NANOPARTICLES-SURFACTANT FOAM AND CRUDE OIL INTERACTION IN POROUS MEDIA

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To the Almighty God be the glory for his love, mercies and favour.
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ABSTRACT

Nanoparticles and surfactant stabilized foams have versatile applications in enhanced oil recovery process. The synergistic advantages of surface tension reduction by surfactant and nanoparticles adsorption at the foam lamellae can be exploited for producing foam with high foamability and longtime stability in the oil producing reservoir. However, the influence of nanoparticles on the static and the dynamic stability of conventional foam is not yet explicit due to limited studies. Moreover, only few studies have considered the pore-scale mechanisms of the nanoparticles-surfactant foams flow process in porous media and the minimization of surfactant adsorption in presence of nanoparticles. Due to limited research in this area, this study was conducted to understand the influence of silicon dioxide (SiO₂) and aluminum oxide (Al₂O₃) nanoparticles on the surfactant foam bulk and dynamic stability and surfactant adsorption on clay mineral. Four main experimental studies comprising the influence of the nanoparticles on surfactant adsorption on kaolinite, bulk and bubble-scale foam stability evaluation in presence of oil and salts, pore-scale visualization studies in etched glass micromodels, and fluid diversion process experiments were conducted. Results of this study showed that the adsorