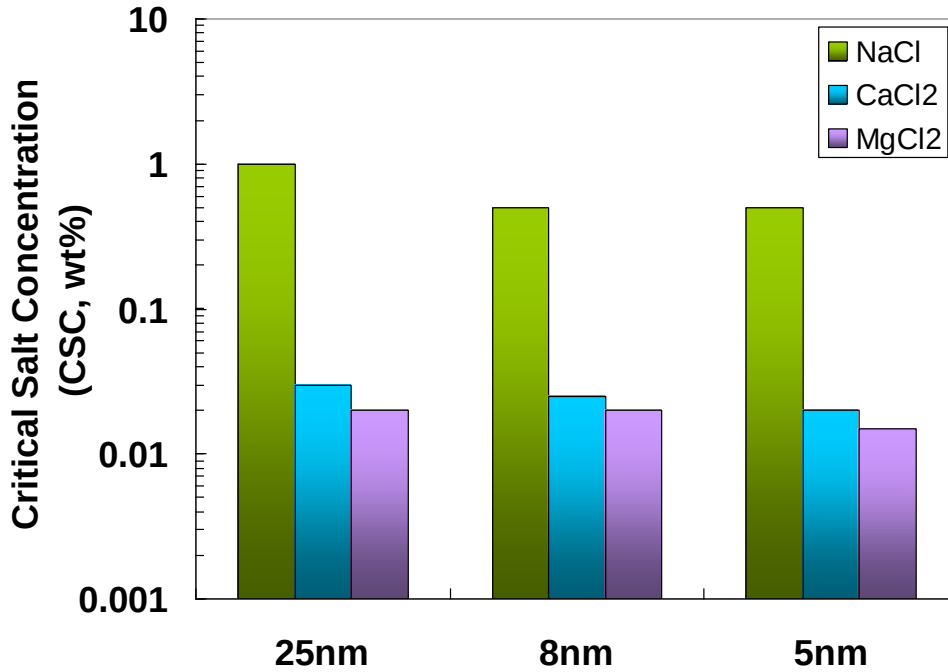


Figure 2.15- The effect of particle size and divalent cations on CSC of unmodified silica nanoparticle dispersions. The values on x-axis are the diameter of silica particles that were studied.

DLVO theory is used to explain the CSC for 5nm particles. The electrostatic repulsion energy term in Equation 2.2 cannot be used because the condition of $\kappa a > 10$ is not satisfied for 5 nm particles. Instead, Equation 2.4 is used where the electrostatic

repulsion term is approximated for the case where $\kappa a < 5$ (Lu 2008). The van der Waals attraction in Equation 2.1 holds true and by adding Equation 2.1 to 2.4 the total interaction potential is obtained. The results are presented in Fig. 2.16.

$$V_R = 2\pi\epsilon_o\epsilon_r a\zeta^2 \exp(-\kappa h) \quad \text{for } \kappa a < 5 \quad (2.4)$$

When the potential curves are compared for 25 (Figure 2.13) and 5 nm (Figure 2.16a) particles, the absence of a secondary minimum in the potential curve for 5 nm particles is observed. However, the maximum in potential curves are much smaller for 5 nm than for 25 nm particles. This result is expected since DLVO theory predicts that interaction potential decreases as particle size decreases (He et al. 2008). Although smaller particles are predicted to be more susceptible to aggregation, the difference in CSC is not significant. This could be explained by the absence of a secondary minimum for 5 nm particles. Moreover, the transition region from a stable dispersion to an unstable dispersion (Figure 2.16b) occurs at similar regions for 5 and 25 nm unmodified particles, which also agrees with our experimental results on CSC.

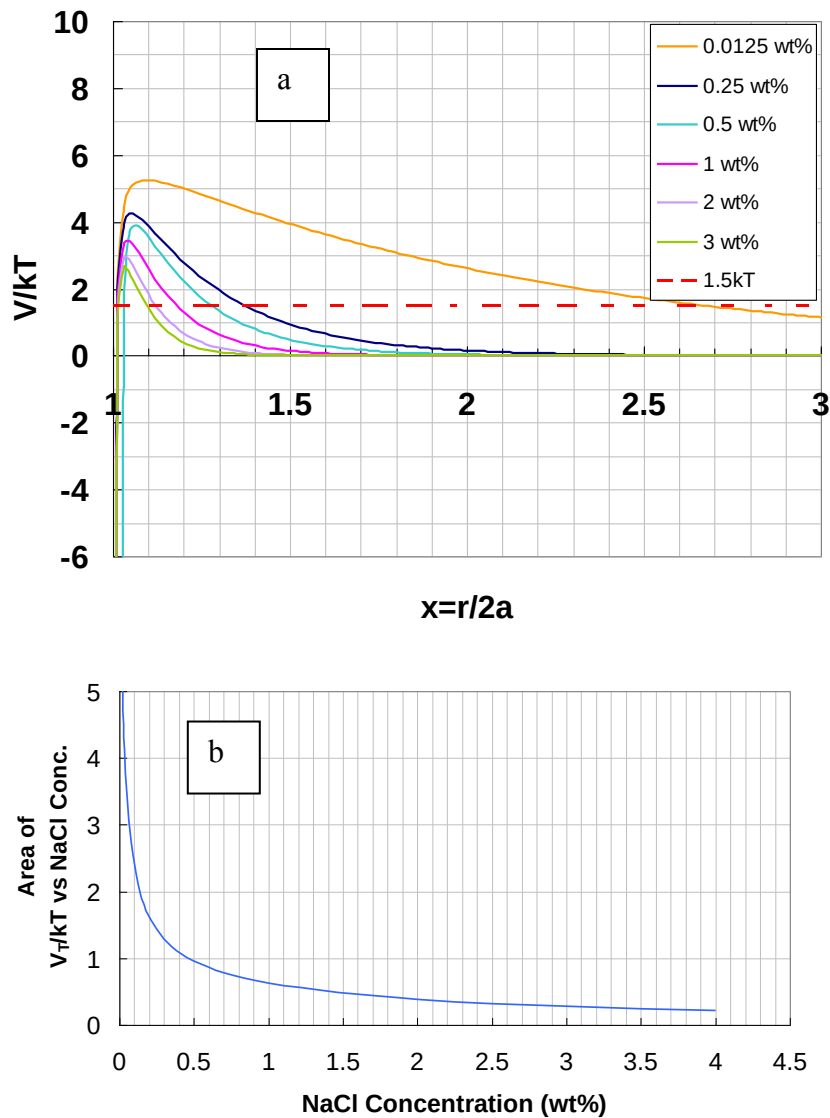


Figure 2.16- (a) The total interaction potential as a function of dimensionless distance according to DLVO for 5nm unmodified particles and NaCl (b) Relationship between electrolyte concentration and the amount of energy (V_T / kT) required to bring two nanoparticles from infinity to a critical distance, x_c , for NaCl.

2.3.5 Effect of Surface Modification on CSC

The effects of surface modification on CSC of NaCl, MgCl₂ and CaCl₂ are studied at 3 different particle sizes such as 5, 8 and 25 nm diameter. Figure 2.17 presents the results for sulfonate modified silica nanoparticle dispersions. The effect of particle size is insignificant for sulfonate modified silica nanoparticles as discussed previously for unmodified silica nanoparticles. Moreover, an increase in CSC is observed for all electrolytes studied when compared to CSC's for unmodified silica nanoparticles (Figure 2.15). This improvement in CSC is more significant for divalent cations than monovalent cations.

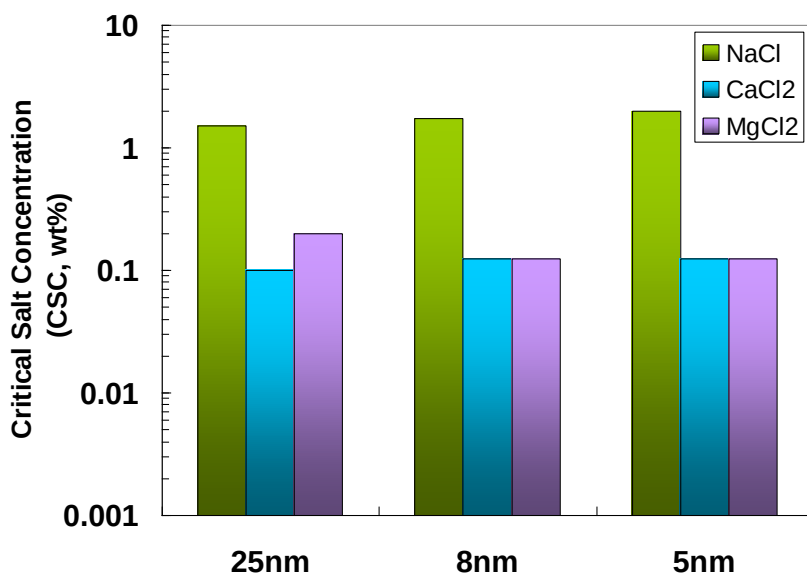


Figure 2.17- The effect of particle size and divalent cations on CSC of sulfonate coated silica nanoparticle dispersions. The values on the x-axis are the diameter of silica particles studied.

Another type of surface modification studied is polyethylene glycol (PEG), covalently bond to the surface of silica nanoparticles. A significant improvement in CSC for both monovalent and divalent cations are observed with PEG modified silica

nanoparticles at 25°C (Fig. 2.18). Comparing the results of CSC's for sulfonate and PEG modified silica nanoparticles, a significant improvement in CSC's for PEG modified particles is observed. However, at higher temperature such as 70°C, CSC of PEG modified particles shifts to lower concentrations. The effect of temperature on CSC for PEG modified particles is discussed in details below. A very important finding is observed with MgCl_2 at 70°C. The dispersions stay clear but the size measurements shifted to larger values as shown in Figure 2.18.

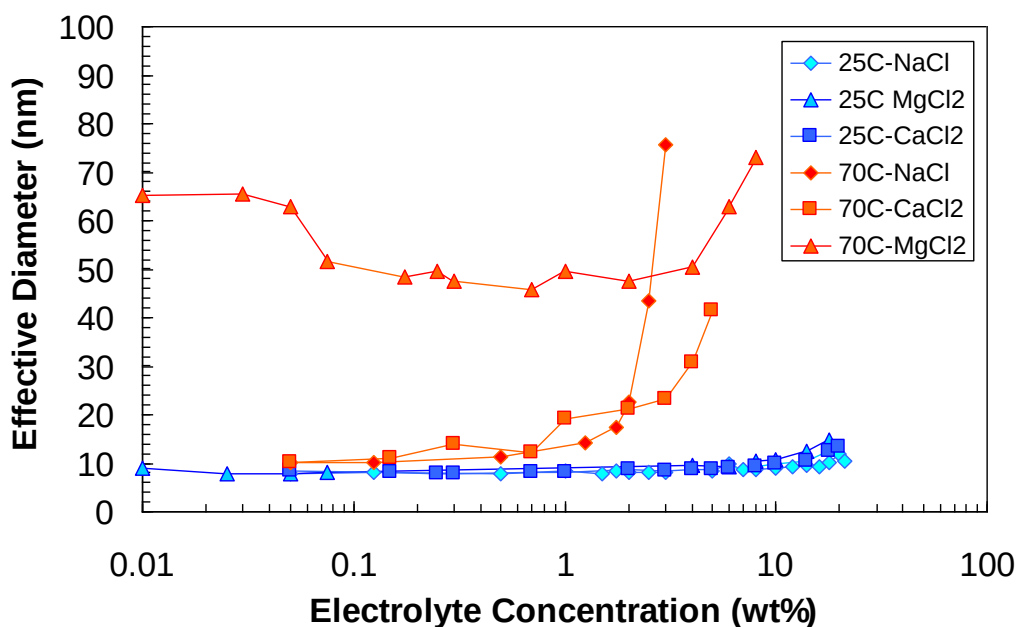


Figure 2.18- The effect of divalent cations and temperature on CSC for 5nm PEG modified silica nanoparticle dispersions.

The interaction forces between unmodified or modified silica particles have been an important research area. Valle-Delgado et al. (2005) measured the interaction forces between silica surfaces at different salt concentrations using atomic force microscopy (AFM). They observed short range repulsive forces at separation below 2 nm and

compared these experimental results with the theoretical models available in literature. The origin of the short range repulsive hydration forces could differ from system to system. The authors concluded that in the case of silica, the formation and rupture of hydrogen bonds between silanol groups on the surface and neighboring water molecules were responsible for the short range repulsive hydration forces.

Manciu and Ruckenstein (2001) suggested that the colloidal stability at high electrolyte concentrations could be a result of hydration repulsive force due to ion pairs present on the particle surface (surface dipole density). They studied the model developed by Schiby and Ruckenstein (1983) using information of adsorption of sodium dodecyl sulfate available in literature. They concluded that at the same surface density of ion pairs, the magnitude of the hydration force was influenced by the dipole moment of the surface ion pairs and the local dielectric constant next to the surface.

Vigil et al. (1994) studied the interactions between silica surfaces. They proposed that the surface of hydrophilic silica swelled, meaning that a 1 to 2 nm thick silica gel layer of silanol and silicic acid grew on the surface due to water adsorption. Therefore, the origin of the short range repulsive force was related to the steric repulsion force between protruding surface groups, silica hairs. Furthermore, the authors suggested based on the adhesion measurements that the protruding reactive groups on both silica surfaces, which were brought together, slowly sintered in the presence of water. At large separations, DLVO forces were found to be effective but at smaller separations steric repulsion was dominant and the outer Helmholtz plane (OHP) was believed to be pushed out by 1 nm from the surface by the water swollen silica gel layer. This shift in OHP enhanced the contribution of electrical double layer repulsion to the net force.

To determine the stability of sulfonate or PEG coated silica nanoparticles theoretically, we need to modify the DLVO theory by adding a steric potential term. It is known that the steric potential is a function of Flory-Huggins parameter defined as

$$\chi = \frac{V_m}{RT} (\delta_p - \delta_{solvent})^2 \quad (2.5)$$

where δ_p and $\delta_{solvent}$ are the Hildebrand solubility parameters for the polymer and solvent respectively, V_m the molar volume, R the universal gas constant and T is. The solvent is considered as a good solvent for the given polymer for $\chi < 0.5$. Then, for $L < h < 2L$, the steric potential is defined by Lu (2008) as

$$V_s = \frac{32\pi kTa}{5\nu} \frac{V_f^2}{L^4} \left(\frac{1}{2} - \chi \right) \left(L - \frac{h}{2} \right)^6 \quad (2.6)$$

where a is the particle radius, k the Boltzmann constant, ν molecular volume of dispersing medium, V_f average volume fraction of polymer segment in the adsorbed layer, h particle separation distance, L length of polymer.

For short particle separations, where $h < L$ the steric potential and elastic interaction energy of polymer chains are as follows

$$V_s = \frac{4\pi kTa}{\nu} L^2 V_f^2 \left(\frac{1}{2} - \chi \right) \left(\frac{h}{2L} - \frac{1}{4} - \ln \left(\frac{h}{L} \right) \right) \quad (2.7)$$

$$V_{elastic} = \frac{2\pi kTa}{M_w} L^2 \rho V_f^2 \left(\frac{h}{L} \ln \left(\frac{h}{L} \left(\frac{3-h/L}{2} \right)^2 \right) - 6 \ln \left(\frac{3-h/L}{2} \right) + 3 \left(1 - \frac{h}{L} \right) \right) \quad (2.8)$$

where M_w is the molecular weight and ρ is the density of adsorbed polymer dispersant. In the case where the separation distance h is larger than $2L$ ($h > 2L$) there is no steric interaction.

From the above equations, we can say that the magnitude and sign of the steric interaction is a function of $\left(\frac{1}{2} - \chi\right)$. Therefore, the determination of the Flory-Huggins parameter is crucial to predict the steric interaction. Instead of using Hildebrand solubility parameter, which does not take into account the energies from dipolar and hydrogen bonds, we calculated Hansen solubility parameters (Hansen, 2007). The results for sulfonate and PEG are as follows

$$\chi_{\text{Sulfonate}} = 2.01$$

$$\chi_{\text{PEG}} = 4.8$$

Calculating the term $\left(\frac{1}{2} - \chi\right)$ we obtain negative values for steric interaction ($V_s < 0$) which indicates that the surface coating of silica nanoparticles with these molecules brings an additional attractive part to the total interaction potential. This result contradicts with the experimental observation where an improvement in colloidal stability occurred for sulfonate and PEG coated particles. As stated by Hubbard (2002), in the presence of polymers and surfactants, the understanding of stabilization is much more incomplete. Therefore, molecular dynamics (MD) simulations may greatly contribute to our understanding of colloidal stability of surface modified nanoparticle dispersions.

Another surface modification studied is alumina modified silica nanoparticles. They were purchased from Sigma-Aldrich as an aqueous dispersion. The zeta potential of alumina modified silica nanoparticles is +45 mV as measured by zeta analyzer. These nanoparticle dispersions are not stable at pH greater than 6 which is the isoelectric point for alumina. Therefore the stability measurements are carried out at pH 5 and below. The

effect of divalent cations on CSC is shown in Figure 2.19. One important remark is that the CSC is same for NaCl, CaCl₂ and MgCl₂ and is around 1 wt%. This result is expected because the particles are positively charged and the counterions matter for stability, being Cl⁻ for all those salts. Therefore a divalent anion SO₄²⁻ is introduced. Then, CSC shifts from 1 wt% to 0.25 wt%. Similar observations are made at 70 °C. The effect of pH on CSC is also studied for alumina modified silica nanoparticles. The results are presented in Figure 2.20 where the effective particle diameter is plotted against electrolyte concentration for dispersions at pH 3.2, 4.2 and 5.2 at 25 and 70 °C. The CSC is independent of pH for the range studied.

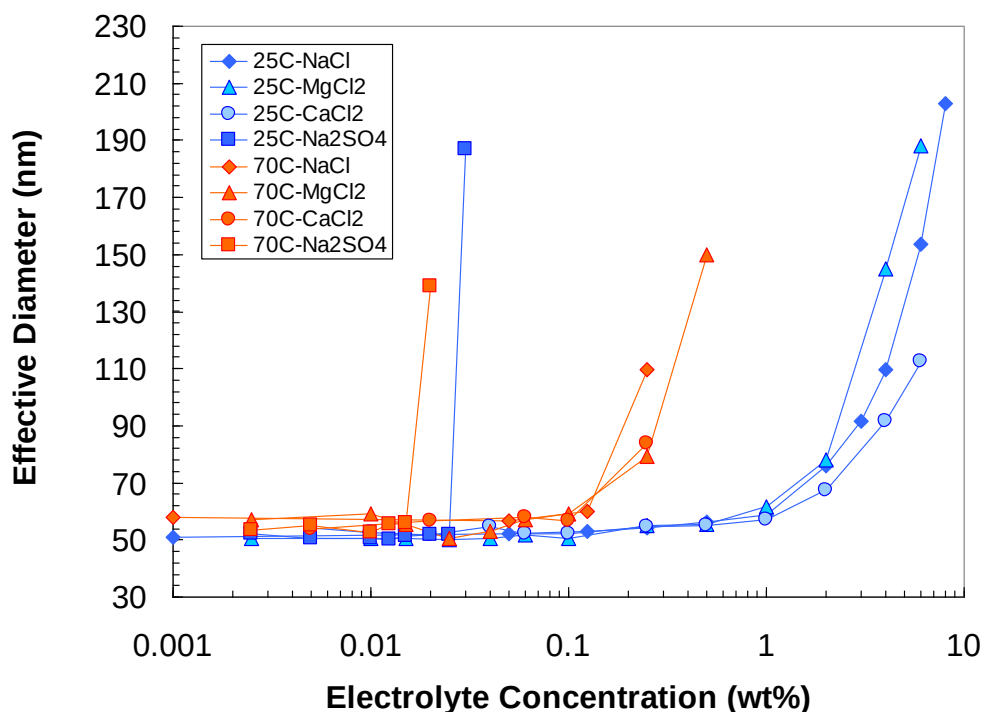


Figure 2.19- The effect of divalent cations, anions and temperature on CSC for 5nm alumina modified silica nanoparticle dispersions.

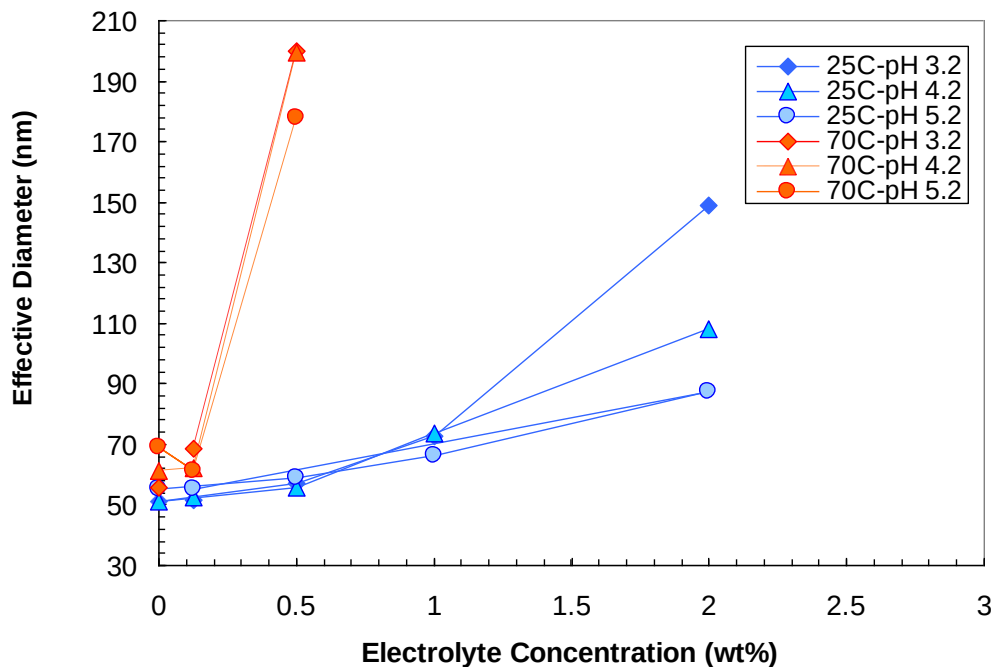


Figure 2.20- The effect of pH on the CSC for NaCl for 5nm alumina modified silica nanoparticle dispersions.

2.3.6 Effect of Temperature on Critical Salt Concentration

To investigate the effect of temperature on the CSC, DLS is used to measure particle size on a series of 1 wt% unmodified silica dispersions with different salt types (NaCl, CaCl₂ and MgCl₂) and concentrations at 25 and 70°C. The results, shown in Figure 2.21, indicate that the CSC is significantly reduced as temperature increases. This observation may be explained based on relative magnitude of the energy barrier and the average kinetic energy of nanoparticles as shown in Figures 2.13 and 2.14. An increase of the average kinetic energy with temperature gives rise to the particle collisions that result in aggregation. As a consequence, a higher energy barrier (i.e. lower salt concentration) is required to maintain the aqueous stability of a nanoparticle dispersion.

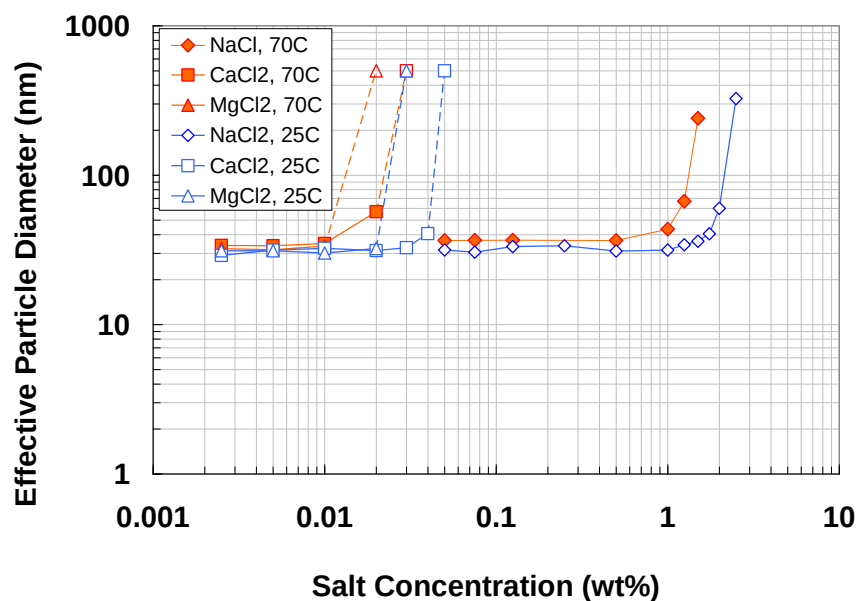


Figure 2.21- DLS measurements of 1 wt% silica dispersion in the presence of different salts (NaCl, CaCl₂ and MgCl₂) at 25°C and 70°C. DLS measurements are taken after 18 days.

Figure 2.22 presents the results on CSC's of NaCl, CaCl₂ and MgCl₂ at 25 and 70°C for 25 nm diameter unmodified silica nanoparticle dispersions on a bar chart. The effects of divalent cations and high temperature are significant in lowering CSC as observed from this figure. The effect of particle size for unmodified nanoparticles on CSC at 70 °C is shown in Figure 2.23. As observed with nanoparticles at 25 °C, the effect of size is not very significant for the ranges studied. However, CSC's are lower at this temperature than those at 25°C (in comparison with Figure 2.15).

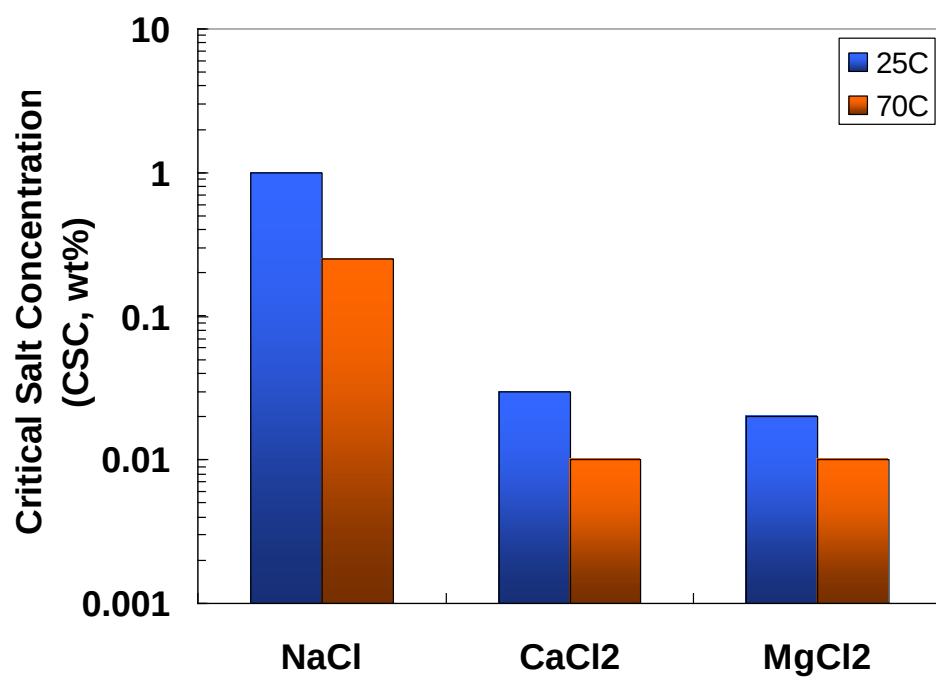


Figure 2.22- Critical salt concentration (CSC) for 25 nm diameter unmodified silica nanoparticle dispersions. The effects of divalent cations and temperature are presented.

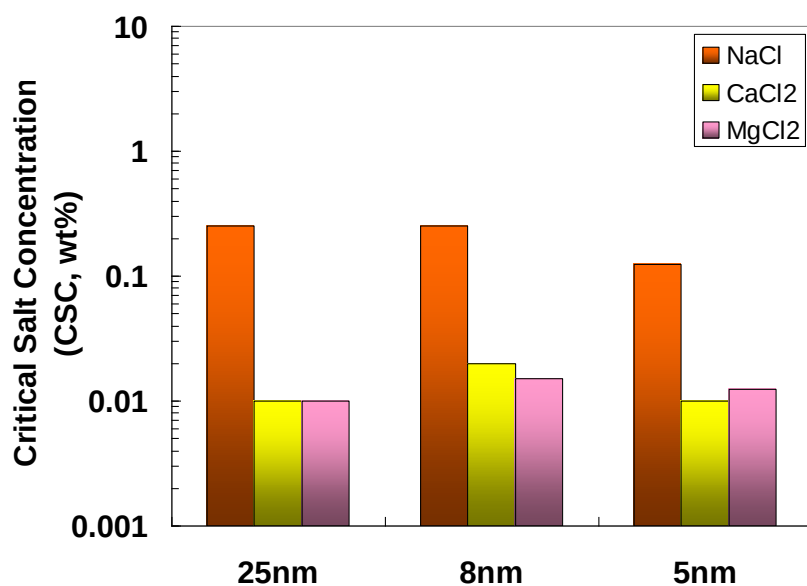


Figure 2.23- The effect of particle size and divalent cations on CSC of unmodified silica nanoparticle dispersions at 70°C. The values on x-axis are the diameter of silica particles that was studied.

The silica nanoparticles modified with sulfonate still have larger CSC's at 70°C than those for unmodified nanoparticles at the same temperature. However, CSC's at 70°C (Figure 2.24) are much lower when compared with sulfonate coated silica nanoparticles at 25°C (Figure 2.17). The particle size does not significantly influence CSC's for sulfonate modified silica nanoparticles at 70 °C (see Figure 2.25).

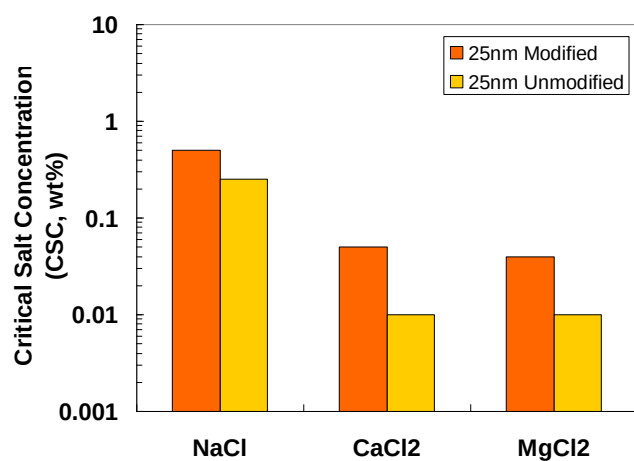


Figure 2.24- The effect of divalent cations on CSC of unmodified and sulfonate modified silica nanoparticle dispersions at 70°C.

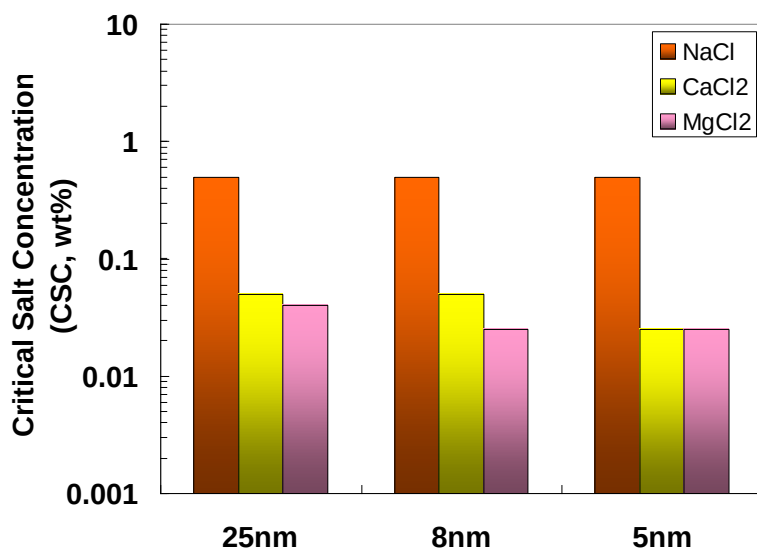


Figure 2.25- The effect of particle size and divalent cations on CSC of sulfonate coated silica nanoparticle dispersions at 70°C. The values on x-axis are the diameter of silica particles that we studied.

The results on the effect of temperature on CSC's of PEG coated particles are presented in the previous section. It was observed that up to the CSC at 2 wt% MgCl_2 the dispersion consists of very stable and well dispersed aggregates of average diameter 60 nm. Below 2 wt% MgCl_2 the dispersion is extremely stable. We believe that the explanation for this observation lies in the interaction between PEG, the electrolytes Mg^{2+} , Cl^- and the surface structure of silica nanoparticle.

2.4 CONCLUSIONS

In this chapter, the stability of silica nanoparticles in aqueous solutions under changing pH, salt concentration (NaCl , MgCl_2 , CaCl_2 and BaCl_2), particle size, surface type and temperature are presented using ATR-FTIR, UV-Vis spectrophotometer, DLS and a zeta potential analyzer. Spectral analysis of the Si-O bond at 1110 cm^{-1} with the ATR-FTIR indicates a structural change on the surface of silica particles because of the change in the pH of the solution, which agrees with zeta potential results. Changing the pH does not affect the aggregation in the absence of electrolyte for the range of pH studied. However, the addition of different types of salts (NaCl , CaCl_2 , MgCl_2 and BaCl_2) causes aggregation of the silica nanoparticles.

It was observed a critical salt concentration (CSC) for a given electrolyte below which the silica nanoparticles are well dispersed in an aqueous phase and above which flocculation of silica nanoparticles occur and the aggregates settle by gravity. The CSC depends on electrolyte type, but is not influenced by silica nanoparticle concentration.

Divalent cations Mg^{+2} , Ca^{+2} and Ba^{2+} are more effective in destabilizing (i.e. causing aggregation) the nanoparticle dispersion than the monovalent cation Na^+ . The CSC for Na^+ is about 100 times larger than that of divalent cations. Among these divalent

cations, Mg^{2+} is the most effective in aggregating the silica particles. The presence of the CSC for the electrolytes studied in this work could be explained by the DLVO theory.

Surface modification (sulfonate or PEG) improves stability for monovalent and divalent cations. However, PEG gives much larger CSC than sulfonate surfactants at relatively low temperature, 25°C. For positively charged alumina modified silica nanoparticles CSC is same for NaCl, MgCl_2 , and CaCl_2 but much lower for Na_2SO_4 . The valence of the counterions determine the CSC.

An increase in temperature from 25°C to 70°C increases the aggregation rate, and hence lowers the CSC. The reduction in CSC is more significant for monovalent cation Na^+ than it is for divalent cations Mg^{2+} and Ca^{2+} . This suggests that the effect of cation valance is dominant over the effect of thermal energy within the range of temperature used in this work.

2.5 REFERENCES

- Asay DB, Kim SH (2005) Evolution of the adsorbed water layer structure on silicon oxide at room temperature. *J Phys Chem B* 109:16760-16763.
- ASTM Standard D 4187-82, Zeta Potential of Colloids in Water and Waste Water, 1985.
- Colic M, Fisher ML, Franks GV (1998) Influence of ion size on short-range repulsive forces between silica surfaces. *Langmuir* 14:6107-6112.
- Derjaguin BV, Landau L (1941) Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim USSR* 14:633-662.
- Dumont F (2006) Stability of sols: Do the silica hydrosols obey the DLVO theory? In: Bergna HE, Roberts WO (eds) *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 243-245.
- Elimelech M, Gregory J, Jia X, Williams RA (1998) *Particle deposition and aggregation: Measurement, modelling and simulation*. Butterworth-Heinemann, Woburn.
- Franks GV (2002) Zeta potentials and yield stresses of silica suspensions in concentrated monovalent electrolytes: Isoelectric point shift and additional attraction. *J Colloid Interface Sci* 249:44-51.

- C. Hansen, Charles, Hansen Solubility Parameters: A user's handbook, CRC Press, Boca Raton, 2007.
- Hair ML (2006) Surface chemistry of silica. In: Bergna HE, Roberts WO (eds), Colloidal silica: Fundamentals and applications, CRC Press, Boca Raton, pp 257-260.
- Healy TW (2006) Stability of aqueous silica sols. In: Bergna HE, Roberts WO (eds), Colloidal silica: Fundamentals and applications, CRC Press, Boca Raton, pp 247-252.
- Y.T. He, J. Wan, T. Tokunga, J. Nanopart. Res. 10 (2008) 321-332.
- Hofmann U, Endell K, Wilm D (1934) Röntgeno-graphische und kolloidchemische Untersuchungen über Ton. *Angew Chem* 47:539-558.
- A.T. Hubbard, Encyclopedia of Surface and Colloid Science, Marcel Dekker, New York, 2002.
- Hunter RJ (2001) Foundations of colloid science. Oxford University Press, New York.
- Iler RK (1971) The chemistry of silica. Wiley & Sons, New York.
- Israelachvili J, Wennerstrom H (1996) Role of hydration and water structure in biological and colloidal interactions. *Nature* 379:219-225.
- Jenkins S, Kirk SR, Persson M, Carlen J, Abbas Z (2007) Molecular dynamics simulation of nanocolloidal amorphous silica particles: Part I. *J Chem Phys* 127:224711-1-10.
- Jenkins S, Kirk SR, Persson M, Carlen J, Abbas Z (2008) Molecular dynamics simulation of nanocolloidal amorphous silica particles: Part II. *J Chem Phys* 128:164711-1-10.
- Kissa E (1999) Dispersions: Characterizations testing, and measurement. Marcel Dekker, New York.
- Kitchener JA (1971) General discussion. *Faraday Disc* 52:372-380.
- Lane JMD, Ismail AE, Chandross M, Lorenz CD, Grest GS (2009) Forces between functionalized silica nanoparticles in solution. *Phys Rev E* 79:050501-1-4.
- K. Lu, *Ceramics Int.* 34 (2008) 1353-1360.
- M. Manciú, E. Ruckenstein, *Langmuir* 17 (2001) 7061-7070.
- Mokhatab S, Fresky MA, Islam MR (2006) Applications of nanotechnology in oil and gas E&P. *J Pet Technol Online* 58:4.
- Morrow BA, Molapo DT (2006) Infrared studies of chemically modified silica. In: Bergna HE, Roberts WO (eds), Colloidal silica: Fundamentals and applications, CRC Press, Boca Raton, pp 287-294.

- Plaza RC, Quirantes A, Delgado AV (2002) Stability of dispersions of colloidal hematite/yttrium oxide core-shell particles. *J Colloid Interface Sci* 252:102-108.
- Roberts WO (2006) Manufacturing and applications of waterborne colloidal silica. In: Bergna HE, Roberts WO (eds.), *Colloidal silica: fundamentals and applications*, CRC Press, Boca Raton, pp131-176.
- D. Schiby, E. Ruckenstein, E. Chem. Phys. Lett. 95 (1983) 435.
- Torrie GM, Kusalik PG, Patey GN (1989) Theory of the electrical double layer: Ion size effects in a molecular solvent. *J Chem Phys* 91:6367-6375.
- J.J. Valle-Delgado et al., *J. Chem Phys.* 123 (2005) 034708.
- Van Blaarderen A, Vrij A (2006) Synthesis and characterization of colloidal model particles made from organoalkoxysilane. In: H.E. Bergna, W.O. Roberts (Eds.), *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 65-80.
- EJW Verwey, JThG Overbeek, *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
- G. Vigil, Z. Xu, S. Steinber, J. Israelachvili, *J. Coll. Int. Sci.* 165 (1994) 367-385.
- Yalamanchili MR, Atia AA, Miller JD (1996) Analysis of interfacial water at a hydrophilic silicon surface by in-situ FTIR/internal reflection spectroscopy. *Langmuir* 12:4176-4184.
- LT Zhuravlev (1987) Concentration of hydroxyl groups on the surface of amorphous silicas. *Langmuir* 3:316-318.

Chapter 3: Shear Rheology of Silica Nanoparticle Dispersions

The effects of particle concentration, particle size and temperature on the shear rheology of suspensions of silica nanoparticles are studied. Sterically or electrostatically stabilized silica nanoparticle dispersions with sizes ranging from 5-75 nm and particle volume fractions ranging from 0.22-25% exhibited a constant viscosity within the shear rate range of 1-200 s⁻¹. There is a non-linear relationship between the concentration and the viscosity of these dispersions that depends on the radii and surface energy of these nanoparticles. It is proposed that an effective maximum packing fraction model based on the concept of an effective particle radius, which takes into account the thickness of the electrical double layer and the surface coating material. The viscosities of all the dispersions collapse onto a universal curve as a function of the volume fraction normalized by the effective maximum packing fraction.

3.1 INTRODUCTION

The rheological behavior of colloidal dispersions has practical applications to many fields (Mokhatab 2006). Recent advances in engineering of nanoparticles have expanded potential application of nanoparticle dispersions into the characterization and production of natural hydrocarbon formations. Current subsurface technologies are insufficient to measure matrix and fracture properties between wells or to monitor changes in fluid saturation as reservoir pressure changes with respect to hydrocarbon production. An improved understanding of spatial distribution of fluids in the reservoir and their properties could significantly increase hydrocarbon recovery rates. This has inspired the use of sensors composed of nanoparticles to enhance knowledge of subsurface systems. For example, paramagnetic nanoparticles may be used as contrast agents to determine hydrocarbon saturation in reservoir rock with downhole magnetic

imaging (Prodanovic *et al.* 2010). In addition to reservoir characterization, the use of polymeric nanoparticle has been found to increase the efficiency of hydrocarbon displacement during water flooding (Moon 2008). In the above applications, propagation and emplacement of nanoparticles are strongly influenced by the mobility of nanoparticles which is partially defined by rheological principles of particle dispersions.

Fundamental studies on the mobility control of nanoparticles in reservoir rocks have been carried out with silica nanoparticles because of their low fabrication cost and controlled stability at reservoir conditions through silica surface modification. The injection of silica particles in an aqueous phase is preferable for most subsurface applications. The rheology of nanofluids is one of the most important transport properties which would determine the operating conditions during the injection process and the flow behavior in subsurface environments. The modeling of nanoparticle transport in such media requires a comprehensive understanding of the rheological behavior of these nanofluids as a function of the size, concentration, and surface properties of particles at varying environmental temperature. While the rheology of larger colloidal dispersions has been experimentally and theoretically studied (Russel *et al.* 2007; Chow 1993; Petrie 1999; Larson 2005; Bergenholtz 2001; Stickel 2005), the viscosity of suspensions of silica nanoparticles has not been well characterized (Namburu *et al.* 2007).

It has been reported that nanofluids, defined as suspensions of nanoparticles with at least one of their critical dimensions less than 100 nm (Choi 1995), exhibit both Newtonian behavior (e.g., Al₂O₃/water (Das *et al.* 2003; Wang *et al.* 1999); Al₂O₃/ethylene glycol (Wang *et al.* 1999); copper nanofluids/water (Xuan and Li 2000); and Al₂O₃/propylene glycol (Prasher *et al.* 2006) and non-Newtonian behavior (e.g., carbon nanotube/water (Ding *et al.* 2006); carbon nanotube/epoxy resin (Ma *et al.* 2008); TiO₂/water (He *et al.* 2007; Tseng and Lin 2003); CuO nanorod/ethylene glycol (Kwak

and Kim 2005); Al_2O_3 /mixture of methyl ketone and toluene (Studart *et al.* 2006)). Newtonian behavior was observed in these studies at shear rates above 150 s^{-1} . The results from these previous studies suggest that the properties of the base fluid and nanoparticle-fluid interactions play a significant role in determining the rheological properties of nanofluids. The particle concentration and shape are strong influencing factors. Jung and Kim (2008) studied the rheological properties of diamond/ethylene glycol, alumina/transfer oil and silica/water nanofluids over a wide range of shear rate (from 0.1 to 1000 s^{-1}). These nanofluids were shear thinning, especially at higher particle concentrations (i.e. between 3 and 6 wt %). However, at lower particle concentrations, Newtonian behavior was observed. In that study very few data are shown and there is no theory explaining the observations. Non-Newtonian behavior was also observed with TiO_2 /water nanofluids (2007), where the viscosity leveled off at higher shear rates ($>100 \text{ s}^{-1}$).

There are very few studies investigating the effect of particle size on the viscosity of nanoparticle dispersions. Prasher *et al.* (2006) showed that nanoparticle volume fraction directly affected the viscosity of alumina-based nanofluids (alumina nanoparticles dispersed in propylene glycol) but the size of nanoparticles did not have a significant influence on the viscosity. However, Lu and Kessler (2006) observed that 38-nm alumina particles dispersed in water/glycerol mixture with ammonium poly (methacrylic acid) and poly (acrylic acid) as dispersants show greater viscosity than $0.2\text{-}\mu\text{m}$ -alumina particle dispersions at the same solid volume fraction. Different dispersing phases were used in these studies, which may account for the discrepancy in the reported particle size dependence of dispersion viscosity. Moreover, the TiO_2 /water system exhibits a different behavior as reported by He *et al.* (2007). They observed experimentally that the effective viscosity increases with particle size at a given particle

volume fraction. McPhie *et al.* (2006) used molecular dynamics simulations to study shear rate dependence of the solution viscosity of nanoparticle dispersions. The authors observed that the viscosity of the dispersion became shear thinning as the solute to solvent mass ratio or size ratio increased. The hydrodynamic radius was calculated to be larger than bare spherical radius of particles assuming a perfect slip boundary condition. Rudyak *et al.* (2009) carried out molecular dynamics (MD) simulations to investigate the effective viscosity of nanoparticle dispersions. Their results showed that larger nanoparticles have lower viscosity than smaller nanoparticles. The authors argued that the motion of molecules of the carrier medium was strongly correlated with the thermal motion of nanoparticles. The fluid molecules around the nanoparticles move in the same direction as the particle. Relaxation correlation function hence decreases and the viscosity of the suspensions increases. The volume of this region is ten times the volume of the particle for the system that the authors studied (Rudyak *et al.* 2009). Rudyak *et al.* (2009) observed an increase in viscosity as particle size decreases

Although the silica nanoparticles are inexpensive with many practical applications, few rheological studies have been performed with silica nanofluids (Moon 2008; Liu *et al.* 1994; Fagan and Zukoski 1997; Chevalier *et al.* 2007; Thwala *et al.* 2008; Starck *et al.* 2007). Non-Newtonian behavior has been observed with silica nanoparticles dispersed in ethylene glycol and water mixture at sub-zero temperatures (Moon 2008), silica particles of 500 nm dispersed in glycol (Thwala *et al.* 2008) at low shear rates, and aqueous silica dispersions coated with zwitterionic polymers (Starck 2007).

However, the role of surface treatment, particle size and temperature of silica nanofluids is not well understood. In this chapter a systematic study on the characterization of the shear rheology of silica nanoparticle dispersions is presented. The

effects of particle size, concentration, and surface type and temperature on the viscosity of silica nanoparticle dispersions are quantified. A methodology is proposed for predicting viscosity of silica nanoparticle dispersions at a given solid volume fraction based on the concept of effective maximum packing fraction. This concept is used to scale all the measured viscosity data.

3.2 MATERIAL AND METHODS

Aqueous dispersions of different size (5, 8, 25 and 75 nm diameter) and surface type of silica particles (unmodified or sulfonate modified) were provided by 3M, Co (St. Paul, MN, USA). The shape of silica nanoparticles was found to be spherical as determined by scanning transmission electron microscope (STEM) images. The unmodified silica nanoparticles have a bare surface, and they are electrostatically stabilized in an aqueous medium resulting in a particle zeta potential value of -45 mV at pH = 9. The surface modified silica nanoparticles coated with sulfonate surfactant were well dispersed in an aqueous solution at pH = 8.5 in which they have a zeta potential value of -45 mV. Stock solutions of the nanoparticle dispersions were diluted to the desired concentration by weight percentage. All samples remained stable (*i.e.*, nanoparticles stayed well dispersed in water) during the experiments. This was verified by measuring the effective particle sizes before and after the experiments using the dynamic light scattering technique. A dispersion is considered stable if the particle size remains unchanged.

A strain controlled rheometer with double-wall Couette fixture was used to determine the rheology of the nanoparticle dispersions at different shear rates. Most experiments were carried out at 25°C to evaluate the effect of shear rate, silica particle

concentration, size and surface type on the viscosity. Additional experiments were conducted at 50 and 80°C to observe the effect of temperature. The maximum volume fraction of silica nanoparticles used in these experiments was 0.25 by volume.

3.3 RESULTS AND DISCUSSION

It was observed that at a given particle size (*e.g.*, 25 nm in Figure 3.1) and concentration (maximum of 24% by volume), silica nanoparticle dispersions exhibit a Newtonian behavior within the shear rate range studied (1-200 s⁻¹). This range represents typical shear rate values for flow in a wellbore and permeable hydrocarbon formation as shown in Table 3.1. In this table the shear rates for wellbore and reservoir flows were calculated using Equations 3.1 and 3.2, respectively. A detailed description of these equations can be found in Lake (1989).

$$\dot{\gamma}_{wall} = \frac{4v}{R} \quad (3.1)$$

$$\dot{\gamma}_{eq} = 4v \left(\frac{\varepsilon}{8k} \right)^{1/2} \quad (3.2)$$

where $\dot{\gamma}_{wall}$ is the wall shear rate; v is the average velocity; R is the pipe radius; $\dot{\gamma}_{eq}$ is the equivalent shear rate in permeable media; ε is the porosity; k is the permeability.

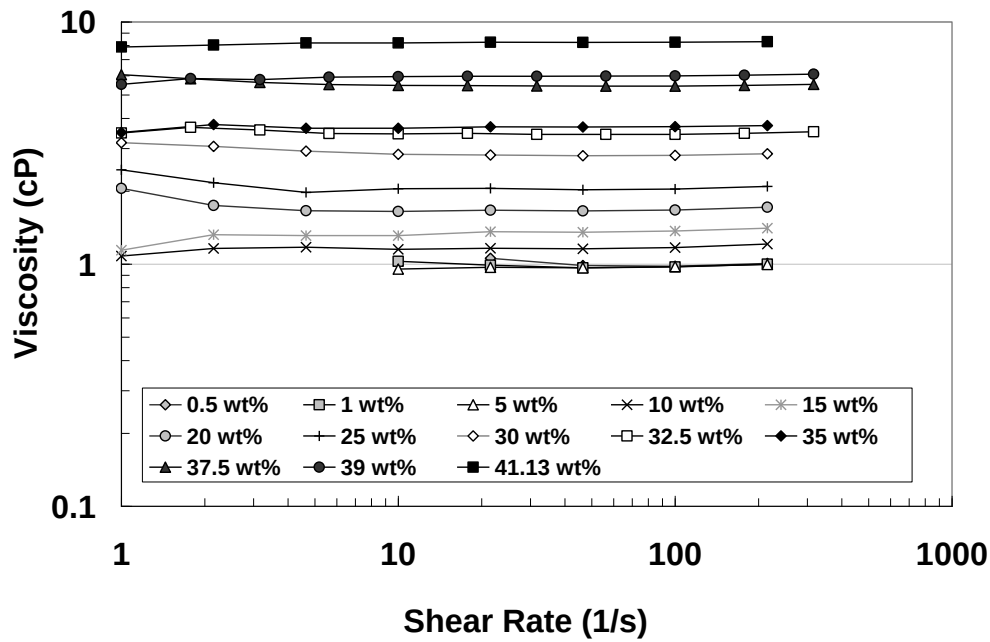


Figure 3.1- Viscosity of 25 nm unmodified silica particle dispersions as a function of shear rate at different particle concentrations. Shear rate-independent viscosity indicates a Newtonian behavior of the dispersions.

Table 3.1- Shear rates encountered in hydrocarbon recovery applications

Flow in Pipes			Flow in Porous Media			
Pipe Diameter (in)	Flow Rate (bbl/d)	Shear Rate (Eq.3.1) (1/s)	Permeability (Darcy)	Porosity (%)	Velocity (ft/d)	Shear Rate (Eq.3.2) (1/s)
3-5	1000-6000	10-250	0.0001-3	10-40	0.5-2	0.5-650

As shown in Figure 3.2, the viscosity of silica nanoparticle dispersions displays a nonlinear behavior with respect to nanoparticle concentration. Several viscosity models available in the literature are evaluated to fit our experimental data. The viscosity models

proposed by Einstein (1956), Mooney (1951), Chong *et al.* (1971), Thomas (1965), Fedors (1974) and Krieger and Dougherty (1959) are listed in Table 3.2.

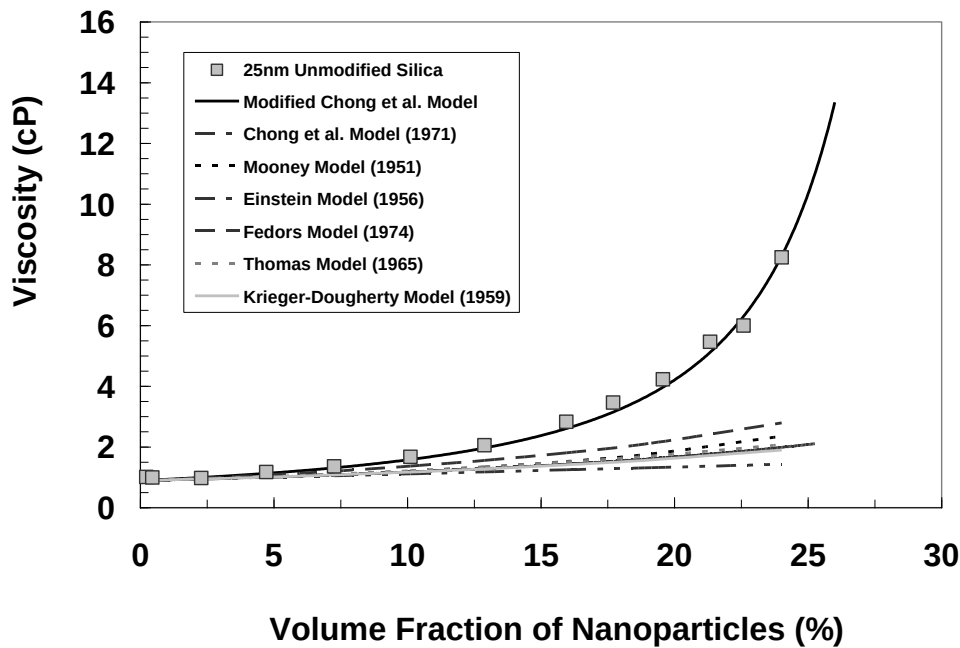


Figure 3.2- Comparison of the fit of viscosity models present in the literature to the experimental data of 25 nm unmodified silica dispersions.

Figure 3.2 shows the performance of these models (Equations 3.3-3.8 in Table 3.2) with respect to the experimental data. As seen from this figure, these models underestimate the viscosity of the silica dispersion. Previous studies on the rheology of nanoparticle dispersions (Prasher *et al.* 2006; Murshed *et al.* 2008) have emphasized that Einstein's (1956) model (Equation 3.3) underestimates the viscosity of these dispersions. Mackay *et al.* (2003) studied the viscosity of polystyrene nanoparticle dispersions and also found that the hydrodynamic contribution of nanoparticles to the viscosity does not follow Einstein's (1956) model.

The viscosity model proposed by Chong *et al.* [35] is modified based on the maximum packing fraction. For the 25 nm unmodified silica particles (Figure 3.2), ϕ_{max} is determined from experimental results as 0.328. The large deviation in ϕ_{max} (0.328) from the random close packed concentration of 0.63 for nominally spherical particles can be explained with the concept of an effective particle diameter (Equation 3.9). The details are presented in the following section where we discuss the effect of particle size on the viscosity of silica dispersions. The modified model shows excellent agreement with the experimental data (Figure 3.2).

Table 3.2- The existing viscosity models of colloidal dispersions evaluated in this study

$\eta_r = \frac{\eta}{\eta_o} = 1 + 2.5\phi$	Einstein (1956)	Eq.3.3
$\eta_r = \exp \left[2.5 \frac{\phi}{\left(1 - \frac{\phi}{\phi_{max}} \right)} \right]; \quad \phi_{max} = 0.63$	Mooney (1951)	Eq.3.4
$\eta_r = \left[1 + 0.75 \frac{\phi / \phi_{max}}{\left(1 - \frac{\phi}{\phi_{max}} \right)} \right]^2; \quad \phi_{max} = 0.63$	Chong <i>et al.</i> (1971)	Eq.3.5
$\eta_r = \left[1 + 1.25 \frac{\phi}{(\phi_{max} - \phi)} \right]^2; \quad \phi_{max} = 0.63$	Fedors (1974)	Eq.3.6
$\eta_r = 1 + 2.5\phi + 10.05\phi^2 + A\exp(B\phi)$ A=0.00273 and B=16.6	Thomas (1965)	Eq.3.7
$\eta_r = \left(1 - \frac{\phi}{\phi_{max}} \right)^{-[\eta]\phi_{max}}; \quad \phi_{max} = 0.63; [\eta] = 2.5 \text{ for spheres}$	Krieger-Dougherty (1959)	Eq.3.8

3.3.1 The Effect of Temperature on the Viscosity of Silica Nanoparticle Dispersions

The effect of temperature on the viscosity of silica nanoparticle is important for potential applications of these dispersions in high temperature hydrocarbon reservoirs. Therefore, the dependence of the viscosity of silica nanoparticle dispersions on the temperature has been investigated in this study. Figure 3.3 shows the relative viscosity as a function of the silica nanoparticle (25 nm diameter, unmodified surface) volume fraction at different temperatures (*e.g.* 25, 50 and 80 °C) and the theoretical predictions based on the modified Chong *et al.* model (1971). The results show that an increase in temperature greatly affects the viscosity of the suspending medium (water) rather than the particle-fluid interaction. Hence, the relative viscosity concept (η/η_0) successfully scales the experimental data at different temperatures in a single curve, indicating that the temperature does not affect the viscosity of silica nanoparticle dispersions. A similar observation was reported by Prasher *et al.* (2006) in their experimental study with alumina-based nanofluids, i.e. the relative viscosity of alumina-based nanofluids was independent of temperature.

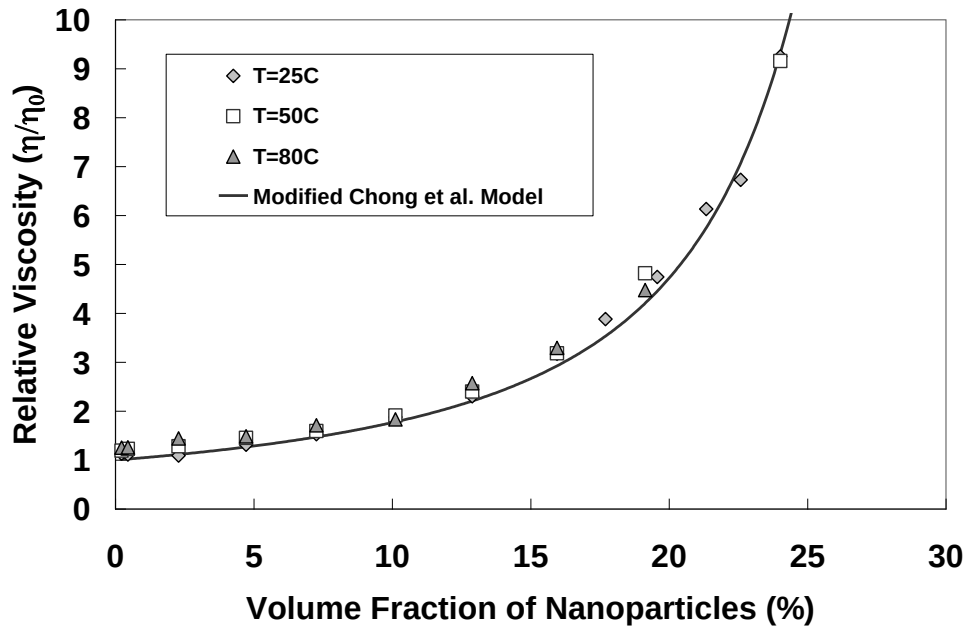


Figure 3.3- Relative viscosity, the ratio of the viscosity of silica dispersion to the viscosity of water, is plotted as a function of nanoparticle volume fractions at three different temperatures: 25, 50 and 80°C. The relative viscosity of 25 nm unmodified silica particles is independent of temperature.

3.3.2 The Effect of Particle Size on the Viscosity of Silica Nanoparticle Dispersions

The dependence of dispersion viscosity on particle size has not been taken into account in the models presented previously (see Table 3.2) because of the hard sphere assumptions. As a consequence, the viscosity is a unique function of the maximum packing fraction, independent of the particle size. In this study we find that the effect of particle size and the electrical double layer on the viscosity of unmodified silica nanoparticle dispersions is significant. It should be noted that the silica colloids used in our experiments are electrostatically stabilized with negative charges on the surface at pH

= 9. To capture these effects, we proposed an effective maximum packing fraction, $\phi_{\max}^{\text{eff}}$, to be incorporated into the modified Chong *et al.* (1971) model as follows:

$$\eta_r = \left[1 + 0.75 \frac{\phi}{(\phi_{\max}^{\text{eff}} - \phi)} \right]^2. \quad (3.9)$$

Figure 3.4 summarizes our experimental results carried out with four different sizes of unmodified silica nanoparticles: 5, 8, 25 and 75 nm. The lines correspond to the modified Chong *et al.* (1971) model by fitting $\phi_{\max}^{\text{eff}}$ to the experimental data. An important observation from this figure is that the viscosity increases as nanoparticle size decreases at a given nanoparticle volume fraction. The deviation from the hard sphere assumption ($\phi_{\max}$) could be confirmed by comparing the experimental results with the curve at the lower end corresponding to $\phi_{\max} = 0.63$. As particle size gets smaller, the effect of $\phi_{\max}^{\text{eff}}$ becomes more significant.

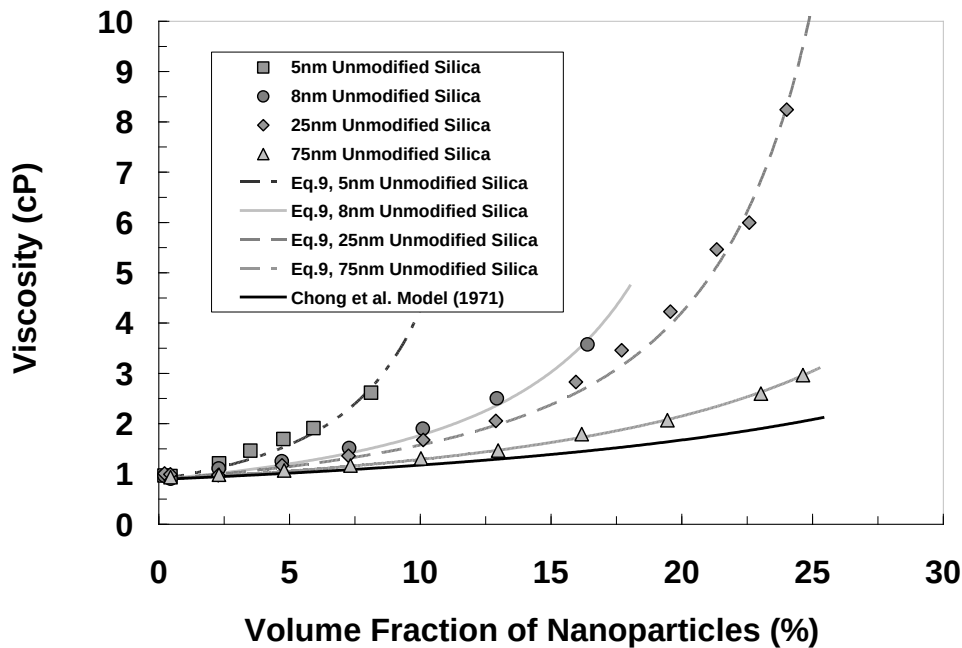


Figure 3.4- The viscosity of unmodified silica dispersions is plotted as a function of particle volume fraction for various particle diameters of 5, 8, 25 and 75 nm. The viscosity decreases as particle size increases at a given volume fraction of nanoparticles. The lines represent the modified Chong *et al.* model by fitting the effective maximum packing fraction to experimental data. The estimated $\phi_{\max}^{\text{eff}}$ values are presented in Table 3.3.

3.3.3 The Effect of Surface Modification on the Viscosity of Silica Nanoparticle Dispersions

The surface coating of silica nanoparticles with small alkyl chain attached to sulfonate group yield notable results when compared with unmodified silica dispersions. Only 5 and 25 nm silica particles are presented in Figure 3.5 for simplicity. The variation of viscosity with particle volume fraction is similar for both bare and surface modified silica nanoparticles. However, it could be clearly seen from this figure that the magnitude of volume fraction effect is significantly different between unmodified and modified

silica nanoparticles. Surface coated silica dispersions have lower viscosity than unmodified silica dispersions. Starck *et al.* (2007) studied the rheological behavior of silica nanoparticles coated with zwitterionic polymers. At concentrations greater than saturation coverage of polymer, the silica particles are sterically stabilized. The authors observed that the viscosity of the suspensions is lower than in the polymer-free suspension. This observation is in agreement with our experimental results for sulfonate coated silica nanoparticle dispersions. The estimated $\phi_{\max}^{\text{eff}}$ values are 0.302 and 0.437 for 5 and 25 nm surface modified particles, respectively. A summary of the properties of the experimental systems studied and the effective maximum packing fractions estimated is presented in Table 3.3. The variation of $\phi_{\max}^{\text{eff}}$ is to account for differences in surface properties of the nanoparticles. The nanoparticle volume fraction ϕ represents the true solid volume fraction.

Table 3.3- The summary of experimental systems studied

Particle diameter / Surface type	Maximum solid volume fraction	Effective maximum packing fraction, $\phi_{\max}^{\text{eff}}$
5nm / Unmodified	0.081	0.163
8nm / Unmodified	0.164	0.284
25nm / Unmodified	0.240	0.328
75nm / Unmodified	0.248	0.471
5nm / Sulfonate	0.099	0.302
8nm / Sulfonate	0.190	0.347
25nm / Sulfonate	0.222	0.437
75nm / Sulfonate	0.191	0.498

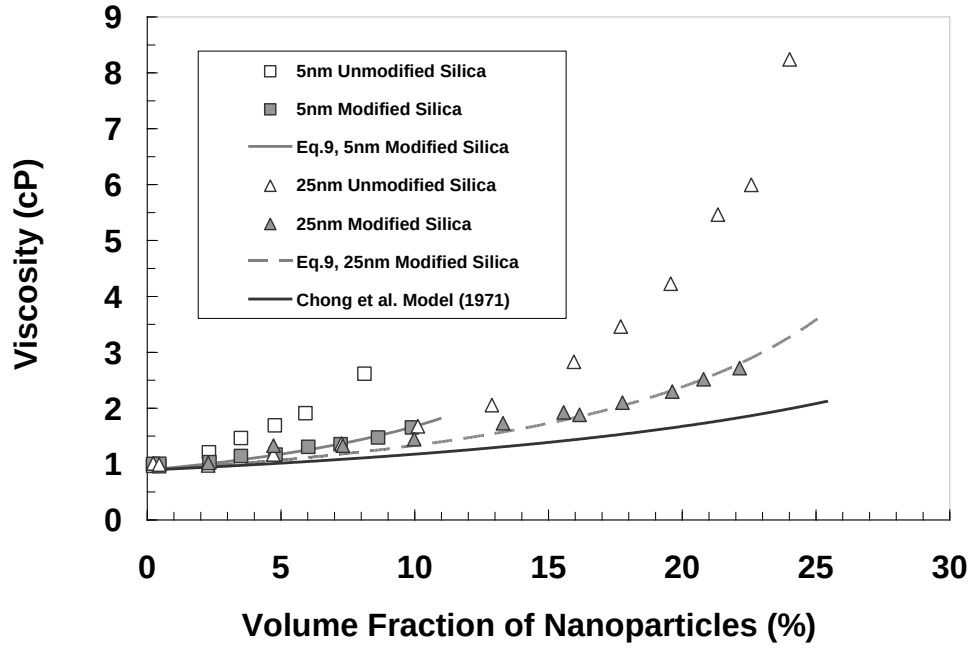


Figure 3.5- The dispersions of silica nanoparticles with surface modification by sulfonate group attached to a short chain of hydrocarbon, exhibit smaller viscosities compared to unmodified silica dispersions value at a given volume fraction.

3.3.4 The Unified Model

We propose a correlation between $\phi_{\max}^{eff}$ and $\phi_{\max}$ based on a simple cubic packing of spherical particles with an electrical double layer (Equation 3.10).

$$\phi_{\max}^{eff} = \phi_{\max} \frac{1}{\left(1 + A \frac{\kappa^{-1}}{a}\right)^3} \quad (3.10)$$

where κ^{-1} is the Debye length; a is the silica nanoparticle radius; and A is a constant. The effect of particle radius could be clearly seen in Equation 3.10; as particle size increases $\phi_{\max}^{eff}$ approaches the hard sphere maximum packing fraction, $\phi_{\max}$.

The effect of electrical double layer on the viscosity of alumina/water nanofluids was studied by Anoop *et al.* (2009). The electroviscous effects are found to be responsible for the additional increase in viscosity when compared to Einstein's model (1956). The authors modified the intrinsic viscosity by introducing a term based on electrical double layer. Our model agrees closely with their experimental results of alumina/water nanofluids.

For the case of sterically stabilized particles, we propose an equation where the effective length of the surface coating material l is taken into account, similar to the effect of electrical double layer thickness described in Equation 3.10, namely

$$\phi_{\max}^{eff} = \phi_{\max} \frac{1}{\left(1 + \frac{l}{a}\right)^3} . \quad (3.11)$$

The conceptual models proposed for the electrostatically and sterically stabilized silica nanoparticle dispersions are presented schematically in Figures 3.6a and 3.6b respectively. A simple cubic packing of particles is assumed in this study since the largest nanoparticle concentration used is less than 25% by volume and the nanoparticles are well dispersed in water.

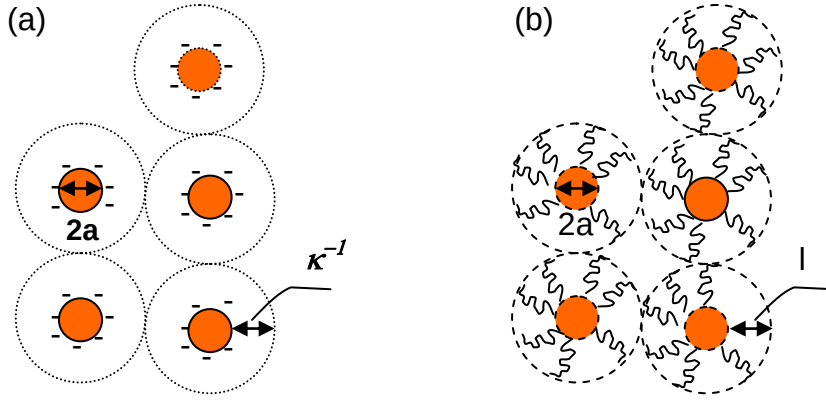


Figure 3.6- Schematic view of the proposed model of effective maximum packing fraction for (a) unmodified and (b) surface modified silica particles.

The reduced volume fraction of silica nanoparticles $\phi / \phi_{\max}^{\text{eff}}$ captures the effect of size and surface type on the viscosity. In Figure 3.7 all the experimental data with four different silica nanoparticle sizes and two different surface types collapse onto a single curve that agrees very well with the unified model. The experimental data of 500-nm silica particles with surface modification by monoethylene glycol (MEG) (Thwala *et al.* 2008) are also presented in Figure 3.7. The effective maximum packing fraction is calculated from Equation 3.9 where l is 7.8 nm as reported by the authors (Fagan and Zukoski 1997). The proposed model works well for silica particles whose sizes range from 5 to 500 nm.

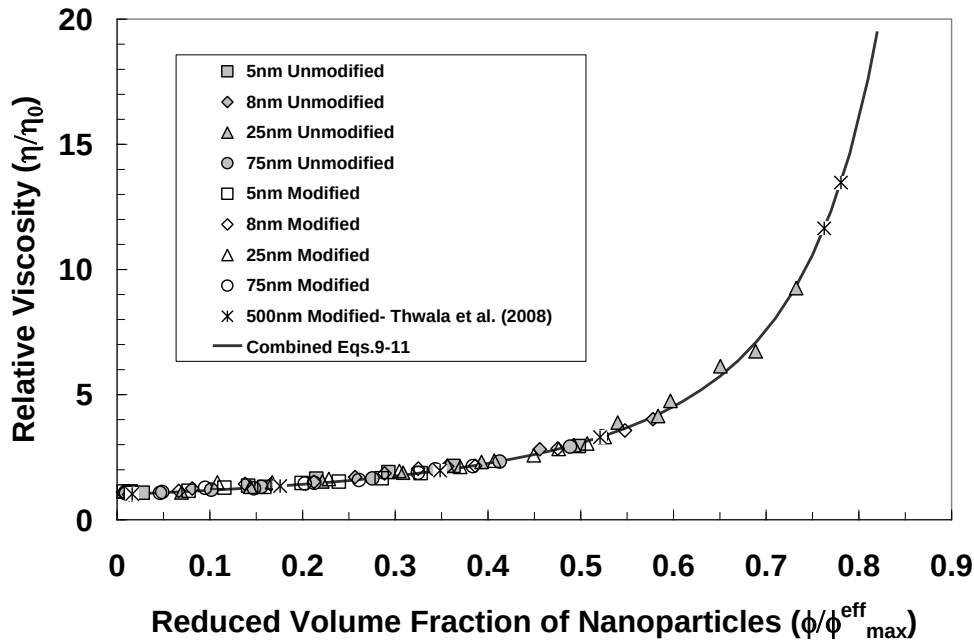


Figure 3.7- Viscosity ratio as a function of volume fraction of silica nanoparticles of various sizes (5, 8, 25 and 75 nm) and two different surface types (unmodified and sulfonate coated). Data from Thwala *et al.* (2008) for much larger particles are also shown. The volume fractions are normalized to the corresponding effective maximum packing fraction. All the data collapse onto a single curve that is well represented by our unified model.

The parameters A and l were computed based on experimental data. The results are shown in Figure 3.8 as a function of particle radius. The parameter l increases as particle size increases. Although the surface modifying material is the same for 5, 25 and 75 nm particles, the surface coverage of sulfonate is greater for larger particles. Therefore the outer surface of modified nanoparticles may be more hydrated by water for larger particles. This may explain why the parameter l increases slightly as particle size increases. The double layer thickness around the unmodified silica nanoparticle is taken as 2 nm according to Roberts (2006), which is also consistent with the particle size

measurements with dynamic light scattering (DLS). The parameters A and l are determined by Equations 3.10 and 3.11 based on the fitting of effective maximum packing fraction to the experimental data. The $O(1)$ values for A and the magnitudes of l are consistent with the conceptual picture of the effective particle diameter set by either an electrostatic double-layer or a steric layer. Normalized effective maximum packing fraction $\phi_{\max}^{\text{eff}}/\phi_{\max}$ is presented in Figure 3.9 as a function of dimensionless length l/a for surface modified and $A\kappa^{-1}/a$ for unmodified silica particles. The nonlinear dependence of $\phi_{\max}^{\text{eff}}/\phi_{\max}$ on dimensionless length described by Equations 3.10 and 3.11 is shown in Figure 3.9. The relationship between $\phi_{\max}^{\text{eff}}/\phi_{\max}$ and $A\kappa^{-1}/a$ or l/a indicates a significant deviation of $\phi_{\max}^{\text{eff}}$ from $\phi_{\max}$ (0.63) especially at small particle sizes (Figure 3.9).

We used our viscosity model (Equations 3.9-3.10/3.11) to predict the measured viscosity of alumina and silica dispersions at different volume fractions and sizes from Das *et al.* (2003), Wang *et al.* (1999), Thwala *et al.* (2008) and Mackay *et al.* (2003). The particle sizes reported in these references were used to determine the corresponding model parameters (A or l) based on Figure 3.8. These model parameters were then used to calculate the viscosity (Equations 3.9-3.10/3.11). We assumed a double layer thickness of 5 nm since the information on the electrical double layer thickness was not given in these studies. All the calculated viscosities and their measured values from the references were plotted versus particle volume in Figure 3.10. The relative viscosities of these dispersions collapse onto a single curve (Figure 3.10) as represented by the unified model (Equations 3.9-3.11).

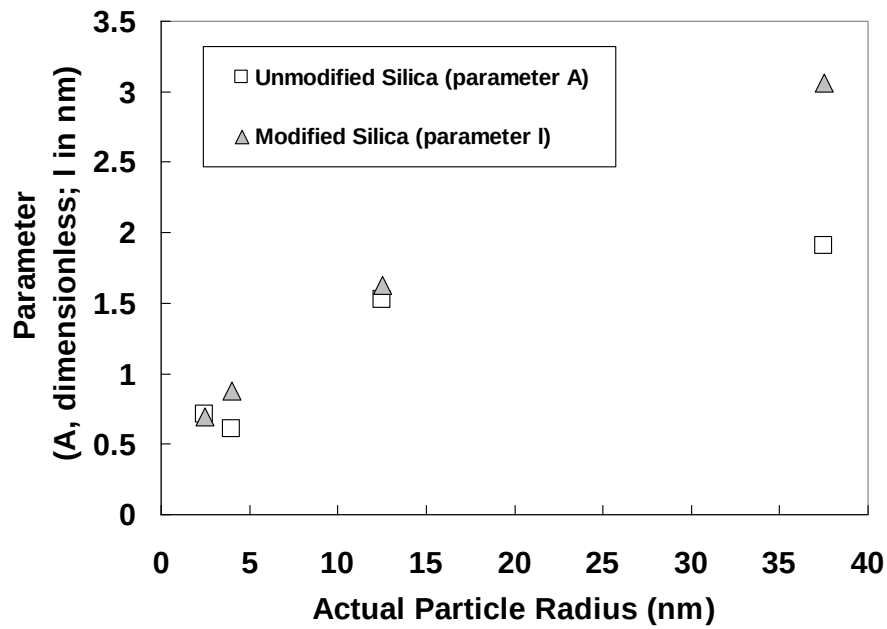


Figure 3.8- The parameters A (for unmodified silica nanoparticles) and l (for modified silica nanoparticles) of the proposed model (Equations 3.10 and 3.11) as a function of particle radius.

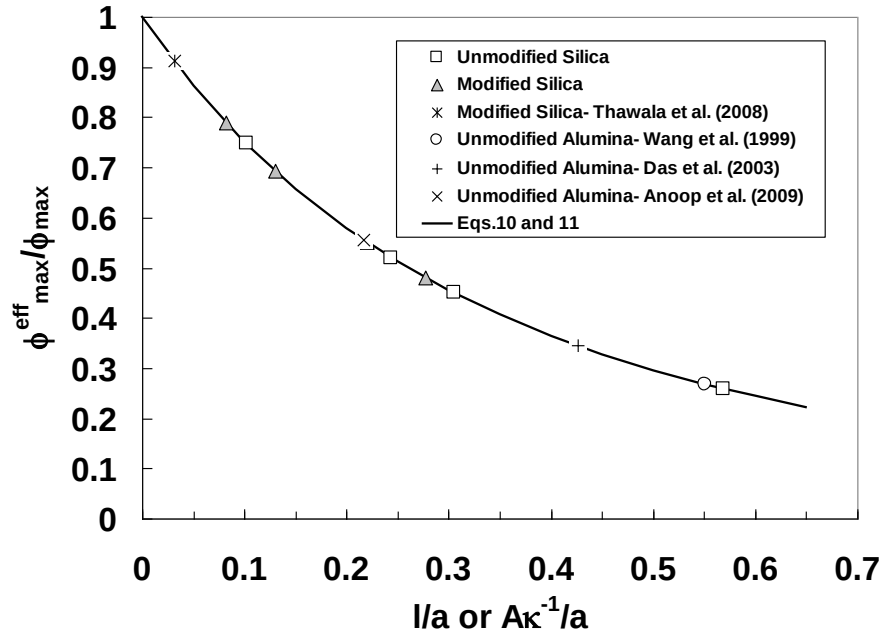


Figure 3.9- The normalized effective maximum packing fraction with respect to maximum packing fraction, $\phi_{\max}^{\text{eff}}/\phi_{\max}$, as a function of dimensionless parameter l/a for modified surface and $A\kappa^{-1}/a$ for unmodified surface. The solid line is constructed using Equations 3.10 and 3.11.

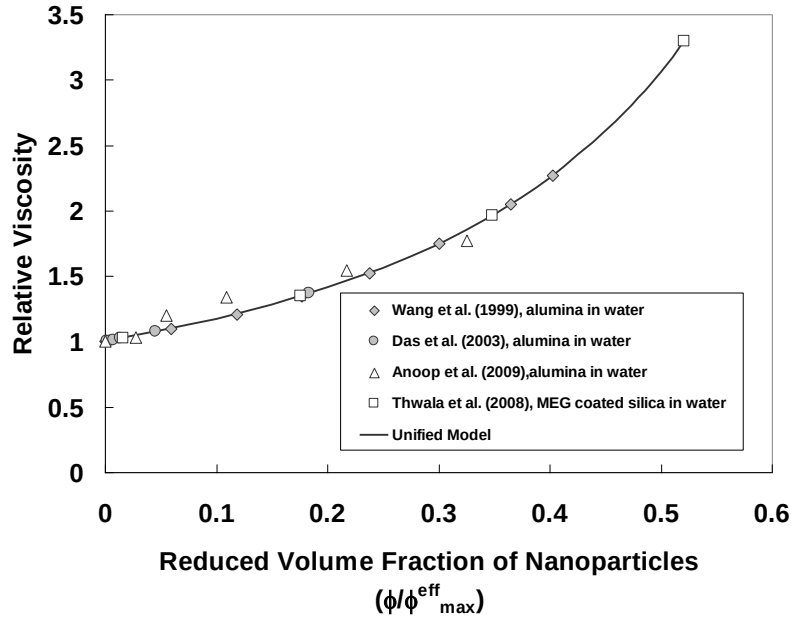


Figure 3.10- Viscosity ratio as a function of volume fraction of alumina nanoparticles in dispersed in water (Das *et al.* 2003; Wang *et al.* 1999; Mackay *et al.* 2003) and MEG coated silica nanoparticle dispersions (Thwala *et al.* 2008). The effective maximum volume fractions are determined by Equations 3.9-3.11. All the data collapse onto a single curve that is well represented by our unified model.

3.4 CONCLUSIONS

This chapter has shown that silica nanoparticle dispersions exhibit a Newtonian behavior for shear rates ranging from 1-200 s⁻¹ and particle concentrations ranging from 0.22-25% by volume. The relative viscosity is a non-linear function of particle volume fraction and independent of temperature. The particle size and the surface type are also found to significantly influence the viscosity. The dispersion viscosity increases as particle size decreases. The unmodified, electrostatically stabilized silica nanoparticles

exhibit greater viscosity than sulfonate coated, sterically stabilized silica nanoparticles at a given particle size and volume fraction.

A significant deviation from the predictions of hard sphere viscosity model occurs with our experimental results. Therefore, the electrostatic or steric interactions between silica nanoparticles should be taken into account. A unified model is proposed to predict accurately the viscosity of silica nanoparticle dispersions at a given solid volume fraction by introducing the concept of effective maximum packing fraction. The model parameters (A or I) could be determined experimentally or numerically based on, for instance molecular dynamics simulation. These parameters depend on nanoparticle size and surface properties. All the experimental data are successfully scaled by normalizing the volume fraction by the effective maximum packing fraction. A correlation is obtained between the effective maximum packing fraction and particle radius.

3.5 REFERENCES

- Anoop KB, Kabelac A, Sundararajan T, Das SK: Rheological and flow characteristics of nanofluids: Influence of electroviscous effects and particle agglomeration, *J. App. Phys.* 106 (2009) 034909-1-7.
- Bergenholtz J: Theory of rheology of colloidal dispersions, *Current Opinion in Colloid Int. Sci.* 6 (2001) 484-488.
- Chevalier J, Tillement O, Ayela F: Rheological properties of nanofluids flowing through microchannels, *App. Phy. Lett.* 91 (2007) 233103-1-3.
- Choi SUS: Enhancing thermal conductivity of fluids with nanoparticles, in *Developments and applications of non-Newtonian flows*, Siginer DA and Wang HP (Eds), FED-Vol 231/MD-Vol 66, pp. 99-105, ASME, New York, 1995.
- Chong JS, Christiansen EB, Baer AD: Rheology of concentrated suspensions, *J. Appl. Polym. Sci.* 15 (1971) 2007-2021.
- Chow TS: Viscosities of concentrated dispersions, *Phys. Rev. E* 48 (1993) 1977-1983.
- Das SK, Putra N, Roetzel W: Pool boiling characteristics of nano-fluids, *Int. J. Heat Mass Transfer* 46 (2003) 851-862.

- Ding YL, Alias H, Wen DS, Williams RA: Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids), *Int. J. Heat and Mass Transfer* 49 (2006) 240-250.
- Einstein A: *Investigations on the theory of the Brownian movement*, Dover, New York, 1956.
- Fagan ME, Zukoski CF: The rheology of charge stabilized silica suspensions, *J. Rheol.* 41 (1997) 373-397.
- Fedors RF: Relations between viscosity and concentration for Newtonian suspensions, *J. Colloid Interface Sci.* 46 (1974) 545-547.
- He Y, Jin Y, Chen H, Ding Y, Cang D, Lu H: Heat transfer and flow behaviour of aqueous suspensions of TiO₂ nanoparticles (nanofluids) flowing upward through a vertical pipe, *Int. J. Heat and Mass Transfer* 50 (2007) 2272-2281.
- Jung K-M, Kim SH: Rheological properties and transfer phenomena of nanofluids, XVth International Congress on Rheology, The Society of Rheology 80th Annual Meeting, (2008) 773-775.
- Krieger IM, Dougherty RJ: A mechanism for non-Newtonian flow in suspensions of rigid spheres, *Trans. Soc. Rheol.* 3 (1959) 137-152.
- Kwak K, Kim C: Viscosity and thermal conductivity of copper oxide nanofluid dispersed in ethylene glycol, *Korea-Australia Rheology J.* 17 (2005) 35-40.
- Lake LW: *Enhanced oil recovery*, Prentice Hall, New Jersey, 1989.
- Larson RG: The rheology of dilute solutions of flexible polymers: Progress and problems, *J. Rheology* 49 (2005) 1-70.
- Liu SF, Lafuma F, Audebert R: Rheological behavior of moderately concentrated silica suspensions in the presence of adsorbed poly(ethylene oxide), *Colloid Polym. Sci.* 272 (1994) 196-203.
- Lu K, Kessler C: Colloidal dispersion and rheology study of nanoparticles, *J. Mater. Sci.* 41 (2006) 5613-5618.
- Ma AWK, Chinesta F, Mackley MR, Ammar A: The rheological modeling of carbon nanotube (CNT) suspensions in steady shear flow, *Int. J. Mater. Form.* 1 (2008) 83-88.
- Mackay ME, Dao TT, Tuteja A, Ho DL, Van Horn B, Kim H-C, Hawker CJ: Nanoscale effects leading to non-Einstein-like decrease in viscosity, *Nature Materials* 2 (2003) 762-766.
- McPhie MG, Davis PJ, Snook IK: Viscosity of a binary mixture: Approach to the hydrodynamic limit, *Phys. Rev. E* 74 (2006) 031201-1-13.
- Mokhatab S, Fresky MA, Islam MR: Applications of nanotechnology in oil and gas E&P, *J. Pet. Technol. Online* 58 (2006) 4.

- Moon T: Nanotechnology collaborative takes aim at EOR, JPT online (2008)
<http://www.spe.org/jpt/2008/12/nanotechnology-collaborative-takes-aim-at-eor/#more-1870>
- Mooney M: The viscosity of a concentrated suspension of spherical particles, J. Colloid Sci. 6 (1951) 162-170.
- Murshed SMS, Tan S-H, Nguyen N-T: Temperature dependence of interfacial properties and viscosity of nanofluids for droplet-based microfluidics, J. Phys. D: Appl. Phys. 41 (2008) 085502-1-5.
- Namburu PK, Kulkarni DP, Dandekar A, Das DK: Experimental investigation of viscosity and specific heat of silicon dioxide nanofluids, Micro & Nano Letters 2 (2007) 67-71.
- Nanotechnology for oil and gas operations, <http://www.offshore-mag.com/index/article-tools-template.articles.offshore.regional-reports.north-sea-northwest-europe.2009.09.nanotechnology-shows.html>
- Petrie CJS: The rheology of fiber suspensions, J. Non-Newtonian Fluid Mech. 87 (1999) 369-402.
- Prasher R, Song D, Wang J, Phelan P: Measurements of nanofluid viscosity and its implications for thermal applications, Appl. Phys. Lett. 89 (2006) 133108-1-3.
- Prodanovic M, Ryoo S, Rahmani AR, Kuranov R, Kotsmar C, Milner TE, Johnston KP, Bryant SL, Huh C: Effects of magnetic field on the motion of multiphase fluids containing paramagnetic nanoparticles in porous media, SPE 129850, SPE IOR Symp., 2010.
- Roberts WO: Colloidal Silica: Fundamentals and Applications, Bergna HE, Roberts WO (Eds.), CRC Press, Boca Raton, 2006.
- Rudyak VYa, Belkin AA, Egorov VV: Effective viscosity coefficient of nanosuspensions, Rarefied Gas Dynamics, 26th International Symposium, Ame. Inst. Of Phys. (2009) 489-494.
- Russel WB, Saville DA, Scholwater WR: Colloidal dispersions, Cambridge University Press, Cambridge, 1991.
- Starck P, Mosse WKJ, Nicholas NJ, Spiniello M, Tyrrell J, Nelson A, Qiao GG, Ducker WA: Surface chemistry and rheology of polysulfobetaine-coated silica, Langmuir 23 (2007) 7587-7593.
- Stickel JJ, Powell RL: Fluid mechanics and rheology of dense suspensions, Ann. Rev. Fluid Mech. 37 (2005) 129-149.
- Stuart AR, Amstad E, Antoni M, Gauckler LJ: Rheology of concentrated suspensions containing weakly attractive alumina nanoparticles, J. Am. Ceram. Soc. 89 (2006) 2418-25.

- Thomas DG: Transport characteristics of suspension: VIII. A note on the viscosity of Newtonian suspensions of uniform spherical particles, J. Colloid Sci. 20 (1965) 267-277.
- Thwala JM, Goodwin JW, Mills PD: Viscoelastic and shear viscosity studies of colloidal silica particles dispersed in monoethylene glycol (MEG), diethylene Glycol (DEG) and dodecane stabilized by dodecyl hexaethylene glycol monoether, Langmuir 24 (2008) 12858-12866.
- Tseng WJ, Lin KC: Rheology and colloidal structure of aqueous TiO₂ nanoparticle suspensions, Mater: Sci. Eng. A 355 (2003) 186-192.
- Wang XW, Xu XF, Choi SUS: Thermal conductivity of nanoparticle - Fluid Mixture, J. Thermophys. Heat Transfer 13 (1999) 474-480.
- Xuan YM, Li Q: Heat transfer enhancement of nanofluids, Int. J. Heat Fluid Flow 21 (2000) 58-64.

Chapter 4: Aggregation Kinetics and Shear Rheology of Aqueous Silica Suspensions

The kinetics of aggregation of silica nanoparticle dispersions at different NaCl and silica concentrations is studied experimentally and theoretically. Silica nanoparticles form fractal aggregates due to the collapse of the electrical double layer at high salt concentrations and resulting reduction in stabilizing repulsive force. A convenient model is proposed to describe the aggregation of silica nanoparticles and the growth of their aggregate size that depends on particle size and concentration and salt concentration. The aggregation curves of all the suspensions studied collapse onto a single master curve by using appropriate dimensionless diameter and time. The aggregation of silica nanoparticles also affects the rheology of the suspension. An equilibrium approach for sediment volume fraction is proposed to determine the maximum effective packing fraction. The results for the relative viscosity of silica aggregates agree well with the proposed viscosity model, which also collapses onto a single master curve.

4.1 INTRODUCTION

The potential application of nanoparticle dispersions as formation stimulation agents, contrast agents or simply as tracers in upstream oil and gas industry requires knowledge of the dispersion properties of these nanoparticles. Silica nanoparticles are commonly used because of their low cost for fabrication and surface modification. The control of the stability of nanoparticle dispersions is crucial under reservoir salinity and temperature, which are often quite severe. Transport of nanoparticles to target zones in the reservoir is key to achieving the goal of improved recovery. Therefore, transport properties such as the mobility of nanoparticles and the dispersion rheology are very

important. These properties depend on several things, such as particle size and concentration. Therefore, determining the rate of change in the size of aggregates formed by nanoparticles is essential for an effective displacement of unstable suspensions of nanoparticles in reservoir rock.

The aggregation kinetics of colloidal particles is commonly modeled by fractal dimension, stability ratio theories (Smoluchowski 1916, 1917; Fuchs 1934), or population balance models (Hounslow *et al.* 1988). The absolute rates of fast or slow aggregation regimes are determined experimentally, by turbidity or size measurements, or numerically by a stability ratio approach. These methods take into account only the early time of aggregation where single particles collide and form doublets. Therefore the confirming experiments must be performed in such a way that the data correspond to the early stage of aggregation. Under such conditions, the selection of particle size and concentration, and electrolyte type and concentration becomes challenging, especially when using nanoparticles, because of their size and relatively small light scattering properties. Taboada-Serrano *et al.* (2005) presented a overview of the recent contributions to the understanding of aggregation.

Aqueous suspensions of silica nanoparticles have been studied for their aggregation behavior by light scattering (Aubert and Cannell 1986; Schaefer and Martin 1984; Lin *et al.* 1990; Dietler *et al.* 1986; Schaefer and Martin 1984; Martin 1987) and x-ray scattering (Schaefer and Martin 1984; Dale *et al.* 1984). Fractal dimensions for slow and fast aggregation regimes are calculated by these authors. Schaefer *et al.* (1984) observed a power law behavior of aggregation, which was claimed to be a signature of fractal structures. They proposed that the structure of fast aggregating clusters could change and become more compact after a long time to approach a fractal dimension of 2.12. Aubert and Cannell (1986) also observed a restructuring to a fractal dimension from

1.75 to 2.08 for rapid aggregation. Giordano-Palmino *et al.* (1994) studied the effect of an adsorbed layer of nonionic surfactant in silica suspensions on the dispersion stability and aggregation kinetics. Rapid flocculation was observed by a drastic increase in UV-Vis absorbance data. The authors suggested that bridging of surface micelles were responsible for the aggregation of these particles. Gorrepati *et al.* (2010) showed how silica precipitation proceeded under very acidic conditions (below pH 0) below silica's isoelectric point and at low temperature, 5°C. The authors modified Smoluchowski equation by incorporating a geometric population balance to simulate the aggregation of particles. An exponential increase in particle size was observed experimentally and also predicted by their simulation study.

In chapter 2, the critical salt concentration (CSC) is defined below which the silica nanoparticles stay well dispersed in solution. This chapter focuses on how the aggregation of silica nanoparticles evolves in time in the presence of NaCl above the CSC. A systematic study of the aggregation of silica nanoparticle dispersions and their rheological behavior under the pH and NaCl conditions in hydrocarbon reservoirs is presented. The effect of the size of the primary silica nanoparticles, NaCl and particle concentration on the aggregation kinetics of silica is determined by measuring the change in aggregate size as a function of time. A new model is proposed to describe the aggregation kinetics and use experimental data or theory to determine the model parameters. The model proposed is very convenient to use and provides a framework to collapse all the data onto a single curve by using dimensionless numbers. The rheology of unstable silica suspensions is modeled by using the effective maximum packing fraction concept coupled with effective aggregate volume fraction.

4.2 MATERIAL AND METHODS

The material under study is an aqueous dispersion of silica nanoparticles as provided by 3M, Co (St. Paul, MN, USA). The mean diameters of the primary particles are 5, 25 and 75 nm and they have an unmodified surface. The particles are monodisperse. The shape of silica nanoparticles is spherical as determined by images of a scanning transmission electron microscope (STEM). The silica nanoparticles are electrostatically stabilized in an aqueous medium with a zeta potential of around -45 mV at pH = 9. Stock solutions containing 16-41% by weight silica nanoparticles were diluted with deionized water up to a desired silica concentration. In the absence of electrolyte, the silica nanoparticles were well dispersed and did not aggregate as determined by size measurements. Analytical grade NaCl was added to silica nanoparticle dispersions to study the aggregation kinetics and the rheology of silica nanoparticle aggregates in suspension.

Delsa Nano dynamic light scattering (DLS) was used to study the effective diameter of silica nanoparticle aggregates as a function of time. The experiments were carried out at 25°C.

A strain controlled rheometer with double-wall Couette fixture was used to determine the rheology of the silica aggregates in suspension at different shear rates at 25°C. The effect of shear rate, aggregate size and effective volume fraction on the shear viscosity is evaluated.

4.3 RESULTS AND DISCUSSION

4.3.1 Aggregation Kinetics

The aggregation of silica nanoparticles takes place at salt concentrations greater than the critical salt concentration (CSC) as discussed in detail by Metin *et al.* (2011a). For 25 nm diameter silica nanoparticles, the CSC occurs approximately at 1 wt% NaCl. Figure 4.1 represents the effect of NaCl concentration on the aggregation kinetics of silica nanoparticles at concentrations greater than the CSC. An S-shape curve on a semi-logarithm of time scale occurs for all samples. As the NaCl concentration increases the rate of aggregation of the silica nanoparticles increases as does the maximum effective diameter of the aggregate.

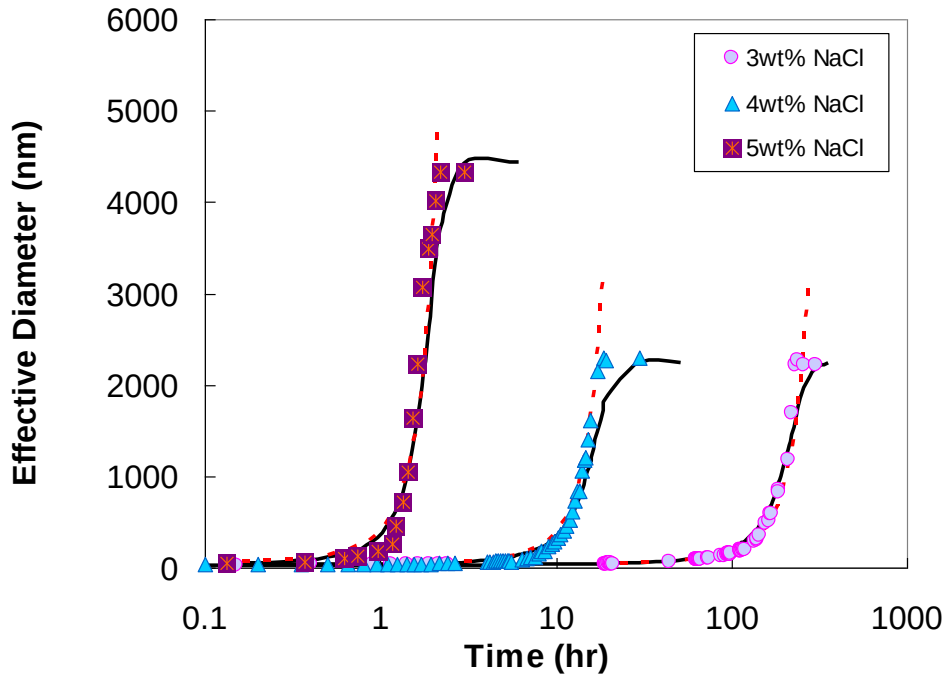


Figure 4.1- Effect of NaCl concentration on the rate of aggregation expressed as diameter growth. The samples are at 25°C and contain 1wt% of 25 nm diameter primary silica nanoparticles. The solid lines correspond to the model proposed in Equation 4.7 and the dashed lines correspond to the exponential model in Equation 4.8.

The effect of NaCl on this aggregation behavior could be explained by considering the interaction potential between two charged spherical nanoparticles as described by DLVO theory (Derjaguin and Landau 1941; Verwey and Overbeek 1948). The repulsion energy, which is a function of electrical double layer thickness, κ^{-1} , decreases as electrolyte concentration increases. Therefore, the total interaction energy changes as a function of electrolyte concentration. The maximum total interaction energy or the energy barrier, V_{Tmax} , decreases as the electrolyte concentration increases. Reerink

and Overbeek (1954) showed that the aggregation rate is proportional to the energy barrier as shown by Equation 4.1. This theory was first developed by Fuchs (1934).

$$W \approx \frac{1}{2\kappa a} e^{\left(\frac{V_{T \max}}{k_B T}\right)} = \frac{k_{fast}}{k_s} \quad (4.1)$$

In Equation 4.1, a is the particle radius, k_B , the Boltzmann constant and T is the temperature. The stability ratio, W , is the ratio of fast aggregation to slow aggregation rates. The aggregation kinetics of colloidal suspensions divides into two regimes: fast and slow aggregation. In the fast aggregation regime, the absence of potential energy barrier occurs because large concentrations of electrolyte are present in the solution and the double layer thickness is suppressed. Therefore, each collision between particles is controlled by the rate of diffusion of the particles towards each other. On the other hand in the slow aggregation regime, the presence of a potential barrier decreases the number of successful collisions between particles, and hence the magnitude of this potential barrier controls the kinetics of aggregation. The aggregation rate constant k_{fast} is in the fast aggregation regime and derived by von Smoluchowski (1916, 1917) as $k_{fast} = \frac{8k_B T}{3\eta}$.

For the slow aggregation regime, where the presence of an energy barrier decreases the number of successful collisions between particles, the actual aggregation rate constant, k_s , can be estimated from Equation 4.1 by using the DLVO curves presented in chapter 2. The data shown in Figure 4.2 corresponds to the slow aggregation regime and we can compare the rate constant in Equation 4.1 to experimentally determined k_s . The latter is obtained from the rate of change of effective particle diameter (hydrodynamic diameter) in DLS measurements at early time of aggregation (Schudel *et*

al. 1997) by $\left. \frac{dD}{dt} \right|_{t \rightarrow 0} = k_s N_0$ as presented in Figure 4.2. Here N_0 , the initial particle number concentration, can be calculated from initial particle weight concentration, c_0 , by using the correlation $N_0 = c_0 \frac{3}{4\pi a^3 \rho}$, where ρ is the density of silica.

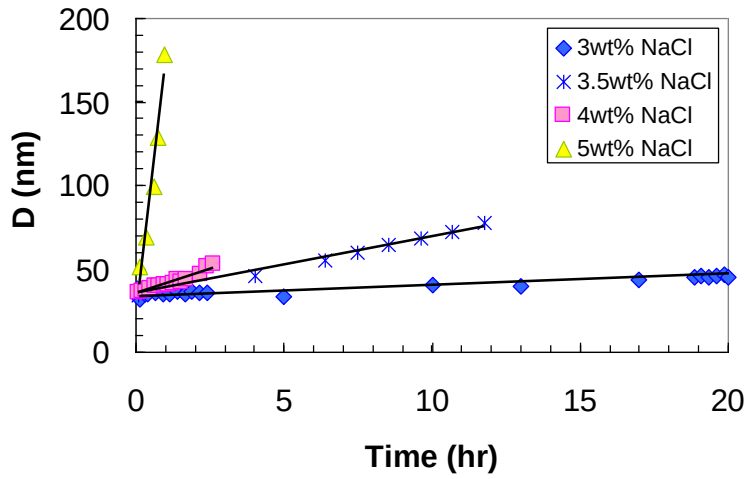


Figure 4.2- Effective particle diameter as a function of time as measured by DLS for 25 nm diameter primary particles at early aggregation times. Lines correspond to a linear fit to experimental data.

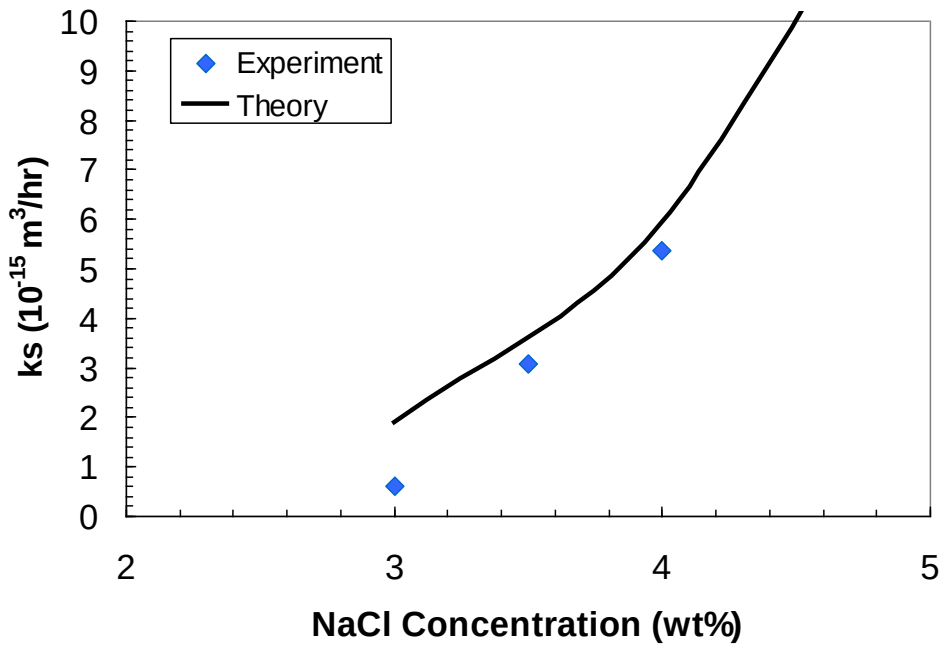


Figure 4.3- Comparison of the slow aggregation rate constant, k_s , in Equation 4.1 and experimental results for 25 nm unmodified nanoparticles.

Figure 4.3 presents k_s as a function of NaCl concentration for 25 nm unmodified nanoparticles. As NaCl concentration increases, the rate constant k_s also increases as discussed above. At NaCl concentration smaller than 5 wt% we obtained a very good agreement between the values of k_s determined experimentally and calculated from the theory presented in Equation 4.1. The concentration of NaCl is used for the calculation of electrical double layer thickness and the maximum total interaction energy in Equation 4.1. The double layer thickness is calculated to be 0.44 nm for 1 wt% silica with 3 wt% NaCl sample. At 5 wt% NaCl concentration, the aggregation is fast and the initial data on aggregate size are limited by the resolution of DLS in time. At high ionic strengths, non-DLVO repulsion may come into play such as silica hairs (Iler 1979; Vigil *et al.* 1994; Israelachvili *et al.* 1996). These thin silica hairs on the surface could push the double

layer repulsion out to extend further than van der Waals attraction and also generate an additional short-range steric repulsion.

The effect of silica concentration on aggregation kinetics is similar to the effect of NaCl in the sense that increasing particle concentration accelerates aggregation, Figure 4.4. However, the physics behind this increase in aggregation rate is different for each effect. From an equilibrium perspective, we have shown that the CSC is independent of particle concentration but we cannot explain our observations from the concept of CSC because it is not a kinetic parameter. The model presented in Equation 4.1 does not explain these observations either because the DLVO theory is about interaction potential between 2 particles. The parameters in Equation 4.1 are not a function of particle concentration. However, k_s is a function of silica nanoparticle concentration and as the particle concentration increases the aggregation rate increases significantly. Experimental results of k_s as a function of silica nanoparticle concentration by weight percent, c_0 , is in Figure 4.5. The correlation is given in Equation 4.2.

$$k_s = 5 \times 10^{-16} c_0^{1.3} \quad (4.2)$$

To understand the effect of particle concentration on aggregation kinetics, we take a close look at how these nanoparticles come in contact and how aggregation develops. The particles must travel a certain distance with a certain diffusivity to come close to each other, and then form an aggregate with a probability of sticking that depends on the extent of the energy barrier, V_{Tmax} . For a fixed electrolyte concentration, the extent of the energy barrier and hence the sticking probability are fixed. However, the mean distance that particles travel before each collision will be small at large particle concentrations, which in turn will increase aggregation rates. Therefore, we argue that the effect of

separation distance between particles is significant on the aggregation behavior of silica nanoparticles at different concentrations. Note that the largest nanoparticle concentration we studied is 5 wt%, for which the diffusion coefficient may be the same as that of a more dilute concentration, 1 wt%.

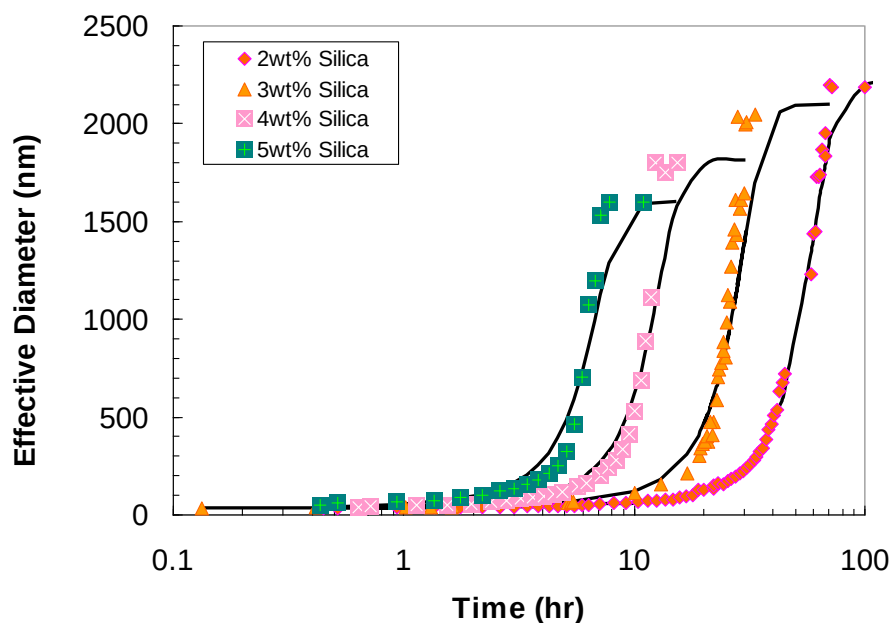


Figure 4.4- Effect of silica concentration on the kinetics of aggregation. The samples are at 25°C and contain 3wt% NaCl. The primary particle diameter is 25 nm. The lines are from the model proposed in Equation 4.7.

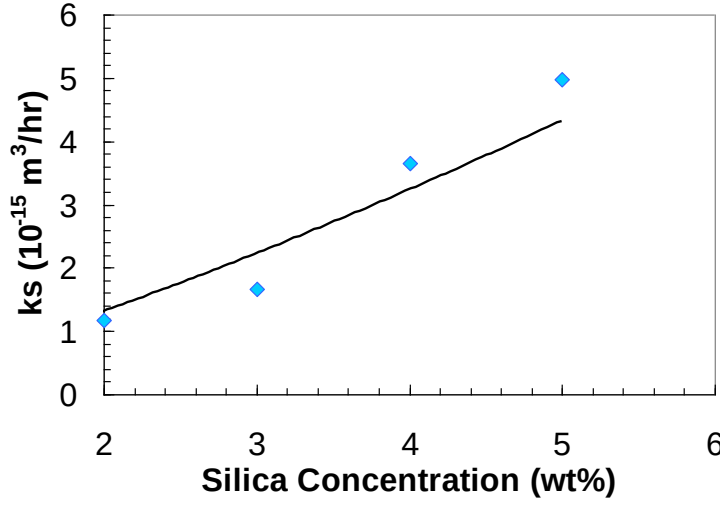


Figure 4.5- The slow aggregation rate constant, k_s , as a function of initial silica particle concentration. The solid line corresponds to Equation 4.2.

To model the experimental observations on the aggregation kinetics of silica nanoparticle dispersions not only at the early time of aggregation but also at late time, we propose a model for the growth of an aggregate size as a function of time. We assume that there are enough particles in the vicinity of the aggregate and hence the growth is not diffusion limited (see Figure 4.6). The mass of the aggregate scales as $m \propto \alpha D^{d_f}$. Since we assume that the fractal dimension, d_f , is 2.05 (Aubert and Cannell 1986; Martin 1987) we can simplify the equation above as $m \approx \alpha D^2$.

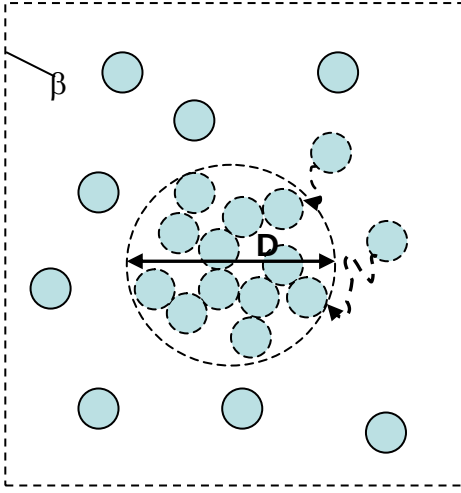


Figure 4.6- Schematic for the growth of an aggregate of diameter D in a cell of volume β .

The rate of change in mass of the aggregate is then given as

$$\frac{dm}{dt} = 4\pi m_p k \left(\frac{D}{2} \right)^2 n_1 \quad (4.3)$$

where m is the mass of an aggregate, m_p the mass of a single particle, k the rate constant and n_1 the number concentration of single particles in a volume β of the dispersion. The rate of change of the number concentration of single particles can then be expressed as

$$\frac{dn_1}{dt} = -\frac{1}{m_p \beta} \frac{dm}{dt} = -\frac{k\pi}{\beta} D^2 n_1 = -k_2 D^2 n_1 \quad (4.4)$$

The mass of an aggregate, m , can be expressed in terms of diameter of the aggregate, D by the correlation $m \approx \alpha D^3$, Equation 4.5 so that

$$\frac{dD}{dt} = \frac{m_p k \pi}{2\alpha} D n_1 = k_1 n_1 D \quad (4.5)$$

At the early time of aggregation, where n_1 can be assumed constant, Equation 4.5 has an analytical solution with an exponential growth term for the diameter. This equation explicitly shows why such an exponential growth is observed experimentally in the aggregation study of silica nanoparticle solutions.

Equation 4.5 can be expressed as a function of diameter by dividing Equation 4.5 by Equation 4.4 and solving the resultant equation with the condition at infinite time that $n_1=0$ and $D=D_{eq}$, so that

$$\frac{dD}{dt} = -\frac{k_2}{2} D (D^2 - D_{eq}^2) \quad (4.6)$$

Equation 4.6 has an analytical solution in the following form with the initial condition of $D=D_0$, the diameter of the primary particles at the beginning of the aggregation stage at $t=0$.

$$\frac{D(t)}{D_{eq}} = \frac{1}{\left\{ \left[\left(\frac{D_{eq}^2}{D_0^2} - 1 \right) e^{-k_2 t D_{eq}^2} \right] + 1 \right\}^{1/2}} \quad (4.7)$$

The model in Equation 4.7 is used to fit our experimental data for aggregate size as a function of time as measured by DLS. Then, the model parameter, k_2 is determined. The results are shown in Figures 4.1 and 4.4 for different NaCl and silica concentrations, respectively.

At the beginning of the aggregation, our model well represents the change in aggregate diameter in time. However, as D approaches D_{eq} , the model in Equation 4.7 deviates slightly from experimental data. In the proposed model, we do not allow aggregates to collide with each other unless they grow big enough that adjacent aggregates become a part of a network. On the other hand, in the experiments, aggregate-to-aggregate collisions occur and D_{eq} is reached earlier than prediction.

We present the fitting parameter k_2 as a function of NaCl and nanoparticle concentration in Figure 4.7. As discussed previously, an increase in the aggregation rate occurs as NaCl or nanoparticle concentration increases.

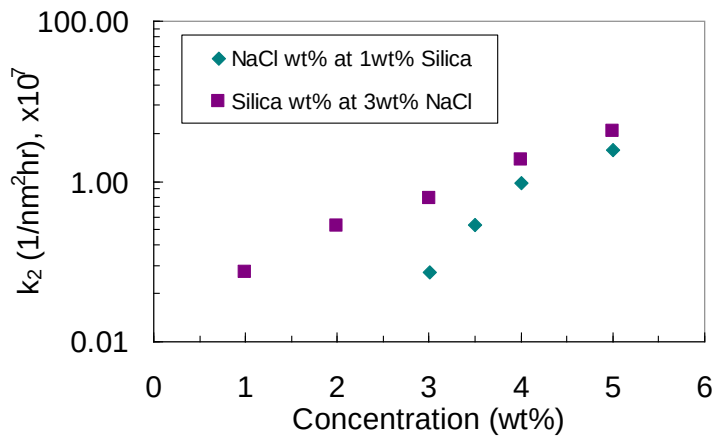


Figure 4.7- The model parameter, k_2 , in Equation 4.7 as a function of NaCl and silica concentration for 25 nm diameter primary particles.

For the early time of aggregation of nanoparticles, where $D \ll D_{eq}$, Equation 4.6 reduces to $\frac{dD}{dt} = \frac{k_2 D_{eq}^2}{2} D$ with an analytical solution of $D(t) = D_0 e^{st}$ where $s = \frac{k_2 D_{eq}^2}{2}$.

This equation is same as the class-II exponential growth model in reaction limited

aggregation (RLA) regime (or slow aggregation regime) for which general analytical solutions of the Smoluchowski equation have not yet been obtained (Martin 1987). Aggregation processes are thought to be described by the Smoluchowski equation (Martin 1987) with the reaction kernels determining the characteristics of the aggregation behavior. In the slow aggregation regime, the aggregate size will grow exponentially in time as

$$D \approx D_0 e^{ct} \quad (4.8)$$

where c is an exponential constant determining the rate of aggregation kinetics and is similar in magnitude to the rate constant $s = \frac{k_2 D_{eq}^2}{2}$ in Equation 4.7. The exponential growth is widely used in the literature to describe the aggregation in reaction limited regime.

At late time aggregation, a limiting value for aggregate diameter is reached. In this period, the model in Equation 4.7 slightly underestimates the growth of aggregates. If individual aggregates grow large enough they may undergo significant sedimentation before aggregates collide with each other and span the space. The ratio of gravitational force to Brownian diffusion is expressed as a gravitational Peclet number, Pe_g as follows (Poon and Haw 1997)

$$Pe_g = \frac{2\pi\Delta\rho g a^4}{9k_B T} \left(\frac{D}{D_0} \right)^{d_f+1} \quad (4.9)$$

where $\Delta\rho$ is the density difference between the particles and dispersion medium. A maximum size that an aggregate could reach can be expressed depending on particle concentration. The aggregates grow and span space at this critical size, D_c , which is a function of particle volume fraction, ϕ_0 and fractal dimension, d_f as follows (Poon and Haw 1997)

$$D_c \approx 2a\phi_0^{1/(d_f-3)} \quad (4.10)$$

If this critical size occurs when $Pe_g < 1$ then D_c is the limiting length scale for D_{eq} . Otherwise, gravitational force will limit D_{eq} . In our experiments, Pe_g is smaller than 1 for silica concentrations equal and greater than 2 wt%. Within that range of silica concentration, our experimental results show that D_{eq} is almost same as D_c from Equation 4.10. Therefore we can predict the maximum aggregate size reached before sedimentation becomes prevalent. Note that D_c decreases as nanoparticle concentration increases.

The parameters in Equation 4.7, the rate constant $s = \frac{k_2 D_{eq}^2}{2}$ and the equilibrium diameter D_{eq} , are presented as a function of silica and NaCl concentrations in Figures 4.8 and 4.9 for 25 nm silica nanoparticles. A power law relationship occurs between the rate constant and NaCl or silica concentrations. However, the equilibrium diameter seems to change slightly (is at same order of magnitude) over the range of NaCl and silica concentrations studied. Figure 4.8 also compares the rate constant c in Equation 4.8 with the rate constant, s , in our proposed model. There is good agreement between these two constants and these two theories since they both represent an exponential growth in time as discussed previously. The comparison between D_{eq} and D_c is in Figure 4.9 as a

function of silica concentrations. A good agreement again occurs between these two parameters for silica concentrations greater than 2 wt% where Pe_g is less than 1.

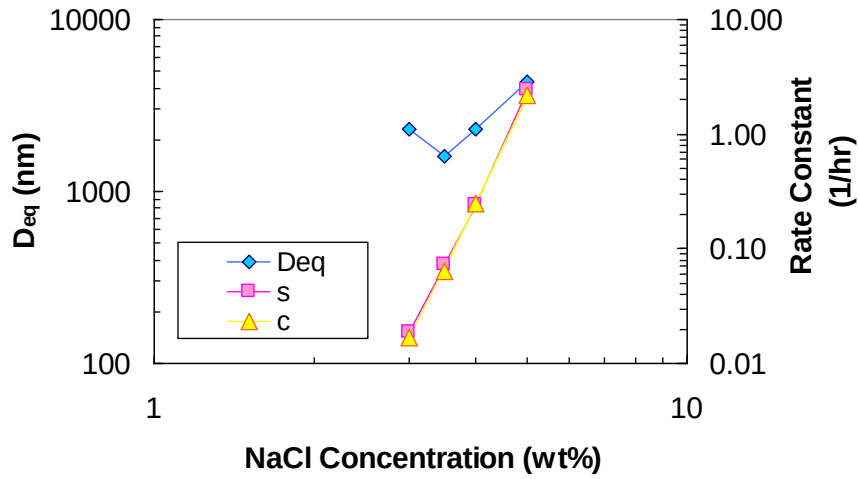


Figure 4.8- The equilibrium diameter and comparison between the rate constant, $s = \frac{k_2 D_{eq}^2}{2}$, in Equation 4.7 and c the exponent of the slow aggregation regime in Equation 4.8, as a function of NaCl concentration at 1 wt% silica particles of 25 nm primary diameter.

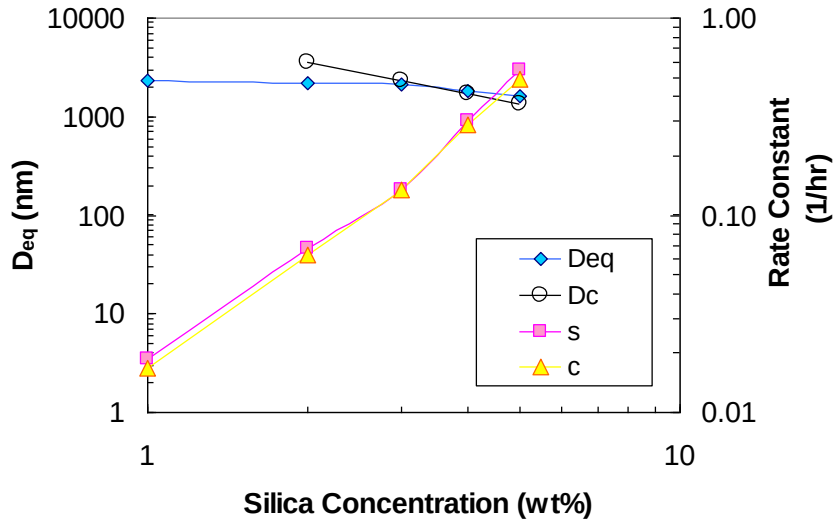


Figure 4.9- The equilibrium diameter and comparison between the rate constant, $s = \frac{k_2 D_{eq}^2}{2}$, in Equation 4.7 and the constant c in Equation 4.8 as a function of silica concentration at 3 wt% NaCl. The primary silica particles are of 25 nm in diameter.

Once the rate constant, s , in the proposed model and its relation with c in the widely used the exponential model are determined, the parameters constituting s , $s = \frac{k_2 D_{eq}^2}{2}$, are investigated where k_2 is

$$k_2 = \frac{k\pi}{\beta} \quad (4.11)$$

The parameters β and k can be determined from Equations 4.12 and 4.13.

$$k \approx \left(\frac{D_{diff}}{l} \right) \frac{1}{2\kappa a} \exp \left(-\frac{V_{Tmax}}{k_B T} \right) \quad (4.12)$$

where l is the width of the secondary minimum in the DLVO curve. The diffusion coefficient, D_{diff} , is calculated from Einstein-Stokes equation as $D_{diff} = \frac{k_B T}{6\mu\pi a}$

$$\beta = \frac{n}{n_0} = \left(\frac{D_{eq}}{0.8D_0} \right)^{d_f} \left(\frac{D_0^3 \pi}{6\phi_0} \right) \quad (4.13)$$

where n is the number of single particles forming an aggregate of size D_{eq} and n_0 is the initial number of single particles per total volume. We calculate β from Equation 4.13 and compare with that obtained from Equation 4.11. The parameter k is determined from Equation 4.12 and k_2 from experimental data. The values for β agree well for various silica concentrations at 3 wt% NaCl, Figure 4.10. However, we observe a deviation between the values obtained by these two approaches for NaCl concentrations at 4 and 5 wt% with 1 wt% nanoparticle concentration. Similarly, we can determine k from Equation 4.12 and compare it with Equation 4.11 where β is calculated from Equation 4.13. The results are in the same order of magnitude, Figure 4.10.

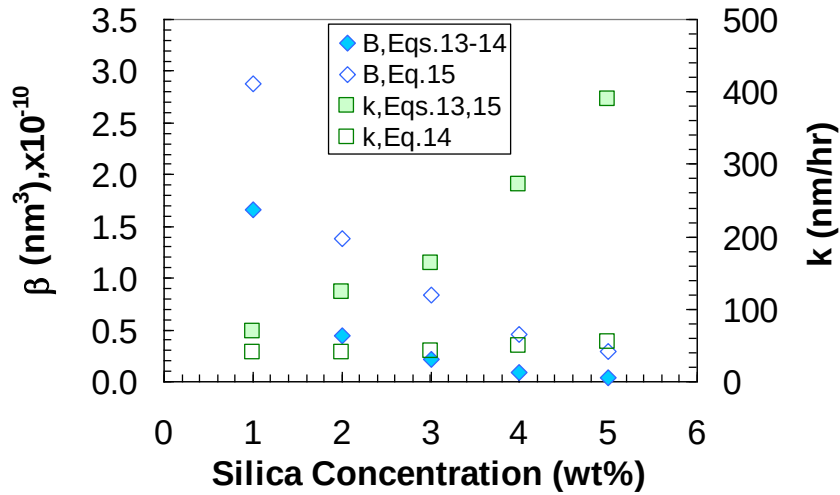


Figure 4.10- The comparison of parameter β obtained by Equations 4.11-4.12 with Equation 4.13 as a function of silica concentration at 3 wt% NaCl. The primary silica particles are 25 nm in diameter.

The effect of primary particle size on the aggregation growth of silica nanoparticles is in Figure 4.11. Both attractive and repulsive interaction potentials are functions of particle size and enhanced colloidal stability occurs at larger particle sizes (He *et al.* 2008). A significant difference in aggregation time is observed between 25 and 75nm diameter primary particles at 5 wt% NaCl. Although the aggregation times for the 5 and 25nm particles at 4 wt% NaCl are similar, the sediment volume fraction is almost 1 for small particles (5nm diameter) at the end of aggregation at equilibrium. However, bigger particles (25 and 75nm diameter) formed a sediment with a volume fraction less than 0.5 after the aggregates settled. The size measurements by DLS are evaluated for homogeneous turbid phase before the aggregates sediment out of the suspension. The time frame of measurements was short enough compared to aggregation time to collect representative data of aggregates.

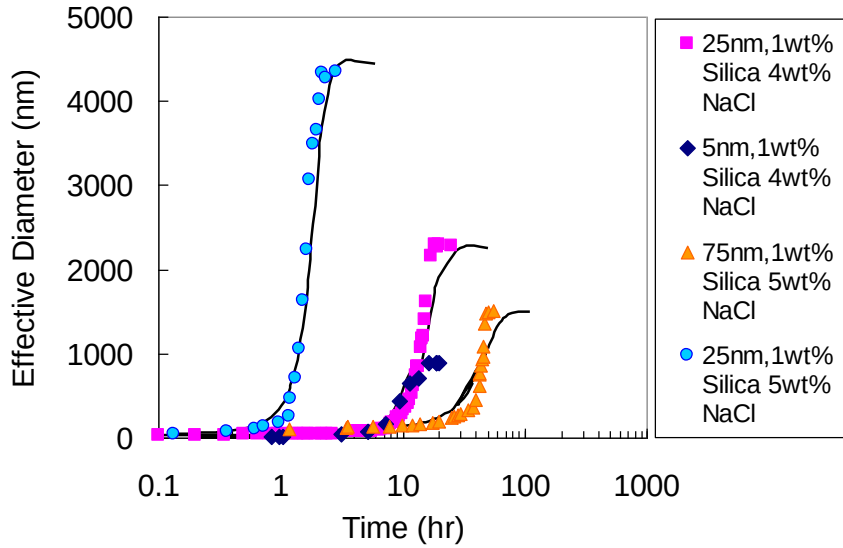


Figure 4.11- Effect of particle size on the kinetics of aggregation at 25°C. The samples contain 4wt% NaCl for the samples with the primary particle diameter of 5 and 25 nm and 5wt% NaCl for those with 25 and 75nm diameter. The change in aggregate diameter, measured by DLS in time is presented. The lines are from the model in Equation 4.7.

The data on aggregation of silica nanoparticles at different particle sizes and electrolyte concentrations are scaled by using dimensionless parameters of time $\tau = k_2 D_{eq}^2 t$ and diameter $D_{norm} = \left(\frac{D^2 - D_{eq}^2}{D^2} \right) \left(\frac{D_0^2}{D_{eq}^2 - D_0^2} \right)$. We obtain these dimensionless parameters by grouping similar terms in Equation 4.7. Figure 4.12 collapses all the curves onto a single curve. The line in Figure 4.12 corresponds to Equation 4.14.

$$D_{norm} = e^{-\tau} \quad (4.14)$$

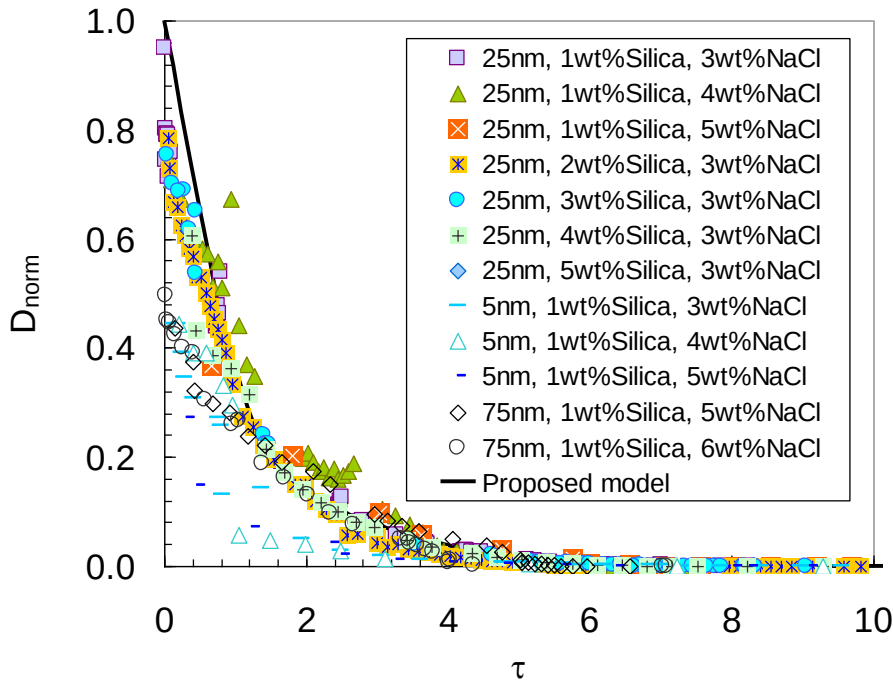


Figure 4.12- Scaling of the aggregation data by Equation 4.14. The samples are at 25°C and contain primary silica particles of 5, 25 and 75 nm diameters.

4.3.2 Shear Rheology of Silica Suspensions

In chapter 3, a model for the rheology of stable silica nanoparticle dispersions is presented. The unified model could collapse all the data onto a single curve by using the concept of maximum effective packing fraction (Metin *et al.* 2011b). It was shown that the viscosity of silica nanoparticle dispersions is a strong function of particle volume fraction. Here, the rheology of unstable silica dispersions is studied and a model is proposed.

The aggregation of silica nanoparticles affects the rheology of the suspension because the size of the aggregate changes in time. In suspensions undergoing significant aggregation, the volume fraction of the aggregate becomes the effective solid volume

fraction. We present our results on the shear rheology of unstable silica nanoparticle suspensions. Figure 4.13 shows the viscosity of 1 wt% silica nanoparticles as a function of shear rate at various aggregate sizes. The aggregation rate is slow compared to time required to take steady shear viscosity measurement because of which we can assume equilibrium during each steady shear rate measurement. Newtonian behavior is observed within the shear rate ranges studied. The viscosity of the suspension is low ($< 2\text{cP}$); therefore, the accuracy of the rheometer restricts the shear rate range where we can obtain a reliable and reproducible data.

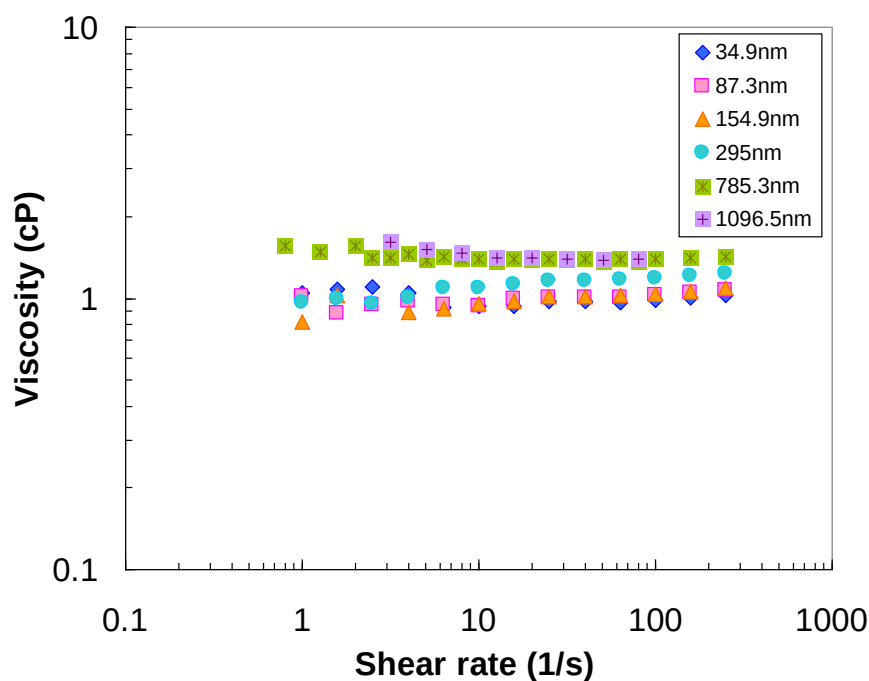


Figure 4.13- Viscosity of 1 wt% unmodified silica nanoparticle with 3 wt% NaCl at different aggregation stages as presented by the effective diameter of the aggregate in Figure 4.1.

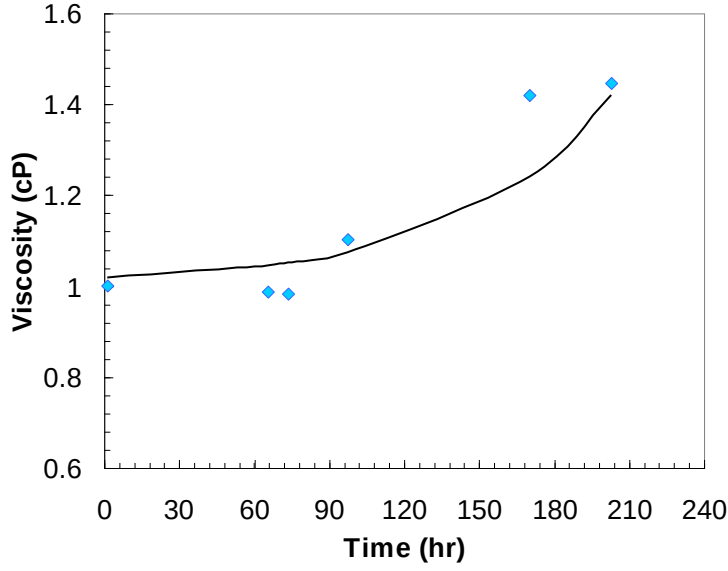


Figure 4.14- Evolution of average viscosity over the range of shear rates from 1-300 s⁻¹ of 1 wt% unmodified silica nanoparticle with 3 wt% NaCl in time. The line is from Equation 4.16 combined with Equations 4.7 and 4.15.

The viscosity of the suspension changes in time (Figure 4.14) with respect to the aggregate size. To model the rheology of unstable dispersions, the effective volume fraction of the aggregates, ϕ_{Agg} , needs to be determined from Equation 4.15.

$$\phi_{Agg} = \phi_0 \left(\frac{D}{D_0} \right)^{3-d_f} \quad (4.15)$$

The size of the aggregate at a specific time during the aggregation stage can be estimated using the models we proposed above. The model for relative viscosity, η_r , is modified to take into account the effective volume fraction of the aggregate as follows

$$\eta_r = \left[1 + 0.75 \frac{\phi_{Agg}}{(\phi_{max}^{eff} - \phi_{Agg})} \right]^2 \quad (4.16)$$

where ϕ_{max}^{eff} is the maximum effective packing fraction and is a function of particle size for stable nanoparticle dispersions, where the extent of electrical double layer or steric layer is important (Metin *et al.* 2011b). However, for the unstable unmodified silica nanoparticle suspensions, the thickness of electrical double layer is reduced significantly because of the presence of electrolytes and the aggregates can be assumed as hard spheres in terms of interactions. We can estimate the maximum effective packing fraction by an equilibrium approach. The phase behavior of 25 nm unmodified silica nanoparticles at 3 wt% NaCl for 0.5-3 wt% silica concentration is presented in Figure 4.15. As the nanoparticle concentration increases the aggregate volume or the sediment volume fraction increases as well.

Let us assume that n single silica particles form one aggregate. At equilibrium all the single particles become part of aggregates and there is no free single particle in the supernatant (Equation 4.17).

$$\begin{aligned} nP &\rightarrow A_{(s)} \\ C_p^T &= nC_A \\ C_p^T &= n\phi_{max}^{eff} C_{sed} v \end{aligned} \quad (4.17)$$

where C_p^T is the total concentration of single silica particles, C_A is the concentration of aggregates, ϕ_{max}^{eff} is the maximum effective packing fraction of aggregates in the sediment, C_{sed} is the concentration of sediment and v is the reciprocal of the volume of a single aggregate. The number of particles, n , forming the aggregate is determined from

$$n = \left(\frac{D_{eq}}{0.8D_0} \right)^{d_f}$$
 where D_{eq} is the equilibrium aggregate diameter as described by the aggregation kinetics model. From the equilibrium approach, it is possible to determine the volume fraction of aggregates in the sediment by simply plotting C_p^T vs. $nC_{sed}v = Y$ as shown in Figure 4.15. The slope corresponds to ϕ_{max}^{eff} equals to 0.68. This result is close to a cubic packing of aggregates within a sediment and indicates that the structure of the sediment is the same for all silica concentrations studied.

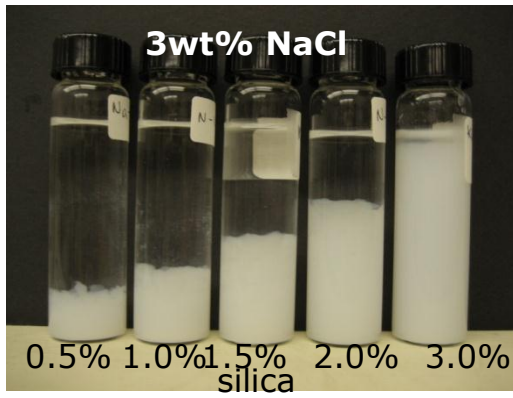


Figure 4.15- Test tubes containing 3 wt% NaCl and 0.5-3 wt% silica nanoparticles of 25 nm diameter. As silica concentration increases the sediment height also increases.

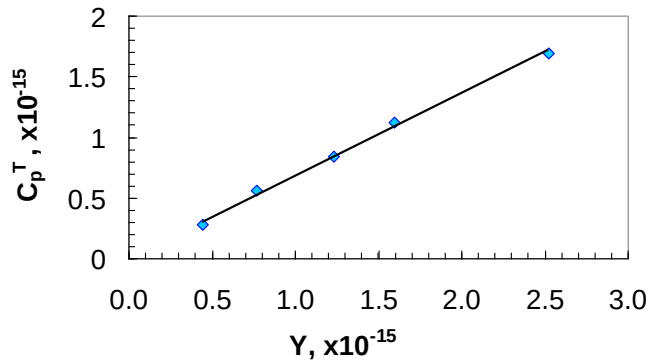


Figure 4.16- The determination of the aggregate volume fraction by the proposed equilibrium approach. The slope of the line corresponds to the aggregate volume fraction, $\phi_{\max}^{eff}=0.68$.

Once the maximum effective packing fraction is determined, it is possible to estimate the relative viscosity of the unstable silica aggregates from Equation 4.16 and collapse all the data onto a single curve regardless the size of primary particles or electrolyte concentration as shown in Figure 4.17. The data presented in Figure 4.17 correspond to a homogeneous turbid phase of the aggregation.

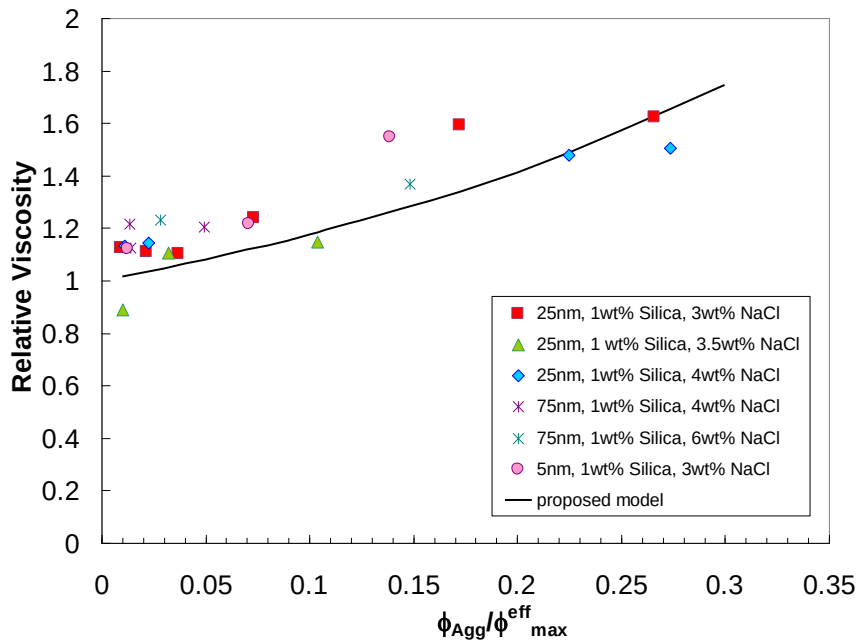


Figure 4.17- Comparison of the proposed model with experimental data of relative viscosity of silica nanoparticle dispersions.

4.4 CONCLUSIONS

The aggregation kinetics of unmodified silica nanoparticles of 5, 25 and 75nm primary diameter are studied as a function of particle and NaCl concentration above the CSC. The aggregation kinetics is strongly influenced by initial particle size, particle and salt concentrations. The proposed model is very convenient to use and successfully described the aggregation kinetics. The model parameters; equilibrium diameter and rate constant, were determined using experimental data and also estimated independently assuming DLVO theory. The proposed model provided the framework to collapse all the data onto a single master curve of dimensionless diameter and time. The early time of aggregation follows an exponential growth that is a characteristic of the slow aggregation

regime. This behavior is successfully captured by the proposed model, is consistent with the Smoluchowski theory. The parameters in the proposed model are shown to be calculable independently from the proposed equations.

Maximum effective packing fraction is estimated from an equilibrium approach model of sediment volume fraction to be 0.68. The results for the relative viscosity of silica aggregates in turbid phase agree well with the proposed viscosity model and collapse onto a single curve. Unstable particle suspensions exhibits Newtonian behavior, which could be predicted by our viscosity model developed for stable dispersions.

Footnote:

Analytical solution to the model proposed in this study with an arbitrary fractal dimension, d_f

$$d_f \left\{ -\frac{1}{2D^2} + \frac{\text{Hypergeometric2F1}\left[-\frac{2}{d_f}, 1, 1 - \frac{2}{d_f}, \left(\frac{D}{D_{eq}}\right)^{d_f}\right]}{2D^2} \right\} = \frac{k\pi t}{\beta} + \text{const.}$$

4.5 REFERENCES

- Aubert C and Cannell DS (1986) Resturcturing of colloidal silica aggregates. Phys. Rev. Lett. 56:738-741.
- Derjaguin BV, Landau L (1941) Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. Acta Physicochim USSR 14:633-662.
- Dietler G, Aubert C and Cannell DS (1986) Gelation of colloidal silica. Phys. Rev. Lett. 57:3117-3120.
- Fuchs N (1934) Uber die stabilitat und ausfladung der aerosole. Z. Physik., 89:736-743.
- Goodwin J (2009) Colloids and interfaces with surfactants and polymers. Wiley, New Delhi.

- Gorrepati EA, Wongthahan P, Raha S and Fogler HS (2010) Silica precipitation in acidic solutions: mechanism, pH effect, and salt effect. *Langmuir* 26 (13) 10467-10474.
- He YT, Wan J and Tokunga T (2008) Kinetic stability of hematite nanoparticles: the effect of particle sizes. *J. Nanoparticle Res.* 10:321-332.
- Hounslow MJ, Ryall RL and Marshall VR (1988) Discretized population balance for nucleation, growth, and aggregation. *AIChE* 34 (11) 1821-1832.
- Hunter RJ (2001) *Foundations of colloid science*. Oxford University Press, New York.
- Israelachvili J, Wennerstrom H (1996) Role of hydration and water structure in biological and colloidal interactions. *Nature* 379:219-225.
- Lin MY, Lindsay HM, Weitz DA, Ball RC, Klein R and Meakin P (1990) Universal reaction-limited aggregation. *Phys. Rev. A* 41:2005-2020.
- Martin JE (1987) Slow aggregation of colloidal silica. *Phys. Rev. A* 36:3415-3426.
- Metin CO, Lake LW, Miranda CR and Nguyen QP (2011a) Stability of aqueous silica nanoparticle dispersions. *J. Nanopart. Res.* 13:839-850.
- Metin CO, Bonnecaze RT and Nguyen QP (2011b) Shear rheology of silica nanoparticle dispersions. *Appl. Rheol.* 21:13146.
- Poon WCK and Haw MD (1997) Mesoscopic structure formation in colloidal aggregation and gelation. *Adv. Colloid Int. Sci.* 73:71-126.
- Reerink H and Overbeek JThG (1954) The rate of coagulation as a measure of the stability of silver iodide sols. *Discuss. Faraday Soc.* 18:74-84.
- Schaefer DW, Martin JE (1984) Fractal geometry of colloidal aggregates. *Phys. Rev. Lett.* 52:2371-2375.
- Schudel M, Behrens SH, Holthoff H, Kretzschmar R and Borkovec M (1997) Absolute aggregation rate constants of hematite particles in aqueous suspensions: a comparison of two different morphologies. *J. Colloid Int. Sci.* 196:241-253.
- Senis D and Allain C (1997) Scaling analysis of sediment equilibrium in aggregated colloidal suspensions. *Phys. Rev. E* 55:7797-7800.
- M. von Smoluchowski (1916) Drei vorträge über diffusion, Brownsche molekularebewegung und koagulation von kolloidteilchen. *Physik. Z.* 17:557-571, 585-599; (1917) *Z. Phys. Chem.* 92:129.
- Taboada-Serrano P, Chin C-J, Yiacoumi S and Tsouris C. (2005) Modeling aggregation of colloidal particles. *Current Opinion in Coll. Int. Sci.*, 10, 123-132.
- Tsoularis A and Wallace J (2002) Analysis of logistic growth models. *Mathematical Biosci.* 179:21-55.
- Verhulst PF (1838) Notice sur la loi que la population suit dans son accroissement. *Curr. Math. Phys.* 10:113.

- Verwey EJW and Overbeek JThG (1948) Theory of stability of lyophobic colloids. Elsevier, Amsterdam.
- Vigil G, Xu Z, Steinberg S, and Israelachvili J (1994) Interactions of Silica Surfaces. J. Colloid Int. Sci. 165:367-385.

Chapter 5: Phase Behavior and Rheological Characterization of Silica Nanoparticle Gel

Over a certain range of salinities, silica nanoparticle suspensions form a gel. An accurate description of nanoparticle solution phase behavior is necessary before advancing their uses in the petroleum industry. In this chapter, the equilibrium phase behavior of silica nanoparticle solutions is presented in the presence of sodium chloride (NaCl) and phase regions are classified as a function of salinity and nanoparticle concentration. Rheology experiments of silica nanoparticle gels are carried out. Gelation time decreases exponentially as a function of silica, salinity, or temperature. Following a power law behavior, the storage modulus, G' , increases with particle concentration. Steady shear measurements show that silica nanoparticle gels exhibit non-Newtonian, shear thinning behavior.

5.1 INTRODUCTION

As discussed in chapter 2, in the presence of electrolytes, the nanoparticle dispersions become unstable above a critical salt concentration. Over a certain range of salinities, the unstable solutions form a gel. Previous efforts (e.g. Jurinak and Summers 1991, Burns *et al.* 2008, Dai *et al.* 2010, Stavland *et al.* 2011) focused on silica gel controlled by pH at high silica concentrations. In contrast, this work is focused on the effect of salinity on the gelation at much lower silica concentrations. Note that the stability of the silica nanoparticle dispersions used in this work is not sensitive to pH as discussed in Chapter 2.

In this chapter, the results of equilibrium phase behavior of silica nanoparticle dispersions in the presence of sodium chloride (NaCl) are presented. The rheology of

particle dispersions in the gel region is also investigated. The characteristic time for the onset of gelation as a function of silica and NaCl concentration and temperature are determined.

5.2 MATERIALS AND METHODS

The material under study is aqueous dispersions of silica nanoparticles. The nanoparticles provided by 3M, Co. (St. Paul, MN) have a mean diameter of 5 and 25 nm. We also tested NexSil5 silica nanoparticles purchased from Nycol for rheology measurements.

Rheological measurements were carried out on a strain controlled rheometer using a parallel plate fixture. The diameter of the parallel plate was 50 mm and the set gap between the lower and upper plate was 1 mm. The measurements were conducted at 25, 40, 55 and 75 °C. A solvent trap was used to prevent the evaporation of water from the solution. Dynamic and steady shear experiments were carried out. The nanoparticle dispersion was mixed with NaCl solution and placed on the lower fixture of the parallel plate. A dynamic time sweep test was first conducted at the frequency 1 rad/s and 1% strain. We measured the time evolution of storage and loss modulus, G' and G'' , for 10,000 seconds after the onset of gelation. Then, frequency sweep and strain sweep tests were carried out. After these tests, steady shear rates were applied and viscosity was recorded as a function of shear rate.

5.3 RESULTS AND DISCUSSION

The results on phase behavior of silica nanoparticle suspensions as a function of NaCl and nanoparticle concentration are presented in this section. The rheological measurements of samples in the gel region are discussed in detail in the next section.

5.3.1 Phase Behavior

There are three phases in the nanoparticle phase diagram. Below the critical salt concentration (CSC), the nanoparticle dispersion is stable and appears as a homogeneous clear liquid. Above the CSC, the suspension is unstable. The unstable suspensions have two distinct behaviors. At salinities above the CSC but below the upper gelation salt concentration, the unstable solution forms a gel phase. Above the upper gelation salt concentration, the solution forms a viscous liquid. The major difference between the two phases is that the gel does not flow when the sample is tilted but the viscous liquid does. In the viscous liquid region, we think that the network of aggregates, which is essential for gel formation, is absent because the repulsive electrostatic interaction between aggregates is screened at very high salt concentration. Therefore, the dynamically arrested state of clusters may be absent and the aggregates can no longer act as building blocks of a gel network (see Campbell et al. 2005 for discussion of dynamic arrest). It is known that strongly-aggregating colloidal suspensions form gels, whose stability depends on the volume fraction of the particles (Senis *et al.* 2001). Within the gel region, two types of gels are observed. At lower silica concentrations, the solution has two phases. A solid gel phase is topped by a clear supernatant liquid. At higher silica concentrations, the solution is a single-phase gel. Two-phase gels are a result of insufficient number of aggregates to incorporate the entire volume of water into the gel. Figures 5.1 and 5.2 show example phase behavior diagrams for the 25 nm and 5 nm particles, respectively, at 25 °C. The monodisperse silica nanoparticles have a wide gel region with respect to salinity. The boundary between single-phase and two-phase gel is only a function of

silica concentration for 5 nm particles and a function of both silica and NaCl concentration for 25 nm particles.

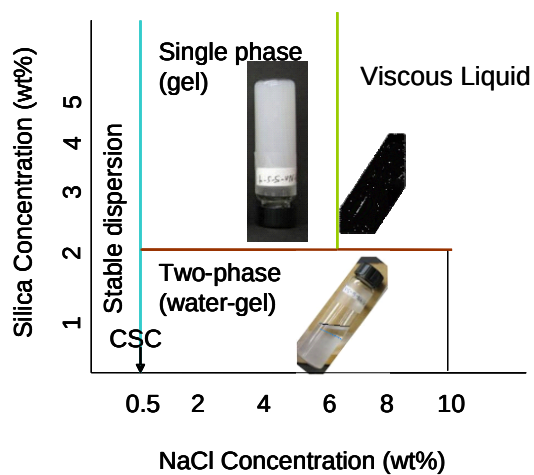


Figure 5.1- Phase behavior diagram of 5 nm unmodified silica nanoparticles at 25 °C.

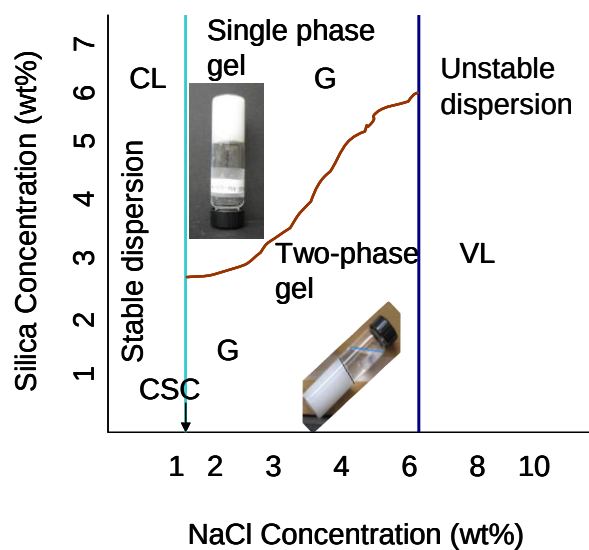


Figure 5.2- Phase behavior diagram of 25 nm unmodified silica nanoparticles at 25 °C.

When particle volume fraction is small, isolated large flocs may form which are denser than the suspending medium, and can form a sediment under gravity. However, for large particle volume fraction, gelation usually occurs and sedimentation is then avoided unless the gel structure is so fragile that it collapses under its own weight (Larson 1999). The structure of the aggregates within the sediment, such as the solid volume fraction, is discussed based on the equilibrium approach in chapter 4. To establish the relationship between the sediment volume fraction and the particle concentration, the force balance on a sediment layer under gravity was suggested by Senis and C. Allain (1997). Figure 5.3 is a schematic presentation of sedimentation and gelation of aggregates.

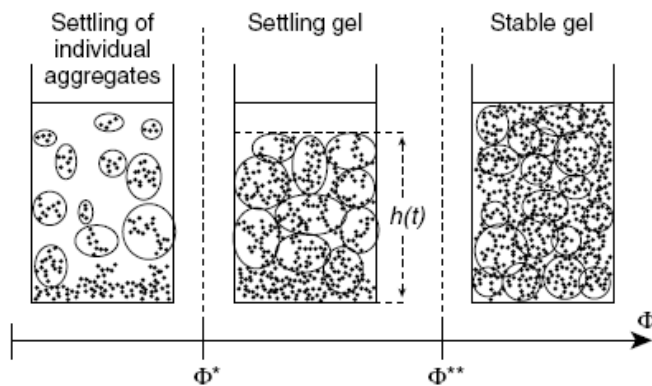


Figure 5.3- Schematic presentation of sedimentation and gel behavior of aggregates as proposed by Senis and Allain (1997).

The force balance on a sediment layer under gravity is

$$\begin{aligned}
-\Delta\rho g\phi &= \frac{\partial\sigma_z}{\partial z} - \frac{4}{D}\sigma_w \\
\sigma_w &= f_f\sigma_{radial} = f_f\alpha\sigma_z \\
\sigma_z^Y(\phi) &= \sigma_0\phi^\kappa
\end{aligned} \tag{5.1}$$

where $\Delta\rho$ is the density difference between the particle and the fluid, g the gravitational acceleration, ϕ the solid volume fraction, σ_z the stress, z the vertical direction, D the diameter of the test vial, σ_w wall stress, σ_z^Y the yield stress, f_f , σ_0 and κ are constants. If the friction at the wall is neglected, then the integration of Equation 5.1 gives

$$\frac{H_s}{H} = \frac{\kappa}{\kappa-1} \left(\frac{H}{\Lambda} \right)^{-1/\kappa} = \frac{\kappa}{\kappa-1} \left(\frac{H}{\Lambda_0} \right)^{-1/\kappa} \phi^{(\kappa-1)/\kappa} \tag{5.2}$$

where H_s is the height of the sediment, H the total height of the solution and Λ is the characteristic length. Equation 5.2 was fit to experimental data for 25 nm unmodified silica nanoparticles (Figure 5.4). The model parameter κ , can be determined as presented in Table 5.1. The results are in the same order of magnitude as the ones reported by Senis and Allain (1997).

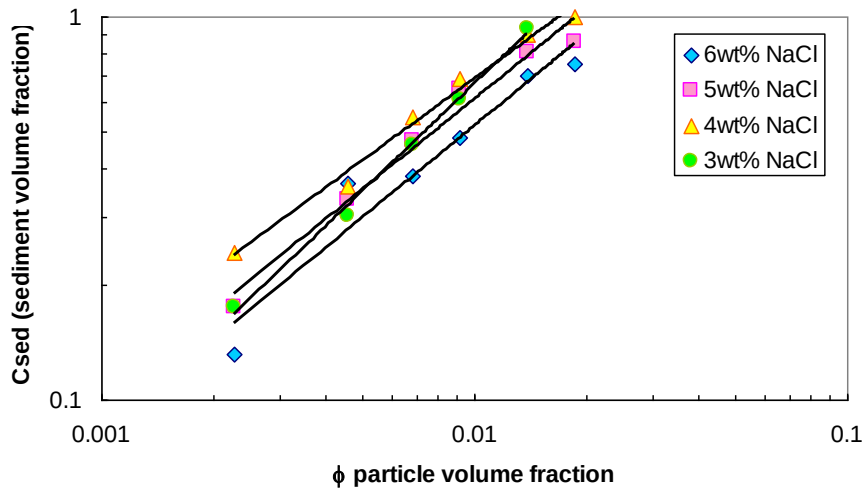


Figure 5.4- The volume fraction of sediment, C_{sed} , vs. particle volume fraction for 25 nm unmodified silica nanoparticle dispersions. The lines correspond to Eq. 5.2.

Table 2.1- The model parameter κ in Eq. 5.2 for 25 nm unmodified silica nanoparticles.

	K
3wt% NaCl	14.6
4wt% NaCl	3.5
5wt% NaCl	2.2
6wt% NaCl	5.0

A map of sediment volume fraction as a function of silica and NaCl concentration is presented in Figure 5.5. The sediment volume fraction significantly depends upon the silica nanoparticle concentration. Above 3 wt% silica concentrations, almost all the volume is occupied by the sediment and a gel is observed. The critical particle concentration Φ^{**} above which the suspension forms a gel that does not collapse under gravity occurs at $H_s/H=1$. This critical gel concentration is determined for 25 nm unmodified silica nanoparticle suspensions at various NaCl concentrations using

Equation 5.2. The points on the map in Figure 5.5 correspond to Φ^{**} as a function of NaCl. The calculations coincide with experiments (see Figure 5.5). The unstable suspensions made with 5 nm silica nanoparticles show gel behavior at silica concentrations much smaller than that of 25 nm particles, as shown in Figure 5.6. For a given nanoparticle concentration by weight, the number of nanoparticles for 5 nm nanoparticle dispersions are $\left(\frac{25}{5}\right)^3 = 125$ times larger than for 25 nm nanoparticle dispersions. Therefore, it is not surprising that gelation occurs at a much smaller particle concentration in 5 nm nanoparticle dispersions because there are enough particles to form a network of aggregates even with a small concentration. Equation 5.2 cannot be applied because the sediment height ratio, or sediment volume fraction, reaches 0.9-1 very quickly. The experimental results for the sediment volume fraction are presented as a 2D map in Figure 5.6.

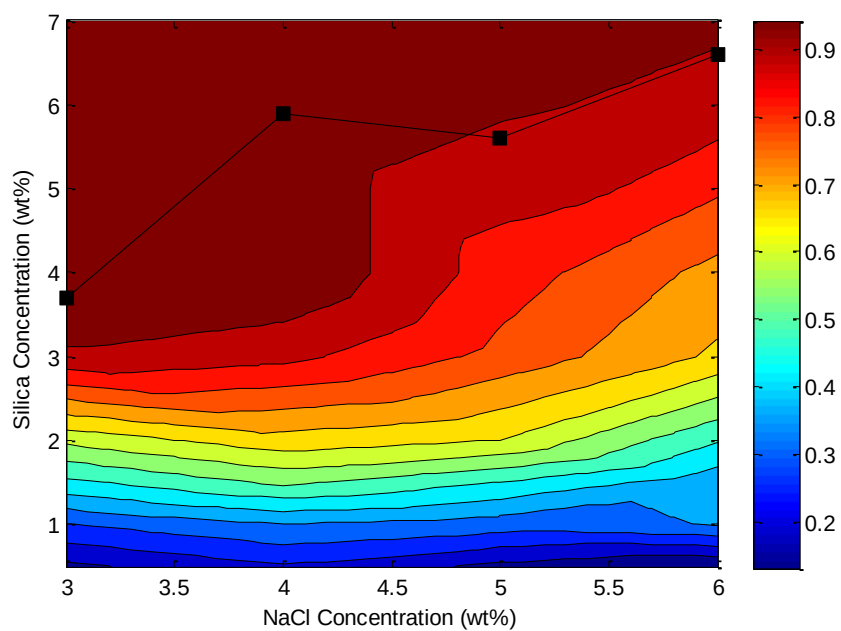


Figure 5.5- The map of the volume fraction of sediment as a function of NaCl and silica concentration for 25 nm unmodified silica nanoparticles. The points on the map correspond to Φ^{**} as a function of NaCl.

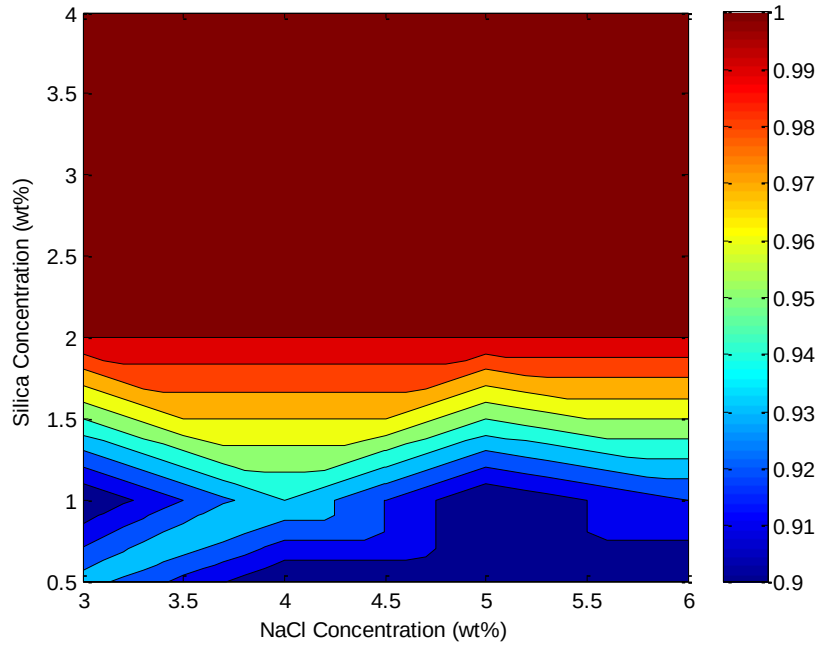


Figure 5.6- The map of the volume fraction of sediment as a function of NaCl and silica concentration for 5 nm unmodified silica nanoparticles.

5.3.2 Rheological Measurements

In addition to understanding the equilibrium behavior of the solutions in order to correctly identify the gel region, it is also important to understand the kinetics of the gelation. A way to explore rates of structural rearrangement within a complex fluid without significantly deforming the fluid's microstructure is to apply small-amplitude oscillatory shearing (Larson 1999). The sinusoidally varying stress can be represented as

$$\sigma(t) = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)] \quad (5.3)$$

Shear stress $\sigma(t)$ is proportional to the amplitude of the strain γ_0 . In Equation 5.3 $G'(\omega)$ is called storage modulus and is in phase with the strain. $G''(\omega)$ is the loss modulus and is in phase with the rate of strain. The storage modulus represents storage of elastic energy and the loss modulus represents the viscous dissipation of that energy (Larson 1999). The ratio $G''/G' \gg 1$ represents materials that are liquid-like and the ratio $G''/G' \ll 1$ represents solid-like materials.

Early on, aggregate size grows exponentially in time until these fractal aggregates become large enough to form a network and fill the entire volume of the solution. The system then crosses over to the critical growth associated with gelation (Martin and Wilcoxon 1989). Measurements taken with DLS and UV-Vis confirm the exponential growth of aggregate size in time before the onset of gelation

Dynamic time sweep tests were conducted to quantify the gelation time as a function of silica concentration, salinity, and temperature. Only the 5 nm particles were studied because they gel at smaller nanoparticle concentrations than 25 nm particles. For the silica concentration scan, the temperature was constant at 25 °C with a salinity of 3 wt% NaCl. For the salinity scan, the temperature was constant at 25 °C with a silica concentration of 4 wt%. The samples studied are presented graphically in Figure 5.7. For the temperature scan, the silica concentration was 3 wt% with a salinity of 3 wt%.

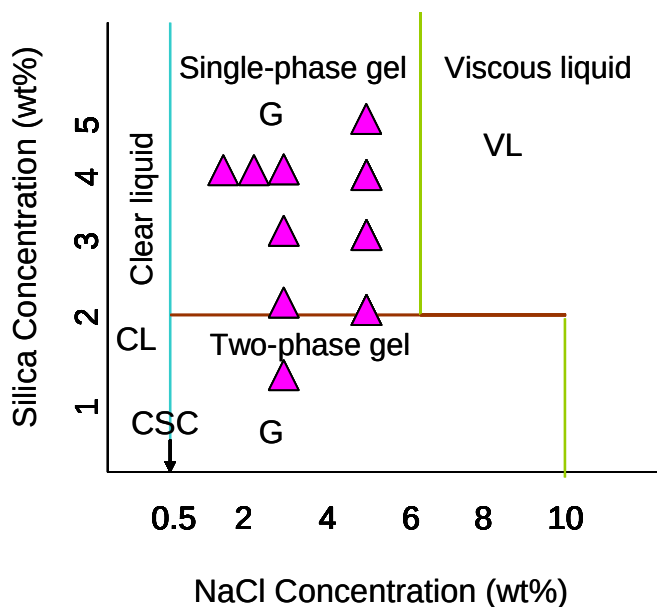


Figure 5.7- Schematic presentation of the samples studied during rheology experiments.

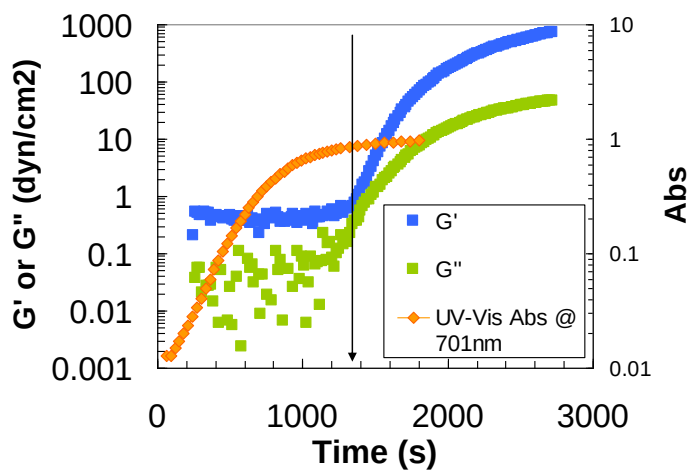


Figure 5.8- Dynamic time sweep test and UV-Vis absorbance of 4 wt% silica and 5 wt% NaCl.

The onset of gelation is determined by using a UV-Vis spectrophotometer and strain-controlled rheometer. The evolution of G' and G'' are recorded as a function of

time and the onset of gelation is determined based on the sudden increase of G' , as shown with an arrow in Figure 5.8. The onset of gelation, estimated by evaluating the sudden change in G' in the rheology experiments, agrees well with that determined by the change in absorbance at a specific wavelength (700 nm in this case) as measured by a UV-Vis spectrophotometer. It has been shown in chapter 2 that a change in aggregate size could be captured by measuring the absorbance using a UV-Vis spectrophotometer. Here in Figure 5.8 the increase in absorbance corresponds to the increase in aggregate size and when the network is formed, a plateau is reached. The transition corresponds to the onset of gelation as determined by G' in rheology experiments. After the gelation time, G' increases significantly, while the ratio G''/G' becomes much smaller than 1 which indicates that the sample has a solid-like behavior. The storage modulus increases during the dynamic measurements suggesting that the gel network gets stronger and stronger over time. Maley *et al.* (2005) also showed that colloidal silica gels stiffen with time through light scattering and rheological measurements. The authors argued that there was no change in the gel structure but the interparticle spring constant was time-dependent and responsible for the increase in G' . According to their hypotheses, the kinetics of bond formation is reaction limited, which leads to an increase in the contact area between network forming particles.

The onset of gelation or the gelation time decreases as silica concentration increases (see Figure 5.9). This observation is in agreement with the way in which the kinetics of the aggregation of silica nanoparticle suspensions change as a function of silica, as discussed in chapter 4. At low salt concentration, 3 wt% NaCl, the change in gelation time is more significant than it is at 5 wt% NaCl, Figure 5.9. Polydisperse unmodified silica nanoparticle dispersions were purchased from Nycol. NexSil5 has a bimodal size distribution with peaks at 3 nm and 18 nm diameter with an average

hydrodynamic diameter of 16 nm. The effect of particle size distribution on gelation time is also presented in Figure 5.9. The polydispersity seems to increase the gelation time but the rate of decrease in gelation time as nanoparticle concentration increases is the same as that for monodisperse 5nm 3M particles.

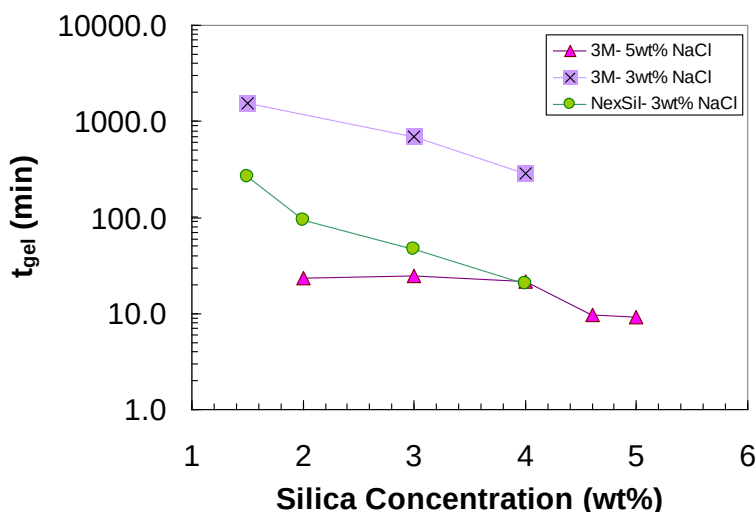


Figure 5.9- Gelation time as a function of silica concentration at 25 °C as measured using a rheometer.

An increase in salinity decreases the gelation time (see Figure 5.10). This observation is also in close agreement with the way in which the kinetics of aggregation of silica nanoparticle suspensions change, as discussed in chapter 4. The gelation time changes in order of magnitude as the NaCl concentration is increased. Polydisperse particles show more significant decrease in gelation time than a suspension with monodisperse particles (see the slope in Figure 5.10). They also have a smaller window of gelation (Metin *et al.* 2012).

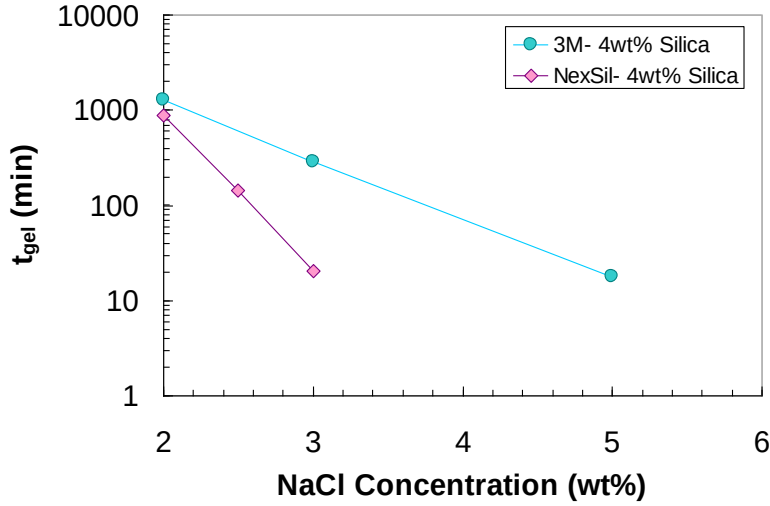


Figure 5.10- Gelation time as a function of salinity for 4 wt% silica suspensions at 25 °C as measured using a rheometer.

Temperature is another important factor that significantly effects the gelation time. An increase in temperature decreases the gelation time (see Figure 5.11). The activation energy (E_a) for kinetically controlled cross-linking was used by Amiri *et al.* (2011) to characterize the temperature dependency of the gelation time for silica suspensions.

$$\ln t_g = \frac{E_a}{RT} + A \quad (5.4)$$

where t_g is the gelation time, R the gas constant, T temperature in Kelvin and A is a constant. The activation energy is calculated using data in Figure 5.11 to be 84 and 73 kJ/mol for mono disperse 3M particles and polydisperse NexSil particles. These apparent activation energies for bridging of aggregates are within the range of 37.5 to 83 kJ/mol as reported by Silva and Vasconcelos (1999), Wang and Zhang (2009) and Amiri *et al.*

(2011). The decrease in gelation time at high temperature was attributed to larger Brownian motion of the particles resulting in faster collisions as discussed in chapter 4. Similar results for gelation time were reported for silica particles suspended in ethanol by Smith and Zukoski (2006).

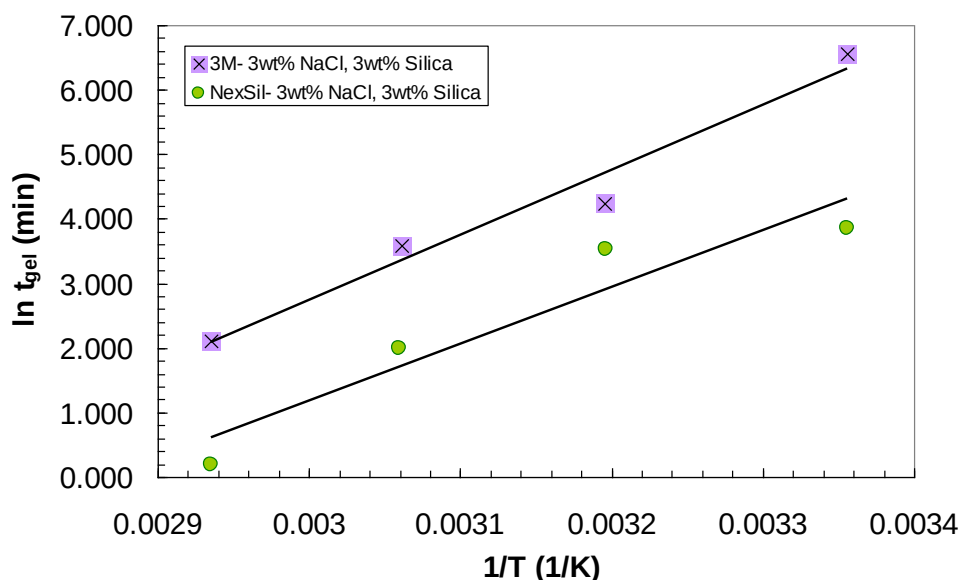


Figure 5.11- Gelation time as a function of temperature for 3 wt% silica suspensions with 3 wt% NaCl as measured using a rheometer. The lines correspond to Equation 5.4.

The gelation time can change in order of magnitude with changes in the primary control variables. The dependence of gelation time on silica, NaCl concentration or temperature follows an exponential decrease (Figures 5.9-5.11). Other rheological quantities that are important for strongly flocculated gels include: linear and nonlinear storage moduli at high and low frequencies and shear rate dependent viscosity. The dependencies of these on particle size, particle concentration, and particle-particle

interactions are of obvious importance for the processing of colloidal gels (Larson 1999). The silica nanoparticle gels show solid-like behavior which is shown by the profile of storage and loss modulus in Figures 5.12-5.15 (see Larson 1999 for detailed explanation of properties of complex fluids). The profile of storage and loss modulus (G' and G'') as a function of strain is strong strain overshoot (Hyun *et al.* 2002) with most of the samples studied: G' and G'' increase followed by a decrease (Figures 5.12-5.15).

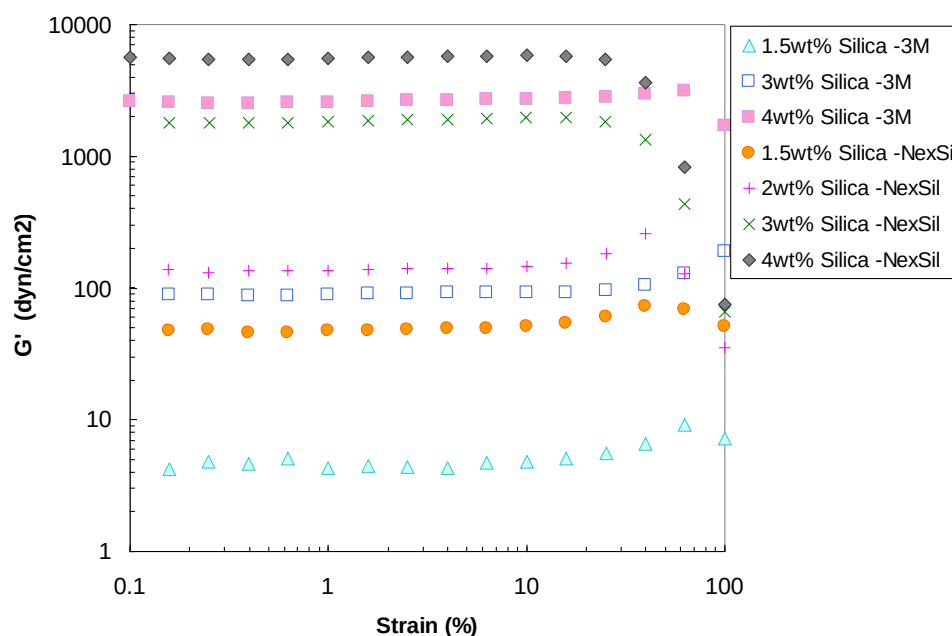


Figure 5.12- Storage modulus G' as a function of silica concentration at 25 °C.

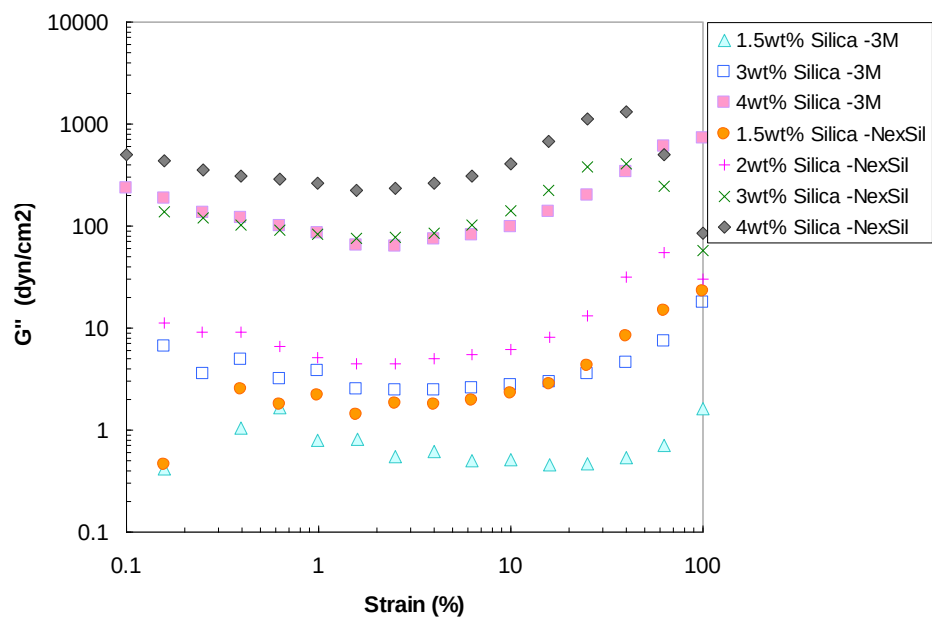


Figure 5.13- Loss modulus G'' as a function of silica concentration at 25 °C.

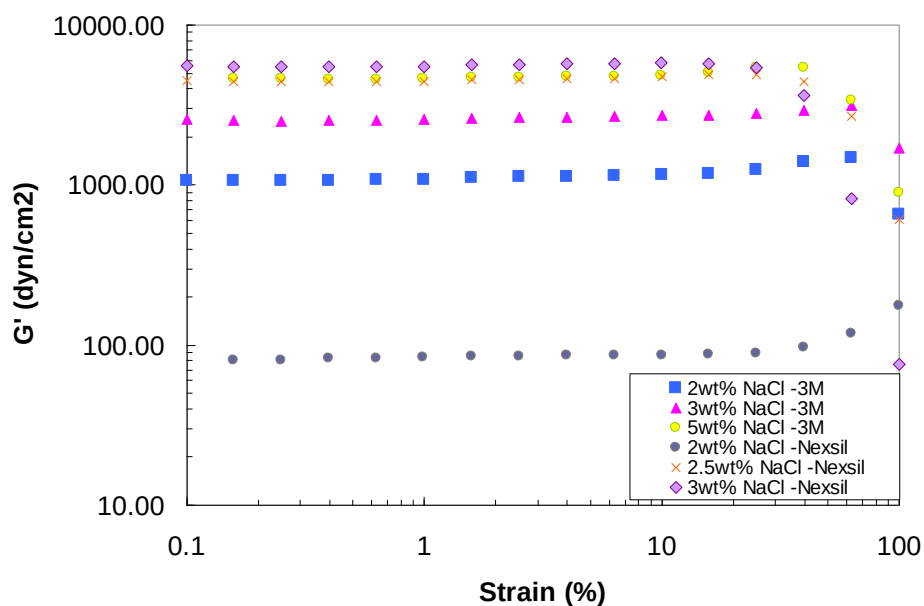


Figure 5.14- Storage modulus G' as a function of NaCl concentration at 25 °C.

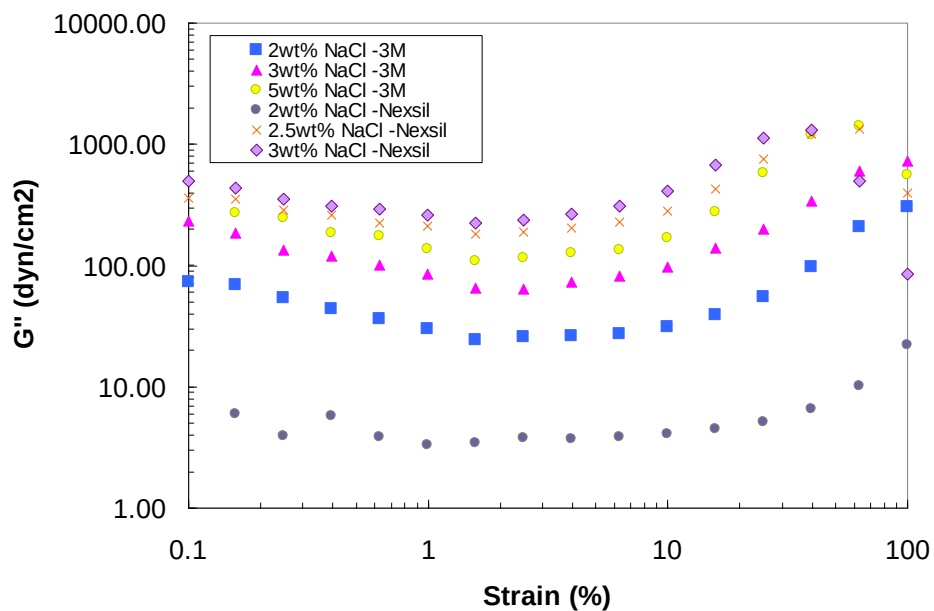


Figure 5.15- Loss modulus G'' as a function of NaCl concentration at 25 °C.

Strain hardening arises from strong secondary bonding effects, like the formation of shear induced network, then the structure breaks down resulting in the decrease in G' and G'' . Initial increase in loss modulus with strain is attributed to structural changes (breakdown of agglomerates to a larger number of smaller size units), which are more dissipative. Destruction of structure or breakdown of the filler network occurs at higher strain and the loss modulus decreases because of further breakdown of the structure (Yziquel *et al.* 1999). It is shown in chapter 4 that aggregate size decreases as the silica concentration increases. That could be the reason why G'' increases as silica concentration increases based on the above argument – smaller units being more dissipative. Martin and Wilcoxon (1989) discussed that at small strain Brownian motion is able to restore the structure to the equilibrium value during oscillation cycle. Therefore, the storage modulus remains constant. After a certain strain, the strain amplitude becomes significant and the Brownian motion is no longer capable of restoring the microstructure. Then the storage modulus decreases (critical strain) and the loss modulus continues to rise with strain amplitude. The silica nanoparticle gels show similar behavior as discussed above.

The critical strain appears to be constant as a function of silica and NaCl concentration. The samples withstand minimum critical strain of 10% before the structure breaks. On the other hand, the critical strain does not have a clear dependency on salt concentration for both types of particles studied. Below the critical strain, G' increases with particle or NaCl concentration (Figures 5.16-5.17). This power law behavior was also reported by Shih *et al.* (1990) with boehmite alumina gels. The authors considered the structure of a gel as a collection of flocs, which are fractal objects closely packed throughout the sample. A continuous network of particles is formed before settling occurs, with the resulting suspension having a very high viscosity and a finite shear

modulus. The authors observed a power law behavior of G' vs $\phi^{4.1}$. In our experiments, m is calculated to be 5.9, 4.2 for 3, 5 wt% NaCl 3M and 5.1 for 3 wt% NaCl NexSil particles. An increase in m shows that the elasticity increases more rapidly and the network becomes more resistive (Yziquel *et al.* 1999).

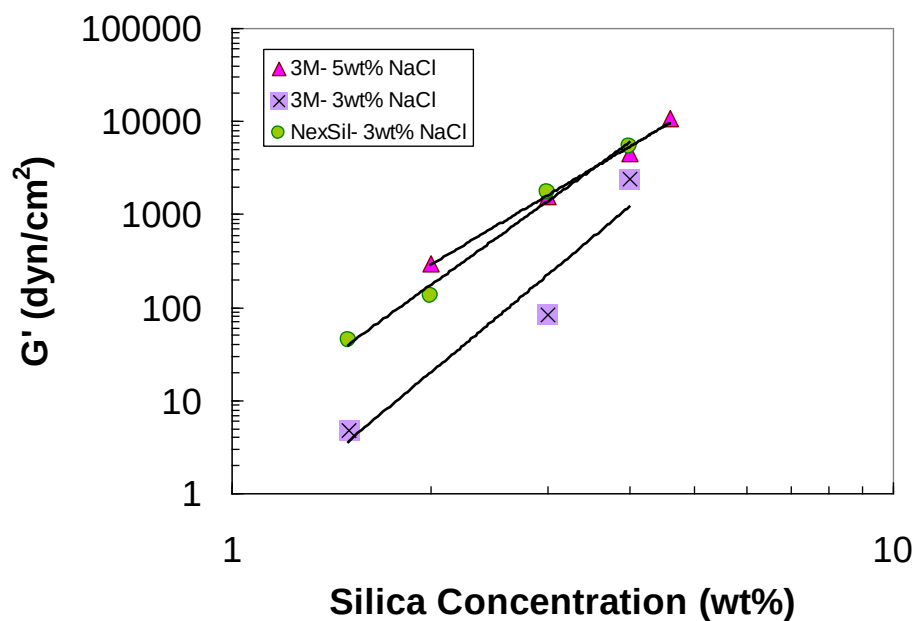


Figure 5.16- Storage modulus G' as a function of silica concentration at 25 °C.

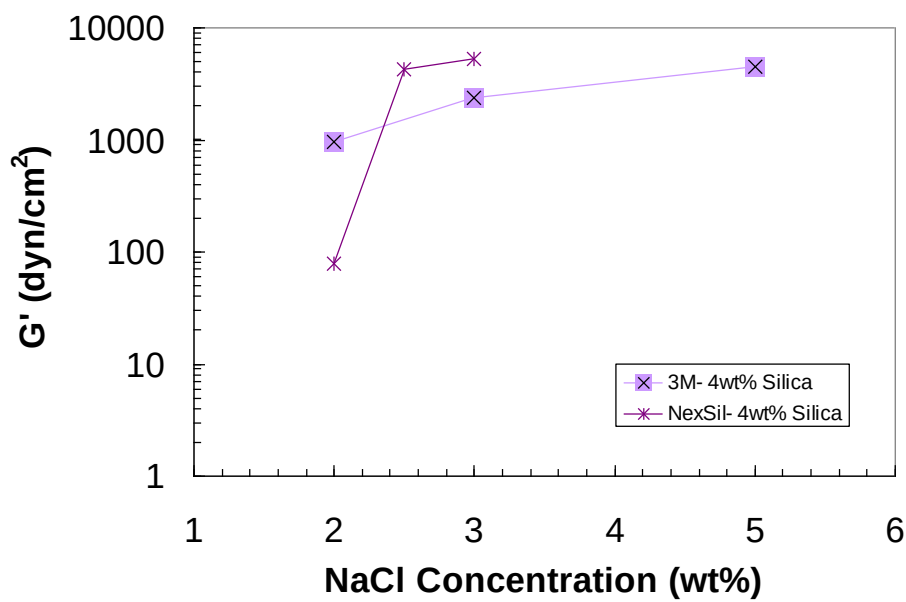


Figure 5.17- Loss modulus G'' as a function of NaCl concentration at 25 °C.

The storage modulus for all samples can be scaled using the ratio strain/critical strain, γ/γ_c and $G_r = G'/G'_{at\ 0.1\% \text{ strain}}$ (Figures 5.18-5.19).

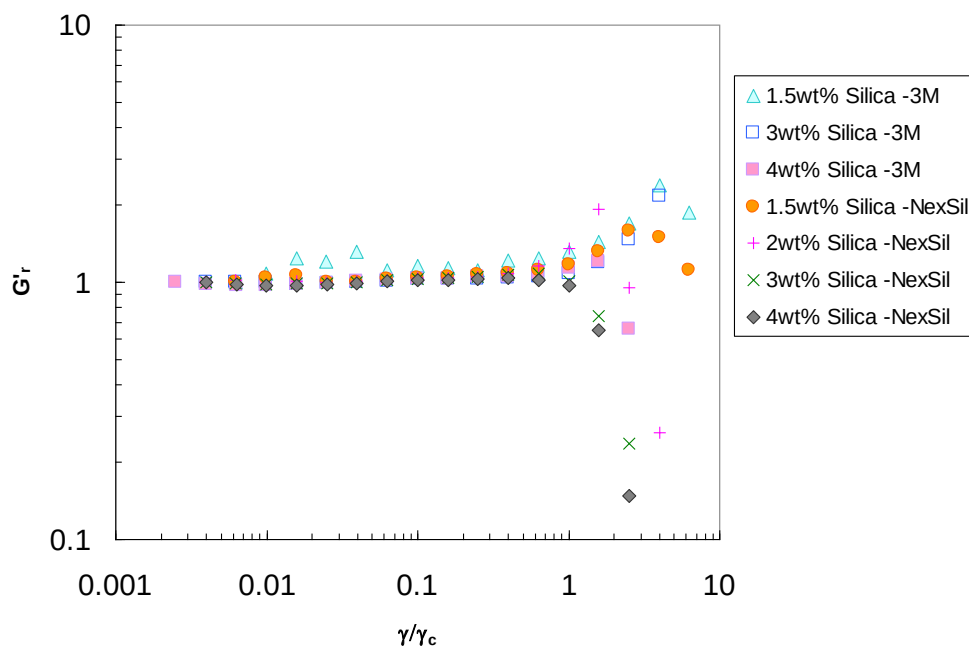


Figure 5.18- Scaling the storage modulus G' as a function of strain at varying silica nanoparticle concentrations 25 °C.

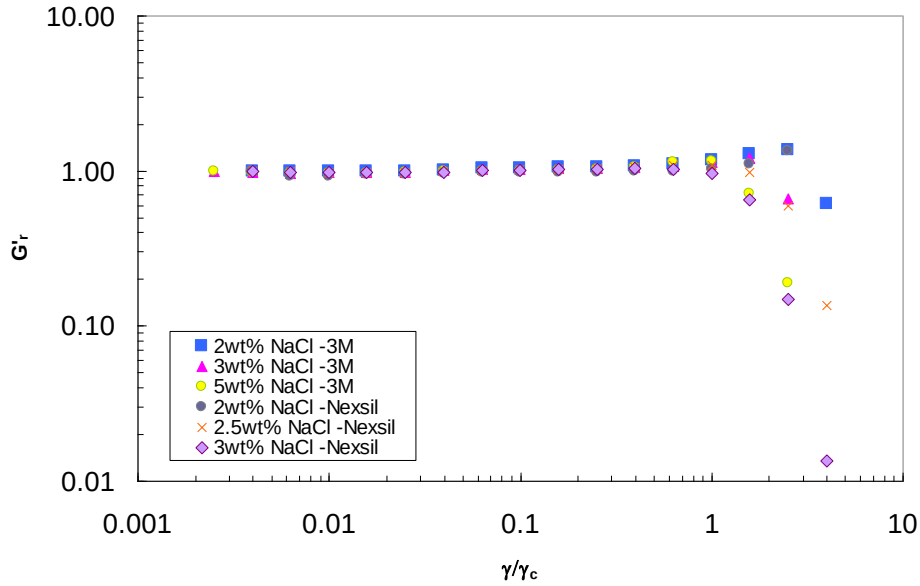


Figure 5.19- Scaling the storage modulus G' as a function of strain at varying NaCl nanoparticle concentrations at 25 °C.

For a solid-like complex fluid, the steady shear stress is independent of shear rate and the shear viscosity, η , decreases with increasing shear rate, $\dot{\gamma}$, as $\eta \propto \dot{\gamma}^{-1}$. A decreasing shear viscosity with increasing shear rate is called shear thinning (Larson 1999). The viscosity for each gel as a function of steady shear rate was measured 10,000 seconds after gelation time had been reached. All of the gels exhibited shear thinning behavior with $\eta \propto \dot{\gamma}^{-1}$. For most of the gels, such as 4.6 wt% silica and 5wt% NaCl 3M samples, a power law model given in Equation 5.5 fits the data well (Figure 5.20). However, the Carreau model given in Equation 5.6 could also represent some of the samples, such as 3wt% NaCl 3M samples as shown in Figure 5.20. The Newtonian plateau region at low shear rates is missing for all the samples. That is why the Carreau model may not be an appropriate choice.

$$\eta = K\dot{\gamma}^n \quad (5.4)$$

where K and n are empirical parameters.

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{\left(1 + (K_1 \dot{\gamma})^2\right)^{m_1/2}} \quad (5.5)$$

where η_0 and η_{∞} are viscosities at zero and infinity shear rates respectively and represent the Newtonian plateau regions. Other empirical parameters in Equation 5.5 are K_1 and m_1 . The parameters of the Carreau model fit to the sample 3 wt% silica, 3 wt% NaCl are 350000 cp, 30 cp, 20 s and 2 for η_0 , η_{∞} , K_1 and m_1 respectively. This sample is the only one showing a significant plateau at high shear rates and steeper slope than -1.

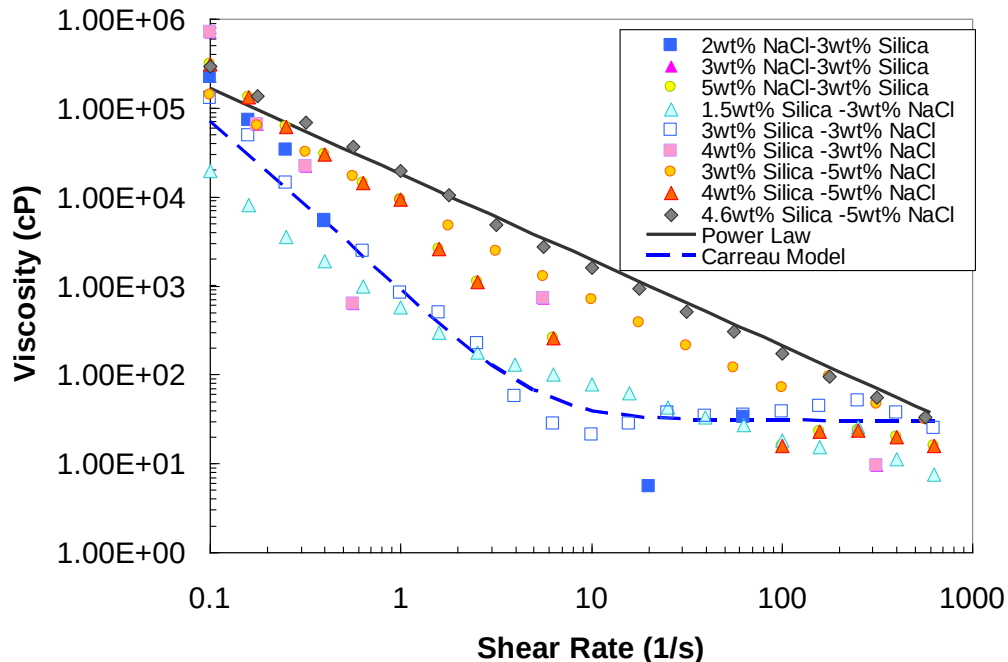


Figure 5.20- Viscosity profile for 3M nanoparticle gels at varying nanoparticle and NaCl concentration. The solid line is power law model and the dashed line corresponds to the Carreau model fit for 3 wt% silica, 3 wt% NaCl sample.

5.4 CONCLUSIONS

We studied the phase behavior of silica nanoparticle suspensions as a function of silica and NaCl concentrations. Monodisperse 3M silica nanoparticles have a wider window of gelation with respect to salinity than polydisperse NexSil particles.

The time to the onset of gelation depends strongly on silica and NaCl concentration and temperature. The gelation time decreases exponentially as a function of silica, NaCl concentration or temperature.

The storage modulus, G' , increases with particle concentration following a power law behavior. The critical strain stays the same for silica concentrations studied. The

samples withstand a minimum critical strain of 10% before the structure breaks. However, the critical strain does not have a clear dependency of salt concentration for both types of particles studied.

Steady shear measurements show that silica nanoparticle gels exhibit non-Newtonian, shear thinning behavior which could be described by the power law model or the Carreau model depending on the particle and NaCl concentration.

5.5 REFERENCES

- Amiri A, Øye G and Sjöblom J (2011) Temperature and pressure effects on stability and gelation properties of silica suspensions. *Colloids and Surfaces A* 378 (1-3): 14-21.
- Burns LD, Burns M, Wilhite P, McCool S, Oglesby K and Glass J (2008) New generation silicate gel system for casing repairs and water shutoff. SPE 113490 presented at SPE/DOE Symposium on Improved Oil Recovery, 20-23 April, Tulsa, Oklahoma.
- Campbell AI, Anderson VJ, van Duijneveldt JS and Betlett P (2005) Dynamical arrest in attractive colloids: the effect of long-range repulsion. *Phys. Rev. Lett.*, 94 208301.
- Dai C, You Q, Zhao LF and Xiong W (2010) Study and field application of profile control agent in high temperature and high salinity reservoir. SPE 132765-MS presented at Trinidad and Tobago Energy Resources Conference, 27-30 June, Port of Spain, Trinidad.
- Hyun K, Kim SH, Ahn KH and Lee SJ (2002) Large Amplitude Oscillatory Shear as a Way to Classify the Complex Fluids. *J. Non-Newtonian Fluid Mech* 107: 51-65.
- Jurinak JJ and Summers LE (1991) Oilfield Applications of Colloidal Silica Gel. *SPE Prod Eng* 6 (11): 406-412. SPE-18505-PA
- Larson G (1999) The structure of complex fluids. Oxford university press, New York.
- Martin JE and Wilcoxon JP (1989) Spatial correlation and growth in dilute gels. *Phys. Rev. A* 39: 252-258.
- Metin CO, Lake LW, Miranda CR and Nguyen QP (2011) Stability of aqueous silica nanoparticle dispersions. *J. Nanopart. Res.* 13:839-850.
- Metin CO, Rankin KM, Nguyen QP (2012) Phase Behavior and Rheological Characterization of Silica Nanoparticle Gel. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* 57 (1), San Diego, March 2012.

- Senis D and Allain C (1997), Scaling analysis of sediment equilibrium in aggregated colloidal suspensions. *Phys. Rev. E* 55:7797-7800.
- Senis D, Talini L, Allain C (2001) Settling in aggregating colloidal suspensions: analysis of cell inclination influence. *Eur. Phys. J. E.* 2, 31.
- Shih WH, Shih WY, Kim SI, Liu J and Aksay IA (1990) Scaling Behavior of the Elastic Properties of Colloidal Gels. *Phys. Rev. A* 42:4772–4779.
- Silva RF and Vasconcelos WL (1999) Influence of processing variables on the pore structure of silica gels obtained with tetraethylorthosilicate. *Materials Research* 2: 197-200.
- Smith WE, Zukoski CF (2006) Aggregation and gelation kinetics of fumed silica–ethanol suspensions. *J. Colloid Int. Sci.* 304: 359-369.
- Stavland A, Jonsbråten HC and Vikane O, Skrettingland K and Fischer H (2011) In-depth water diversion using sodium silicate on snorre - factors controlling in-depth placement. SPE 143836 presented at SPE European Formation Damage Conference, 7-10 June, Noordwijk, The Netherlands.
- Wang GH and Zhang LM (2009) A bio friendly silica gel for insitu protein entrapment: biopolymer-assisted formation and its kinetic mechanism. *J. Phys. Chem* 113: 2688-2694.
- Yziquel F, Carreau P J, Moan M and Tanguy PA (1999) Rheological modeling of concentrated colloidal suspension. *J. Non-Newtonian Fluid Mech.* 86 (1):133–155.

Chapter 6: Adsorption of Surface Functionalized Silica Nanoparticles onto Mineral Surfaces and Decane/Water Interface

The adsorption of silica nanoparticles onto representative mineral surfaces and at the decane/water interface was studied. The effects of particle size, concentration and surface type on the adsorption were studied in detail. Silica nanoparticles with four different surfaces (unmodified, surface modified with anionic (sulfonate), cationic (quaternary ammonium (quat)) or nonionic (polyethylene glycol (PEG)) surfactant) were used. The adsorption of all the nanoparticles (unmodified or surface modified) on quartz and calcite surfaces was found to be insignificant. Interfacial tension (IFT) measurements are used to investigate the adsorption of silica nanoparticles at the decane/water interface. Unmodified nanoparticles or surface modified ones with sulfonate or quat do not significantly affect the interfacial tension (IFT) of the decane/water interface. It also does not appear that the particle size or concentration influences the IFT. However, the presence of PEG as a surface modifying material significantly reduces the IFT. The PEG surface modifier alone in an aqueous solution, without the nanoparticles, yields the same IFT reduction for an equivalent PEG concentration as that used for modifying the surface of nanoparticles. Contact angle measurements of a decane droplet on quartz or calcite plate immersed in water (or aqueous nanoparticle dispersion) showed a slight change in the contact angle in the presence of the studied nanoparticles. The results of contact angle measurements are in good agreement with experiments of adsorption of nanoparticles on mineral surfaces or decane/water interface. This study brings new insights into the understanding and modeling of the adsorption of surface modified silica nanoparticles onto mineral surfaces and water/decane interface.

6.1 INTRODUCTION

The retention of nanoparticles in porous media will play an important role in selecting the types of nanoparticles or surface modifying agents for said nanoparticles. Silica nanoparticles are good candidates for such applications due to their low cost of fabrication, their ready availability, and the ability to modify their surfaces by known chemical methods. The surface modification of silica nanoparticles would allow one to control their hydrophilicity and also to improve their salt tolerance. There exists a critical salt concentration (CSC) below which previously studied silica nanoparticles stayed well dispersed in water (Metin *et al.* 2011). The surface modification significantly improves CSC especially for divalent cations (Ca^{2+} and Mg^{2+}). Therefore, they can be injected in reservoir rocks where brine salinity is large and remain as a stable dispersion.

The interaction of nanoparticles with liquids (water/oil interface) or solids (mineral surfaces) determines the mechanisms of retention of nanoparticles in reservoir rocks. Characterization of the surface charge of nanoparticles by measuring their zeta potential, tracking nanoparticles in the bulk phase or at interface by UV-Visible spectroscopy provided means to analyze the effect of pH, surface modification of nanoparticles and their sizes on the stability of nanoparticles at fluid interfaces. A comprehensive literature review on nanoparticles at fluid interfaces is presented by Bresme and Oettel (2007).

Lin *et al.* (2005) presented an experimental study on the structure of hydrophobically surface modified 4.6nm cadmium selenide nanoparticle assembly at fluid interfaces. They observed that nanoparticles assembled at the interface of two immiscible liquids (toluene and water) as a densely packed monolayer. In the case of particles with different sizes, larger particles displaced smaller particles at a rate consistent with their adsorption energy. The assembly at the water/toluene interface was

liquid-like with no long-range order. Lee *et al.* (2006) studied the monolayer behavior of 500nm silica particles in the presence of a cationic surfactant at the air/water interface. They compared chemically grafted and physically modified nanoparticles and found that modification methods and chain length of modifying agents determined the structure of particle layering at the interface.

Reincke *et al.* (2006) discussed three types of interactions that are dominant for a charged nanoparticle (less than 16nm gold nanoparticles) at a water/oil interface: energy of water/organic, water/particle and particle/organic interfaces, electrostatic repulsion between particles and van der Waals interactions between particles at the interface. They reported that big particles adsorbed more strongly to the interface than small particles. Binks and Fletcher (2001) studied the theoretical adsorption of amphiphilic spherical particles (Janus particles) at the oil/water interface. Later, Binks and Whitby (2005) found that precipitated silica particles with a primary particle size ranging from 3.5-101nm could stabilize oil-in-water emulsions. The emulsion stability was controlled by changing the pH or particle charge. The authors observed that adding cationic surfactants improved the emulsion stability. The average diameter of emulsions increased as the silica nanoparticle size increased. Bresme and Quirke (1999) analyzed the wetting behavior of spherical particles at liquid/water interface by using MD simulation. Young's equation provided an accurate estimation of the contact angle even for particle of size 1.5 nm. Contact line tension appeared to have no effect on the contact angle when the surface tensions were on the order of that of water.

Particle structuring in a wedge film and the role of structural component of disjoining pressure on displacement of the contact line were studied by Wasan and Nikolov (2003).

The authors observed by video microscopy, a crystal like ordering of 1 μm diameter latex particles in the liquid film-meniscus region of wedge-like shape, which resulted in a structural component of disjoining pressure. Then, the authors argued that the structural component of the disjoining pressure was strong enough for a nanofluid composed of 8 nm diameter micelles to move the contact line at oil droplet/glass/aqueous micellar solution interface. This particle structure formation in the wedge film was confirmed by the theoretical results of Boda *et al.* (1999). Further theoretical studies followed their research (Chengara *et al.* 2004; Vafei *et al.* 2006; Matar *et al.* 2007; and Sefiane *et al.* 2008). However, it is not clear that the structural disjoining pressure is the only mechanism influencing this enhanced spreading of a droplet in the presence of nanoparticle suspensions. Vafei *et al.* (2006) conducted contact angle measurements of droplets containing 2.5-nm bismuth telluride nanoparticles, which are surface modified with thioglycolic acid, on glass and silicon wafer substrates in air. The authors observed that the variation in contact angle depended on the solid surface material and nanoparticle size. At a given concentration, smaller diameter nanoparticles resulted in greater changes in contact angle than larger diameter nanoparticles would. The authors argued that greater amount of smaller diameter nanoparticles can fit into this region than larger diameter ones. The spreading of a sessile droplet on solid surface was also studied theoretically by Yang *et al.* (1991), Blake *et al.* (1997), de Ruijter *et al.* (1999a,b), Hwang *et al.* (2001), Choi and Kim (2006) and Voronov *et al.* (2006, 2007).

In this chapter, the interaction of unmodified or surface modified silica nanoparticles with mineral surfaces and decane/water interface is investigated. Adsorption experiments with the silica nanoparticles were conducted onto quartz and calcite surfaces. Interfacial tension (IFT) measurements provide insightful information on the interaction of silica nanoparticles with decane/water interface. The effects of particle

size, concentration and surface type of silica nanoparticles are also studied in detail. The importance of surface modifiers on silica nanoparticles and the design of experiments are highlighted when studying the adsorption of nanoparticles with minerals or water/hydrocarbon interface. Contact angle measurements confirm our findings from nanoparticle dispersion/mineral and nanoparticle dispersion/decane interactions.

6.2 MATERIALS AND METHODS

The materials studied were aqueous dispersions of silica particles as provided by 3M, Co (St. Paul, MN, USA). The mean diameters of primary particles are 5, 25 and 75 nm, which have an unmodified surface or a modified surface with sulfonate, polyethylene glycol (PEG) or quaternary ammonium and PEG. The latter one will be referred to as “quat” throughout this chapter. The surface modifications describe the surface of the particles after using alkoxysilanes as surface modifying agents. The zeta potential of these silica nanoparticles was determined using a Malvern Zetasizer. The values are presented in Table 6.1. We used Iceland spar calcite and Ottawa quartz sand for these studies. The zeta potential of the mineral powders were also and were found to be -55 mV for quartz and -31 mV for calcite.

We used an ultraviolet-visible spectrophotometer (UV-Vis) to determine the concentration of nanoparticles in the supernatant liquid. Interfacial tension measurements were a Wilhemly plate. A contact angle goniometer was used to determine the contact angle of decane droplets on mineral samples immersed in water or nanoparticle dispersion.

Pieces of minerals were submerged in the various nanoparticle dispersions for 24 hours. 3 ml of the supernatant was removed by pipette and centrifuged. The supernatant liquid was then analyzed by UV-Vis spectroscopy to determine the silica nanoparticle concentration remaining in the liquid. Principal Component analysis combined with multiple regression was applied to construct calibration curves for the particle concentration analysis using the Unscrambler chemometric software. The supernatant liquid was centrifuged at 14,000 rpm for 20 minutes to separate fines generated by the mineral grains. The nanoparticle dispersions of 0.04, 0.2 and 1 wt% were added to mineral to 10:1 and 5:2 dispersion to mineral weight ratios. These liquid-to-solid ratios were chosen based on the range of the ratios commonly used during sorption experiments published in literature (Antelmi and Spalla 1999; Marczewski and Szymula 2002; Flury *et al.* 2004)

The calcite mineral was first ground using an agate mortar and pestle set and sieved using meshed sieves ranging from 20 to 100 mesh for 20 minutes under the agitation of a Ro-Tap sieve shaker. The grains were then cleaned by deionized water before the adsorption tests. The UV-Vis absorbance of the supernatant was measured as a part of the cleaning procedure to make sure that the substrate was cleaned with deionized (DI) water. Then the clean calcite grains were air dried at room temperature. The same cleaning procedure was applied to the quartz sand. We use 20/35 (841/500 micron) mesh calcite and 20/40 (841/420 micron) mesh quartz sand. To study the effect of mineral size we also choose 60/100 (250/150 micron) mesh calcite and quartz sand.

Table 6.1- Zeta potential of silica nanoparticles dispersed in water

Particle Diameter (nm)	Surface Type	Zeta Potential (mV)
5	PEG	-24.1
25	PEG	-39.3
75	PEG	-50.0
5	Sulfonate	-31.3
25	Sulfonate	-44.2
75	Sulfonate	-52.8
5	Quat	9.3
25	Quat	-1.1
75	Quat	15.2
5	Unmodified	-48.7
25	Unmodified	-60.3
75	Unmodified	-79.8

The surface energy of clean and dry quartz sand and calcite grains were measured using an inverse gas chromatography (IGC) method. IGC involves the sorption of a known adsorbate (vapor) and an unknown adsorbent stationary phase (solid sample). The principle of this method has been described in detail elsewhere (Saint and Papirer, 1982). The experimental procedure can be briefly described as follows. The series of alkanes used for determining the dispersive surface energy were of the High Performance Liquid Chromatography (HPLC) grade. The cleaned calcite or quartz samples were then packed into the column and flushed with the carrier gas, He at 105 °C for two hours to remove any trace of moisture contamination. The column is then conditioned for another two hours by passing the carrier gas, helium at the desired temperature and relative humidity. The possibility of any moisture accumulation is removed because of continuous outgassing of the column first at elevated temperature and then at the desired temperature. Then a series of solvent pulse injections are carried out and their retention

behavior monitored by the Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD) placed at the end of the column. The retention times are recorded and used to determine the total surface energy of the quartz and calcite samples (Saint and Papirer, 1982).

6.3 RESULTS AND DISCUSSION

In this section, I present the adsorption of nanoparticles on minerals and interfacial tension of silica nanoparticle dispersion/decane interface and contact angle measurements.

6.3.1 Adsorption on Minerals

The batch adsorption experiments were carried out with 150 and 500 micron calcite grains using silica nanoparticle concentrations of 0.04, 0.2 and 1.0 wt%. The UV-Vis spectra of the 5 nm unmodified silica nanoparticle dispersions are presented in Figure 6.1 before and after contact with calcite grains. For the silica concentrations studied (0.04, 0.2 and 1 wt%) there is no significant adsorption of nanoparticles on calcite surfaces. The effect of grain size was studied with 60/100 mesh calcite and no significant adsorption is observed.

The effect of electrolyte on adsorption of silica nanoparticles onto a calcite surface was tested by adding 0.25 wt% NaCl to 0.2 wt% unmodified silica nanoparticle dispersion. The NaCl concentration is below critical salt concentration at 0.5 wt% (CSC) (Metin *et al.* 2011) to ensure that the nanoparticle dispersion is stable. Figure 6.2 shows that there is no significant adsorption in the presence of NaCl. Moreover increasing the size of nanoparticles (25 nm diameter) does not influence the adsorption of unmodified silica nanoparticles on calcite surface (Figure 6.2).

The effect of the surface modification of silica nanoparticles on the adsorption behavior was also studied. The results show that there was no significant adsorption of PEG or sulfonate modified nanoparticles on calcite (Figure 6.3).

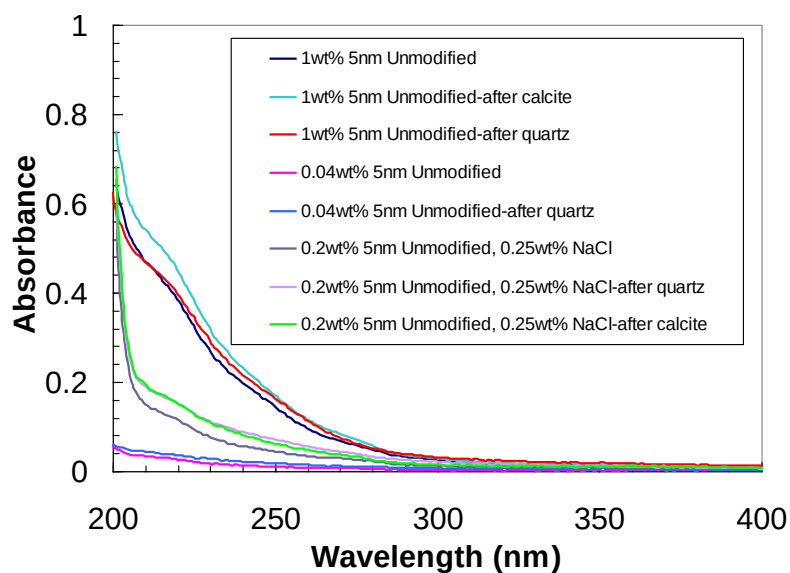


Figure 6.1- UV-Vis spectra of 0.04, 0.2 and 1wt% 5-nm unmodified silica nanoparticle dispersion with and without NaCl before and after contact with quartz sand or calcite grains.

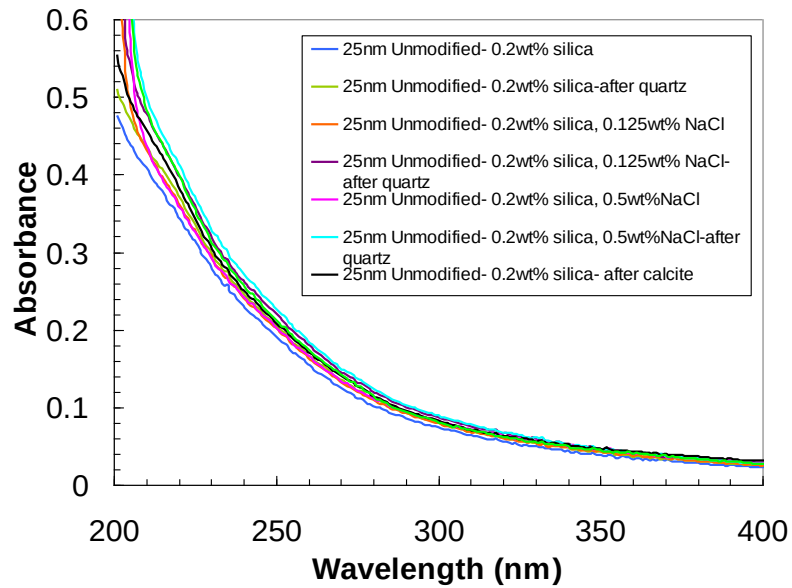


Figure 6.2- UV-Vis spectra of 0.2 wt% 25-nm unmodified silica nanoparticle dispersion with or without NaCl before and after contact with quartz sand or calcite grains.

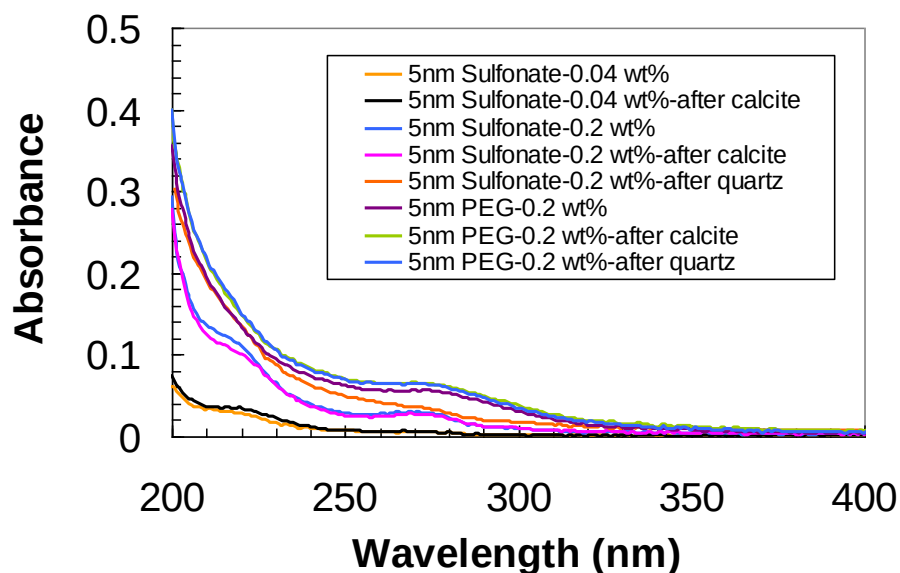


Figure 6.3- UV-Vis spectra of 0.04 and 0.2 wt% 5-nm sulfonate or PEG modified silica nanoparticle dispersion after contact with quartz sand or calcite grains.

The adsorption of silica nanoparticles onto quartz sand was studied with batch adsorption experiments. From Figure 6.1 we concluded that there is no significant adsorption of unmodified silica nanoparticles onto quartz surface. The effect of grain size was studied with 60/100 mesh quartz sand and no significant adsorption was observed. Figure 6.2 shows that at 0.5 wt% NaCl concentration, there was not any significant adsorption of silica nanoparticles on quartz surface.

The effect of the surface treatment is presented in Figure 6.3 for sulfonate and PEG modified particles, respectively. Similar to the observations with unmodified particles there was not any significant adsorption of surface modified particles on quartz sand.

DLVO (Derjaguin and Landau 1941; Verwey and Overbeek 1948) theory was used to model the particle-mineral interactions and compare those results to the experimental results. The electrostatic repulsion energy can be expressed for two parallel, infinite plates with flat double layers as

$$V_R = \frac{\varepsilon\kappa}{8\pi} \left[(\psi_1^2 + \psi_2^2)(1 - \coth \kappa h) + 2\psi_1\psi_2 \operatorname{sech}(\kappa h) \right] \quad (6.1)$$

where ψ_1 and ψ_2 are the surface potential of plate 1 and 2, κ is the inverse of electrical double layer, and h is the separation distance. For two spherical colloidal particles, Derjaguin approximation for $\kappa a \gg 1$ gives

$$V_R = \frac{\varepsilon a_1 a_2 (\psi_1^2 + \psi_2^2)}{4(a_1 + a_2)} \left[\frac{2\psi_1\psi_2}{(\psi_1^2 + \psi_2^2)} \ln \left(\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right) + \ln(1 - \exp(-2\kappa h)) \right] \quad (6.2)$$

where a_1 and a_2 are the radii of particles. Hogg *et al.* (1966) showed that Debye-Huckel approximation works well even at large surface potentials for $h > a$.

Thin, slightly overlapping cloud of a spherical particle and a flat plate gives a repulsive energy approximated by Equation 6.3.

$$V_R = 16\varepsilon a \left(\frac{kT}{ze} \right)^2 \tanh \left(\frac{ze\psi_s}{4kT} \right) \tanh \left(\frac{ze\psi_p}{4kT} \right) \exp(-\kappa h) \quad (6.3)$$

where subscript s and p represent the spherical particle and the flat plate. Derjaguin's approximation is valid for all values of surface potentials provided that $\kappa a \gg \kappa h \gg 1$.

The van der Waals attraction potential between two spheres of radii a_1 and a_2 is given in Equation 6.4.

$$V_A = -\frac{A_{132}}{6} \left[\frac{2a_1a_2}{R^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{R^2 - (a_1 - a_2)^2} + \ln \left(\frac{R^2 - (a_1 + a_2)^2}{R^2 - (a_1 - a_2)^2} \right) \right]$$

$$R = a_1 + a_2 + h$$

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$
(6.4)

where A_{132} , the Hamaker constant of silica nanoparticle (1), water (3) and mineral (2) is calculated from the measured dispersive surface energies of calcite (71.76 mJ/m²) and quartz (107.78 mJ/m²). The results of A_{132} for calcite and quartz are calculated as 1.09×10^{-20} and 1.62×10^{-20} J respectively.

Similarly, the van der Waals attraction between sphere and a planar half-space plate can be expressed as

$$V_A = -\frac{A_{132}a}{6h} \left[1 + \frac{h}{2a+h} + \frac{h}{a} \ln \left(\frac{h}{2a+h} \right) \right]$$
(6.5)

For details of above equations please see Hunter (2001), Goodwin (2009) and Hogg *et al.* (1966).

The total interaction potential $V_T = V_A + V_R$ is calculated for the 25-nm unmodified silica nanoparticles-calcite interaction by using Equations 6.3 and 6.5. The results are shown in Figure 6.4 at various NaCl concentrations. Although the energy barrier is small, the predictions by DLVO indicate that there is no adsorption without background NaCl concentration. However, at 0.5 wt% NaCl concentration the interaction between the silica nanoparticle and the calcite grain is attractive. This prediction does not agree with the

experimental results as shown in Figure 6.2. The interaction potential by DLVO theory was also calculated for 5 nm unmodified silica nanoparticle-calcite interaction. (Note that the condition, $\kappa a \gg 1$, in the approximation of repulsive energy is not satisfied for these small size nanoparticles). The interaction energy is repulsive in the absence of background NaCl concentration, however, the magnitude of the energy barrier is also small which can be easily overcome by the kinetic energy of particles in dispersion.

Similar results in DLVO curves are obtained for 25 nm unmodified silica nanoparticles-quartz interaction potential by using Equations 6.2 and 6.4. Experimental results shown in Figure 6.2 agree well with DLVO predictions (Figure 6.5) for the condition where there is no background electrolyte but we did not observe any significant adsorption at 0.5 wt% NaCl as predicted by DLVO. For 5 nm unmodified silica nanoparticles-quartz interaction potential the particle size is too small to satisfy the condition $\kappa a \gg 1$. A small energy barrier occurs which would be overcome by silica nanoparticles promoting the adsorption on quartz. However, insignificant adsorption is experimentally observed.

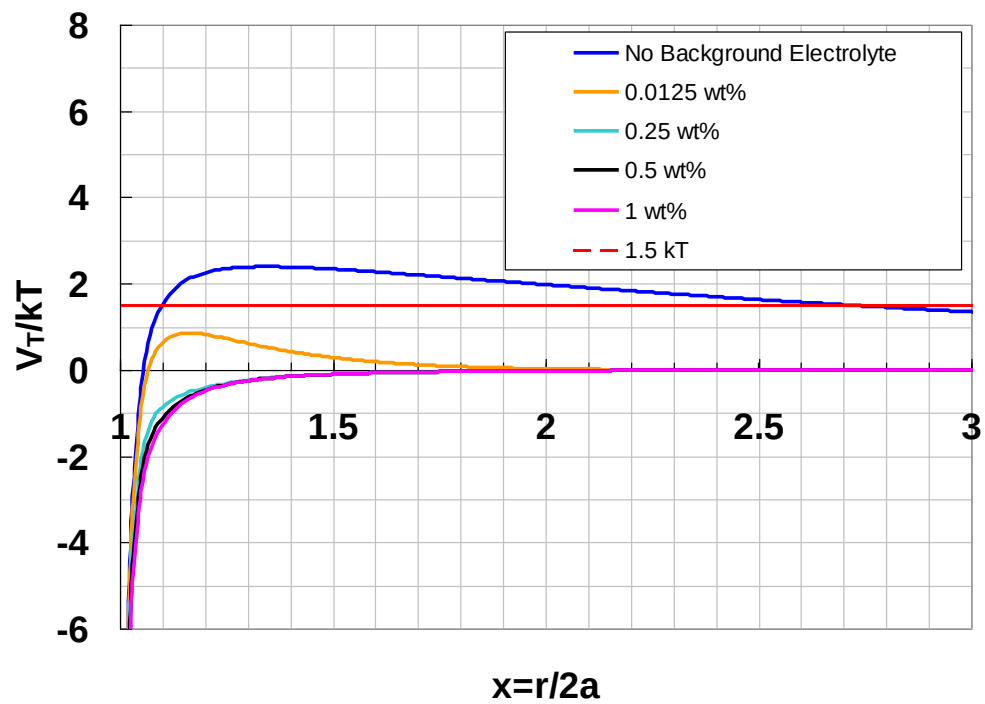


Figure 6.4- Total interaction energy between calcite plate and 25 nm diameter silica nanoparticles as a function of NaCl concentration (Equations 6.3 and 6.5).

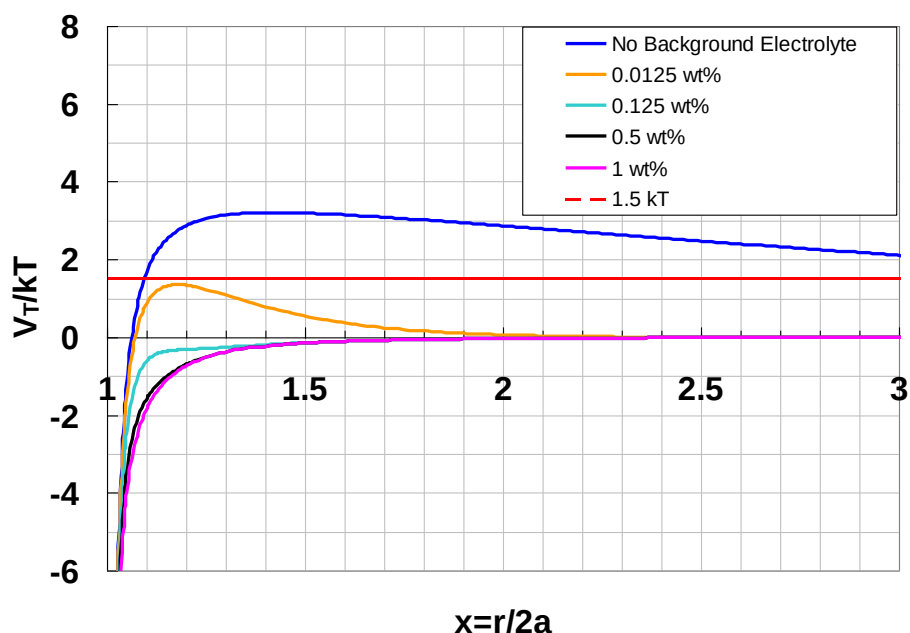


Figure 6.5- Total interaction energy between 420 micron diameter quartz grain and 25 nm diameter silica nanoparticles as a function of NaCl concentration (Equations 6.2 and 6.4).

6.3.2 Interfacial Tension of Silica Nanoparticle Dispersion/Decane Interface

The effects of nanoparticles on interfacial properties are investigated with unmodified and surface modified silica nanoparticle dispersions. The Wilhemy plate method with a Kruss K100 tensiometer was used to determine the effect of nanoparticles on the IFT of decane/water interface. The results are presented in Figures 6.6 and 6.7. The IFT of decane/water is 45 dynes/cm. Unmodified silica nanoparticles at various concentrations do not have any effect on IFT of water/decane interface (43 dynes/cm), as presented in Figures 6.6 and 6.7. The surface modified silica nanoparticles with sulfonate surface modification also do not influence the IFT either. A slight decrease is observed as particle concentration increases but this decrease may be due to the presence of the

sulfonate surface modifier. When the IFT in presence of sulfonate modified particles is compared with just the sulfonate modifier in water, almost the same decrease in IFT is observed. Therefore, the decrease in IFT corresponds to the effect of sulfonate molecules not to the presence of the nanoparticles.

A significant decrease in IFT (24 dynes/cm) occurs with PEG modified silica particles. To determine whether this decrease is because of the PEG itself or not, we prepared a solution having the same PEG concentration, but without nanoparticles. This PEG solution exhibits similar IFT values as the PEG modified nanoparticle dispersions. Therefore, the presence of PEG, attached to silica nanoparticle or free in solution, determines the decrease in IFT of water/decane interface. The presence of the nanoparticle appears not to add to the IFT reduction.

The effect of particle size and concentration is presented in Figure 6.7. The results are consistent with our findings for 5 nm particles (Figure 6.8). All the unmodified silica nanoparticle dispersions (5, 25 and 75 nm) have almost the same IFT value as water/decane and it appears not to be sensitive to particle concentration or size. Based on these findings, it can be concluded that unmodified silica nanoparticles do not stay at the water/interface.

However, with the surface modified nanoparticles, a decrease in IFT is observed as particle concentration increases at a given size or as particle size decreases at a given nanoparticle concentration. These trends are consistent with the increasing amount of the surface modifiers as the nanoparticle concentration increases and the nanoparticle size decreases. In the case of surface modified nanoparticles, deviations from IFT of water/decane occur, especially in case of PEG modified silica nanoparticles, as seen in Figure 6.8. The type and amount of surface treatment attached to silica nanoparticles determines the extent of the change in IFT of water/decane interface. The degree of IFT

change is identical for aqueous solutions of surface modifying material in the absence of nanoparticles.

Insignificant adsorption of unmodified silica nanoparticles at the decane/water interface shows that the silica nanoparticles are not amphiphiles and the surface modification alone determines the adsorption of silica nanoparticles on interfaces as observed with the PEG modified silica nanoparticles (Figure 6.9).

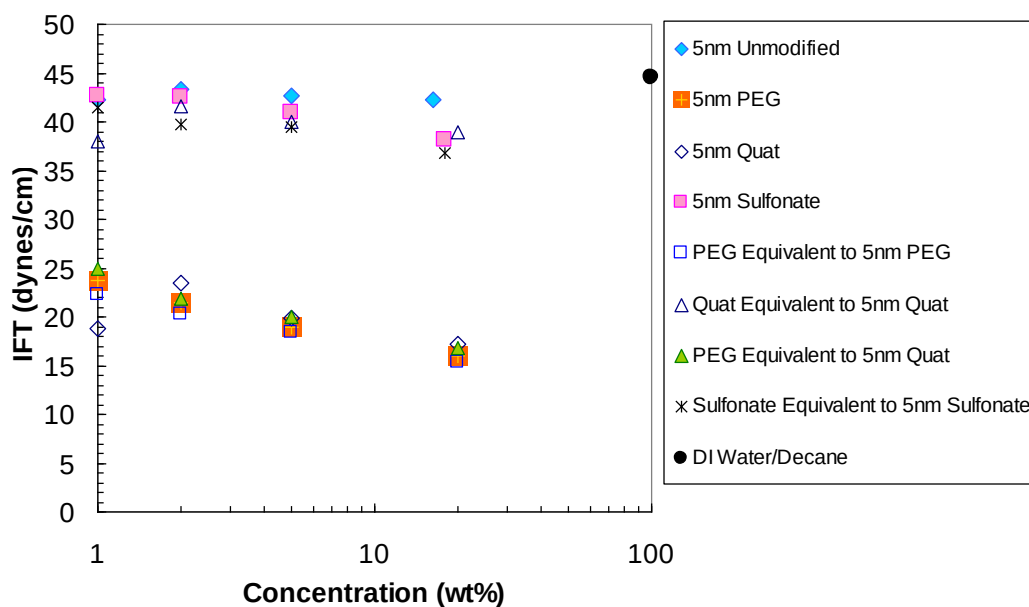


Figure 6.6- IFT of decane/water in presence of 5 nm silica unmodified or surface modified nanoparticles.

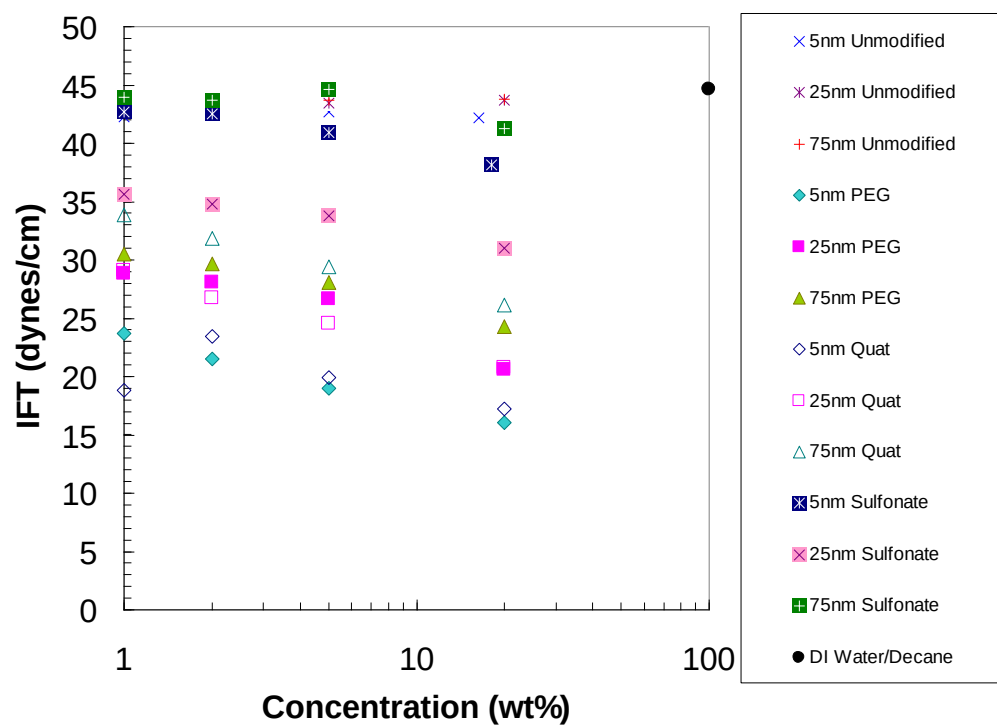


Figure 6.7- IFT of decane/water in presence of nanoparticles. The effect of nanoparticle size and concentration is shown.

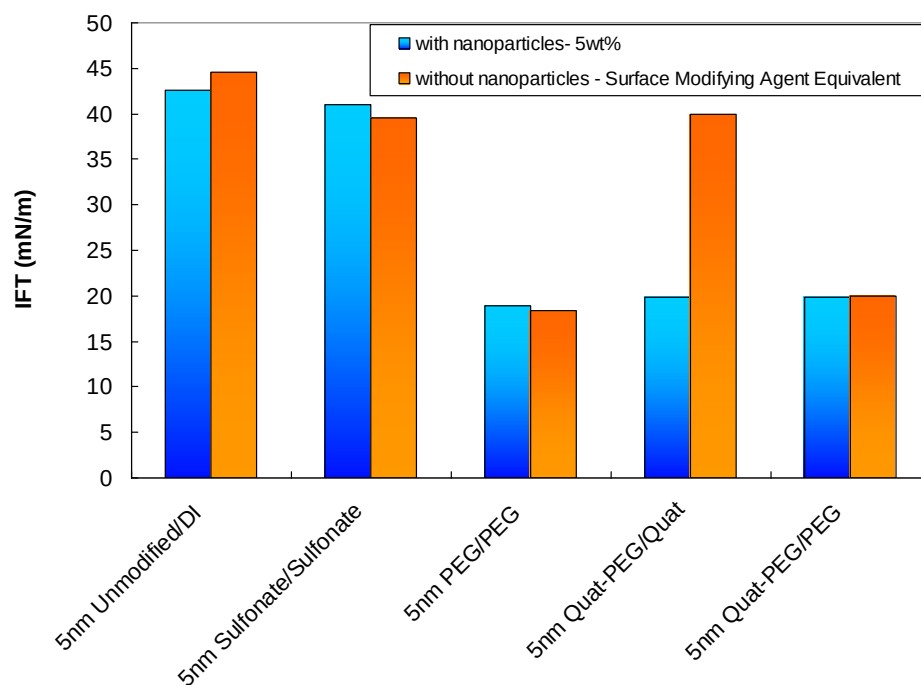


Figure 6.8- The effect of 5 wt% 5nm nanoparticles on IFT of water/decane.

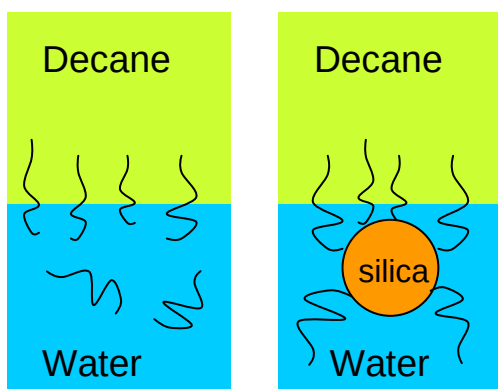


Figure 6.9- Schematic presentation of adsorption of PEG to water/decane interface (a) in the absence of silica nanoparticle and (b) attached to silica nanoparticle.

The concentration of PEG in aqueous solution and PEG attached to silica nanoparticles partitioned to the interface was quantitatively determined by using thermodynamic theory of partitioning (Gibbs equation):

$$\frac{d\gamma}{dC_2} = -\Gamma_2 \frac{RT}{C_2 N_A} \quad (6.6)$$

where R is the universal gas constant; N_A the Avogadro number; T the temperature; C_2 bulk concentration in number of nanoparticles/volume of dispersion; γ interfacial tension and Γ_2 is the nanoparticle or PEG concentration at interface. The results are presented in Figure 6.10. The PEG modified nanoparticles and PEG solution without nanoparticles show same adsorption behavior, which leads us to conclude that only PEG molecules adsorb at the interface, not the nanoparticles (see Figure 6.9). The line corresponds to Langmuir isotherm (Hunter 2001) in Equation 6.7 that is used to fit our data. The model parameters, K and Γ_{max} are 30 and 1.2 (molecules/nm²) respectively. Assuming a surface coverage of PEG molecules as 1 molecule of PEG/nm² nanoparticle, a monolayer of PEG modified nanoparticles occur at the water/decane interface. Either the nanoparticles would place near interface and/or the interface would deform slightly for PEG molecules on the nanoparticles to uniformly cover the interface. This is a consequence of the spherical shape of nanoparticles and short length of PEG molecules (2-3 nm). Monolayer coverage is also in agreement with Langmuir isotherm. We can conclude that the results obtained from Gibbs' equation correspond to the adsorption of PEG molecules/nm² interface but not nanoparticles/nm² interface. If the latter was correct then 30 layers of 5 nm nanoparticles with a cubic packing would need to be at the interface corresponding to the maximum adsorption of 1.2 nanoparticle/nm².

$$\Gamma_2 = \Gamma_{\max} \frac{KC_2}{1 + KC_2} \quad (6.7)$$

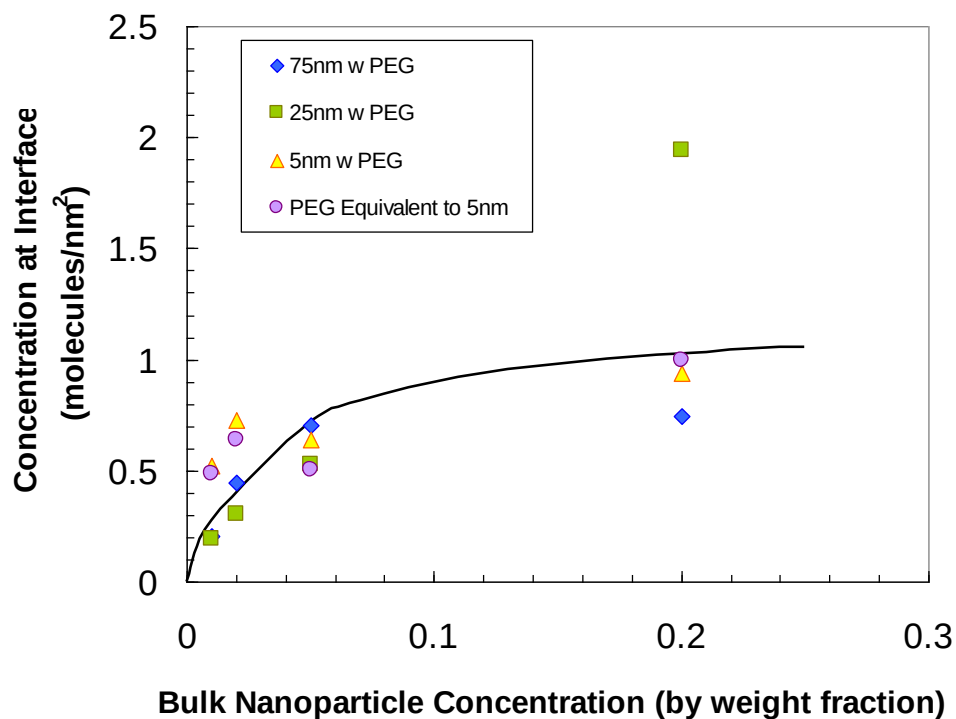


Figure 6.10- Adsorption of PEG or PEG modified silica nanoparticles on decane/water interface. The line corresponds to Langmuir isotherm.

6.3.3 Contact Angle Measurements

The contact angle goniometer was used to monitor and measure the contact angle of decane droplet on quartz or calcite plate immersed in silica nanoparticle dispersions. The contact angle is measured through the denser phase (water or nanoparticle dispersion). A schematic is shown in Figure 6.11. The contact angle $\theta=0^\circ$ corresponds to

a surface completely water wet and $\theta=180^\circ$ corresponds to completely oil wet surface. For effective displacement of oil by water, we need $\theta<90^\circ$.

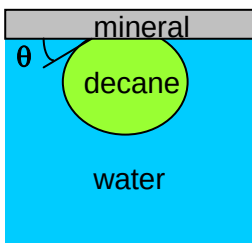


Figure 6.11- Schematic of an oil droplet on a solid substrate (mineral) immersed in water

Calcite and quartz plates were immersed in decane for one week before the contact angle experiments. The pictures of a decane droplet immersed in water or silica nanoparticle dispersion are presented in Figures 6.12-6.14. The effect of particle size and surface type on the contact angle of water/decane on a mineral was studied. The decane droplet is injected with an inverted J-syringe underneath the substrate. However the pictures in Figures 6.12-6.14 are digitally inverted using a Pax-it 2+ digital camera connected directly to the microscope for visual purposes. These images are inverted pictures of the actual droplet.

The image on the left side in each figure corresponds to the contact angle of water/decane/mineral without nanoparticles and the image on the right side shows the contact angle at nanoparticle dispersion/decane/mineral. Figures 6.12-6.14 show the effect of unmodified silica nanoparticles and their size on the contact angle on quartz plate. The contact angle does not change significantly in the presence of unmodified nanoparticles of 5, 25 or 75 nm diameter. This observation is consistent with the present

findings of IFT and adsorption. The unmodified nanoparticles do not change IFT of water/decane nor do they adsorb to the quartz surface.

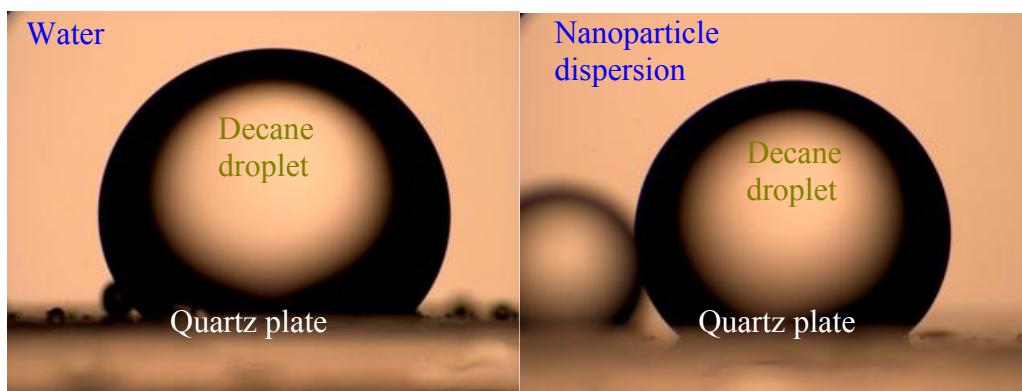


Figure 6.12- Decane droplet on quartz plate immersed in (a) water and (b) 5nm unmodified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 59° and (b) 46° .

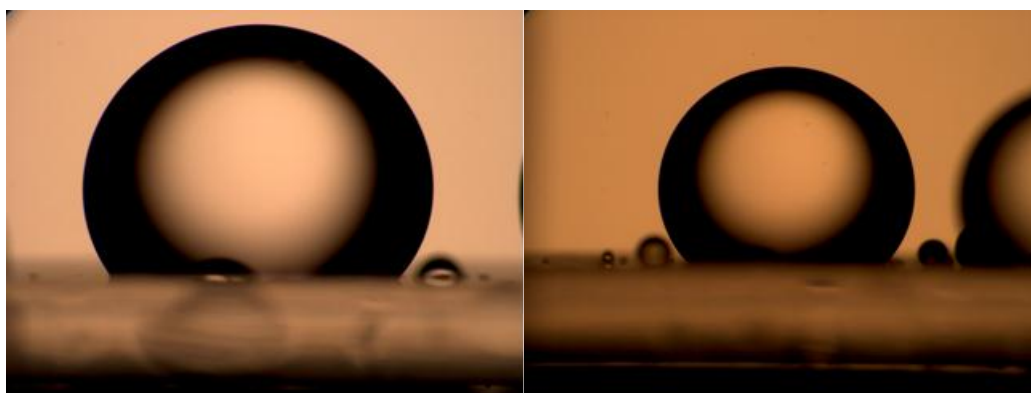


Figure 6.13- Decane droplet on quartz plate immersed in (a) water and (b) 25nm unmodified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 60° and (b) 52° .

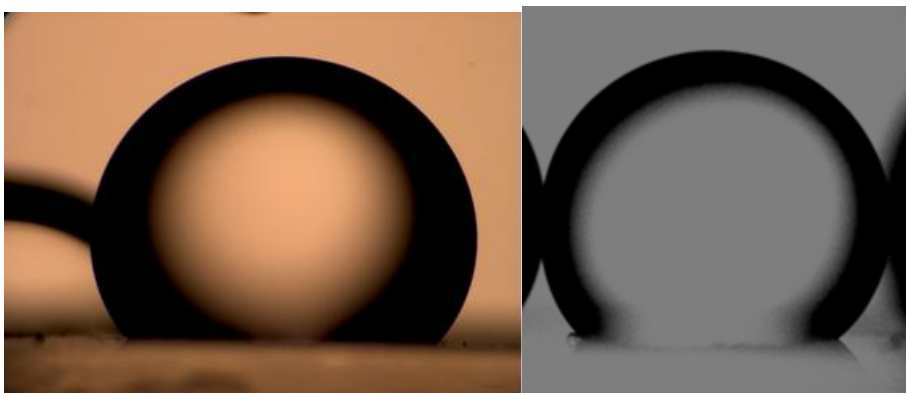


Figure 6.14- Decane droplet on quartz plate immersed in (a) water and (b) 75nm unmodified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 56° and (b) 52° . The color in (b) is digitally altered to more easily see the droplet.

Figures 6.16-6.18 show the effect of sulfonate modified silica nanoparticles and their size on the contact angle on quartz plate. The contact angle does not change significantly in the presence of sulfonate modified nanoparticles of 5, 25 or 75 nm diameter. This observation is consistent with our findings of IFT and adsorption. The sulfonate modified nanoparticles do not significantly change the IFT of water/decane interface nor do they adsorb to the quartz surface. Similar results for contact angle are observed with the quat modified silica nanoparticles of 5, 25 or 75 nm diameter (Figures 6.19-6.21).

Although PEG modified nanoparticles reduce the IFT of water/decane from 45 to 24 dynes/cm there is no significant change in contact angle in the presence of these nanoparticles, under the experimental conditions. Figures 6.22-6.24 show the effect of PEG modified silica nanoparticles and their size on the contact angle on quartz plate. The contact angle does not significantly change in the presence of PEG modified nanoparticles of 5, 25 or 75 nm diameter. This observation is consistent with our findings

from batch adsorption experiments. The effect of temperature is investigated with 5nm PEG modified nanoparticles at 80°C, Figure 6.25. We did not observe any significant change in the contact angle at the higher temperature.

Figures 6.26-6.28 show the effect of sulfonate modified silica nanoparticles and their size on the contact angle on calcite plate. The contact angle does not significantly change in the presence of sulfonate modified nanoparticles of 5, 25 or 75 nm diameter. This observation is also consistent with our findings of IFT and adsorption.

A summary of contact angle measurements is presented in Figure 6.15. The change in contact angle in the presence of nanoparticles is plotted as a function of nanoparticle diameter. The change is less than 10 degrees.

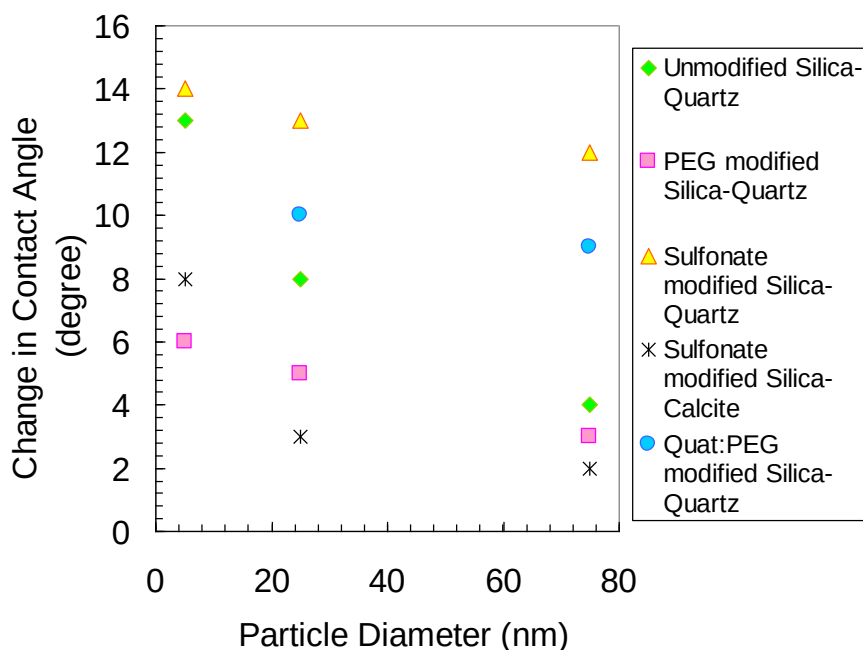


Figure 6.15- The change in contact angle in the presence of 1wt% silica nanoparticles

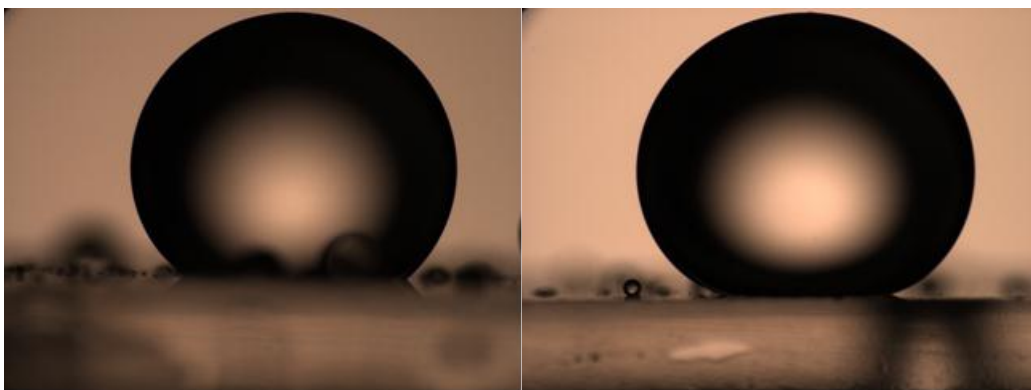


Figure 6.16- Decane droplet on quartz plate immersed in (a) water and (b) 5nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 34° and (b) 20° .

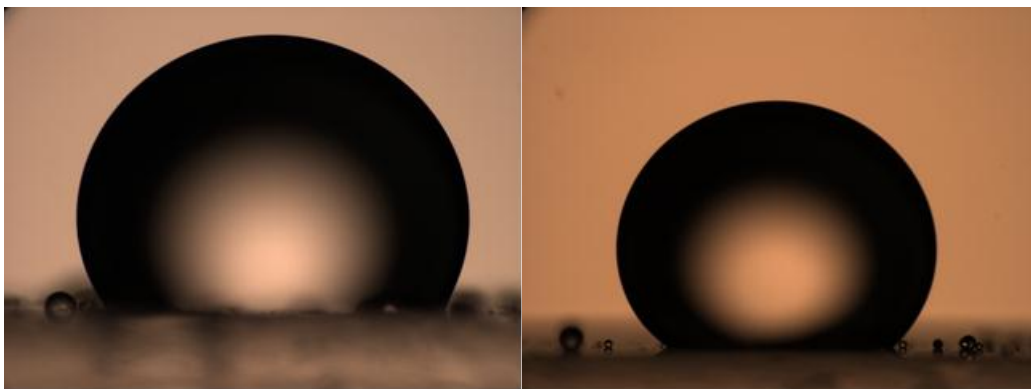


Figure 6.17- Decane droplet on quartz plate immersed in (a) water and (b) 25nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 51° and (b) 38° .

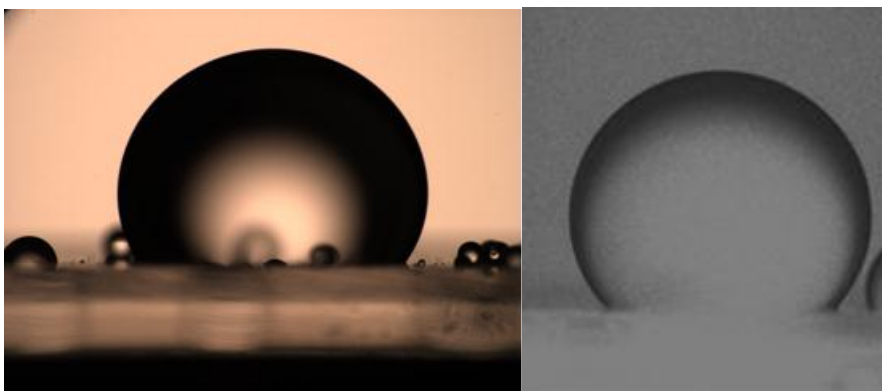


Figure 6.18- Decane droplet on quartz plate immersed in (a) water and (b) 75nm sulfonate modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 55° and (b) 43° . The color in (b) is digitally altered to see the droplet clearly since the light transmittance of nanoparticle dispersion is low because of particle size.

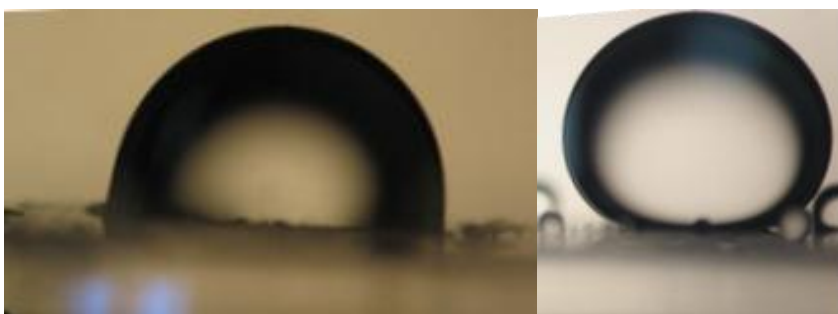


Figure 6.19- Decane droplet on quartz plate immersed in (a) water and (b) 5nm quat/PEG (50:50) modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 91° and (b) 14° .

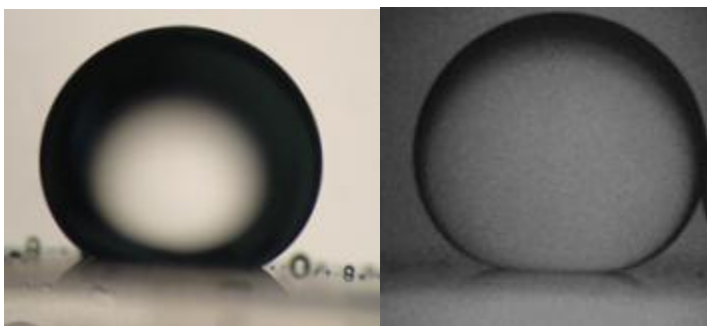


Figure 6.20- Decane droplet on quartz plate immersed in (a) water and (b) 25nm quat/PEG (50:50) modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 30° and (b) 20° .

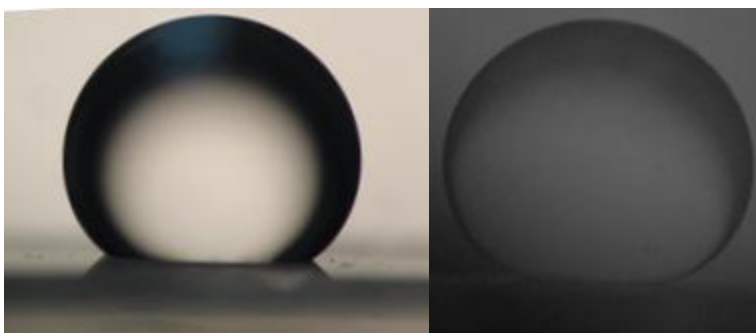


Figure 6.21- Decane droplet on quartz plate immersed in (a) water and (b) 75nm quat/PEG (50:50) modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 35° and (b) 26° .



Figure 6.21- Decane droplet on quartz plate immersed in (a) water and (b) 5nm PEG modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 20° and (b) 14° . The quartz plate in (a) is not tilted.

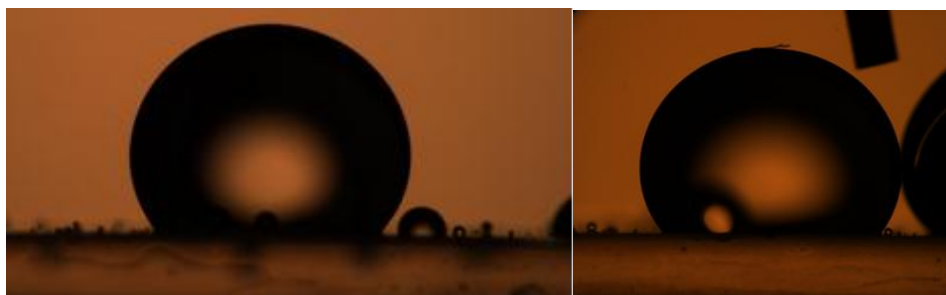


Figure 6.23- Decane droplet on quartz plate immersed in (a) water and (b) 25nm PEG modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 56° and (b) 51° .

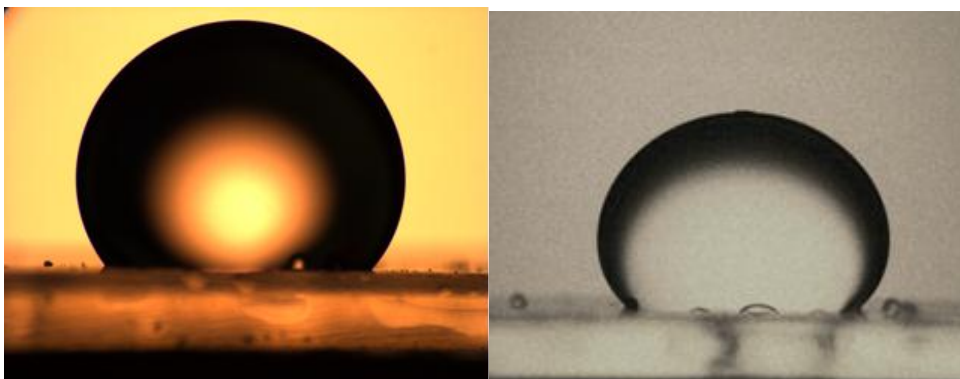


Figure 6.24- Decane droplet on quartz plate immersed in (a) water and (b) 75nm PEG modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 52° and (b) 49° . The color in (b) is digitally altered to see the droplet clearly since the light transmittance of nanoparticle dispersion is low because of particle size.

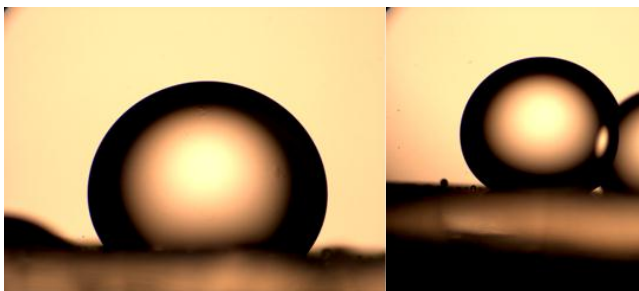


Figure 6.25- Decane droplet on quartz plate immersed in (a) water at 80°C and (b) 5nm PEG modified silica nanoparticle dispersion of 1wt% at 80°C. The contact angle is (a) 59° (b) 45°.

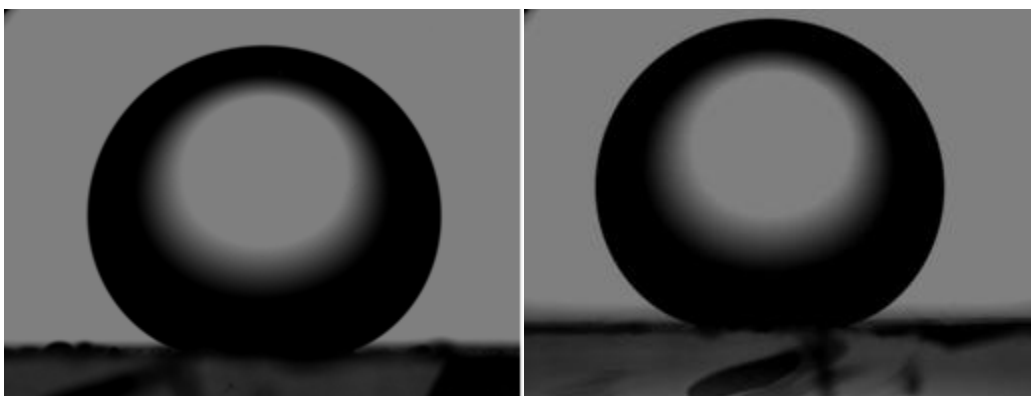


Figure 6.26- Decane droplet on calcite plate immersed in (a) water and (b) 5nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 32° and (b) 24°.

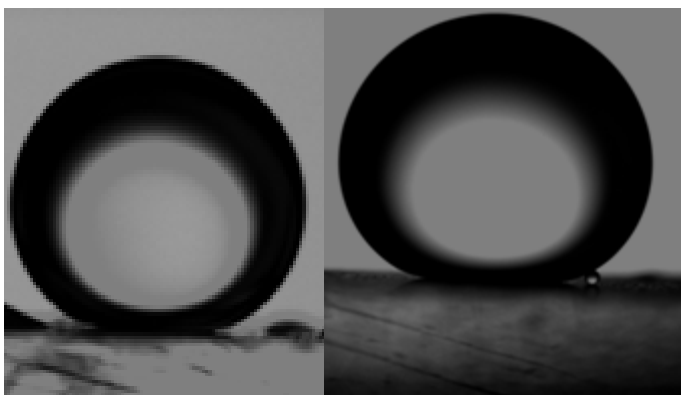


Figure 6.27- Decane droplet on calcite plate immersed in (a) water and (b) 25nm sulfonate modified silica nanoparticle dispersion of 1wt%. The contact angle is (a) 21° and (b) 18°.

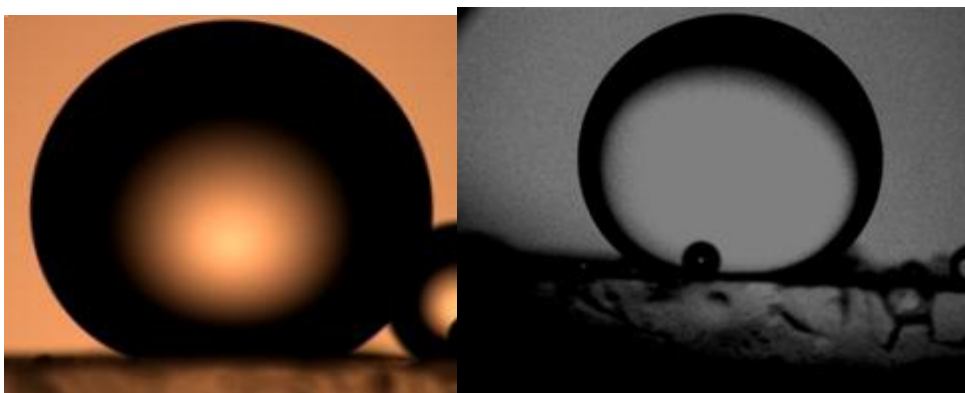


Figure 6.28- Decane droplet on calcite plate immersed in (a) water and (b) 75nm sulfonate modified silica nanoparticle dispersion of 0.5wt%. The contact angle is (a) 38° and (b) 36°.

6.4 CONCLUSIONS

Unmodified, sulfonate or PEG modified silica nanoparticles do not significantly adsorb on quartz and calcite surfaces is not observed under the experimental conditions reported in this chapter. Increase in particle size from 5 to 25 nm or addition of NaCl less than CSC does not promote adsorption of nanoparticles on mineral surfaces.

Unmodified nanoparticles or those with an anionic (sulfonate) or cationic surfactant (quat) do not influence the IFT of water/decane interface. The particle size or concentration does not have any influence on IFT. However, the presence of PEG as a surface coating material significantly decreases the IFT. The degree of change is the same for aqueous solutions of surface modifying materials in the absence of nanoparticles. Based on these results, it can be concluded that silica nanoparticles are not amphiphiles. The surface modification determines the extent of adsorption of silica particles to interfaces.

A slight change in contact angle is observed in the presence of unmodified or surface modified nanoparticles with anionic, cationic or nonionic surfactants (sulfonate, quat or PEG). The size of nanoparticle does not influence contact angle.

We further the study of Wasan and Nikolov (2003), Binks and Whitby (2005) and Lee *et al.* (2006) and investigate the effect of nanoparticles and surface treatment on interfacial tension, adsorption on minerals and finally on contact angle change. We show that surface modified silica nanoparticles have minimal interaction with minerals and the water/decane interface and hence the change in contact angle is not significant. The effect of surface treatment on the IFT change is isolated and conclude that the type and amount of surface treatment attached to silica nanoparticles determines the extent of the change in IFT of water/decane interface.

6.5 REFERENCES

- Antelmi DA and Spalla O (1999) Adsorption of Nanolatex Particles to Mineral Surfaces of Variable Surface Charge. *Langmuir* 15: 7478-7489.
- Aubert C, Cannell DS (1986) Restructuring of colloidal silica aggregates. *Phys. Rev. Lett.* 56:738-741.

- Binks BP, and Fletcher PDI (2001) Particles Adsorbed at the Oil-Water Interface: A Theoretical Comparison Between Spheres of Uniform Wettability and “Janus” Particles. *Langmuir* 17 (16): 4708-4710.
- Binks BP, and Whitby CP (2005) Nanoparticle Silica-Stabilised Oil-In-Water Emulsions: Improving Emulsion Stability. *Colloids and Surfaces A* 253 (1-3): 105-115.
- Blake TD, Clarke A, De Conninck J and de Ruijter M.J (1997) Contact Angle Relaxation During Droplet Spreading: Comparison Between Molecular Kinetic Theory and Molecular Dynamics. *Langmuir* 13 (7): 2164-2166.
- Boda D, Chan K-Y, Henderson D, Wasan DT and Nikolov AD (1999) Structure and Pressure of a Hard Sphere Fluid in a Wedge-Shaped Cell or Meniscus. *Langmuir* 15 (13): 4311-4313. DOI: 10.1021/La981013h.
- Bresme F and Quirke N (1999) Computer Simulation of Wetting and Drying of Spherical Particulates at a Liquid–Vapor Interface. *J. Chem. Phys.* 110 (7): 3536-3547.
- Bresme F and Oettel M (2007) Nanoparticles at Fluid Interfaces. *J. Phys. Condens. Matter* 19: 413101-1-413101-33. DOI: 10.1088/0953-8984/19/41/413101.
- Chengara A, Nikolov AD, Wasan DT, Trokhymchuk A and Henderson D (2004) Spreading of Nanofluids Driven by the Structural Disjoining Pressure Gradient. *J. Colloid Interface Sci.* 280 (1): 192-201.
- Choi C-H and Kim C-J (2006) Large Slip of Aqueous Liquid Flow Over a Nanoengineered Superhydrophobic Surface. *Phys. Rev. Lett.* 96: 066001-1-066001-4. DOI: 10.1103/Physrevlett.96.066001.
- Drummond C and Israelachvili J (2004) Fundamental studies of crude oil–surface water interactions and its relationship to reservoir wettability. *J. Pet. Sci. Eng.* 45 (1-2): 61-81
- Derjaguin BV, Landau L (1941) Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim USSR* 14:633-662.
- Flury M, Czigany S, Chen G and Harsh JB (2004) Cesium Migration in Saturated Silica Sand and Hanford Sediments as Impacted by Ionic Strength. *J. of Contaminant Hydrology* 71: 111-126.
- Goodwin J (2009) Colloids and interfaces with surfactants and polymers. Wiley, New Delhi.
- Hogg RI, Healy TW and Fuerstenau DW (1966) Mutual Coagulation of Colloidal Dispersions. *Trans. Faraday Soc.* 62: 1638–1651.
- Hunter RJ (2001) Foundations of colloid science. Oxford University Press, New York.
- Metin CO, Lake LW, Miranda CR, Nguyen QP (2011) Stability of aqueous silica nanoparticle dispersions. *J. Nanopart. Res.* 13:839-850.

- Hwang C-C, Jeng Y-R, Hsu Y-L and Chang J-G (2001). Molecular Dynamic Simulation of Microscopic Droplet Spread on Rough Surfaces. *J. Phys. Soc. Jpn.* 70 (9): 2626-2632.
- Lee Y, Du Z, Lin W and Yang Y (2006) Monolayer Behavior of Silica Particles at Air/Water Interface: A Comparison Between Chemical and Physical Modifications of Surface. *J. Colloid Interface Sci.* 296 (1): 233-241.
- Lin Y, Böker A, Skaff H, Cookson D, Dinsmore AD, Emrick T and Russell TP (2005) Nanoparticle Assembly at Fluid Interfaces: Structure and Dynamics. *Langmuir* 21 (1): 191-194.
- Marczewski AW and Szymula M (2002) Adsorption of Asphaltenes From Toluene on Mineral Surface. *Colloids and Surfaces A* 208: 259-266.
- Matar OK, Craster RV and Sefiane K (2007) Dynamic Spreading of Droplets Containing Nanoparticles. *Phys. Rev. E* 76 (5): 056315-1-056315-9.
- Reincke F *et al.* (2006) Understanding the Self-Assembly of Charged Nanoparticles at the Water/Oil Interface. *Phys. Chem. Chem. Phys.* 8 (33): 3828-3835.
- de Ruijter MJ, Blake TD, and de Coninck J (1999a) Dynamic Wetting Studied By Molecular Modeling Simulations of Droplet Spreading. *Langmuir* 15 (22): 7836-7847. DOI: 10.1021/La990171l.
- de Ruijter MJ, De Coninck J and Oshanin G (1999b) Droplet Spreading: Partial Wetting Regime Revisited. *Langmuir* 15 (6): 2209-2216.
- Saint Flour C, Papirer E (1982) Gas solid chromatography: A method of measuring surface free energy characteristics of short glass fibres. II. Through retention volumes measured near zero surface coverage. *Ind. Eng. Chem. Process Res. Dev.* 21 : 666.
- Sefiane K, Skilling J and MacGillivray J (2008) Contact Line Motion and Dynamic Wetting of Nanofluid Solutions. *Adv. Colloid Interface Sci.* 138 (2): 101-120. DOI: 10.1016/j.cis.2007.12.003.
- Wasan DT and Nikolov AD (2003) Spreading of Nanofluids on Solids. *Nature* 423 (5): 156-159. DOI: 10.1038/Nature01591.
- Vafaei S, Borca-Tasciuc T, Podowski MZ, Purkayastha A, Ramanath G and Ajayan PM (2006). Effect of Nanoparticles on Sessile Droplet Contact Angle. *Nanotechnology* 17: 2523-2527. DOI: 10.1088/0957-4484/17/10/014.
- Verwey EJW, Overbeek JThG (1948) Theory of stability of lyophobic colloids. Elsevier, Amsterdam.
- Voronov RS, Papavassiliou DV and Lee LL (2006) Boundary Slip and Wetting Properties of Interfaces: Correlation of the Contact Angle with the Slip Length. *J. Chem. Phys.* 124 (20): 2047011-10.

- Voronov RS, Papavassiliou DV and Lee LL (2007) Slip Length and Contact Angle Over Hydrophobic Surfaces. *Chem. Phys. Lett.* 441 (4-6): 273-276. DOI: 10.1016/J.Cplett.2007.05.013.
- Yang Y-X, Koplik J and Banavar JR (1991) Molecular Dynamics of Drop Spreading on a Solid Surface. *Phys. Rev. Lett.* 67 (25): 3539-3542.

Chapter 7: Interaction of Nanoparticles with Clay Mineral

The interaction of silica nanoparticles with montmorillonite clay was investigated by visual swelling tests and analytical techniques such as Fourier Transform Infrared (FTIR) and x-ray diffraction (XRD). The adsorption of silica nanoparticles onto montmorillonite was also studied with a UV-Vis spectrophotometer. The effects of particle size, concentration and surface type on the adsorption were presented in detail. Silica nanoparticles with four different surfaces (unmodified, surface modified with anionic (sulfonate), cationic (quaternary ammonium (quat)) or nonionic (polyethylene glycol (PEG)) surfactant) were used. The adsorption of unmodified and sulfonate modified nanoparticles on clay was found to be insignificant. However, PEG and quat/PEG modified nanoparticles adsorbed significantly on montmorillonite. Adsorption isotherms were calculated for those nanoparticles. Additionally it does not appear that the particle size or concentration influences the extent of adsorption. This study brings new insight into the understanding and modeling of the adsorption of surface modified silica nanoparticles onto clay minerals.

7.1 INTRODUCTION

Most hydrocarbon reservoir rocks contain clay minerals in which kaolinite, montmorillonite, illite, and chlorite are abundant in sandstone. The basic structure of clay minerals consists of a sheet of oxygen or hydroxyl groups embedding heavy metals such as aluminum, iron, or magnesium atoms, and a sheet of silica tetrahedral. Two sheets of silica sandwiching on one sheet of aluminum defines a basic layer of montmorillonite. These layers are separated by thin aqueous films that contain cations and organic materials (Brindley and Pedro 1972). This particular structure of montmorillonite is

mainly responsible for the expansion of montmorillonite in the presence of water. Clay swelling has been an active area of research since 1950s. Especially in drilling and production engineering, clay swelling has significant impacts such as wellbore instability and formation damage. It has been suggested that the silicate structure had a permanent negative charge due to the replacement of Si^{4+} by Al^{3+} or Al^{3+} by Mg^{2+} . These exchangeable cations were situated between the silicate layers, neutralizing their charge. The mechanism of clay swelling was described as water molecules entering interlayer positions to hydrate ions present in that region (Norrish 1954). The interlayer spacing increases from 9.5 Å for the dry material to 20 Å corresponding to 4 layers of water in crystalline swelling. In the second region of swelling, osmotic swelling, Na-montmorillonite takes up 10g H_2O /g clay and increases its volume by about 20 times. At greater water content, the montmorillonite becomes a thixotropic gel, then a sol and this may be regarded as the third stage of water uptake. Na-montmorillonite in contact with water has been reported as taking up to 10g H_2O /g clay and this may represent the maximum water content of $\sim 300\text{Å}$ of normal swelling” (Luckham and Rossi 1999).

The mechanisms and kinetics of clay swelling in petroleum-bearing formations was discussed in detail by Civan (2007). Sensoy *et al.* (2009) reported that nanoparticles at 10 wt% or higher concentrations could plug shale pore throats and reduce permeability to minimize fluid invasion. Sharma *et al.* (2011) argued that the use of nanoparticles in drilling fluids would be the first large scale application of nanotechnology in oil and gas industry. The authors showed experimentally that unmodified nanoparticles could reduce the invasion of water-based drilling fluids into shale.

The mechanisms for clay swelling are well defined as discussed above. However, there is very little work published on the interaction of nanoparticles with clays and the mechanisms are not well understood. In this chapter, the effect of unmodified and

surface modified silica nanoparticles on the clay (montmorillonite) swelling is investigated visually and by analytical methods such as FTIR and x-ray. Moreover, the adsorption of silica nanoparticles on clay is quantified by using a UV-Vis spectrophotometer. The results present new insight into the understanding of the interactions of unmodified and modified nanoparticles with clay.

7.2 MATERIALS AND METHODS

The materials studied were aqueous dispersions of silica particles as provided by 3M, Co (St. Paul, MN, USA). The mean diameters of primary particles are 5 and 25, which have an unmodified surface or a modified surface with sulfonate, polyethylene glycol (PEG) or a mixture of quaternary ammonium and PEG. The latter one will be referred to as “quat/PEG” throughout this chapter. The surface modifications describe the surface of the particles after using alkoxysilanes as surface modifying agents. We used montmorillonite clay purchased from Ward’s Natural Science Establishment, Inc, for these studies. Throughout this chapter montmorillonite is referred as “clay”. An ultraviolet-visible spectrophotometer (UV-Vis) was used to determine the concentration of nanoparticles in the supernatant liquid.

Powder of montmorillonite clay mineral was submerged in the various nanoparticle dispersions for 24 hours. The liquid of an amount of 3 ml was separated from the mineral by pipette and centrifuge. The supernatant liquid was centrifuged 15 minutes at 9,000 rpm to separate fine clay minerals from the liquid, and then analyzed by UV-Vis spectroscopy to determine the silica nanoparticle concentration remaining in the liquid. A calibration curve was built using UV-Vis absorbance at a fixed wavelength as a function of nanoparticle concentration. Different nanoparticle concentrations were used

ranging from 0.04 to 6 wt%. The dispersion to mineral weight ratio was 100:1. This liquid-to-solid ratio was chosen based on the extent of the swelling of clay in water that would give enough supernatant for concentration measurements.

7.3 RESULTS AND DISCUSSION

First, the effect of nanoparticles on swelling of montmorillonite clay was studied by visual observations by adding 0.2 g of clay to 10 g of aqueous nanoparticle dispersion. It is known that there are two types of swelling mechanisms depending on the extent of the increase in the basal spacing between two montmorillonite sheets: crystalline and osmotic swelling. Crystalline swelling results from the adsorption of the monomolecular layers of water on both the external and interlayer surfaces. In osmotic swelling, the interlayer spacing increases abruptly to 30-40 Å and continues to increase to several hundred angstroms (several ten nanometers) with water content (Schechter, 1992). In the presence of electrolytes, the swelling of clay is suppressed. In Figure 7.1, the effect of NaCl concentration on clay swelling is shown. As NaCl concentration increases, the volume of the clay sediment decreases. It is known that K^+ is more effective in inhibiting clay swelling than Na^+ (see Figure 7.2). The effect of unmodified or modified silica nanoparticles on clay swelling is shown in Figure 7.3 for 10 g solution and 0.2 g clay. In the presence of unmodified nanoparticles, the clay swelling is similar to that without any nanoparticles. At a low nanoparticle concentration (~1 wt%), all the nanoparticles (unmodified or modified) show slightly larger sediment volume than that without any nanoparticles. However, as nanoparticle concentration increases, PEG and quat/PEG modified nanoparticles inhibit swelling and the sediment thickness is smaller than that without any nanoparticles. Figures 7.4-7.7 clearly illustrate the effect of nanoparticle

concentration on the clay swelling. Sulfonate modified or unmodified nanoparticles do not show any effect on clay swelling. However, PEG or quat/PEG modified nanoparticles inhibit clay swelling and as nanoparticle concentration increases, the clay swelling becomes less significant. The presence of background electrolyte and nanoparticle is presented in Figure 7.8. For unmodified and sulfonate modified nanoparticle, we did not observe any improved inhibition of clay swelling. However, the presence of PEG or quat/PEG modified nanoparticles decreased the degree of swelling as indicated by the level of sediment height in Figure 7.8.

The interaction between PEG and montmorillonite has been studied in detail by many researchers. Carroll (1959) showed that organic ions, glycerol or glycol, could penetrate between the layers in montmorillonite. Liu *et al.* (2004) observed that in pure PEG, only 60% of swelling height of montmorillonite in water occurred. The authors argued that PEG penetrated into montmorillonite interlayers and caused the swelling. When there was KCl in the solution, the addition of PEG had little effect on the swelling height as measured by a linear swelling test. Liu *et al.* (2004) observed that the more hydrophobic units there were in the polyglycols, the stronger the adsorption was on montmorillonite layers. Water was displaced from clay and complexes are formed in the presence of K^+ . Upon addition of K^+ , the PEO hydration was significantly perturbed and PEO-water pair interaction energy drastically decreased. Quintero (2002) argued that PEG disrupted hydrogen bonding between water molecules and silica or alumina functionalities on clay surface. (Quintero 2002). In water-based drilling fluids, PEG has been demonstrated to be an effective shale inhibitor (Reid *et al.* 1995).

While the precise role of K^+ is still not fully understood, its use in combination with any of the polyols is clearly important for maximum shale inhibition (Reid *et al.* 1995). The authors proposed that the effectiveness may be due to the low hydration

energy of K^+ compared with Na^+ and Ca^{2+} . They showed from infrared measurements that water was displaced from the clay as the polyol was taken up, and thus, it could be determined that the interaction energy between the potassium ion and the polyol was sufficient to remove more of the water molecules solvating K^+ than would be the case for Na^+ and Ca^{2+} where these molecules were more tightly bound (Reid *et al.* 1995).

Amines can also enter into exchange reactions with clay minerals forming organic-clay complexes (Caroll 1959). Anderson *et al.* (2010) showed that cationic quaternary groups might form electrostatic interactions with negatively charged surfaces of the clay, in addition to the hydrogen bonds and enhanced inhibition of swelling.

Our findings on the effect of PEG or quat/PEG modified silica nanoparticles on the inhibition of clay swelling could be explained by the mechanism by which PEG or amines interact with clay. Since quat/PEG modified nanoparticles have both amines and PEG on the surface, they tend to be more effective than PEG-only modified silica nanoparticles (Figure 7.3).



Figure 7.1– Pictures of 10 g solution with 0, 0.5, 0.75, 1, 1.25, 1.5 and 1.75 wt% NaCl with 0.2 g clay.



Figure 7.2– Pictures of 10 g solution with 0.5, 1, 1.5, 1.75, 2 wt% KCl with 0.2 g clay.



Figure 7.3 – Picture of 10 g solution of DI water, 1 wt% 5 nm unmodified, 1 and 5 wt% sulfonate modified, 1 and 5 wt% PEG modified and 1 and 5 wt% quat/PEG modified silica nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.



Figure 7.4 – Picture of 10 g solution of DI water, 1 and 10 wt% 5 nm unmodified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.



Figure 7.5 – Picture of 10 g solution of DI water, 1, 5 and 10 wt% 5 nm sulfonate modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.



Figure 7.6 – Picture of 10 g solution of DI water, 1, 5, and 10 wt% 5 nm PEG modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.



Figure 7.7 – Picture of 10 g solution of DI water, 1, 5, 7.5 and 10 wt% 5 nm quat/PEG modified nanoparticle dispersions. Each sample contains 0.2 g clay and there is no background NaCl in the solution. The picture was taken 4 months after preparation of samples.

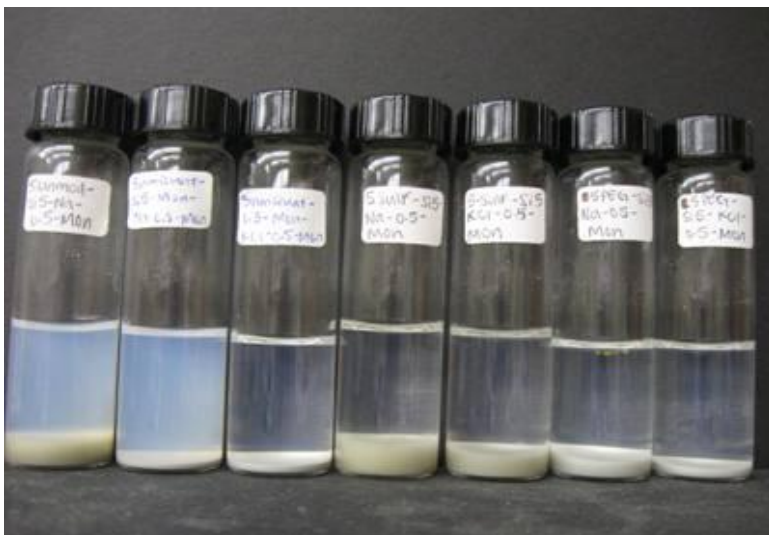


Figure 7.8 – Picture of 10 g solution of 5 wt% 5 nm particles of unmodified and 0.5 wt% NaCl, quat/PEG modified and 0.5 wt% NaCl and 0.5 wt% KCl, sulfonate modified and 0.5 wt% NaCl and 0.5 wt% KCl, PEG modified and 0.5 wt% NaCl and 0.5 wt% KCl. Each sample contains 0.2 g clay. The picture was taken 4 months after preparation of samples.

We carried out an ATR-FTIR study of clay/nanoparticle dispersion mixture to understand the effect of nanoparticles on clay swelling. The samples were prepared as discussed in previous section and 3 g of each sample was pipetted out from the solution and allowed to dry at room temperature for 1 day. Then ATR-FTIR of the dry samples was carried out. Figure 7.9 shows the spectra. Based on FTIR measurements Billingham *et al.* (1997) showed that PEG readily adsorbed onto the clay surface due to the considerable entropic driving force for adsorption. In our study, the band near 1635 cm^{-1} corresponding to water in the clay film was observed. The diagnostic bands for PEG were also present at 1460, 1350, 1295 and 1250 cm^{-1} . The peak assignments are given in Table 7.1. However, the results were not sufficient to make any conclusion about any structural change in clay or water adsorption that nanoparticles may cause.

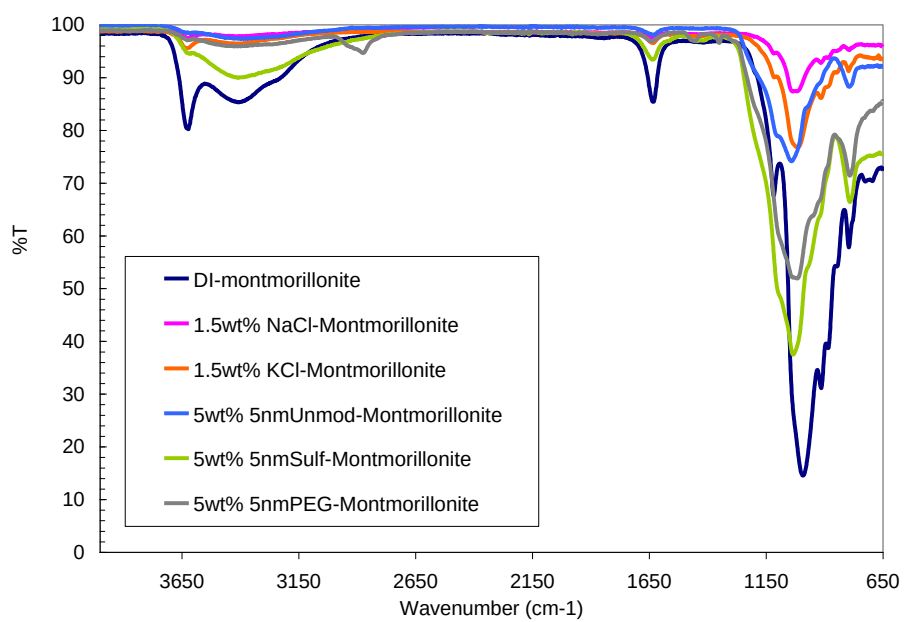


Figure 7.9 – ATR-FTIR spectra of dried clay/nanoparticle dispersion mixture.

Table 7.1- The peak assignments of the clay/nanoparticle mixture by ATR-FTIR.

	DI-Montmorillonite		1.5wt% NaCl-Montmorillonite		1.5wt% KCl-Montmorillonite		5wt% 5nmUnmod-Montmorillonite		5wt% 5nmSulf-Montmorillonite		5wt% 5nmPEG-Montmorillonite	
	Wavenumber (1/cm)	%T	Wavenumber (1/cm)	%T	Wavenumber (1/cm)	%T	Wavenumber (1/cm)	%T	Wavenumber (1/cm)	%T	Wavenumber (1/cm)	%T
OH stretching of structural hydroxyl groups					3630.75	95.53						
OH stretching of inner surface hydroxyl groups	3622.56	80.21	3622.67	97.49								
OH stretching of water					3448.31	96.39						
OH stretching of adsorbed and zeolitic water	3408.03	85.31							3411.2	89.98	3411.89	95.92
OH stretching of zeolitic water							3369.74	97.32				
CH ₂ asymmetric stretching											2873.67	94.66
OH deformation of water	1631.48	85.41	1633.3	97.56	1637.51	96.57	1637.07	98.09	1637.15	93.4	1638.15	96.84
CH ₂ scissoring									1450.64	96.9	1456.86	96.89
CH ₂ bending											1350.52	96.57
Si-O stretching (longitudinal mode)	1117.54	67.6										
in-plane Si-O stretching			1037.23	87.38			1040.4	74.14	1034.83	37.46		
in-plane Si-O stretching					1014.85	76.71					1015.88	51.91
Si-O stretching	991.76	14.53										
Al(OH) deformation	914.71	31.11	915.64	92.77	915.23	86.12						
Al(Fe)OH deformation	884.31	38.68										
Si-O stretching of quartz and silica	796.05	57.79	795.68	95.23	797.64	91.22	795.76	88.28	791.65	66.41	791.88	71.39
Si-O stretching of feldspar	725.6	70.28										
Si-O					689.05	93.53						

We further studied the effect of nanoparticles on clay structure by XRD. Nanoparticle dispersions were prepared from a dilution of the stock solutions to 1 wt% using DI water in 20 ml glass vials. Then 0.2 g of clay was added to 10 g of dispersion. The samples were left undisturbed for 2 days and XRD measurements were conducted. The clay/nanoparticle dispersion mixture was pipetted out from the glass vials into 1 mm diameter glass capillaries. Each sample was scanned for 10 min with 5°/sec rotation speed. The results were then analyzed using EVA software. The results are presented in Figure 7.10. The curves correspond to water and dispersions of unmodified, sulfonate, PEG and quat/PEG modified 5 nm particles mixed with clay as described above. The

most significant peak was observed at a d-spacing of 20 Å for all the samples. Billingham *et al.* (1997) obtained a spacing of 16 Å for PEG of molecular weight 300g/mol, corresponding to one layer of molecules lying flat between the clay lamellae. When its concentration was increased, the basal spacing increased to 18.6 Å corresponding to 2 layers of PEG lying flat between the sheets. In our experiments, a small peak can also be seen at larger d-spacing, 42 Å. The instrument could not measure d-spacing larger than 42 Å because of the size of the x-ray beam. However, all the peaks seem to be common for all the samples studied, with or without nanoparticles. Based on these results, we cannot make any quantitative conclusion on the effect of nanoparticles on clay swelling.

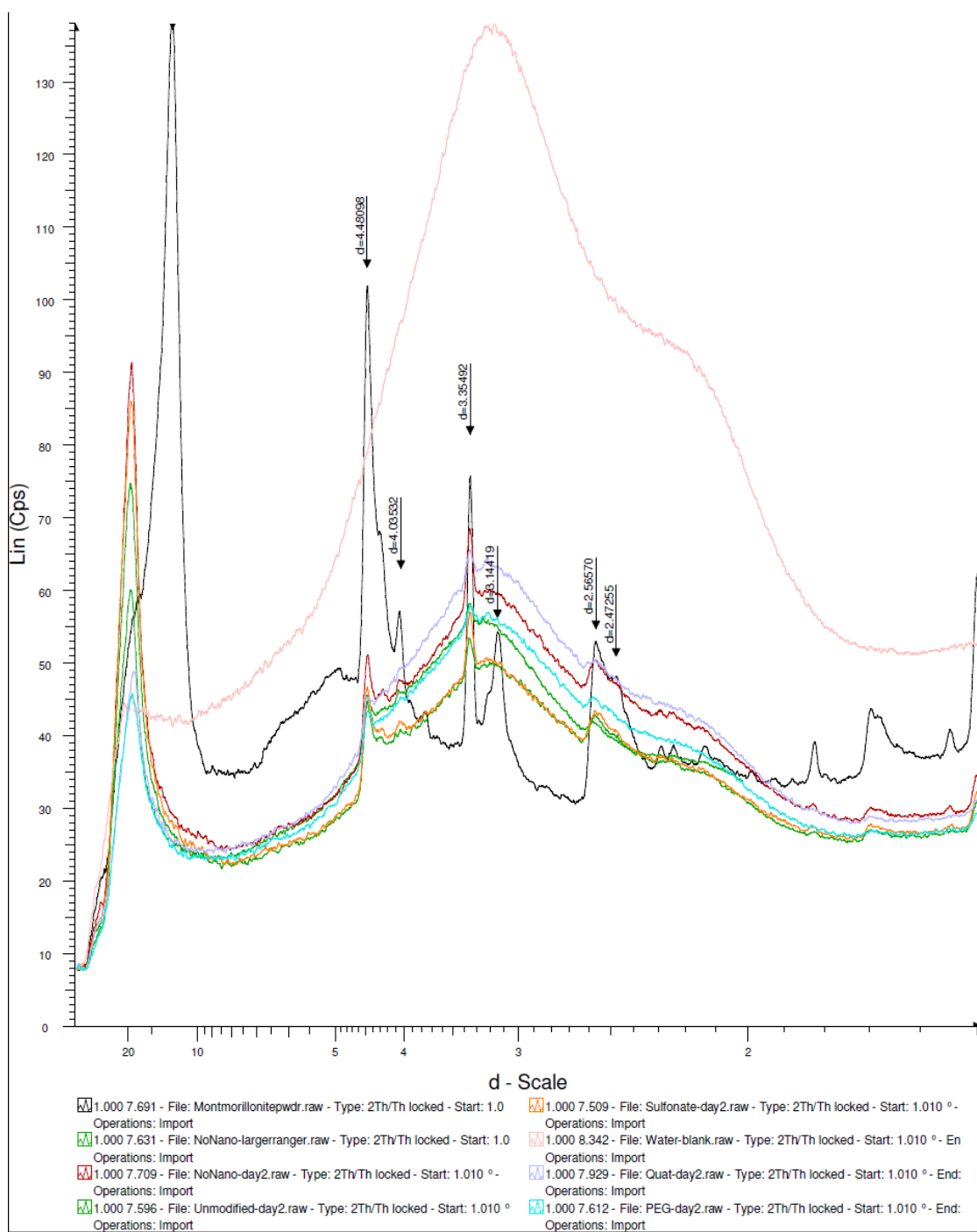


Figure 7.10 – X-ray diffraction of clay/nanoparticle dispersion mixture in glass capillary.

We studied the adsorption of unmodified and modified nanoparticles on clay with a UV-Vis spectrophotometer. We did not observe any significant adsorption with 5 nm unmodified or sulfonate modified silica nanoparticles. This result is in agreement with the visual observations on clay swelling as presented above. However, PEG or quat/PEG modified nanoparticles showed significant adsorption on clay. The picture of adsorption samples is presented in Figure 7.11. A background electrolyte of 1.5 wt% NaCl was chosen to decrease the amount of dispersed clay in solution and decrease the degree of swelling so that we could relate the results for possible oil field applications.



Figure 7.11- Picture of 5g solution of 1.5wt% NaCl with 0.05g clay without nanoparticles and with 5 nm PEG modified nanoparticles at 0.04, 0.06, 0.1, 0.4, 0.6 and 1wt% concentration in dispersion.

A calibration curve was built in UV-Vis to determine the concentration of 5 and 25 nm PEG modified nanoparticles in supernatant (see Figure 7.12). The UV-Vis absorbance spectra for 5 nm PEG modified nanoparticle dispersions is shown in Figure 7.13 before and after the dispersion was in contact with clay. The results of adsorption are shown in Figure 7.14 for both 5 and 25 nm PEG modified nanoparticles. The effect of particle size seems to be negligible on adsorption. Figure 7.15 presents the adsorption isotherm for PEG and quat/PEG modified 5 nm nanoparticles. We observed that PEG or quat/PEG modified silica nanoparticles have a strong affinity for the clay as indicated by the shapes of the isotherms. The effect of cation type was also studied. The results showed that the extent of adsorption of 5 nm PEG modified silica nanoparticles decreased when K^+ was present (see Figure 7.16). We have shown by visual observations that PEG modified nanoparticles were more effective in clay inhibition in the presence of K^+ than Na^+ . In addition to the above discussion on the interaction of PEG and clay in the presence of K^+ and Na^+ , Parfitt and Greenland (1970) suggested that the direct interaction between the exchangeable cations and PEG molecules was not responsible for adsorption (ion-dipole interactions). Instead, it was proposed that the cations retained their hydration shell and that weak bonds were involved between the primary hydration shell of the exchangeable cation and that of the ether oxygen atoms of the polymer to give a water bridge. Burchill *et al.* (1983) demonstrated through neutron scattering studies that hydrophilic polymers were able to displace the non-coordinated water and bind to the silicate surface as well as to the exchangeable cations through water bridge mechanism. The adsorption of PEO onto Na- montmorillonite gave Langmuir type isotherms and the adsorbed amount increased with the molecular weight. Cliffe *et al.* (1995) showed that the adsorption of PEG onto Na- montmorillonite gave Langmuir type isotherms without reaching a plateau. We have presented similar adsorption behavior for PEG or quat/PEG

modified nanoparticles on clay in Figure 7.14-7.16. In these figures, the adsorption results are also presented in terms of a fraction of a monolayer surface coverage of nanoparticles on clay mineral. Assuming a cubic packing of nanoparticles on clay surface, 4×10^{16} and 1.6×10^{15} nanoparticles of 5 and 25 nm diameter respectively can pack on 1 m^2 surface area of clay. The specific surface area of clay used in calculations is $560 \text{ m}^2/\text{g}$ (Edwards and Quirk 1962). It is observed that for larger nanoparticles (25 nm) the surface coverage on clay is much smaller than with 5 nm nanoparticles (see Figure 7.14). This suggests that 25 nm particles has more sparse packing on the clay surface compared to 5 nm particles.

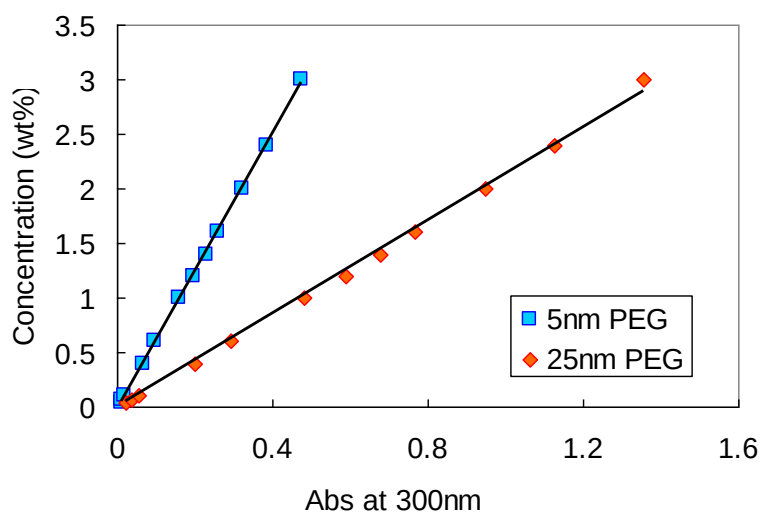


Figure 7.12- Calibration curve for 5 and 25nm diameter PEG modified nanoparticle dispersions by UV-Vis spectrophotometer.

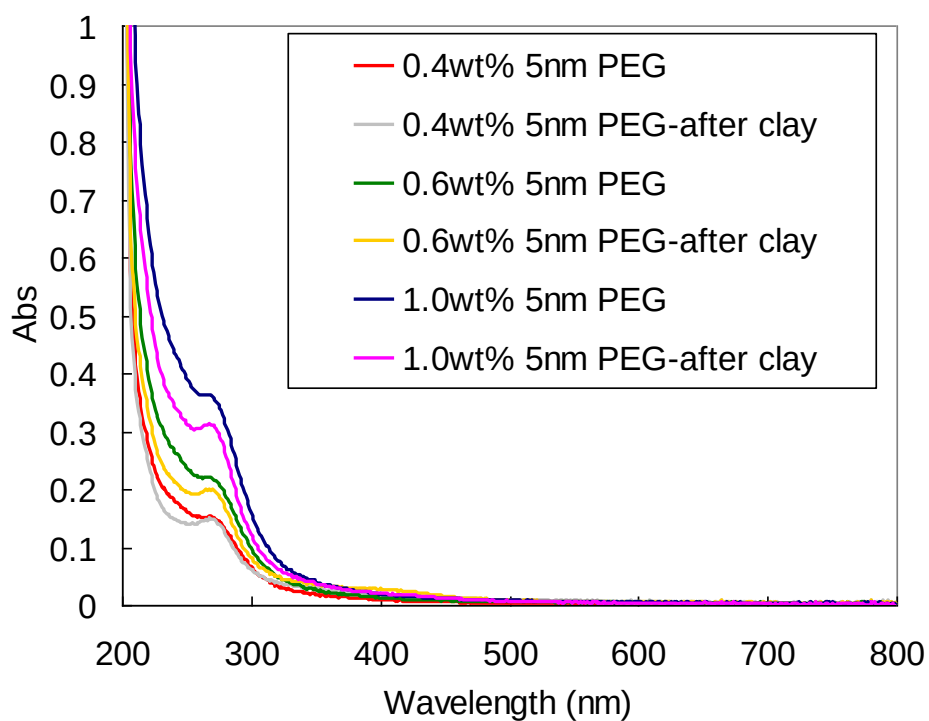


Figure 7.13- UV-Vis spectra for 5 nm PEG modified silica nanoparticle dispersions before and after in contact with clay.

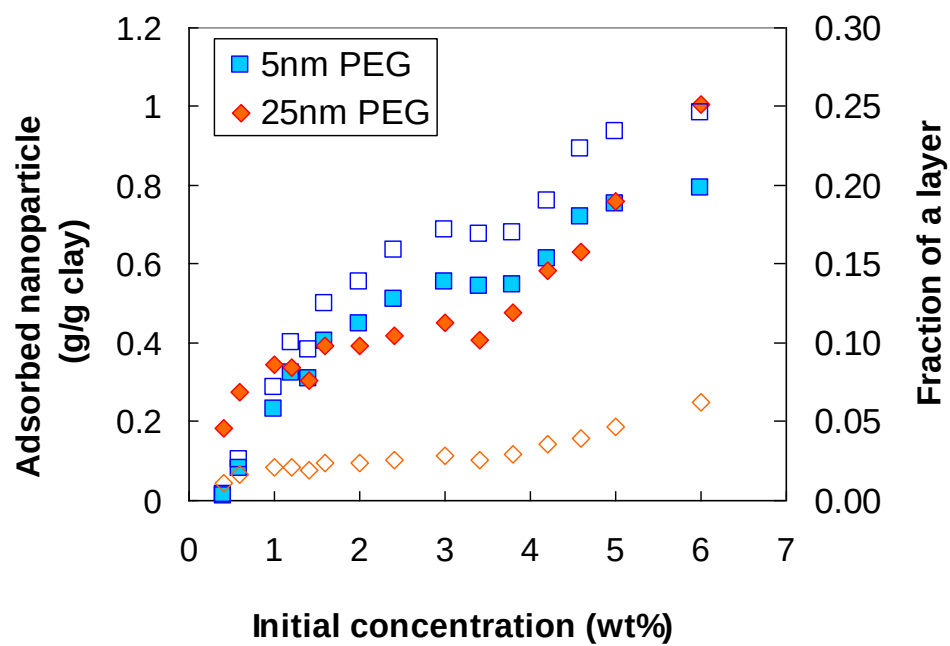


Figure 7.14- Adsorption of PEG modified silica nanoparticles on clay at 1.5wt% NaCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.

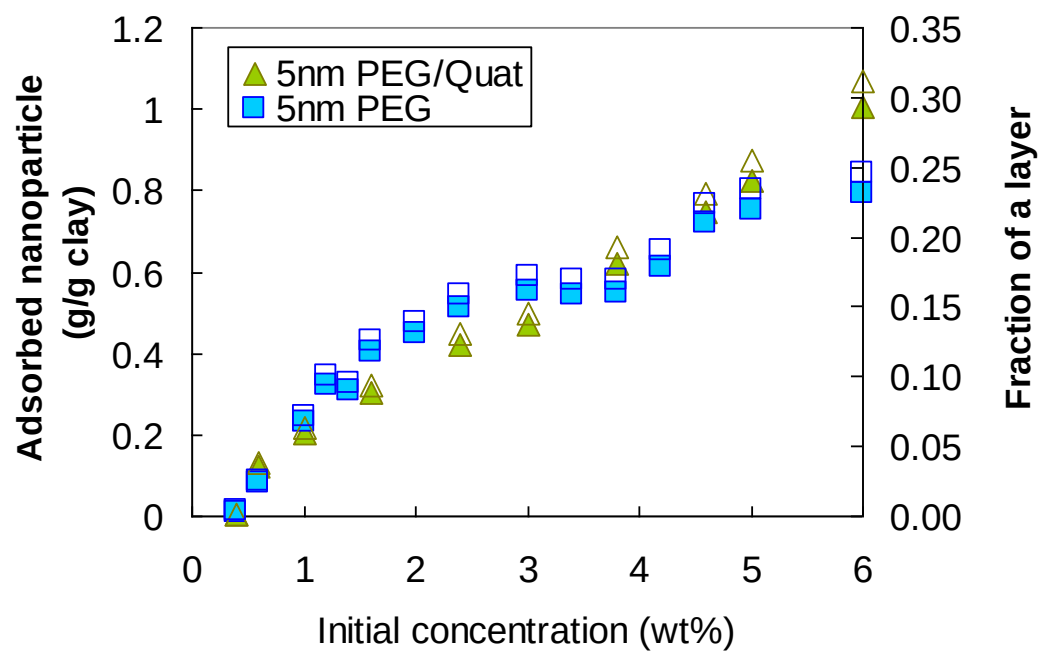


Figure 7.15- Adsorption of PEG or quat/PEG modified silica nanoparticles on clay at 1.5wt% NaCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.

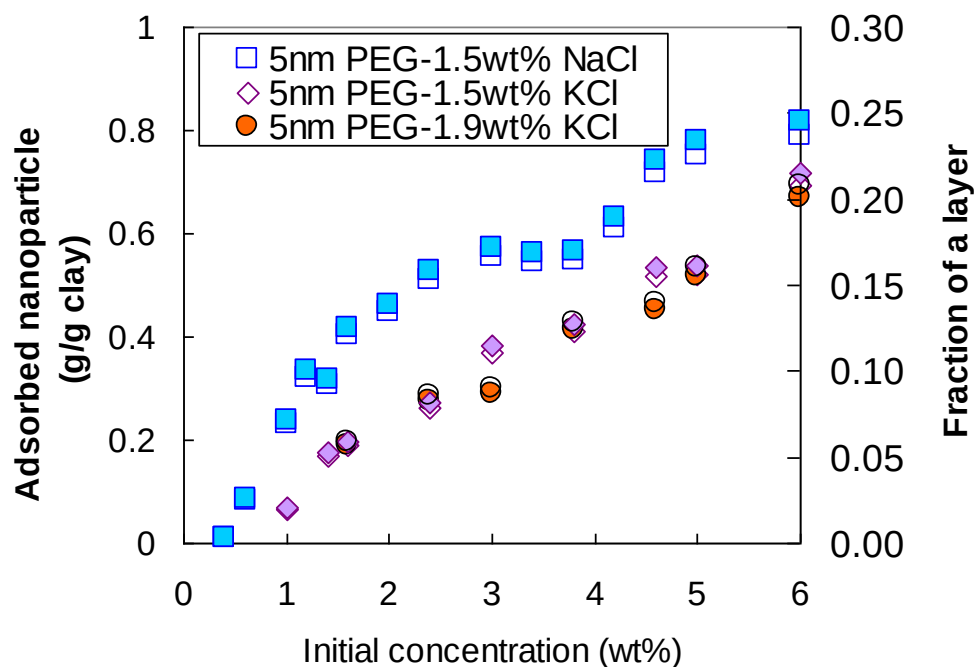


Figure 7.16- Adsorption of PEG modified silica nanoparticles on clay at 1.5wt% NaCl and 1.5 wt% KCl solution. The data with open symbols correspond to the secondary y-axis of fraction of a layer.

7.4 CONCLUSIONS

The study of clay swelling in the presence of unmodified or modified silica nanoparticles is presented by visual observations, analytical methods and adsorption isotherms. It is concluded that unmodified or sulfonate modified silica nanoparticles do not have any effect on clay swelling. However, PEG modified or quat/PEG modified silica nanoparticles decrease the extent of clay swelling. The presence of K^+ improves the effectiveness of the inhibition of clay swelling by these nanoparticles. Unmodified or sulfonate modified nanoparticles do not show any significant adsorption on clay. However, PEG or quat/PEG significantly modified nanoparticles' adsorption on clay. The

size of the nanoparticles affects the surface coverage of nanoparticles on clay. The adsorption isotherms do not level off at the concentration range of nanoparticles studied.

7.5 REFERENCES

- Anderson RL, Ratcliffe I, Greenwell HC, Williams PA, Cliffe S, Coveney PV (2010) Clay swelling - A challenge in the oilfield. *Earth-Science Reviews*, 98 (3-4):201-216.
- Billingham J, Breen C, and Yarwood J (1997) Adsorption of polyamine, polyacrylic acid and polyethylene glycol on montmorillonite: An in situ study using ATR-FTIR. *Vibrational Spectroscopy*, 14, 19-34.
- Brindley G W and Pedro G (1972) Report of the AIPEA Nomenclature Committee. *AIPEA Newsletter* No. 7, 8-13.
- Burchill S, Hall PL, Harrison R, Hayes MHB, Langford JI, Livingston WR, Smedley RJ, Ross DK, Tuck JJ (1983) Smectite-polymer interactions in aqueous systems. *Clay Miner.*, 18 :373-397.
- Cai J, Chenevert ME, Sharma MM and Friedheim J (2011) Decreasing water invasion into Atoka shale using nonmodified silica nanoparticles. Paper SPE 146979 presented at SPE Annual Technical Conference and Exhibition, Denver 30 October-2 November.
- Carroll 1959, Bulletin of the geological soc. of America, 70, 749-780.
- Civan F (2007) Reservoir formation damage: fundamentals, modeling, assessment and mitigation, Elsevier, Burlington, MA.
- Cliffe S, Dolan B and Reid P (1995) Mechanism of shale inhibition by polyols in water based drilling fluids. SPE 28960 presented at SPE Symp. Oil Field Chem., 14-17 Feb, San Antonio.
- Edwards DG and Quirk JP (1962) Repulsion of chloride by montmorillonite. *J. Colloid Int. Sci.*, 17 (9) :872-882.
- Liu S, Mo X., Sun D., Mu C. and Zhang C (2004) Swelling Inhibition by Polyglycols in Montmorillonite Dispersions. *Journal of Dispersion Science and Technology*, 25 (1):63-66.
- Luckham PF and Rossi S (1999) The colloidal and rheological properties of bentonite suspensions. *Advances in Colloid and Interface Science*, 82 (1-3):43-92.
- Norrish K (1954) The swelling of montmorillonite. *Discuss. Faraday Soc.* 18, 120-134.

- Parfitt RL and Greenland DJ (1970) The adsorption of poly(ethylene glycols) on clay minerals. *Clay Miner.* 8, 305-315.
- Quintero L (2002) An overview of surfactant applications in drilling fluids for the petroleum industry. *Journal of Dispersion Science and Technology*, 23 (1-3): 393-404.
- Reid PI, Elliott GP, Minton RC, Chambers BD and Burt DA (1993) Reduced environmental impact and improved drilling performance with water-based muds containing glycols. Paper SPE 25989SPE/EPA Exploration and Production Environmental Conference, San Antonio (TX) March 7-10
- Schechter SR (1992) Oil well stimulation, Prentice-Hall, Inc. Englewood Cliffs, New Jersey.
- Sensoy T, Chenevert ME and Sharma MM (2009) Minimizing water invasion in shales using nanonparticles. Paper SPE 124429 presented at the SPE Annual Technical Conference and Exhibition, New Orleans 4-6 October.

Chapter 8: Flow of Silica Nanoparticles in Permeable Media

The potential application of nanoparticle dispersions requires knowledge of the flow properties of these complex fluids, particularly comprehensive understanding of the rheological behavior.

The aqueous silica nanoparticle dispersions show Newtonian behavior under steady shear measurements, measured by a rheometer, as discussed in chapter 3. The viscosity of nanoparticle dispersions depends strongly on the particle concentration and that this correlation can be depicted by a unified rheological model as described in chapter 3. During flow in permeable media, the variation of shear associated with complex pore structure and the interactions between the nanoparticles and tortuous flow channels can also affect the viscosity of nanoparticle dispersion. The latter is particularly important where the concentration of nanoparticles in dispersion may change because of nanoparticle adsorption on mineral/fluid and oil/water interfaces or by mechanical trapping of nanoparticles.

In this chapter, the flow of silica nanoparticle dispersions through different permeable media is investigated. The rheological behaviors of the dispersions are compared with those determined using a rheometer. We established a correlation between the nanoparticle concentration and dispersion viscosity in porous media for various nanoparticle sizes. The effect of pore structure and shear rate are also studied. We have confirmed that the concept of effective maximum packing fraction can be applied to describe the viscosity of aqueous nanoparticle dispersions in both bulk flow and flow in porous media with high permeability and regular pore structures but not at low permeability probably because of mechanical trapping. Our work provides new insight into engineering nanoparticle rheology for subsurface applications.

8.1 INTRODUCTION

The transport of colloids in porous media is a well-established research area. Extensive work has been done to model colloidal transport in subsurface environments with applications in groundwater contamination and treatment (Biggs, *et al.* 2002; Sen, *et al.* 2003). Zhang *et al.* (2011) provided an overview of the recent developments in the application of nanotechnology for reservoir engineering and improved oil recovery. LeCoanet *et al.* (2004) studied the mobility of nanomaterials such as silica, fullerol, clusters of C₆₀ and single-wall carbon nanotubes in porous media composed of spherical glass beads. They measured the concentration of nanomaterials in the effluent using a UV-Visible spectrophotometer. They found that these nanomaterials could travel 10-14m in a sandy aquifer where the velocity of ground water is around 9m/day.

Hydrodynamic conditions have an important effect on colloid retention at the air/water interface in a microchannel and DLVO theory alone is inadequate to describe the experimental results (Lazouskaya *et al.* 2006). Non-DLVO interactions such as hydration, steric and hydrodynamic potentials must be included to better understand the colloid-air/water interface interactions (Lazouskaya and Jin 2008). Rodriguez *et al.* (2009) studied the migration of surface modified nanoparticles in sedimentary rocks. The authors observed that PEG-modified silica nanoparticles could be transported through sedimentary rocks. The retention mechanism for these nanoparticles was identified as reversible adsorption on the pore wall because of adsorption by van der Waals attraction between particles and minerals on the pore walls and desorption governed by Brownian diffusion of nanoparticles. The authors argued that the apparent viscosity measured during the flow of nanoparticle dispersions was smaller than that measured at rheometer

because of a possible slippage at the pore walls. Caldelas *et al.* (2011) furthered the study of Rodriguez *et al.* (2009) to investigate the factors governing the propagation of nanoparticles in porous media. They confirmed the findings of Rodriguez *et al.* (2009) on the retention mechanism and showed that the nanoparticles could travel several meters in porous media.

Ju *et al.* (2006) proposed a mathematical model for the migration and adsorption of hydrophilic nanoparticles through porous media. They evaluated the change in porosity, absolute permeability and relative permeability after core flooding with hydrophilic nanoparticles. Oil recovery increased by 9.3% when 2% volume hydrophilic nanoparticles were added to water. The numerical results showed that nanoparticles were retained in the pores (adsorbed on the pore walls) and the absolute permeability and porosity decreased. Relative permeability to oil increased whereas relative permeability to water decreased after injecting nanoparticles.

Gu *et al.* (2007) investigated the flow of hydrophobic nanoparticles through porous media and they proposed a slip velocity model for capillary flow and slip boundary condition. The authors experimentally observed that hydrophobic nanoparticles could adsorb on porous walls which changed the contact angle from preferentially water wet to preferentially oil wet. The core flood experiments showed that effective permeability of water increased by 47% after hydrophobic nanoparticle suspensions were injected. Sun *et al.* (2006) found that the motion of nanoparticles in the laminar flow was mainly Brownian and that the deposition of particles was independent of flow velocity. In this sense, smaller particles deposited on the wall surface more easily than large ones.

However, most previous studies of nanoparticle mobility in porous media have not taken into account the correlation between nanoparticle retention and the rheological behavior of nanoparticle dispersions. The latter is rarely found in literature. In this

chapter, the flow of silica nanoparticle dispersions through permeable media is presented systematically beginning with a high permeability pack of spherical glass beads and followed by the effect of pore structure with high permeability sand packs. The effect of pore morphology and permeability is then further investigated with sandstone and limestone cores. The concentration of nanoparticles in the effluent is compared that of conservative tracers. Then the viscosity results are given in comparison with the bulk rheology measurements presented in chapter 3. This chapter brings new insight to the understanding of the transport mechanism of nanoparticles in permeable media by using previously established knowledge of interaction of nanoparticles with minerals and the characterization of their rheology as a function of particle concentration.

8.2 MATERIALS AND METHODS

The material under study is an aqueous dispersion of silica nanoparticles. The mean diameters of the primary particles are 5 and 25 nanometers; they have an unmodified surface. The particles are monodisperse in aqueous solution. The shape of silica nanoparticles is spherical as determined by images of a scanning transmission electron microscope (STEM). The silica nanoparticles are electrostatically stabilized in an aqueous medium with a zeta potential of around -45 mV at pH = 9. Stock solutions containing 16-41% by weight silica nanoparticles were diluted with deionized water up to a desired silica concentration. In the absence of electrolyte, the silica nanoparticles were well dispersed and did not aggregate as determined by size measurements.

The materials used to prepare the unconsolidated permeable media were glass beads of 100-140 mesh size (0.10-0.15 mm). The sand used was Ottawa quartz sand of size 100-140 mesh (0.10-0.15 mm). Berea sandstone and French limestone were the

consolidated permeable media studied in this work. The glass beads and sand were cleaned with distilled water, dried in an oven set at 100 °C for a couple of days and sieved using several meshes stacked on top of each other, ranging from 40 to 170, for 20 minutes under the agitation of a sieve shaker. The grains collected at 100-140 mesh were used to pack the glass column. A flow adapter and glass column of 2.5 cm diameter and 30 cm long were used for the preparation of both the glass beads and sand pack. Glass columns of 4.8 cm diameter were used to store the fluid to be injected. A pump delivered mineral oil to the glass column displacing the injected fluid to the permeable media. The pressure drop across the permeable media was measured with differential pressure transducers connected in parallel to the inlet and outlet. Low (0-1 psid) and mid range (0-10 psid) transducers were used. A bleeding line was connected to the pressure transducer to displace any air bubbles trapped in the tubes before each experiment started. The effluent was collected in a fraction collector in 15 ml plastic centrifuge tubes. A schematic presentation of the flow loop is in Figure 8.1 and pictures of the experimental setup are in Figures 8.2-8.4. An epoxy coated core was also used to study the flow of nanoparticles in permeable media. Cores of 2.54 cm diameter and 15 cm long were drilled from large blocks of clean sandstone and limestone. Then the cores were dried in an oven at 100 °C for a couple of days. The dried cores were then coated with epoxy in a 1.5 in diameter polycarbonate tubing and the epoxy was cured for 24 hours.

The glass bead pack, sand pack and the epoxy coated cores were put under vacuum and saturated with deionized (DI) water. The effective pore volume was calculated from the difference in weight of saturated and dry sand/glass bead pack or core. The saturated permeable media was then connected to the flow loop and a tracer test of 0.05 wt% NaCl was conducted. The concentration of NaCl in the effluent was analyzed by a conductivity probe. The calibration curve is presented in Figure 8.5. From

the concentration of NaCl in the effluent, the pore volume (PV) was calculated. In Figure 8.6 the normalized concentration, C_{norm} , in Equation 8.1 is presented as function of injected fluid. Then 10-20 pore volumes of DI water were injected to clean the permeable media from tracer. Once the conductivity of the effluent reached that of the DI water, injection of nanoparticle dispersion was started. The concentration of the nanoparticles in the effluent was determined using a calibration curve built by a UV-Vis spectrophotometer. The data from pressure transducers was collected with LabVIEW.

$$C_{norm} = \frac{C - C_{res}}{C_{inj} - C_{res}} \quad (8.1)$$

where C is the concentration of the tracer or nanoparticle in the effluent, C_{res} the concentration in the resident fluid and C_{inj} is the concentration in the injected fluid.

From the concentration of NaCl in the effluent, the pore volume (PV) was calculated and compared with that determined based on the mass balance method. The permeability, k , was determined using Darcy's law. Then 20 pore volumes of DI water were injected to clean the permeable media from tracer. Once the conductivity of the effluent reached that of the DI water, injection of nanoparticle dispersion was started. The concentration of the nanoparticles in the effluent was determined using a calibration curve built by a UV-Vis spectrophotometer. The data from pressure transducers was collected with LabVIEW. Note that the above procedure was not applied for the Berea core because the injection of low salinity water causes swelling of clay as further discussed below. The permeability of the sandstone core was determined using air.

Darcy's law (Equation 8.2) was also used to determine the viscosity of nanoparticle dispersion over a wide range of flow rates. The flow rates were set on the

pump to 150 ml/hr x 50%, 100% and 400 ml/hr x 50%, 70% and 90%. However, the actual flow rates were determined using a graduated glass test tube at the fraction collector and measuring the time required to fill 4 ml of liquid. These flow rates correspond to shear rates of 16, 32, 42, 60 and 68 s⁻¹ as determined by Equation 3.2. The use of different flow rates is to verify if all the nanoparticle dispersions exhibit Newtonian behavior.

$$\frac{Q}{A} = \frac{k}{\mu} \frac{\Delta P}{L} \quad (8.2)$$

where k is the permeability; Q is the volumetric flow rate; A the cross-sectional area of the permeable media; μ the viscosity of the fluid and ΔP , the pressure drop across length L of the glass bead pack.

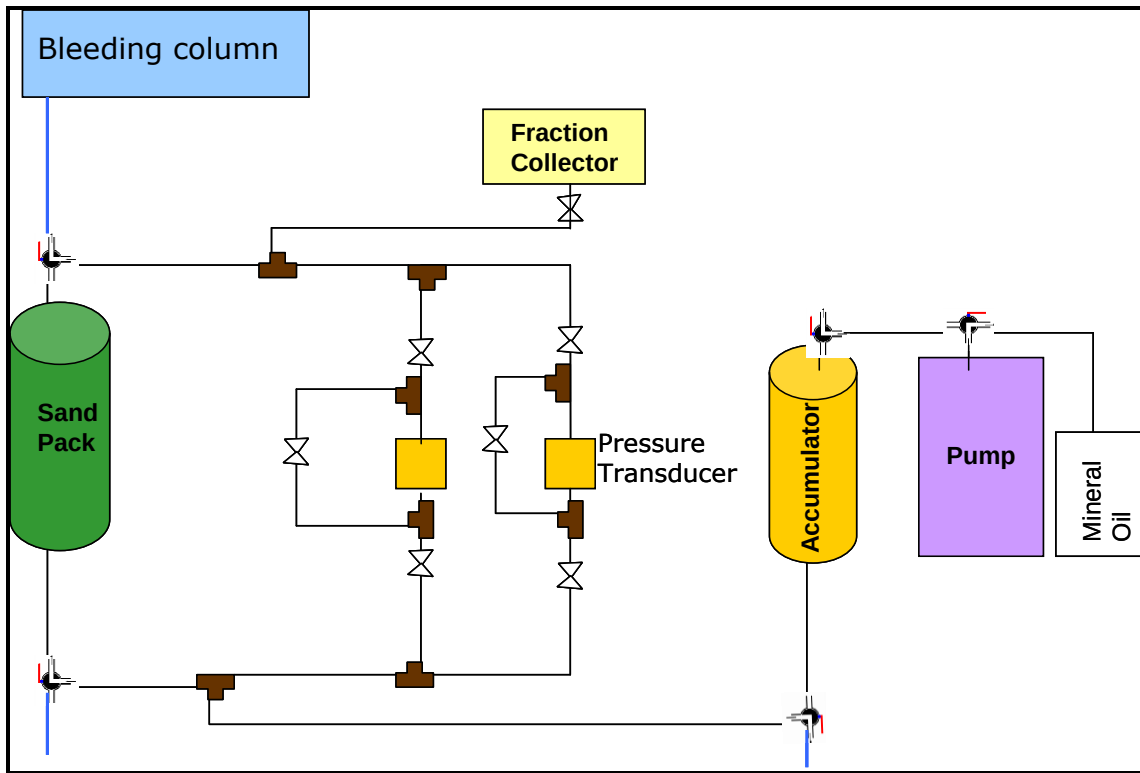


Figure 8.1- Schematic presentation of the experimental setup for determination of viscosity of nanoparticle dispersions in porous media.



Figure 8.2- Picture of the flow loop with glass beads packed in a glass column of 2.5 cm diameter and 18 cm long.

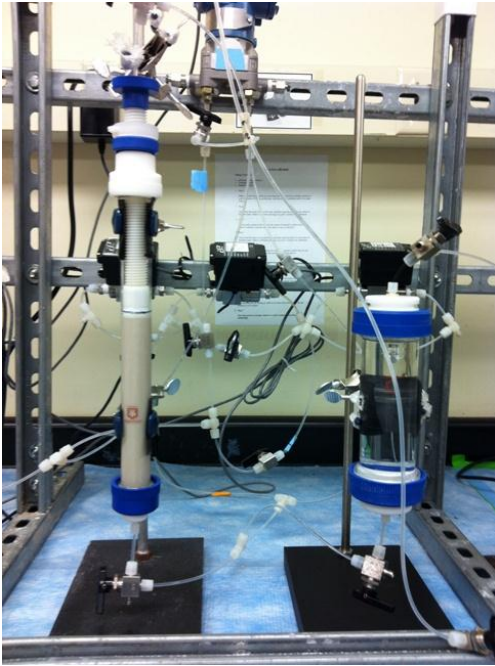


Figure 8.3- Picture of sand pack flow loop.

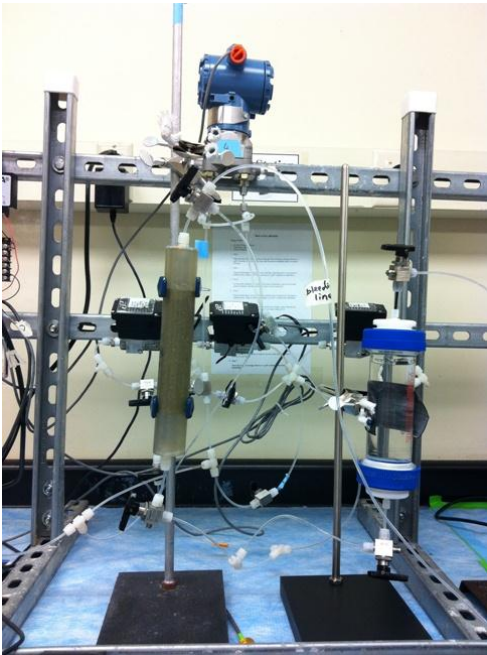


Figure 8.4- Picture of epoxy coated Berea sandstone core.

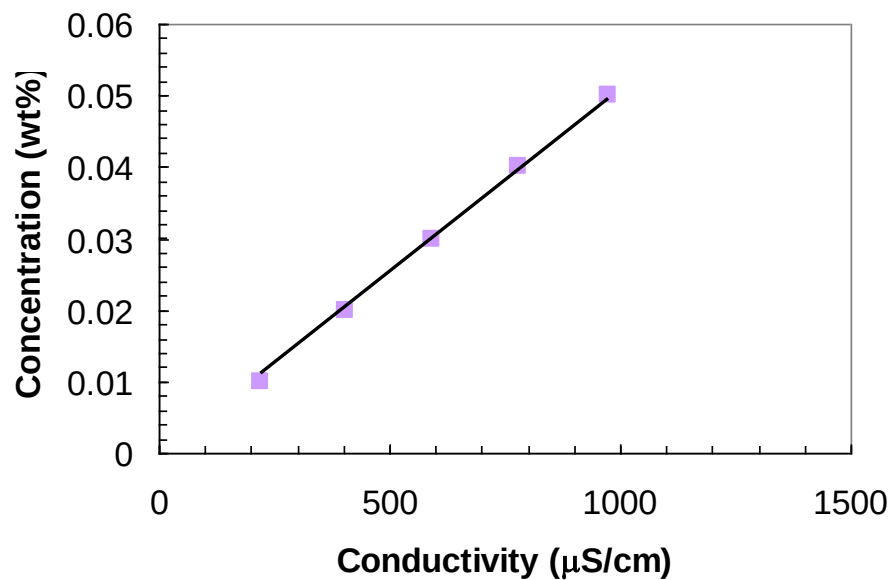


Figure 8.5– Calibration curve for NaCl concentration using a conductivity probe.

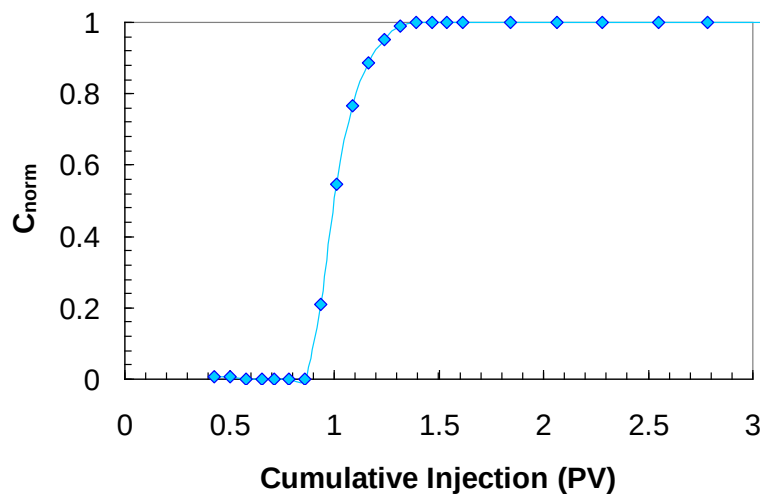


Figure 8.6– Normalized concentration of the tracer vs. cumulative injection through sand pack. The line connecting the data points is for visual purpose.

8.3 RESULTS AND DISCUSSION

The results of nanoparticle flow through unconsolidated (glass bead and sand packs) and consolidated permeable media (sandstone and limestone) are presented in this section. Table 8.1 shows the measured porosity and brine permeability of the unconsolidated (glass bead and sand packs) and consolidated media (sandstone and limestone cores). The mass balance based and tracer methods gave almost the same porosity value for all the media. The grain size of the glass beads and the sand were similar (100-140 mesh); therefore, it is not surprising that the permeability of the sand pack was also found to be around 7 D with a porosity of 43%. For the limestone core, the permeability was calculated to be 54 mD with a porosity of 25%. The sandstone had an air permeability of 500 mD. However, this value decreased to 12.1 mD during the tracer test because the concentration of NaCl in the injected liquid was much lower than the critical concentration required to inhibit clay swelling (Civan 2007). The dimensions of the porous media studied are also given in Table 8.1.

Table 8.1- Properties of porous media studied

Porous Media	Permeability* (D)	Porosity (%)	Diameter (cm)	Length (cm)
Glass bead pack	7.0	40.3	2.50	18.0
Sand pack	6.7	43.5	2.50	17.3
Limestone	0.054	24.9	2.45	15.2
Sandstone	0.105**	12.6	2.49	14.6
*Permeability to brine at 0.05 wt% NaCl; **Permeability to brine at 3 wt% NaCl				

The permeability was calculated as 7 D from the slope of the line in Figure 8.7 obtained from the injection of DI water for glass bead pack.

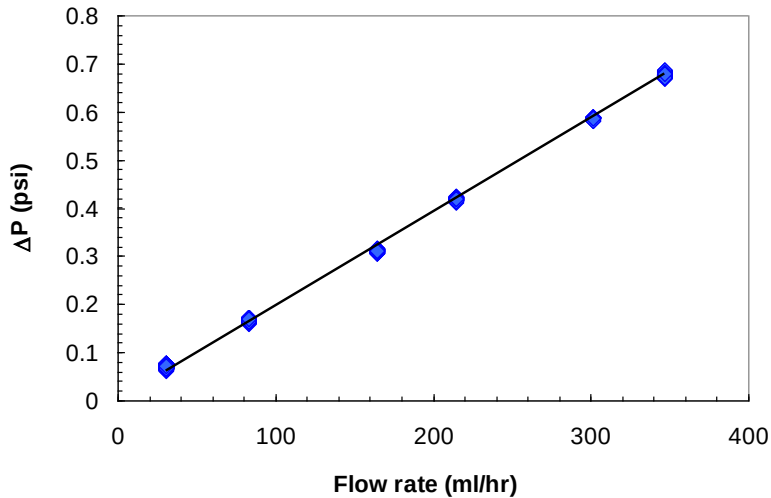


Figure 8.7- Pressure drop across the glass bead pack.

Figure 8.8 shows the respective effluent concentration profiles for the tracer and the 1 wt% of 5 nm unmodified nanoparticle dispersion in the glass bead pack. It appears from the shape of the normalized concentration profile in Figure 8.8 that the dispersivity of the pack is very small. The two profiles collapse on the same trend, indicating insignificant retention of nanoparticles in the glass bead pack. This result is consistent with our recent findings of the interaction of unmodified and surface modified silica nanoparticles with mineral surfaces (see chapter 6). Based on batch adsorption experiments with the silica nanoparticles onto quartz and calcite surfaces, we concluded that significant adsorption of unmodified silica nanoparticles on quartz and calcite surfaces was not observed under the experimental conditions studied.

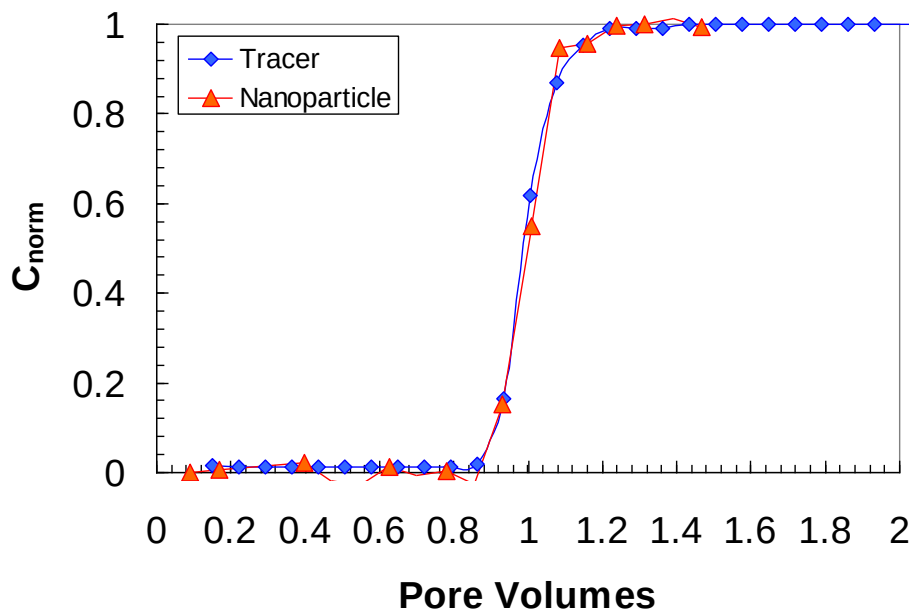


Figure 8.8- Normalized concentration vs. cumulative injection in terms of pore volume (PV) for tracer (NaCl) and nanoparticle dispersion in flow through glass bead pack.

For all nanoparticle concentrations used in the glass bead pack flow experiment, the pressure drop reached a constant value once the effluent nanoparticle concentration was equal to the injected concentration. This steady state pressure drop was used to calculate the viscosity of the nanoparticle dispersion. The results are shown in Figure 8.9 for 1, 10 and 16 wt% 5 nm and 35 wt% for 25 nm unmodified nanoparticle dispersions. The pressure drop increased linearly with the flow rate in accordance with Darcy's law, confirming Newtonian behavior of the dispersions over the range of nanoparticle concentration.

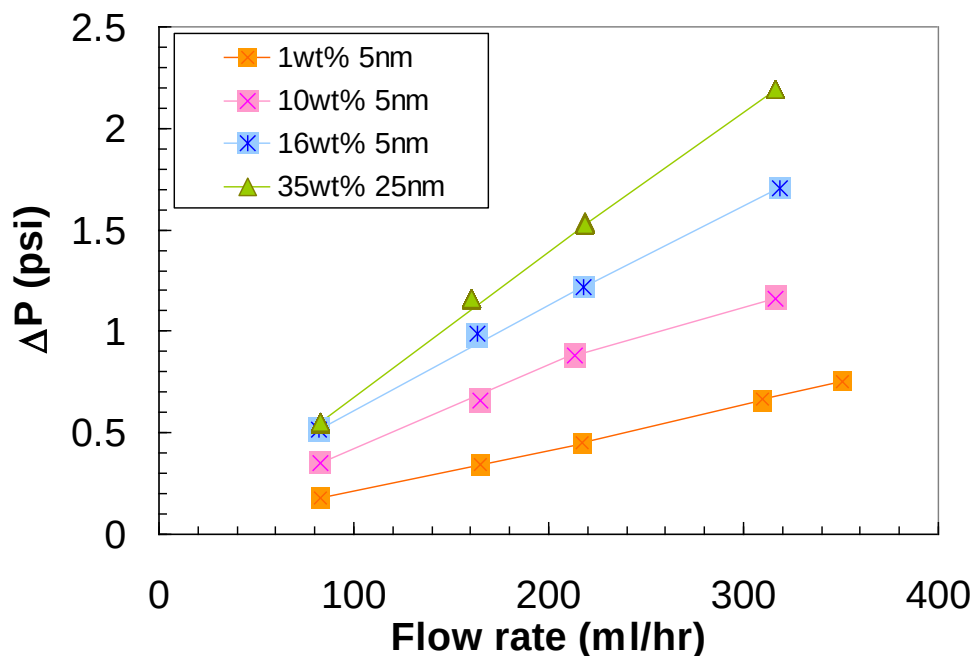


Figure 8.9- Pressure drop across the glass bead pack vs. flow rate for 5nm and 25nm unmodified nanoparticle dispersions.

For the sand pack, only the flow of 1, 16.17 wt% 5nm and 35 wt% 25 nm unmodified nanoparticle dispersions were studied. The pressure drop as a function of volumetric flow rate for these three nanoparticle dispersions is shown in Figure 8.10. Note that the same linear dependency of pressure drop on flow rate was observed as it was shown for the glass bead pack. For both glass bead pack and sand pack, the permeability after cleaning the packs stayed the same as it was before the injection of nanoparticles.

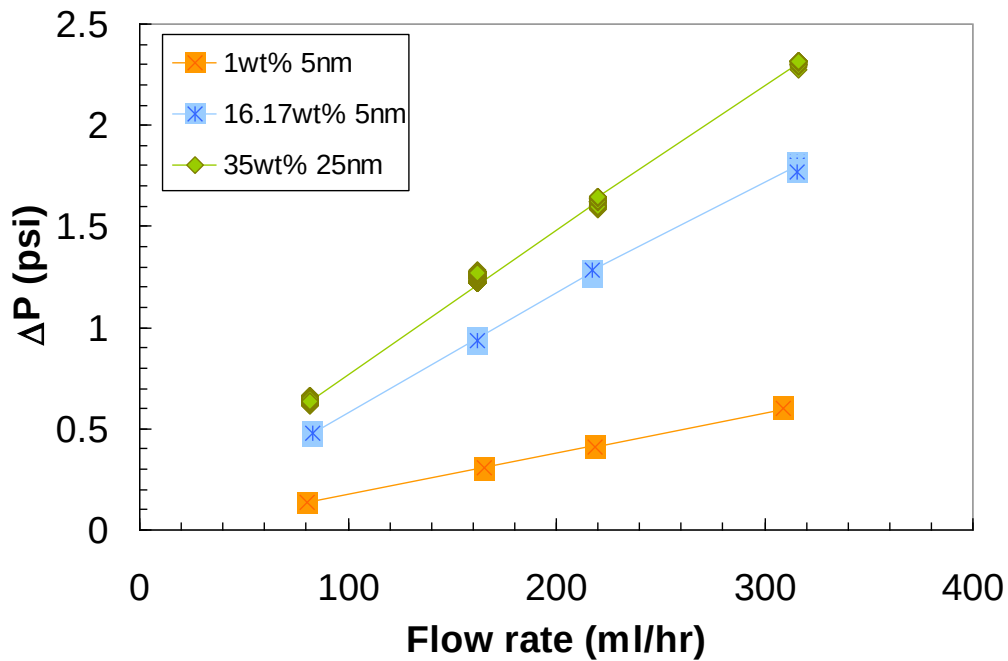


Figure 8.10- Pressure drop across the sand pack vs. flow rate for 5nm and 25nm unmodified nanoparticle dispersions

A limestone core with properties shown in Table 8.1 was used as a consolidated permeable medium to study the effect of permeability on the rheology of nanoparticle dispersions. The respective pressure drops for steady flow of water with and without 1 wt% 5 nm particles at different flow rates are shown in Figure 8.11, which are very similar to those observed in the unconsolidated media above (Figures 8.9 and 8.10). After these two experiments, the core was flooded with water for more than 20 pore volumes and the original permeability of 54 mD was not changed.

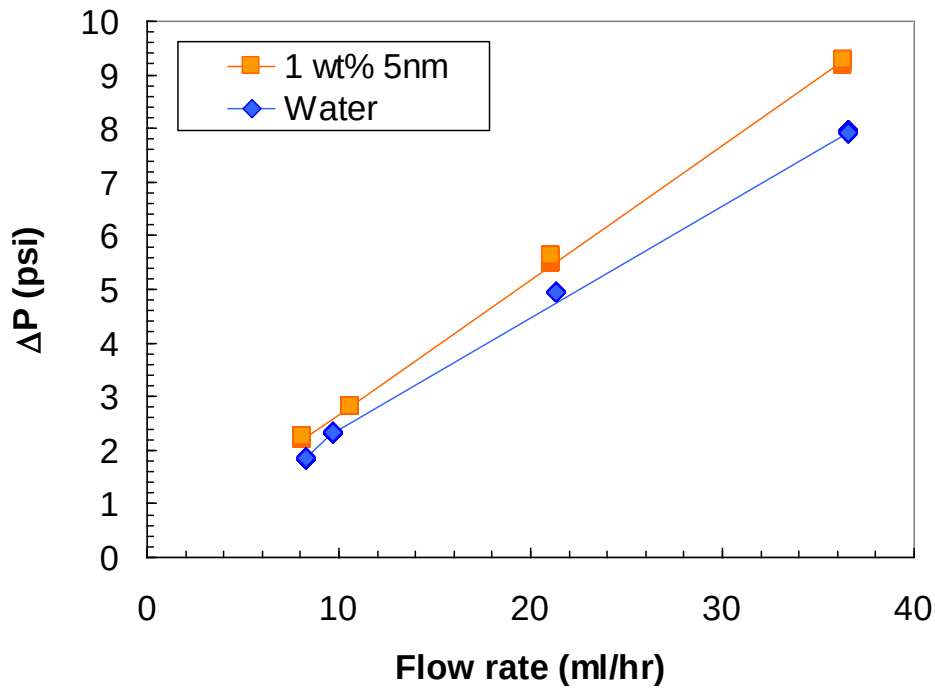


Figure 8.11- Pressure drop as a function of flow rate for 1 wt% 5 nm unmodified nanoparticle dispersion and for water.

Based on our bulk rheology experiments (see chapter 3), it was found that at a given particle size and concentration, silica nanoparticle dispersions exhibit a Newtonian behavior within the shear rate range studied ($1\text{--}200\text{ s}^{-1}$). This range of shear rate covers that used in the core flood experiments in this work according to the correlation in Equation 3.2 between the average velocity and the equivalent shear rate for flow in porous media. Therefore, the Newtonian behavior observed in our bulk rheology experiments is still valid for flow through porous media with different pore morphologies and over a wide range of permeability (54 mD to 7000 mD). However, the bulk viscosity of nanoparticle dispersion is a strong function of particle concentration and size. This relationship can be predicted by our scaled viscosity model presented in chapter 3.

In this chapter, the viscosity ratio, η_r , of the nanoparticle dispersions flowing through porous media is calculated from the ratio of the slopes shown in Figures 8.9, 8.10 and 8.11 divided by that from water runs. Then, the effective maximum packing fraction was calculated as discussed in chapter 3. We previously showed that the reduced volume fraction of silica nanoparticles captures the effect of size and surface type on the viscosity and the proposed model predicts well the viscosity of aqueous dispersion of silica particles whose sizes range from 5 to 500 nm. Therefore, we used the same method to compare the viscosity of nanoparticle dispersions obtained in this section to those from bulk rheology measurements. The results are presented in Figure 8.13. The symbols in grey scale are those obtained from bulk rheology measurements (see chapter 3) and the symbols in color are those calculated from the flow through porous media experiments. The unified model proposed in Equation 3.9 was able to collapse all the data from the bulk rheology measurements and flow in porous media experiments onto a single curve.

However, the retention of nanoparticle can influence the interpretation of the rheological behavior of the nanoparticle dispersion in porous media if it induces a significant variation of particle concentration in flow. This effect could be demonstrated on a low permeability rock such as the sandstone studied in this work. The pressure drops during the injection of 0.05 wt% NaCl solution for 4 hours followed by 1 wt% 5 nm particle dispersion are shown in Figure 8.12. For the brine injection, the pressure drop increases sharply in the first 20 minutes and then much more gradually. The pressure drop after 4 hours is about 20 psi which is significantly higher than the expected value of 2.3 psi for 105 mD at 20 ml/hr. Note that the permeability of 105 mD was determined using a 3 wt% NaCl solution. This salt concentration is sufficiently higher than the critical concentration (about 1.5 wt% NaCl from Civan (2007)) below which significant swelling of clay occurs. Therefore, the higher pressure drop during the injection of 0.05

wt% NaCl solution is due to the clay swelling induced reduction of the sandstone core permeability from 105 mD to 12 mD. As a consequence, when the injection of 1 wt% 5nm unmodified nanoparticle dispersion started; the pressure drop across the core increased sharply (Figure 8.12). The injection of the nanoparticle dispersion is stopped after 60 minutes because the pressure drop reached the maximum of the transducer. Very little effluent was produced which indicted that nanoparticles had been trapped mechanically and plugged the core. The filtration of nanoparticle can induce a large gradient of nanoparticle concentration in flow, which in turn influences the rheological behavior of flow according to Equation 3.9. The interplay between nanoparticle retention and rheological variation determine the mobility of nanoparticles in porous media. Therefore, we believe that the viscosity model (Equation 3.9) is still valid in the presence of nanoparticle retention and very useful in identification and evaluation of the significance of retention mechanisms separate from the effect of dynamic rheology.

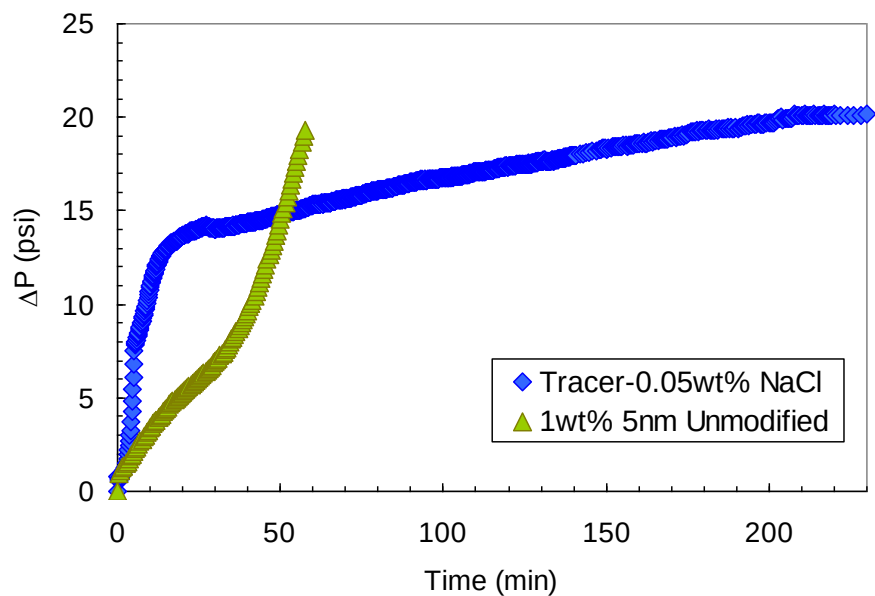


Figure 8.12- Pressure drop profile in time for a tracer (0.05 wt% NaCl) and 1 wt% 5 nm unmodified nanoparticle dispersion flowing through sandstone core.

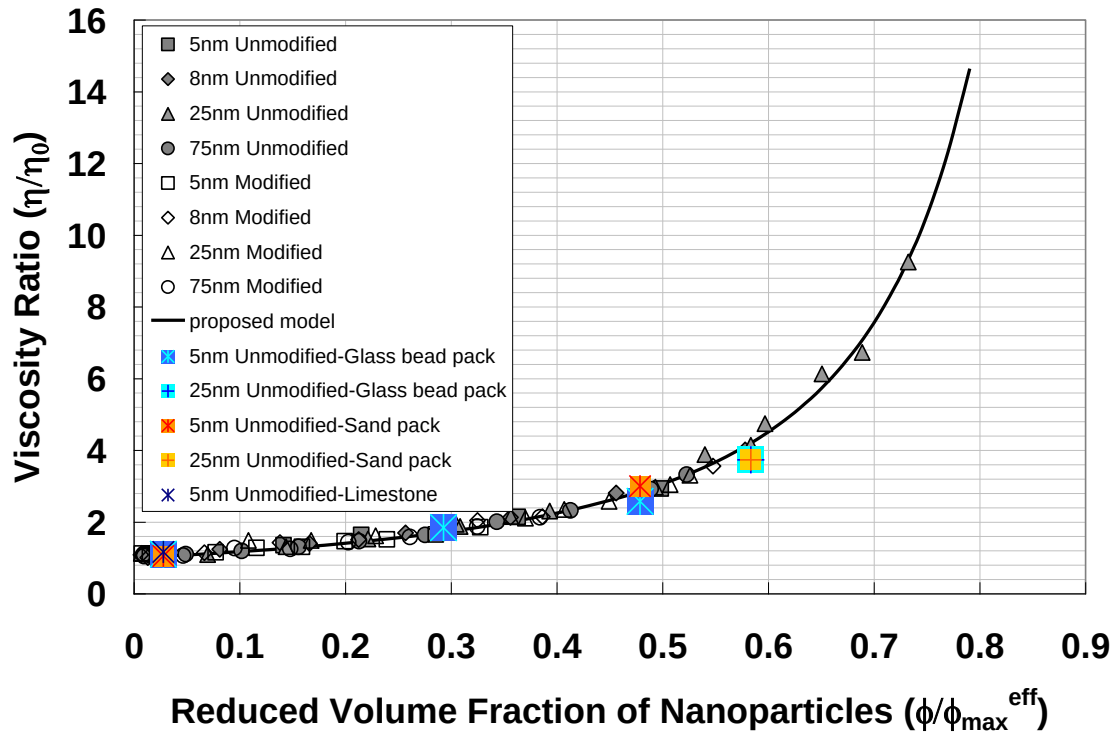


Figure 8.13- Viscosity ratio as a function of volume fraction of silica nanoparticles of various sizes (5, 8, 25 and 75 nm) and two different surface types (unmodified and sulfonate coated). The volume fractions are normalized to the corresponding effective maximum packing fraction. All the data collapsed onto a single curve that is well represented by the unified model. The results obtained from glass bead, sand pack and limestone follow the same curve as the bulk rheology data.

8.4 CONCLUSIONS

The transport properties of nanoparticle dispersion was studied in unconsolidated (glass bead and sand pack) and consolidated (limestone and sandstone cores) porous media. Unmodified nanoparticles showed no significant retention in high permeability glass bead and sand packs as well as limestone core as the tracer and nanoparticle showed the same effluent concentration profiles. The nanoparticle dispersions studied exhibit a

Newtonian behavior. The viscosity of unmodified nanoparticles in porous media was in very good agreement with those determined using a rheometer. The viscosity depends strongly on the particle concentration and this relationship can be described with a scaled rheological model. Based on our model and experimental results, the effect of slippage at the pore walls that may cause a detectable difference in viscosity between rheometer and porous media was not observed in our work.

We established a correlation between the nanoparticle concentration and dispersion viscosity in porous media for various nanoparticle sizes. The pore structure showed no observable effect on the viscosity for high permeability media, such as glass bead and sand packs. For lower permeability limestone, the measured viscosity of nanoparticle dispersion also agrees well with the model for 1 wt% nanoparticle concentration. However, nanoparticles were retained in the sandstone core as a consequence of clay swelling. This effect and its interaction with the dynamic viscosity of nanoparticle dispersion will be further investigated in a future work.

8.5 REFERENCES

- Biggs MJ, Humby SJ, Buts A and Tuzun U (2003) Explicit numerical simulation of suspension flow with deposition in porous media: influence of local flow field variation on deposition processes predicted by trajectory methods. *Chemical Engineering Science* 58: 1271 – 1288
- Caldelas F., Murphy M, Huh C and Bryant SL (2011) Factors Governing Distance of Nanoparticle Propagation in Porous Media. SPE Production and Operations Symposium, Oklahoma City. SPE 142305.
- Civan F. (2007) Reservoir Formation Damage: Fundamentals, Modeling, Assessment and Mitigation, Elsevier, Burlington, MA.
- Gu, C.-Y., Di, Q.-F. and Fang, H.-P. 2007. Slip Velocity Model of Porous Walls Absorbed by Hydrophobic Nanoparticles SiO₂. *J. Hydrodynamics* **19** (3): 365-371.

- Ju, B., Fan, T. and Ma, M. 2006. Enhanced Oil Recovery by Flooding With Hydrophilic Nanoparticles. *China Particuology* **4** (1): 41-46.
- Lazouskaya, V. and Jin, Y. 2008. Colloid Retention at Air-Water Interface in a Capillary Channel. *Colloids Surface A* in press.
- Lazouskaya, V, Jin, Y. and Or, D. 2006. Interfacial Interactions and Colloid Retention Under Steady Flows in a Capillary Channel. *J. Colloid Interface Sci.* **303** (1): 171-184
- LeCoanet, H.F., Bottero, J-Y. and Wiesner, M.R. 2004. Laboratory Assessment of the Mobility of Nanomaterials in Porous Media. *Environ. Sci. Technol.* **38** (19): 5164-5169.
- Rodriguez E, Roberts MR, Yu H, Huh C and Bryant SL (2009) Enhanced Migration of Surface-Treated Nanoparticles in Sedimentary Rocks. SPE Annual Technical Conference and Exhibition, New Orleans. SPE 124418.
- Sen TK, Shanbhag S and Khilar KC (2004) Subsurface colloids in groundwater contamination: a mathematical model. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **232**: 29–38.
- Sun, L., Lin, J-Z. and Bao, F-B. 2006. Numerical Simulation on the Deposition of Nanoparticles Under Laminar Conditions. *J. Hydrodynamics* **18** (6): 676-680.
- Thielmann F (2004) Introduction into the characterisation of porous materials by inverse gas chromatography. *Journal of Chromatography A*, 1037: 115–123.
- Zhang T. et al. (2011) Engineered Nanoparticles as Harsh-Condition Emulsion and Foam Stabilizers and as Novel Sensors. Offshore Technology Conference, Houston. OTC 21212.

Chapter 9: Retention of Nanoparticles at Oil/Water Interface

The retention of silica nanoparticles at water/crude oil interface is studied in this chapter. Silica nanoparticles with three different surfaces (unmodified, surface modified with anionic (sulfonate), or nonionic (PEG) surfactant) are used. Interfacial tension (IFT) measurements provide us the means to investigate the adsorption of silica nanoparticles at the crude oil/water interface. Unmodified nanoparticles do not change the IFT of crude oil/water interface. However, the presence of sulfonate or PEG modified nanoparticles in solution lower the IFT. Moreover, the presence of unmodified or surface-modified nanoparticles in solution does not alter the contact angle of a crude oil droplet on clean calcite (water-wet) or aged calcite plate (oil-wet). We also carried out flow experiments with PEG modified silica nanoparticles through a glass bead pack. In the absence of crude oil, the nanoparticles act like a conservative tracer with insignificant interaction with the glass beads. This result is in agreement with our previous work on the adsorption of silica nanoparticles on mineral surfaces. However, at the residual oil saturation of 12%, PEG modified silica nanoparticles are retained at crude oil/water interface, as shown by the concentration history. These results are also in agreement with IFT and the contact angle measurements carried out in this study.

9.1 INTRODUCTION

The interaction of nanoparticles with liquids (water/oil interface) or solids (mineral surfaces) determines the mechanisms of retention of nanoparticles in reservoir rocks. Previously, we investigated the adsorption of silica nanoparticles onto quartz and calcite surfaces and at the decane/water interface (Metin et al. 2011). Insignificant adsorption of unmodified, sulfonate or PEG modified silica nanoparticles on quartz and

calcite surface was observed. The type and amount of surface treatment attached to silica nanoparticles determined the extent of the change in interfacial tension (IFT) of decane/water interface (Metin et al. 2011). Similarly, Lee et al. (2006) observed that the modification methods and chain length of modifying agents on silica nanoparticles determined the structure of particle layering at the air/water interface in the presence of a cationic surfactant. Binks and Whitby (2005) studied the effect of precipitated silica nanoparticles on stabilizing oil-in-water emulsions. The emulsion stability was controlled by changing the pH or particle charge. The authors observed that adding cationic surfactants improved the emulsion stability. A comprehensive literature review on nanoparticles at fluid interfaces was presented by Bresme and Oettel (2007).

In this work, we investigate the retention of silica nanoparticles at water/crude oil interface. Silica nanoparticles with three different surfaces (unmodified, surface modified with anionic (sulfonate), or nonionic (PEG) surfactant) are used. Interfacial tension (IFT) measurements provide us the means to investigate the adsorption of silica nanoparticles at the crude oil/water interface. The effect of pH was investigated with IFT and phase behavior measurements of crude oil/water (or nanoparticle dispersion). The flow of nanoparticles in glass bead packs was also studied in the presence of residual oil.

9.2 MATERIALS AND METHODS

Interfacial tensions were measured with a surface tension instrument by using pendant drop method (Rame-Hart). An oil droplet was formed at the end of a J-needle in an optical glass cell filled with 100 ml of aqueous solution (water or nanoparticle dispersion). Then the drop was imaged with a video camera. The interfacial tension was calculated using DROPimage software by analyzing the shape of the drop and the

evolution of IFT in time was monitored. On the basis of the Young-Laplace equation describing the drop profile of pendant, DROPimage software calculated the surface tension from digitized picture data (DROPimage). The same glass cell was used for contact angle measurement. A calcite plate was inserted on a small stand made of Teflon tubing immersed in water or a nanoparticle dispersion. Then a droplet of oil was deposited underneath the calcite. The image of the droplet was captured by the camera and DROPimage software was used to determine the contact angles. The oil used in the study presented in this chapter was Yates crude oil.

A phase behavior study was carried out using crude oil and nanoparticle dispersions. 2 ml of aqueous phase was brought in contact with 1 ml of oil in glass pipettes. Then pipettes were sealed using a torch and the samples were shaken by hand for 2 minutes. They were put in an upright position and let settle. The mixing procedure was repeated a couple times a day for 2 days. Visual observations and volume measurements were taken after a week, at which point the samples were shaken once again by hand for 2 minutes. The samples were then allowed to settle and measurements were retaken every week for 1 month.

The flow experiments were conducted in the flow loop as described in chapter 8. The permeable media used in this section was composed of 100-140 mesh size glass beads. The glass bead pack was prepared as described in chapter 8 and porosity and permeability were determined accordingly. The concentration of nanoparticles in the effluent was determined using a conductivity probe and a UV-Vis spectrophotometer. Calibration curves for 5 nm PEG modified nanoparticle dispersions are presented in Figure 9.1.

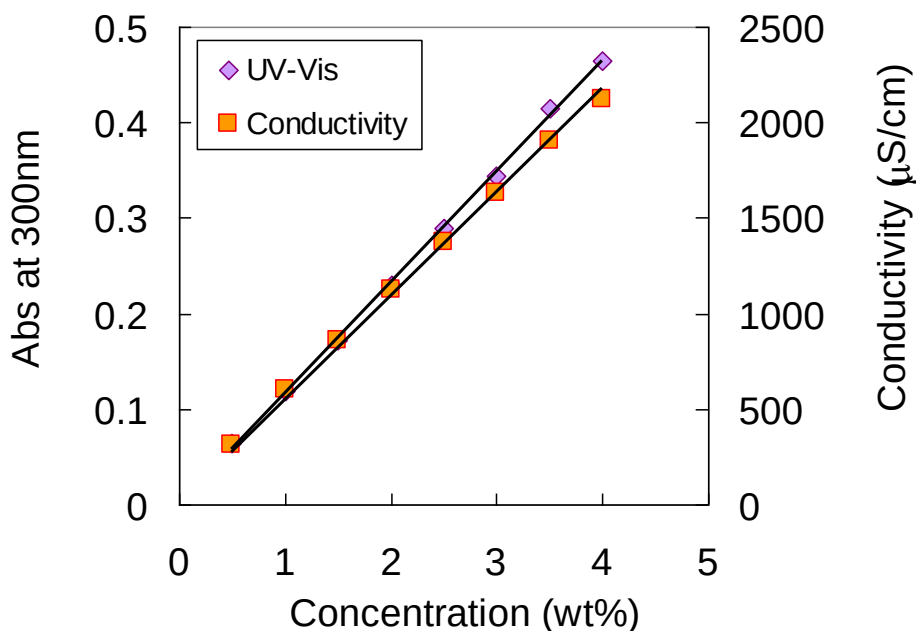


Figure 9.1– Calibration curve for 5nm PEG coated nanoparticle dispersions by a using conductivity probe and a UV-Vis spectrophotometer.

9.3 RESULTS AND DISCUSSION

The interaction between nanoparticles and crude oil was investigated by interfacial tension (IFT) measurements. Figure 9.2 presents the pictures of the oil droplet and how its shape changes as the PEG modified nanoparticle concentration changes. The change in IFT as a function of nanoparticle concentration at pH 7 is also shown graphically in Figure 9.3. The change in IFT of water/crude oil from 22.4 to 12 mN/m in the presence of 1 wt% 5 nm PEG modified nanoparticles in dispersion shows adsorption of nanoparticles at the interface. The concentration of nanoparticles at the interface was calculated using Equation 6.6. The adsorption isotherms are given in Figure 9.4. The effect of pH was also studied. The change in IFT as a function of nanoparticle

concentration at pH 9 is shown in Figure 9.3. In the absence of nanoparticles, the IFT of crude oil/water at this pH was 6.1 mN/m. As nanoparticle concentration increased, IFT decreased further. However, it reached a plateau around 3 mN/m for concentrations > 10 wt%. A similar behavior was observed with nanoparticle dispersions at pH 7. This observation can also be made with the plateau in adsorbed concentration in Figure 9.4. The results show that a monolayer coverage of PEG modified nanoparticles at the interface following the discussion in chapter 6 on the adsorption of PEG modified nanoparticles at water/decane interface. If the results from Gibbs' equation were in terms of nanoparticle/nm² then 10-25 layers of nanoparticles at the interface would occur, which is not likely because the nanoparticles on these layers far from the interface wouldn't feel the presence of water/oil interface. This would also mean an aggregation of nanoparticles but PEG modified nanoparticle dispersions are colloidal stable (see chapter 2).

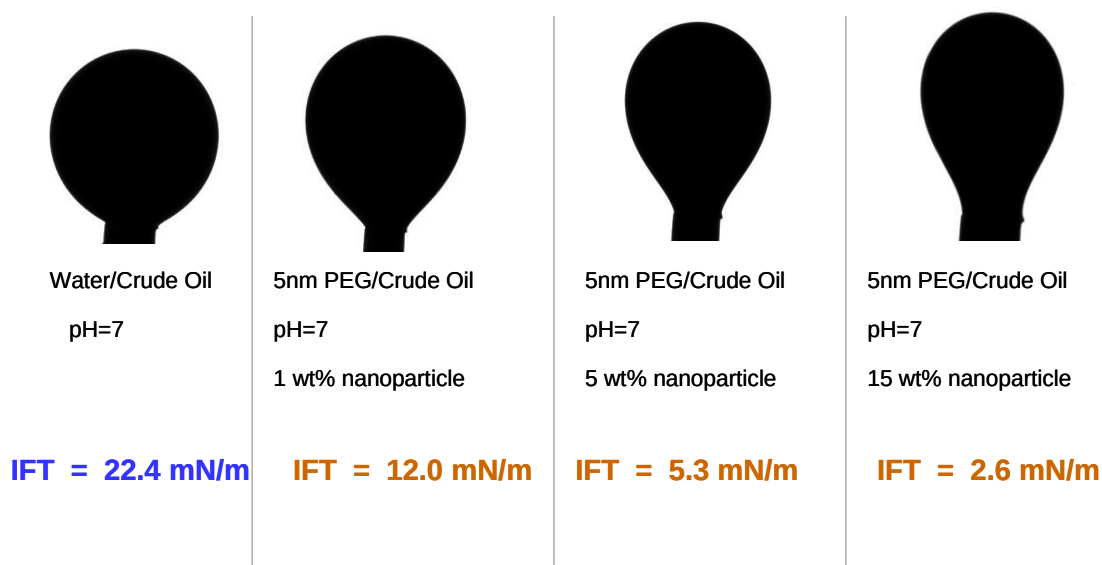


Figure 9.2– Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 7 and there is no background electrolyte. Picture of an oil drop at the tip of the J-needle immersed into water or silica nanoparticle dispersion is shown for different nanoparticle concentrations.

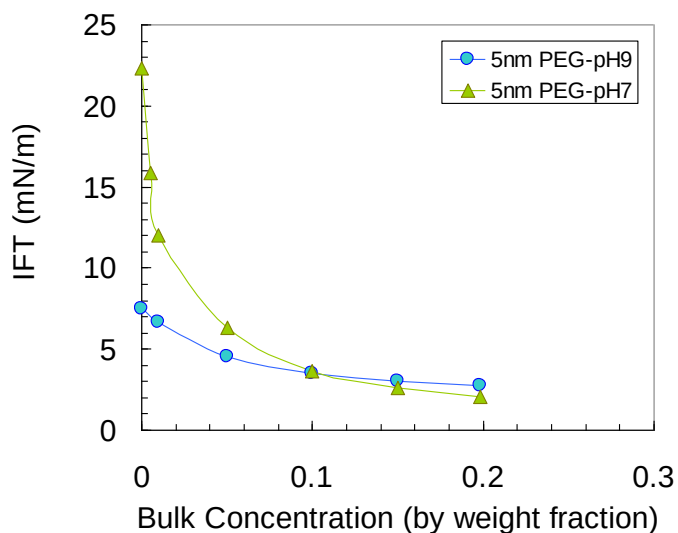


Figure 9.3– The change in IFT of crude oil/water as a function of 5 nm PEG modified nanoparticles at pH 7 and 9.

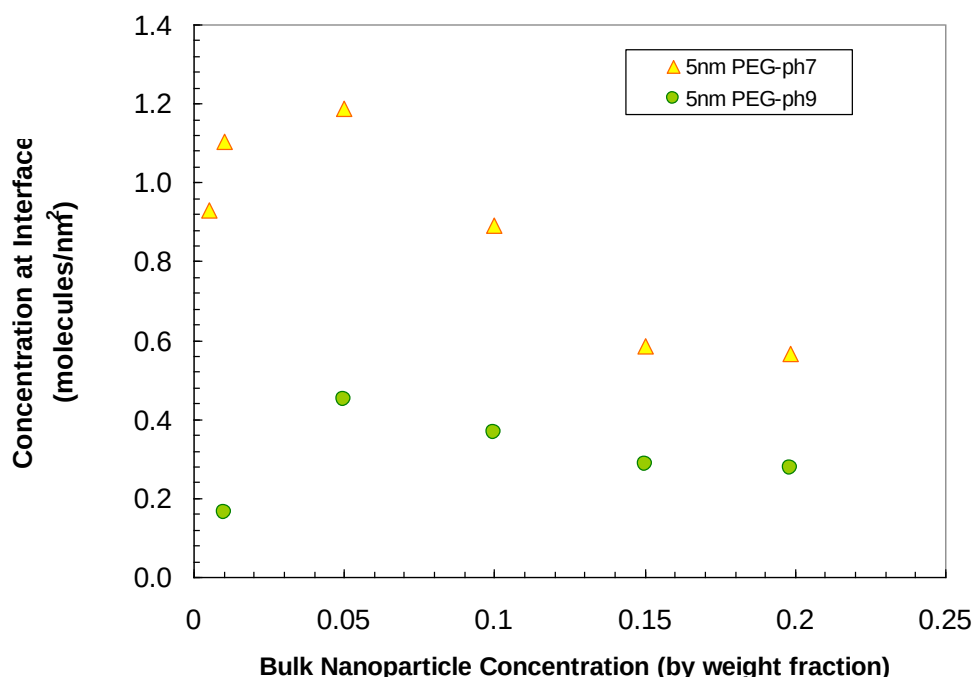


Figure 9.4– The adsorption of nanoparticles at the crude oil/water interface. The equivalent molecules of PEG concentration at the interface as a function of bulk nanoparticle concentration at pH 7 and 9

The temporal variation of IFT of water/oil in the presence of 5nm PEG modified nanoparticles was also determined. This is particularly important for flow experiments where nanoparticles flow through a permeable media in the presence of oil. Choosing an appropriate transport model depends on how fast the adsorption of nanoparticles on the interface takes place. In Figure 9.5, the change in IFT as a function of time is plotted for various nanoparticle concentrations. The IFT first decreased sharply as nanoparticles adsorb at the interface until it reached an equilibrium value. A similar behavior was observed by Serrien et al. (1992) for the adsorption of proteins. The diffusion process of proteins was very fast. The authors argued that the IFT change observed experimentally was the reorganization of molecules at the interface. They described that process Equation 9.1.

$$\gamma = \gamma_{eq} + (\gamma_0 - \gamma_{eq})e^{-t/\tau} \quad (9.1)$$

where τ is the characteristic time for the reorganization process, γ_0 is the initial surface tension, γ_{eq} the equilibrium surface tension and t is the time. We determined the characteristic time and equilibrium value of IFT for 5 nm PEG nanoparticles. Figure 9.6 shows how the characteristic time and equilibrium value of IFT depend on the nanoparticle concentration. As the nanoparticle concentration increases in the bulk phase the characteristic time also increases. This may indicate that the interaction between PEG modified silica nanoparticles are attractive, which is why it becomes more difficult for these particles to move to the water/oil interface. However, the adsorption rate of nanoparticles should increase with bulk concentration, resulting in a reduction in the characteristic time. This might not be captured in our experiment because the measurement time might be relatively longer than the characteristic time. In this sense, the secondary characteristic time defines transient IFT observed for high nanoparticle concentration. Jeribi et al. (2002) observed an increase in IFT in time between a toluene solution of asphaltenes and an aqueous solution of surfactant. The authors argued that this phenomenon indicates the presence of transfer across the interface. Ferrari et al. (1997) studied the adsorption kinetics of alkylphosphine oxide at the water/hexane interface. They observed a steep minimum and a subsequent leveling off at a certain value in the dynamic IFT curves in the case of aqueous solution drop of alkylphosphine oxide immersed in hexane. The solubility of alkylphosphine oxide in hexane was very large. The authors argued that the minimum corresponded to a maximum in the amount adsorbed at the interface. After the minimum had been passed, the IFT increased and reached a final value which depended on the distribution coefficient, the initial surfactant

bulk concentration in the drop and the volume ratio of the two phases. The authors did not observe such behavior in the dynamic IFT curves for the case where hexane drop was immersed into the aqueous solution. The authors argued that the relative magnitude of surfactant fluxes in water and oil phase was responsible for the shapes of IFT curves. A minimum was observed for a larger surfactant flux in oil than in aqueous phase. On the other hand, a monotonic adsorption was observed at the liquid/liquid interface in the case of the larger surfactant flux in water than in oil phase.

Under some conditions such fluxes could produce hydrodynamic instabilities at the interface resulting in macroscopic IFT oscillations (Linde and Schwartz 1979). The driving force for the instability is $\frac{\Delta\gamma}{\Delta c} \frac{\Delta c}{\Delta x}$. We have seen such variations in IFT especially at large nanoparticle concentrations suggesting that PEG modified nanoparticles transfer into the oil. The equilibrium is reached faster at smaller nanoparticle concentrations. We observed macroscopic oscillations of the volume of the oil drop especially at large nanoparticle concentrations (≥ 10 wt %) in aqueous phase. Figure 9.7 shows how the volume of the drop and the IFT varies over time

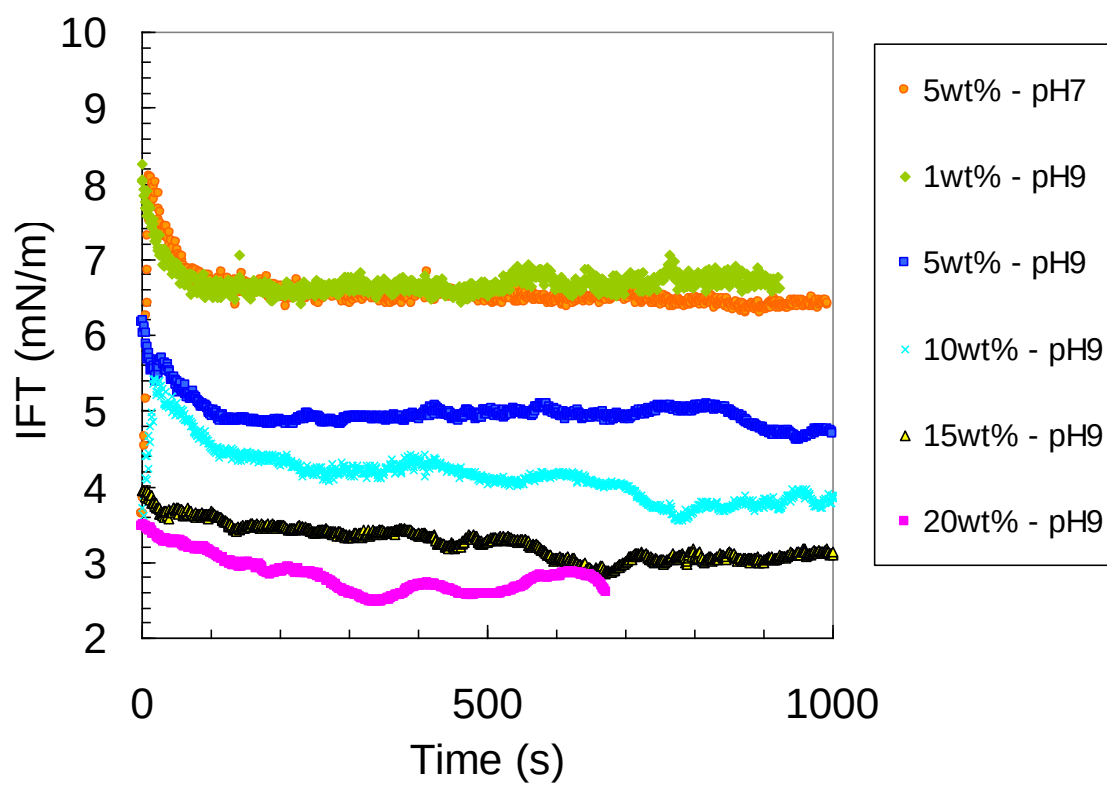


Figure 9.5– The change in IFT of crude oil/water with time in the presence of 5 nm PEG modified nanoparticles at pH 7 and 9.

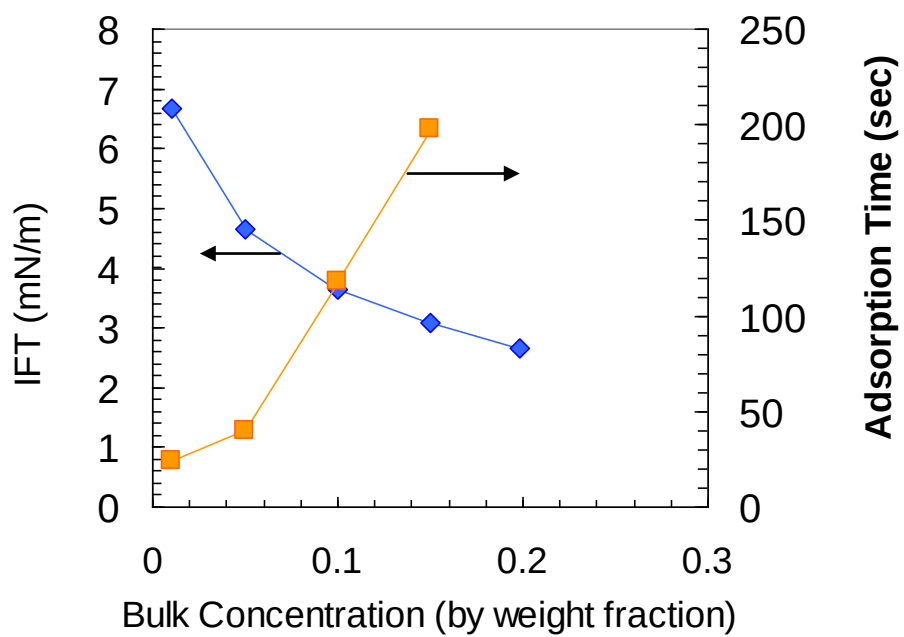


Figure 9.6— The variation of IFT and adsorption time as a function of 5 nm PEG modified nanoparticle concentration in the bulk phase at pH 9.

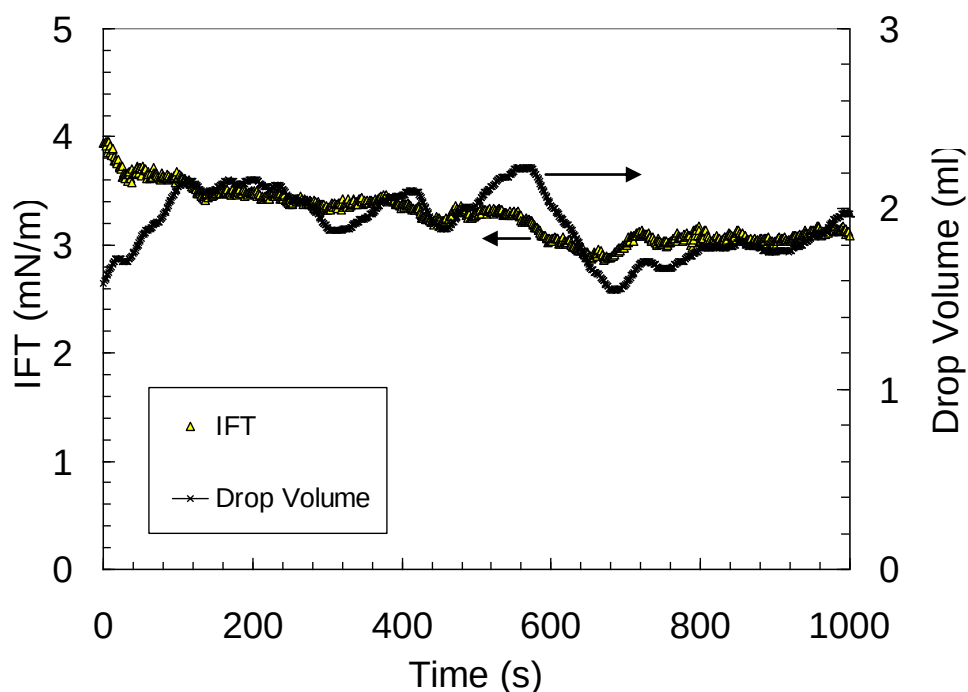


Figure 9.7– The change in IFT of crude oil/water and volume of oil drop used in the measurements in time for 5 nm PEG modified nanoparticles at pH 9.

The phase behavior of crude oil and water (or nanoparticle dispersions) was conducted in sealed glass pipettes as discussed in the previous section. In Figure 9.8, oil and water phase behavior at pH at different NaCl concentrations are shown. The samples did not show any middle phase (or Winsor type III microemulsion) and oil blobs were attached to glass wall of the pipette in aqueous phase. However, in the presence of 5 wt% PEG modified nanoparticles, there were no oil blobs attached to the glass wall in the aqueous phase (see Figure 9.9). Note that the IFT changes from 22.4 to 5.3 mN/m in the presence of nanoparticles. It seems that nanoparticles help clean the walls of the pipettes from oil. The effect of pH on phase behavior was also studied. As discussed above, increasing pH from neutral to 9 reduces IFT to 8 mN/m. The glass pipettes in Figure 9.10 shows the phase behavior of water at pH 9 at various NaCl concentrations. At this low

IFT, there were no oil blobs attached to the walls of the pipettes as observed in the presence of nanoparticles at pH 7. In the presence of 5 wt% PEG modified nanoparticles at pH 9, a middle phase was observed (see Figure 9.12). The change in volume of the middle phase is presented in Figure 9.13 as a function of NaCl concentration. The presence of a middle phase indicates that in the presence of PEG modified nanoparticles, soap was generated. It is accepted that acids present in the crude oil react with the alkaline solution to produce in situ surfactants which lower the water/oil interfacial tension. The acid partition from the oil in the aqueous phase and the presence of alkali causes the acids dissociation. The ionized acid forms soap with the sodium ions present in the aqueous phase. This soap partitions into the oil phase and causes the surface concentration to reach a maximum and then drop to its equilibrium value (Chatterjee and Wasan 1998).

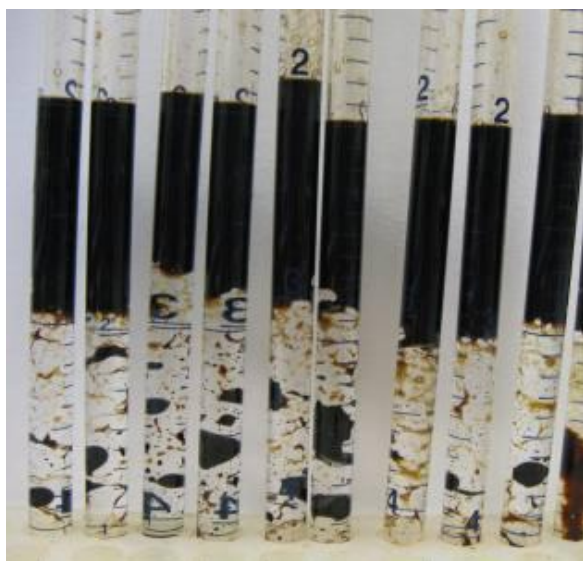


Figure 9.8– Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5. The initial pH of aqueous phase is 7.

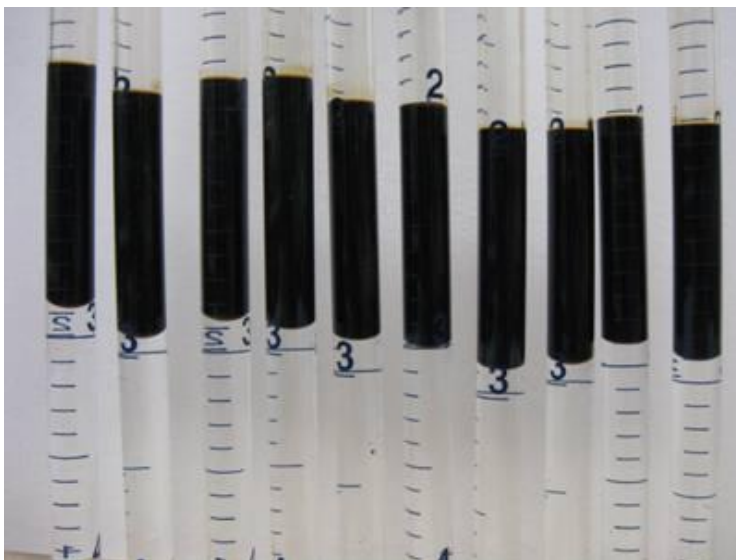


Figure 9.9– Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The initial pH of aqueous phase is 7 and the concentration of 5 nm PEG-modified nanoparticles is 5 wt% in aqueous phase.

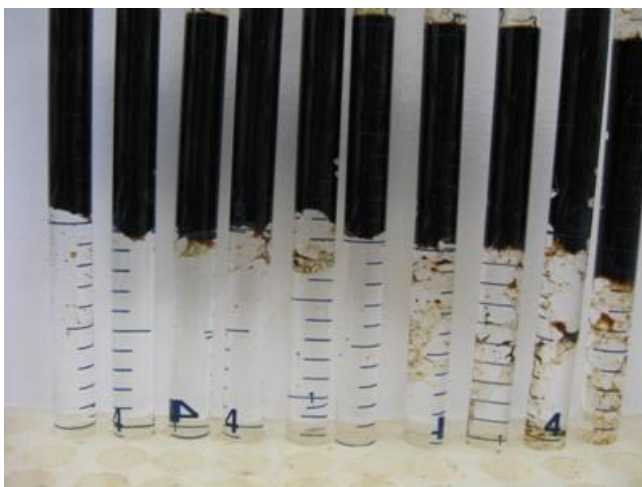


Figure 9.10– Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The initial pH of aqueous phase is 9.

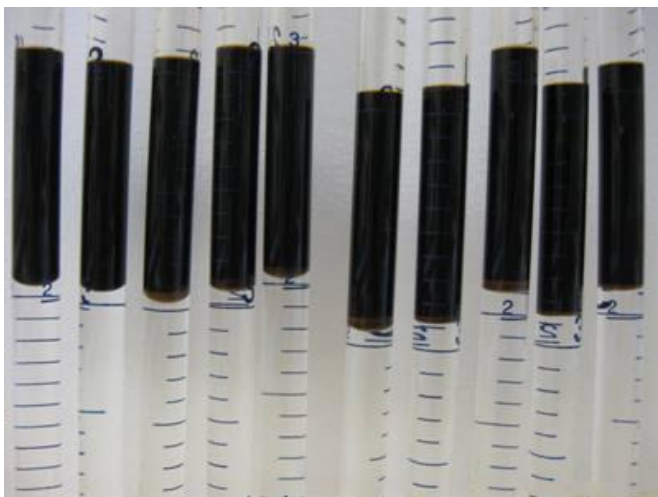


Figure 9.11– Phase behavior as a function of NaCl concentration. WOR=2:1, 1 month settling at 25 °C. NaCl (wt%) from left to right :0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0. The initial pH of aqueous phase is 9 and the concentration of 5 nm PEG modified nanoparticles is 5 wt% in aqueous phase.

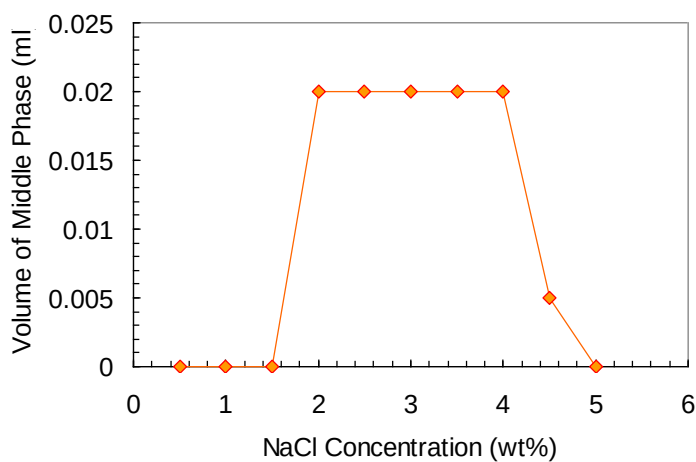


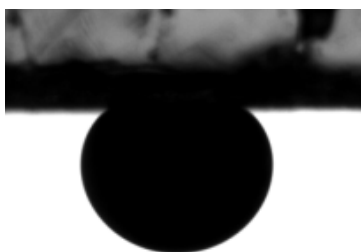
Figure 9.12– Volume of middle phase as a function of NaCl concentration. The initial pH of aqueous phase is 9 and the concentration of 5 nm PEG modified nanoparticles is 5 wt% in aqueous phase.

The effect of nanoparticles on the contact angle of a crude oil drop on calcite immersed in an aqueous solution was also investigated. We chose calcite because more than 60% of world's oil reserves are in carbonate reservoirs (Schlumberger 2008) most of which are mixed wet or preferentially oil wet. The alteration of reservoir wettability from preferentially oil wet or mixed wet towards water wet increases the relative permeability to oil, and thus improves oil recovery by water flooding (Owens and Archer 1971). Surfactant aggregates, which can be characterized as soft nanoparticles, have been extensively studied as effective wettability modifiers. However, most of them exhibit relatively low tolerance to divalent ions and salinity (Tweheyo et al. 2006; Zhang et al. 2006). Other types, high performance surfactants, greatly lower oil/water interfacial tension but do not favor capillary driven imbibition during water flooding (Hirasaki and Zhang 2004; Seethepalli et al. 2004; Abidhatla and Mohanty 2006). Recent advances in nanoparticle engineering have indicated a great potential for the use of nanoparticles as a more robust wettability modifier under broader reservoir conditions than conventional soft nanoparticles.

Here, clean calcite plates were used to determine the effect of nanoparticles on the contact angle of a crude oil droplet. The experimental procedure was presented in the previous section in detail. The results show that the calcite plate was water-wet in water at pH 9 and in the presence of unmodified or modified nanoparticles in water at same pH (see Figure 9.13). Then, we used aged calcite plates in the same crude oil at 60 °C for 1 week. The results in Figure 9.14 show that the aged calcite plate is strongly oil-wet and introducing 5 wt% 5 nm PEG nanoparticles did not change the wettability of the calcite to water-wet. The samples were allowed to equilibrate for a day and the contact angle measurements were repeated.



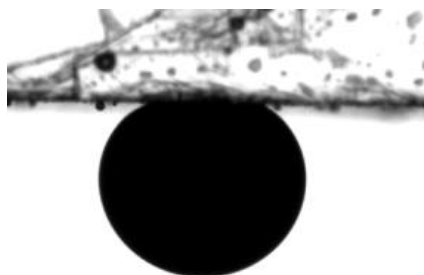
Water at pH 9
Water wet, $\theta=24^\circ$



5nm Sulfonate modified at pH 9
Water wet, $\theta=28^\circ$

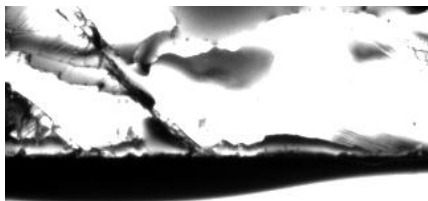


5nm Unmodified at pH 9
Water wet, $\theta=41^\circ$

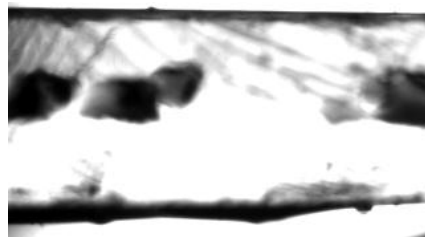


5nm PEG modified at pH 9
Water wet, $\theta=25^\circ$

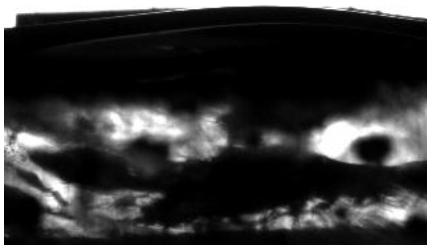
Figure 9.13– Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 9 and there is no background electrolyte.



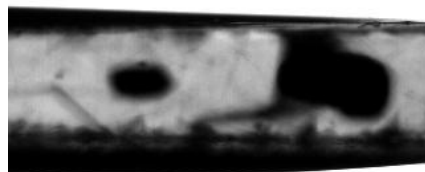
Water at pH9
Oil wet, $\theta=180^\circ$



5nm Unmodified at pH9
Oil wet, $\theta=180^\circ$



5nm Sulfonate modified at pH 9
Oil wet, $\theta=180^\circ$



5nm PEG modified at pH 9
Oil wet, $\theta=180^\circ$

Figure 9.14– Interfacial tension (IFT) measurements for nanoparticle dispersions/crude oil. The aqueous nanoparticle dispersions are at pH 9 and there is no background electrolyte.

From batch experiments of IFT, phase behavior and contact angle we moved to dynamic measurements. Glass bead pack with permeability of 7 D as described in chapter 8 was saturated with crude oil and then flooded with water at pH 7 without any background electrolyte until residual oil saturation was reached. A tracer test of aqueous solution of 0.05 wt% NaCl at pH 7 was injected to determine the residual oil saturation. Then the glass bead pack was flooded with DI water for several pore volumes until the conductivity of effluent reaches that of DI water. The injection of 5 wt% 5nm PEG modified nanoparticles started immediately after the water injection. The flow rates of water, tracer and nanoparticle dispersion are kept the same at 160 ml/hr to eliminate the effect of mobilization of oil because of hydrodynamic force. The effluent was collected to

determine the concentration of tracer and nanoparticle as a function of pore volume injected. A picture of the glass bead pack is shown in Figure 9.15 at the end of water flood. The dark spots are residual oil.

We did not observe any oil recovery for the case of nanoparticle injection. The normalized concentration, $C_{norm} = \frac{C - C_{res}}{C_{inj} - C_{res}}$, is plotted as a function of cumulative injection in terms of pore volume (PV) in Figure 9.16. In the absence of oil, both the tracer and nanoparticle dispersion show same profile as discussed in chapter 8. This result is consistent with our previous findings, showing that the nanoparticles do not adsorb on to glass (silicate) and act as a conservative tracer. The concentration profile of the tracer in the presence of oil shows that the residual oil saturation was 12 % which agrees well with the calculations from the material balance of injected and produced oil. In the presence of oil, PEG modified nanoparticles adsorb at the water/residual oil interface as shown with IFT measurements. Hence, the shape of the normalized concentration curve for nanoparticles is different from that in the absence of oil. Although nanoparticles are retained at the oil/water interface, decreasing the IFT from 22.4 mN/m to 7 mN/m, we did not observe any oil recovery under the conditions as described above. Note that to displace residual oil, a critical value of capillary number must be reached; $N_{Ca}^* = \frac{u\mu_w}{\gamma_{ow}} > 10^{-5}$, where u is the Darcy velocity, μ_w is the viscosity of aqueous phase and γ_{ow} is the IFT of water or nanoparticle dispersion/oil. For our experiments, N_{Ca}^* is 4×10^{-6} for water and 10^{-5} for 5wt% 5nm PEG modified nanoparticle dispersions at pH 7 without any background electrolyte concentration. Therefore our observation of indiscernible oil recovery is supported by theory.

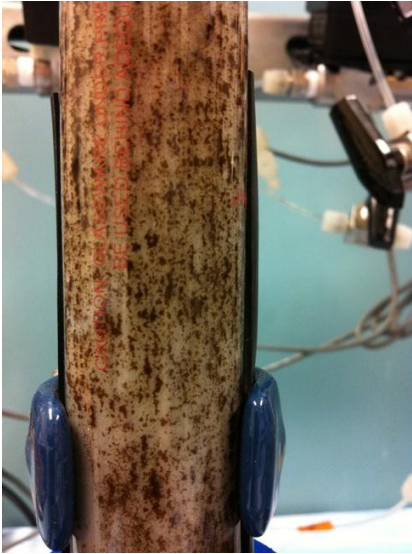


Figure 9.15–Picture of the glass bead pack at residual oil saturation.

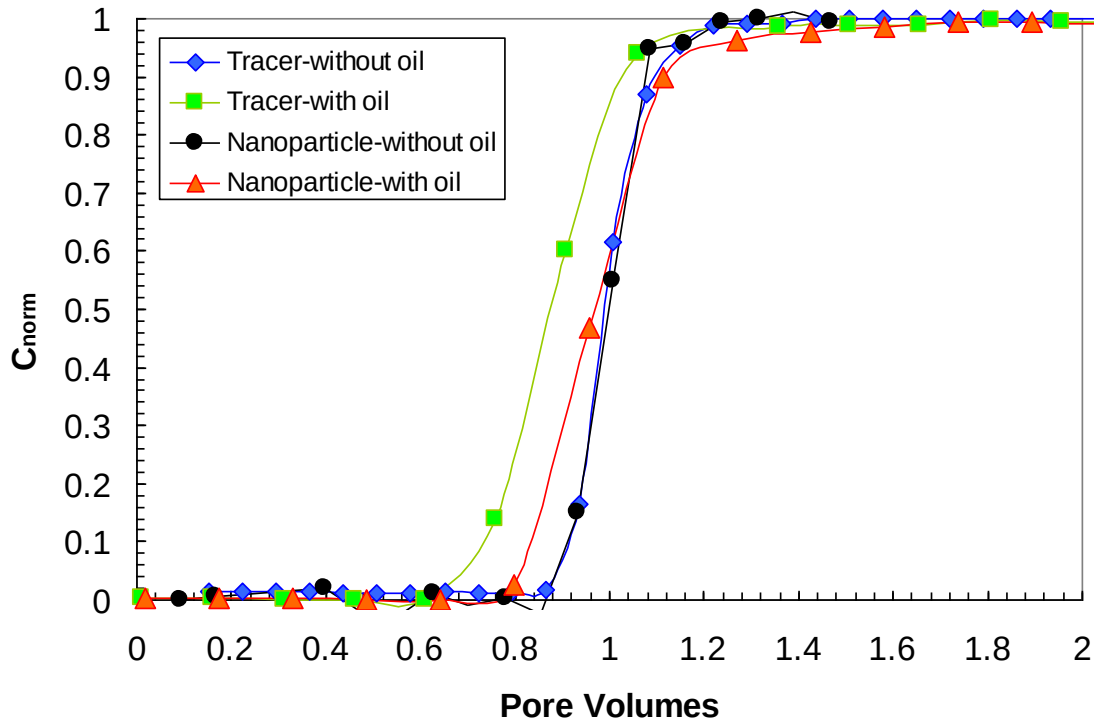


Figure 9.16–The effect of residual oil on the retention of PEG coated silica nanoparticles in glass bead pack.

The delay in breakthrough in the presence of nanoparticles at residual oil saturation is around 0.085 from interpolation of the data in Figure 9.16 at $C_{norm}=0.5$ (Equation 9.2). This delay, D_e , is related to the adsorbed nanoparticle concentration at the water/oil interface by Equation 9.3.

$$t_{breakthrough} = 1 + D_e \quad (9.2)$$

$$D_e = \frac{\Delta S}{\Delta C} \quad (9.3)$$

Where ΔS is the mass of nanoparticles retained at the interface per pore volume and ΔC is equal to the injected nanoparticle concentration. The amount of nanoparticle adsorbed at the water/oil interface can be calculated using Equation 9.4 (Lake *et al.* 2002).

$$\Delta S = A_c a_c \quad (9.4)$$

where A_c is the nanoparticle retention concentration and a_c is the specific interfacial area of water/oil interface per pore volume. The parameter a_c is estimated as 17307.7 1/m from Gladkikh and Bryant (2003) and using a grain specific surface area of $(1-\phi)\frac{3}{r}\frac{1}{\phi} = 86538.5$ 1/m. Then combining Equations 9.3 and 9.4, A_c was calculated as 0.25 g nanoparticles/m² of water/oil interface. This amount of adsorbed nanoparticles corresponds to 43 layers of surface coverage if a cubic packing of nanoparticles at the interface is assumed (see chapter 7). The ordering of nanoparticle at the water/oil interface may be in a staggered structure rather than a cubic packing however, the length of PEG molecules is not very long to support that ordering (i.e. 2-3 nm long). However, a monolayer of nanoparticle adsorption would occur at the interface according to IFT measurements and analysis based on Gibbs' equation (see Figure 9.4). Small errors in calculation may arise from the interpolation of the concentration history and/or the calculation of grain specific surface area, which may lead to an overestimation of the adsorbed nanoparticle concentration. A detailed study on the adsorption of PEG modified nanoparticles at water/oil interface needs to be carried out to determine the structure of adsorbed layers.

9.4 CONCLUSIONS

In this chapter, we conclude that unmodified nanoparticles do not change the IFT of a crude oil/water interface. However, the presence of PEG modified nanoparticles in solution lower the IFT. Moreover, the presence of unmodified or surface-modified nanoparticles at 5 wt% in solution does not alter the contact angle of a crude oil droplet on clean calcite (water-wet) or aged calcite plate (oil-wet).

In the absence of crude oil, the nanoparticles act as a conservative tracer with insignificant interaction with the glass beads. This result is in agreement with our previous work on the adsorption of silica nanoparticles on mineral surfaces. However, at the residual oil saturation of 12%, PEG modified silica nanoparticles are retained at the crude oil/water interface as shown by the concentration history. These results are also in agreement with IFT and contact angle measurements carried out in this study.

9.5 REFERENCES

- Binks BP and Whitby CP (2005) Nanoparticle Silica-Stabilised Oil-In-Water Emulsions: Improving Emulsion Stability. *Colloids and Surfaces A* 253 (1-3): 105-115.
- Bresme F and Oettel M (2007) Nanoparticles at Fluid Interfaces. *J. Phys. Condens. Matter* 19: 413101-1-413101-33.
- Chatterjee J and Wasan DT (1998) A kinetic model for dynamic interfacial tension variation in an acidic oil/alkali/surfactant system. *Chem Eng Sci* 53, 2700-2725.
- DROPimage <http://folk.uio.no/fhansen/dropbroc.html>
- Ferrari M, Liggieri L, Ravera F, Amodio C and Miller R (1997) Adsorption Kinetics of Alkylphosphine Oxides at Water/Hexane Interface: 1. Pendant Drop Experiments. *J. Colloid Int. Sci.* 186 (1): 40-45.
- Gladkikh M and Bryant S (2003) Prediction of interfacial areas during imbibition in simple porous media. *Advances in Water Resources*, 26, 609-622.
- Hirasaki GJ and Zhang DL (2004) Surface Chemistry of Oil Recovery from Fractured, Oil-wet, Carbonate Formations. *SPEJ* 9(2), 151-162.

- Jeribi M, Almir-Assad B, Langevin D, Hénaut I and Argillier JF (2002) Adsorption Kinetics of Asphaltenes at Liquid Interfaces. *J. Colloid Int. Sci.* 256 (2):268-272.
- Lake LW, Bryant SL and Araque-Martinez AN (2002) Geochemistry and fluid flow (Developments in Geochemistry) Elsevier.
- Lee Y, Du Z, Lin W and Yang Y (2006) Monolayer Behavior of Silica Particles at Air/Water Interface: A Comparison Between Chemical and Physical Modifications of Surface. *J. Colloid Interface Sci.* 296 (1): 233-241.
- Linde and Schwartz in, Dissipative structures and nonlinear kinetics of the marangoni-instability, Lecture notes in physics (T.S. Sorensen, Ed.) p. 105. Springer-Verlag, Berlin 1979.
- Metin CO, Baran Jr. JR and Nguyen QP (2011) Adsorption of Surface Functionalized Silica Nanoparticles onto Mineral Surfaces and Decane/Water Interface, *Petroleum Preprints Presented at the 242nd ACS National Meeting*.
- Owens WW and Archer DL (1971) The Effect of Rock Wettability on Oil-Water Relative Permeability Relationships. *JPT* **23**: 873–878.
- Rame-Hart, <http://www.ramehart.com/>
- Schlumberger,
http://www.slb.com/media/services/solutions/reservoir/carbonate_reservoirs.pdf.
- Serrien G, Geeraerts G, Ghosh L and Joos P (1992) Dynamic surface properties of adsorbed protein solutions: BSA, casein and buttermilk. *Colloids and Surfaces* 68 (4) :219-233.
- Tweheyo MT, Zhang P and Austad T (2006) The Effects of Temperature and Potential Determining Ions Present in Seawater on Oil Recovery From Fractured Carbonates. Paper SPE 99438 presented at the Symposium on Improved Oil Recovery, Tulsa, Oklahoma, 22-26 April.

Chapter 10: Contributions and Recommendation

The main contributions of research presented in this dissertation are presented in this chapter. Recommendations for future research are offered based on the findings in this work.

10.1 MAJOR CONTRIBUTIONS

The critical salt concentration is identified for the stability of silica nanoparticle dispersions. The use of DLVO theory for calculation of the CSC is validated for unmodified nanoparticle dispersions.

A unified model is proposed to accurately predict the viscosity of silica nanoparticle dispersions at a given solid volume fraction by introducing the concept of effective maximum packing fraction. This model is accurate for both stable and unstable nanoparticle dispersions.

A convenient model is derived to describe the aggregation of silica nanoparticles and the growth of their aggregate size dependent upon particle size and concentration and salt concentration.

The equilibrium phase diagram of silica nanoparticle solutions is mapped based on experimental data in the presence of sodium chloride (NaCl). The rheology of silica nanoparticle gels and the onset of gelation are determined for control parameters such as silica and NaCl concentration and temperature.

The effect of nanoparticles and surface treatment on interfacial tension (IFT), adsorption on minerals and finally on contact angle change is investigated. The effect of surface treatment on the IFT change is quantified. The type and amount of surface treatment attached to silica nanoparticles determines the extent of the change in IFT of water/decane interface.

The interaction of silica nanoparticles with montmorillonite clay is investigated by visual observations and analytical techniques. Adsorption isotherms are calculated for silica nanoparticles.

The transport of silica nanoparticles is studied in unconsolidated (glass bead and sand packs) and consolidated (sandstone and limestone) permeable media. The unified viscosity model is applicable for flow through highly permeable media i.e., glass bead and sand pack. The pore structure and permeability plays an important role during the transport of nanoparticles through consolidated permeable media.

The interaction between silica nanoparticles and crude oil is determined by IFT, contact angle and phase behavior measurements. The retention of nanoparticles at oil/water interface during flow through glass bead pack is shown. The results validated previous findings on the interaction between nanoparticles and oil.

10.2 RECOMMENDATIONS FOR FUTURE WORK

The following list presents the topics for future research to further the work presented in this dissertation:

- Extension of theoretical work on CSC to include the effect of surface modification on CSC.
- Extension of the aggregation kinetics model in chapter 4 to include the effect of temperature.
- Modeling of the rheology of silica nanoparticle gels with the effect of aggregate size, volume fraction and temperature.
- Extension of analytical measurements to further understand the interaction between nanoparticles and clay.

- Extension of adsorption experiments to other types of clays and different types of nanoparticles like iron oxide nanoparticles.
- Modeling of the trapping of nanoparticles in sandstone with the effect of clays.
- Effect of pH (phase behavior) on the retention of nanoparticles at a water/crude oil interface in permeable media.
- Modeling of the retention of nanoparticles at water/crude oil interface in permeable media with application to the estimation of oil saturation.
- Understanding the structure of nanoparticles (i.e., number of layers, packing pattern) formed at the water/crude oil interface. Interfacial rheology may be insightful for this part.

Appendix A: List of Acronyms

ATR-FTIR: Attenuated total reflectance, Fourier transform infrared

CSC: Critical salt concentration

DI water: Deionized water

DLS: Dynamic light scattering

DLVO theory: Derjaguin-Landau-Verwey-Overbeek theory

FID: Flame ionization detector

HPLC: High performance liquid chromatography

IEP: Isoelectric point

IFT: Interfacial tension

IGC: Inverse gas chromatography

IR: Infrared light

MD simulations: Molecular dynamics simulations

MEG: Monoethylene glycol

OHP: Outer Helmholtz plane

PEG: Polyethylene glycol

PEO: polyethylene oxide

Quat: Quaternary ammonium

STEM: Scanning transmission electron microscope

TCD: Thermal conductivity detector

TEM: Transmission electron microscope

UV-Vis: Ultraviolet-visible

XRD: X-ray diffraction

Appendix B: List of Equipment and Vendors

The list of the instruments and materials used in this work is as follows:

Hitachi-S5500 scanning transmission electron microscope,

A spectrum 100 FTIR spectrometer made by Perkin Elmer,

Cary 50 ultraviolet-visible spectrophotometer,

A zeta potential analyzer (Zeta Plus) with a dynamic light scattering option from
Brookhaven Instruments Corporation,

Delsa Nano dynamic light scattering (DLS) instrument from Beckman Coulter,

A zeta potential analyzer (Zetasizer) from Malvern,

A strain controlled TA Instruments ARES LS-1 rheometer,

Kruss K100 tensiometer equipped with a Wilhemly plate,

A Rame-Hart contact angle goniometer,

The series of alkanes were obtained from Acros Organics,

Montmorillonite clay purchased from Ward's Natural Science Establishment, Inc.,

Rigaku SPIDER XRD system,

Glass beads of 100-140 mesh size purchased from Potters Industry Inc.,

A Ro-Tap sieve shaker,

A flow adapter and glass columns from Kimble Chase,

An Isco pump,

Low (0-1 psid) and mid range (0-10 psid) transducers from Cole-Parmer and Rosemount
Inc.

Bibliography

- Amiri A, Øye G and Sjöblom J (2011) Temperature and pressure effects on stability and gelation properties of silica suspensions. *Colloids and Surfaces A* 378 (1-3): 14-21.
- Anderson RL, Ratcliffe I, Greenwell HC, Williams PA, Cliffe S, Coveney PV (2010) Clay swelling - A challenge in the oilfield. *Earth-Science Reviews*, 98 (3-4):201-216.
- Anoop KB, Kabelac A, Sundararajan T, Das SK: Rheological and flow characteristics of nanofluids: Influence of electroviscous effects and particle agglomeration, *J. App. Phys.* 106 (2009) 034909-1-7.
- Antelmi DA and Spalla O (1999) Adsorption of Nanolatex Particles to Mineral Surfaces of Variable Surface Charge. *Langmuir* 15: 7478-7489.
- Asay DB, Kim SH (2005) Evolution of the adsorbed water layer structure on silicon oxide at room temperature. *J Phys Chem B* 109:16760-16763.
- ASTM Standard D 4187-82, Zeta Potential of Colloids in Water and Waste Water, 1985.
- Aubert C, Cannell DS (1986) Restructuring of colloidal silica aggregates. *Phys. Rev. Lett.* 56:738-741.
- Bergenholtz J: Theory of rheology of colloidal dispersions, *Current Opinion in Colloid Int. Sci.* 6 (2001) 484-488.
- Biggs MJ, Humby SJ, Buts A and Tuzun U (2003) Explicit numerical simulation of suspension flow with deposition in porous media: influence of local flow field variation on deposition processes predicted by trajectory methods. *Chemical Engineering Science* 58: 1271 – 1288.
- Billingham J, Breen C, and Yarwood J (1997) Adsorption of polyamine, polyacrylic acid and polyethylene glycol on montmorillonite: An in situ study using ATR-FTIR. *Vibrational Spectroscopy*, 14, 19-34.
- Binks BP, and Fletcher PDI (2001) Particles Adsorbed at the Oil-Water Interface: A Theoretical Comparison Between Spheres of Uniform Wettability and “Janus” Particles. *Langmuir* 17 (16): 4708-4710.
- Binks BP, and Whitby CP (2005) Nanoparticle Silica-Stabilised Oil-In-Water Emulsions: Improving Emulsion Stability. *Colloids and Surfaces A* 253 (1-3): 105-115.
- van Blaaderen A, Vrij A (2006) Synthesis and characterization of colloidal model particles made from organoalkoxysilane. In: H.E. Bergna, W.O. Roberts (Eds.), *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 65-80.

- Blake TD, Clarke A, De Conninck J and de Ruijter M.J (1997) Contact Angle Relaxation During Droplet Spreading: Comparison Between Molecular Kinetic Theory and Molecular Dynamics. *Langmuir* 13 (7): 2164-2166.
- Boda D, Chan K-Y, Henderson D, Wasan DT and Nikolov AD (1999) Structure and Pressure of a Hard Sphere Fluid in a Wedge-Shaped Cell or Meniscus. *Langmuir* 15 (13): 4311-4313. DOI: 10.1021/La981013h.
- Brindley G W and Pedro G (1972) Report of the AIPEA Nomenclature Committee. *AIPEA Newsletter* No. 7, 8-13.
- Bresme F and Quirke N (1999) Computer Simulation of Wetting and Drying of Spherical Particulates at a Liquid–Vapor Interface. *J. Chem. Phys.* 110 (7): 3536-3547.
- Bresme F and Oettel M (2007) Nanoparticles at Fluid Interfaces. *J. Phys. Condens. Matter* 19: 413101-1-413101-33. DOI: 10.1088/0953-8984/19/41/413101.
- Burchill S, Hall PL, Harrison R, Hayes MHB, Langford JI, Livingston WR, Smedley RJ, Ross DK, Tuck JJ (1983) Smectite-polymer interactions in aqueous systems. *Clay Miner.*, 18 :373-397.
- Burns LD, Burns M, Wilhite P, McCool S, Oglesby K and Glass J (2008) New generation silicate gel system for casing repairs and water shutoff. SPE 113490 presented at SPE/DOE Symposium on Improved Oil Recovery, 20-23 April, Tulsa, Oklahoma.
- Cai J, Chenevert ME, Sharma MM and Friedheim J (2011) Decreasing water invasion into Atoka shale using nonmodified silica nanoparticles. Paper SPE 146979 presented at SPE Annual Technical Conference and Exhibition, Denver 30 October-2 November.
- Caldelas F., Murphy M, Huh C and Bryant SL (2011) Factors Governing Distance of Nanoparticle Propagation in Porous Media. SPE Production and Operations Symposium, Oklahoma City. SPE 142305.
- Campbell AI, Anderson VJ, van Duijneveldt JS and Betlett P (2005) Dynamical arrest in attractive colloids: the effect of long-range repulsion. *Phys. Rev. Lett.*, 94 208301.
- Carroll 1959, Bulletin of the geological soc. of America, 70, 749-780.
- Chatterjee J and Wasan DT (1998) A kinetic model for dynamic interfacial tension variation in an acidic oil/alkali/surfactant system. *Chem Eng Sci* 53, 2700-2725.
- Chengara A, Nikolov AD, Wasan DT, Trokhymchuk A and Henderson D (2004) Spreading of Nanofluids Driven by the Structural Disjoining Pressure Gradient. *J. Colloid Interface Sci.* 280 (1): 192-201.
- Chevalier J, Tillement O, Ayela F: Rheological properties of nanofluids flowing through microchannels, *App. Phy. Lett.* 91 (2007) 233103-1-3.

- Choi SUS: Enhancing thermal conductivity of fluids with nanoparticles, in *Developments and applications of non-Newtonian flows*, Siginer DA and Wang HP (Eds), FED-Vol 231/MD-Vol 66, pp. 99-105, ASME, New York, 1995.
- Choi C-H and Kim C-J (2006) Large Slip of Aqueous Liquid Flow Over a Nanoengineered Superhydrophobic Surface. *Phys. Rev. Lett.* 96: 066001-1-066001-4. DOI: 10.1103/Physrevlett.96.066001.
- Chong JS, Christiansen EB, Baer AD: Rheology of concentrated suspensions, *J. Appl. Polym. Sci.* 15 (1971) 2007-2021.
- Chow TS: Viscosities of concentrated dispersions, *Phys. Rev. E* 48 (1993) 1977-1983.
- Civan F (2007) Reservoir formation damage: fundamentals, modeling, assessment and mitigation, Elsevier, Burlington, MA.
- Cliffe S, Dolan B and Reid P (1995) Mechanism of shale inhibition by polyols in water based drilling fluids. SPE 28960 presented at SPE Symp. Oil Field Chem., 14-17 Feb, San Antonio.
- Colic M, Fisher ML, Franks GV (1998) Influence of ion size on short-range repulsive forces between silica surfaces. *Langmuir* 14:6107-6112.
- Dai C, You Q, Zhao LF and Xiong W (2010) Study and field application of profile control agent in high temperature and high salinity reservoir. SPE 132765-MS presented at Trinidad and Tobago Energy Resources Conference, 27-30 June, Port of Spain, Trinidad.
- Das SK, Putra N, Roetzel W: Pool boiling characteristics of nano-fluids, *Int. J. Heat Mass Transfer* 46 (2003) 851-862.
- Derjaguin BV, Landau L (1941) Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim USSR* 14:633-662.
- Dietler G, Aubert C and Cannell DS (1986) Gelation of colloidal silica. *Phys. Rev. Lett.* 57:3117-3120.
- Ding YL, Alias H, Wen DS, Williams RA: Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids), *Int. J. Heat and Mass Transfer* 49 (2006) 240-250.
- Dumont F (2006) Stability of sols: Do the silica hydrosols obey the DLVO theory? In: Bergna HE, Roberts WO (eds) *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 243-245.
- DROPImage <http://folk.uio.no/fhansen/dropbroc.html>
- Drummond C and Israelachvili J (2004) Fundamental studies of crude oil–surface water interactions and its relationship to reservoir wettability. *J. Pet. Sci. Eng.* 45 (1-2): 61-81.

- Edwards DG and Quirk JP (1962) Repulsion of chloride by montmorillonite. *J. Colloid Int. Sci.*, 17 (9) :872-882.
- Einstein A: Investigations on the theory of the Brownian movement, Dover, New York, 1956.
- Elimelech M, Gregory J, Jia X, Williams RA (1998) Particle deposition and aggregation: Measurement, modelling and simulation. Butterworth-Heinemann, Woburn.
- Fagan ME, Zukoski CF: The rheology of charge stabilized silica suspensions, *J. Rheol.* 41 (1997) 373-397.
- Fedors RF: Relations between viscosity and concentration for Newtonian suspensions, *J. Colloid Interface Sci.* 46 (1974) 545-547.
- Ferrari M, Liggieri L, Ravera F, Amodio C and Miller R (1997) Adsorption Kinetics of Alkylphosphine Oxides at Water/Hexane Interface: 1. Pendant Drop Experiments. *J. Colloid Int. Sci.* 186 (1): 40-45.
- Flury M, Czigany S, Chen G and Harsh JB (2004) Cesium Migration in Saturated Silica Sand and Hanford Sediments as Impacted by Ionic Strength. *J. of Contaminant Hydrology* 71: 111-126.
- Franks GV (2002) Zeta potentials and yield stresses of silica suspensions in concentrated monovalent electrolytes: Isoelectric point shift and additional attraction. *J Colloid Interface Sci* 249:44-51.
- Fuchs N (1934) Über die stabilität und ausladung der aerosole. *Z. Physik.*, 89:736-743.
- Gladkikh M and Bryant S (2003) Prediction of interfacial areas during imbibition in simple porous media. *Advances in Water Resources*, 26, 609-622.
- Goodwin J (2009) Colloids and interfaces with surfactants and polymers. Wiley, New Delhi.
- Gorrepati EA, Wongthahan P, Raha S and Fogler HS (2010) Silica precipitation in acidic solutions: mechanism, pH effect, and salt effect. *Langmuir* 26 (13) 10467-10474.
- Gu C-Y, Di Q-F and Fang H-P (2007) Slip Velocity Model of Porous Walls Absorbed by Hydrophobic Nanoparticles SiO₂. *J. Hydrodynamics* 19 (3): 365-371.
- Hair ML (2006) Surface chemistry of silica. In: Bergna HE, Roberts WO (eds), *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 257-260.
- Hansen C, Hansen Solubility Parameters: A user's handbook, CRC Press, Boca Raton, 2007.
- He Y, Jin Y, Chen H, Ding Y, Cang D, Lu H: Heat transfer and flow behaviour of aqueous suspensions of TiO₂ nanoparticles (nanofluids) flowing upward through a vertical pipe, *Int. J. Heat and Mass Transfer* 50 (2007) 2272-2281.

- He YT, Wan J and Tokunga T (2008) Kinetic stability of hematite nanoparticles: the effect of particle sizes. *J. Nanoparticle Res.* 10:321-332.
- Healy TW (2006) Stability of aqueous silica sols. In: Bergna HE, Roberts WO (eds), *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 247-252.
- Hirasaki GJ and Zhang DL (2004) Surface Chemistry of Oil Recovery from Fractured, Oil-wet, Carbonate Formations. *SPEJ* 9(2), 151–162.
- Hofmann U, Endell K, Wilm D (1934) Röntgeno-graphische und kolloidchemische Untersuchungen über Ton. *Angew Chem* 47:539-558.
- Hogg RI, Healy TW and Fuerstenau DW (1966) Mutual Coagulation of Colloidal Dispersions. *Trans. Faraday Soc.* 62: 1638–1651.
- Hounslow MJ, Ryall RL and Marshall VR (1988) Discretized population balance for nucleation, growth, and aggregation. *AIChE* 34 (11) 1821-1832.
- Hubbard AT, *Encyclopedia of Surface and Colloid Science*, Marcel Dekker, New York, 2002.
- Hunter RJ (2001) *Foundations of colloid science*. Oxford University Press, New York.
- Hwang C-C, Jeng Y-R, Hsu Y-L and Chang J-G (2001). Molecular Dynamic Simulation of Microscopic Droplet Spread on Rough Surfaces. *J. Phys. Soc. Jpn.* 70 (9): 2626-2632.
- Hyun K, Kim SH, Ahn KH and Lee SJ (2002) Large Amplitude Oscillatory Shear as a Way to Classify the Complex Fluids. *J. Non-Newtonian Fluid Mech* 107: 51-65.
- Iler RK (1971) *The chemistry of silica*. Wiley & Sons, New York.
- Israelachvili J, Wennerstrom H (1996) Role of hydration and water structure in biological and colloidal interactions. *Nature* 379:219-225.
- Jenkins S, Kirk SR, Persson M, Carlen J, Abbas Z (2007) Molecular dynamics simulation of nanocolloidal amorphous silica particles: Part I. *J Chem Phys* 127:224711-1-10.
- Jenkins S, Kirk SR, Persson M, Carlen J, Abbas Z (2008) Molecular dynamics simulation of nanocolloidal amorphous silica particles: Part II. *J Chem Phys* 128:164711-1-10.
- Jeribi M, Almir-Assad B, Langevin D, Hénaut I and Argillier JF (2002) Adsorption Kinetics of Asphaltenes at Liquid Interfaces. *J. Colloid Int. Sci.* 256 (2):268-272.
- Ju B, Fan T and Ma M (2006) Enhanced Oil Recovery by Flooding With Hydrophilic Nanoparticles. *China Particuology* 4 (1): 41-46.

- Jung K-M, Kim SH: Rheological properties and transfer phenomena of nanofluids, XVth International Congress on Rheology, The Society of Rheology 80th Annual Meeting, (2008) 773-775.
- Jurinak JJ and Summers LE (1991) Oilfield Applications of Colloidal Silica Gel. *SPE Prod Eng* **6** (11): 406-412. SPE-18505-PA.
- Kissa E (1999) Dispersions: Characterizations testing, and measurement. Marcel Dekker, New York.
- Kitchener JA (1971) General discussion. *Faraday Disc* 52:372-380.
- Krieger IM, Dougherty RJ: A mechanism for non-Newtonian flow in suspensions of rigid spheres, *Trans. Soc. Rheol.* 3 (1959) 137-152.
- Kwak K, Kim C: Viscosity and thermal conductivity of copper oxide nanofluid dispersed in ethylene glycol, *Korea-Australia Rheology J.* 17 (2005) 35-40.
- Lake LW: Enhanced oil recovery, Prentice Hall, New Jersey, 1989.
- Lake LW, Bryant SL and Araque-Martinez AN (2002) *Geochemistry and fluid flow (Developments in Geochemistry)* Elsevier.
- Lane JMD, Ismail AE, Chandross M, Lorenz CD, Grest GS (2009) Forces between functionalized silica nanoparticles in solution. *Phys Rev E* 79:050501-1-4.
- Larson RG (2005) The rheology of dilute solutions of flexible polymers: Progress and problems. *J. Rheology* 49 1-70.
- Larson G (1999) *The structure of complex fluids.* Oxford university press, New York.
- Lazouskaya, V. and Jin, Y. 2008. Colloid Retention at Air-Water Interface in a Capillary Channel. *Colloids Surface A* in press.
- Lazouskaya, V, Jin, Y. and Or, D. 2006. Interfacial Interactions and Colloid Retention Under Steady Flows in a Capillary Channel. *J. Colloid Interface Sci.* **303** (1): 171-184.
- LeCoanet, H.F., Bottero, J-Y. and Wiesner, M.R. 2004. Laboratory Assessment of the Mobility of Nanomaterials in Porous Media. *Environ. Sci. Technol.* **38** (19): 5164-5169.
- Lee Y, Du Z, Lin W and Yang Y (2006) Monolayer Behavior of Silica Particles at Air/Water Interface: A Comparison Between Chemical and Physical Modifications of Surface. *J. Colloid Interface Sci.* 296 (1): 233-241.
- Lin MY, Lindsay HM, Weitz DA, Ball RC, Klein R and Meakin P (1990) Universal reaction-limited aggregation. *Phys. Rev. A* 41:2005-2020.
- Lin Y, Böker A, Skaff H, Cookson D, Dinsmore AD, Emrick T and Russell TP (2005) Nanoparticle Assembly at Fluid Interfaces: Structure and Dynamics. *Langmuir* 21 (1): 191-194.

- Linde and Schwartz in, Dissipative structures and nonlinear kinetics of the marangoni-instability, Lecture notes in physics (T.S. Sorensen, Ed.) p. 105. Springer-Verlag, Berlin 1979.
- Liu S, Mo X., Sun D., Mu C. and Zhang C (2004) Swelling Inhibition by Polyglycols in Montmorillonite Dispersions. *Journal of Dispersion Science and Technology*, 25 (1):63-66.
- Liu SF, Lafuma F, Audebert R: Rheological behavior of moderately concentrated silica suspensions in the presence of adsorbed poly(ethylene oxide), *Colloid Polym. Sci.* 272 (1994) 196-203.
- Lu K, Kessler C: Colloidal dispersion and rheology study of nanoparticles, *J. Mater. Sci.* 41 (2006) 5613-5618.
- Lu K, *Ceramics Int.* 34 (2008) 1353-1360.
- Luckham PF and Rossi S (1999) The colloidal and rheological properties of bentonite suspensions. *Advances in Colloid and Interface Science*, 82 (1-3):43-92.
- Marczewski AW and Szymula M (2002) Adsorption of Asphaltenes From Toluene on Mineral Surface. *Colloids and Surfaces A* 208: 259-266.
- Martin JE and Wilcoxon JP (1989) Spatial correlation and growth in dilute gels. *Phys. Rev. A* 39: 252-258.
- Martin JE (1987) Slow aggregation of colloidal silica. *Phys. Rev. A* 36:3415-3426.
- Matar OK, Craster RV and Sefiane K (2007) Dynamic Spreading of Droplets Containing Nanoparticles. *Phys. Rev. E* 76 (5): 056315-1-056315-9.
- Manciu M, Ruckenstein E, *Langmuir* 17 (2001) 7061-7070.
- Ma AWK, Chinesta F, Mackley MR, Ammar A: The rheological modeling of carbon nanotube (CNT) suspensions in steady shear flow, *Int. J. Mater. Form.* 1 (2008) 83-88.
- Mackay ME, Dao TT, Tuteja A, Ho DL, Van Horn B, Kim H-C, Hawker CJ: Nanoscale effects leading to non-Einstein-like decrease in viscosity, *Nature Materials* 2 (2003) 762-766.
- McPhie MG, Daivis PJ, Snook IK: Viscosity of a binary mixture: Approach to the hydrodynamic limit, *Phys. Rev. E* 74 (2006) 031201-1-13.
- Metin CO, Lake LW, Miranda CR, Nguyen QP (2011) Stability of aqueous silica nanoparticle dispersions. *J. Nanopart. Res.* 13:839-850.
- Metin CO, Baran Jr. JR and Nguyen QP (2011) Adsorption of Surface Functionalized Silica Nanoparticles onto Mineral Surfaces and Decane/Water Interface, *Petroleum Preprints Presented at the 242nd ACS National Meeting*.

- Metin CO, Bonnecaze RT and Nguyen QP (2011) Shear rheology of silica nanoparticle dispersions. *Appl. Rheol.* 21:13146.
- Metin CO, Rankin KM, Nguyen QP (2012) Phase Behavior and Rheological Characterization of Silica Nanoparticle Gel. *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.* 57 (1), San Diego, March 2012.
- Mokhatab S, Fresky MA, Islam MR (2006) Applications of nanotechnology in oil and gas E&P. *J Pet Technol Online* 58:4.
- Moon T: Nanotechnology collaborative takes aim at EOR, *JPT online* (2008)
<http://www.spe.org/jpt/2008/12/nanotechnology-collaborative-takes-aim-at-eor/#more-1870>
- Mooney M: The viscosity of a concentrated suspension of spherical particles, *J. Colloid Sci.* 6 (1951) 162-170.
- Morrow BA, Molapo DT (2006) Infrared studies of chemically modified silica. In: Bergna HE, Roberts WO (eds), *Colloidal silica: Fundamentals and applications*, CRC Press, Boca Raton, pp 287-294.
- Murshed SMS, Tan S-H, Nguyen N-T: Temperature dependence of interfacial properties and viscosity of nanofluids for droplet-based microfluidics, *J. Phys. D: Appl. Phys.* 41 (2008) 085502-1-5.
- Namburu PK, Kulkarni DP, Dandekar A, Das DK: Experimental investigation of viscosity and specific heat of silicon dioxide nanofluids, *Micro & Nano Letters* 2 (2007) 67-71.
- Nanotechnology for oil and gas operations, <http://www.offshore-mag.com/index/article-tools-template.articles.offshore.regional-reports.north-sea-northwest-europe.2009.09.nanotechnology-shows.html>
- Norrish K (1954) The swelling of montmorillonite. *Discuss. Faraday Soc.* 18, 120-134.
- Owens WW and Archer DL (1971) The Effect of Rock Wettability on Oil-Water Relative Permeability Relationships. *JPT* 23: 873–878.
- Parfitt RL and Greenland DJ (1970) The adsorption of poly(ethylene glycols) on clay minerals. *Clay Miner.* 8, 305-315.
- Petrie CJS: The rheology of fiber suspensions, *J. Non-Newtonian Fluid Mech.* 87 (1999) 369-402.
- Plaza RC, Quirantes A, Delgado AV (2002) Stability of dispersions of colloidal hematite/yttrium oxide core-shell particles. *J Colloid Interface Sci* 252:102-108.
- Poon WCK and Haw MD (1997) Mesoscopic structure formation in colloidal aggregation and gelation. *Adv. Colloid Int. Sci.* 73:71-126.

- Prasher R, Song D, Wang J, Phelan P: Measurements of nanofluid viscosity and its implications for thermal applications, *Appl. Phys. Lett.* 89 (2006) 133108-1-3.
- Prodanovic M, Ryoo S, Rahmani AR, Kuranov R, Kotsmar C, Milner TE, Johnston KP, Bryant SL, Huh C: Effects of magnetic field on the motion of multiphase fluids containing paramagnetic nanoparticles in porous media, SPE 129850, SPE IOR Symp., 2010.
- Quintero L (2002) An overview of surfactant applications in drilling fluids for the petroleum industry. *Journal of Dispersion Science and Technology*, 23 (1-3): 393-404.
- Rame-Hart, <http://www.ramehart.com/>
- Reerink H and Overbeek JThG (1954) The rate of coagulation as a measure of the stability of silver iodide sols. *Discuss. Faraday Soc.* 18:74-84.
- Reid PI, Elliott GP, Minton RC, Chambers BD and Burt DA (1993) Reduced environmental impact and improved drilling performance with water-based muds containing glycols. Paper SPE 25989SPE/EPA Exploration and Production Environmental Conference, San Antonio (TX) March 7-10
- Reincke F *et al.* (2006) Understanding the Self-Assembly of Charged Nanoparticles at the Water/Oil Interface. *Phys. Chem. Chem. Phys.* 8 (33): 3828-3835.
- Roberts WO (2006) Manufacturing and applications of waterborne colloidal silica. In: Bergna HE, Roberts WO (eds.), *Colloidal silica: fundamentals and applications*, CRC Press, Boca Raton, pp131-176.
- Roberts WO: *Colloidal Silica: Fundamentals and Applications*, Bergna HE, Roberts WO (Eds.), CRC Press, Boca Raton, 2006.
- Rodriguez E, Roberts MR, Yu H, Huh C and Bryant SL (2009) Enhanced Migration of Surface-Treated Nanoparticles in Sedimentary Rocks. SPE Annual Technical Conference and Exhibition, New Orleans. SPE 124418.
- Rudyak VYa, Belkin AA, Egorov VV: Effective viscosity coefficient of nanosuspensions, *Rarefied Gas Dynamics*, 26th International Symposium, Ame. Inst. Of Phys. (2009) 489-494.
- de Ruijter MJ, Blake TD, and de Coninck J (1999a) Dynamic Wetting Studied By Molecular Modeling Simulations of Droplet Spreading. *Langmuir* 15 (22): 7836-7847. DOI: 10.1021/La990171l.
- de Ruijter MJ, De Coninck J and Oshanin G (1999b) Droplet Spreading: Partial Wetting Regime Revisited. *Langmuir* 15 (6): 2209-2216.
- Russel WB, Saville DA, Scholwater WR: *Colloidal dispersions*, Cambridge University Press, Cambridge, 1991.

- Saint Flour C, Papirer E (1982) Gas solid chromatography: A method of measuring surface free energy characteristics of short glass fibres. II. Through retention volumes measured near zero surface coverage. *Ind. Eng. Chem. Process Res. Dev.* 21 : 666.
- Schaefer DW, Martin JE (1984) Fractal geometry of colloidal aggregates. *Phys. Rev. Lett.* 52:2371-2375.
- Schechter SR (1992) Oil well stimulation, Prentice-Hall, Inc. Englewood Cliffs, New Jersey.
- Schiby D and Ruckenstein E, *Chem. Phys. Lett.* 95 (1983) 435.
- Schudel M, Behrens SH, Holthoff H, Kretschmar R and Borkovec M (1997) Absolute aggregation rate constants of hematite particles in aqueous suspensions: a comparison of two different morphologies. *J. Colloid Int. Sci.* 196:241-253.
- Schlumberger,
http://www.slb.com/media/services/solutions/reservoir/carbonate_reservoirs.pdf.
- Sen TK, Shanbhag S and Khilar KC (2004) Subsurface colloids in groundwater contamination: a mathematical model. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 232: 29–38.
- Senis D and Allain C (1997) Scaling analysis of sediment equilibrium in aggregated colloidal suspensions. *Phys. Rev. E* 55:7797-7800.
- Senis D, Talini L, Allain C (2001) Settling in aggregating colloidal suspensions: analysis of cell inclination influence. *Eur. Phys. J. E.* 2, 31.
- Sensoy T, Chenevert ME and Sharma MM (2009) Minimizing water invasion in shales using nanonparticles. Paper SPE 124429 presented at the SPE Annual Technical Conference and Exhibition, New Orleans 4-6 October.
- Sefiane K, Skilling J and MacGillivray J (2008) Contact Line Motion and Dynamic Wetting of Nanofluid Solutions. *Adv. Colloid Interface Sci.* 138 (2): 101-120. DOI: 10.1016/j.cis.2007.12.003.
- Serrien G, Geeraerts G, Ghosh L and Joos P (1992) Dynamic surface properties of adsorbed protein solutions: BSA, casein and buttermilk. *Colloids and Surfaces* 68 (4) :219-233.
- Shih WH, Shih WY, Kim SI, Liu J and Aksay IA (1990) Scaling Behavior of the Elastic Properties of Colloidal Gels. *Phys. Rev. A* 42:4772–4779.
- Silva RF and Vasconcelos WL (1999) Influence of processing variables on the pore structure of silica gels obtained with tetraethylorthosilicate. *MaterialsResearch* 2: 197-200.
- Smith WE, Zukoski CF (2006) Aggregation and gelation kinetics of fumed silica–ethanol suspensions. *J. Colloid Int. Sci.* 304: 359-369.

- von Smoluchowski M (1916) Drei vorträge über diffusion, Brownsche molekularbewegung und koagulation von kolloidteilchen. Physik. Z. 17:557-571, 585-599; (1917) Z. Phys. Chem. 92:129.
- Starck P, Mosse WKJ, Nicholas NJ, Spiniello M, Tyrrell J, Nelson A, Qiao GG, Ducker WA: Surface chemistry and rheology of polysulfobetaine-coated silica, Langmuir 23 (2007) 7587-7593.
- Stavland A, Jonsbråten HC and Vikane O, Skrettingland K and Fischer H (2011) In-depth water diversion using sodium silicate on snorre - factors controlling in-depth placement. SPE 143836 presented at SPE European Formation Damage Conference, 7-10 June, Noordwijk, The Netherlands.
- Stickel JJ, Powell RL: Fluid mechanics and rheology of dense suspensions, Ann. Rev. Fluid Mech. 37 (2005) 129-149.
- Studart AR, Amstad E, Antoni M, Gauckler LJ: Rheology of concentrated suspensions containing weakly attractive alumina nanoparticles, J. Am. Ceram. Soc. 89 (2006) 2418-25.
- Sun, L., Lin, J-Z. and Bao, F-B. 2006. Numerical Simulation on the Deposition of Nanoparticles Under Laminar Conditions. *J. Hydrodynamics* **18** (6): 676-680.
- Taboada-Serrano P, Chin C-J, Yiacoumi S and Tsouris C. (2005) Modeling aggregation of colloidal particles. *Current Opinion in Coll. Int. Sci.*, 10, 123-132.
- Thielmann F (2004) Introduction into the characterisation of porous materials by inverse gas chromatography. *Journal of Chromatography A*, 1037: 115-123.
- Thomas DG: Transport characteristics of suspension: VIII. A note on the viscosity of Newtonian suspensions of uniform spherical particles, J. Colloid Sci. 20 (1965) 267-277.
- Thwala JM, Goodwin JW, Mills PD: Viscoelastic and shear viscosity studies of colloidal silica particles dispersed in monoethylene glycol (MEG), diethylene Glycol (DEG) and dodecane stabilized by dodecyl hexaethylene glycol monoether, Langmuir 24 (2008) 12858-12866.
- Torrie GM, Kusalik PG, Patey GN (1989) Theory of the electrical double layer: Ion size effects in a molecular solvent. J Chem Phys 91:6367-6375.
- Tweheyo MT, Zhang P and Austad T (2006) The Effects of Temperature and Potential Determining Ions Present in Seawater on Oil Recovery From Fractured Carbonates. Paper SPE 99438 presented at the Symposium on Improved Oil Recovery, Tulsa, Oklahoma, 22-26 April.
- Tseng WJ, Lin KC: Rheology and colloidal structure of aqueous TiO₂ nanoparticle suspensions, Mater: Sci. Eng. A 355 (2003) 186-192.

- Tsoularis A and Wallace J (2002) Analysis of logistic growth models. *Mathematical Biosci.* 179:21-55.
- Wang XW, Xu XF, Choi SUS: Thermal conductivity of nanoparticle - Fluid Mixture, *J. Thermophys. Heat Transfer* 13 (1999) 474-480.
- Wang GH and Zhang LM (2009) A bio friendly silica gel for insitu protein entrapment: biopolymer-assisted formation and its kinetic mechanism. *J. Phys. Chem* 113: 2688-2694.
- Wasan DT and Nikolov AD (2003) Spreading of Nanofluids on Solids. *Nature* 423 (5): 156-159. DOI: 10.1038/Nature01591.
- Xuan YM, Li Q: Heat transfer enhancement of nanofluids, *Int. J. Heat Fluid Flow* 21 (2000) 58-64.
- Valle-Delgado JJ, Molina-Bolívar JA, Galisteo-González F, Gálvez-Ruiz MJ, Feiler A, Rutland MW (2005) Hydration forces between silica surfaces: Experimental data and predictions from different theories. *J. Chem Phys.* 123: 034708.
- Verwey EJW, Overbeek JThG, *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
- G. Vigil, Z. Xu, S. Steinber, J. Israelachvili, *J. Coll. Int. Sci.* 165 (1994) 367-385.
- Verhulst PF (1838) Notice sur la loi que la population suit dans son accroissement. *Curr. Math. Phys.* 10:113.
- Verwey EJW and Overbeek JThG (1948) *Theory of stability of lyophobic colloids*. Elsevier, Amsterdam.
- Vigil G, Xu Z, Steinberg S, and Israelachvili J (1994) Interactions of Silica Surfaces. *J. Colloid Int. Sci.* 165:367-385
- Vafaei S, Borca-Tasciuc T, Podowski MZ, Purkayastha A, Ramanath G and Ajayan PM (2006). Effect of Nanoparticles on Sessile Droplet Contact Angle. *Nanotechnology* 17: 2523-2527. DOI: 10.1088/0957-4484/17/10/014.
- Verwey EJW, Overbeek JThG (1948) *Theory of stability of lyophobic colloids*. Elsevier, Amsterdam.
- Voronov RS, Papavassiliou DV and Lee LL (2006) Boundary Slip and Wetting Properties of Interfaces: Correlation of the Contact Angle with the Slip Length. *J. Chem. Phys.* 124 (20): 2047011-10.
- Voronov RS, Papavassiliou DV and Lee LL (2007) Slip Length and Contact Angle Over Hydrophobic Surfaces. *Chem. Phys. Lett.* 441 (4-6): 273-276. DOI: 10.1016/J.Cplett.2007.05.013.

- Yang Y-X, Koplik J and Banavar JR (1991) Molecular Dynamics of Drop Spreading on a Solid Surface. *Phys. Rev. Lett.* 67 (25): 3539-3542.
- Yalamanchili MR, Atia AA, Miller JD (1996) Analysis of interfacial water at a hydrophilic silicon surface by in-situ ftir/internal reflection spectroscopy. *Langmuir* 12:4176-4184.
- Yziquel F, Carreau P J, Moan M and Tanguy PA (1999) Rheological modeling of concentrated colloidal suspension. *J. Non-Newtonian Fluid Mech.* 86 (1):133–155.
- Zhang T et al. (2011) Engineered Nanoparticles as Harsh-Condition Emulsion and Foam Stabilizers and as Novel Sensors. Offshore Technology Conference, Houston. OTC 21212.
- Zhuravlev LT (1987) Concentration of hydroxyl groups on the surface of amorphous silicas. *Langmuir* 3:316-318.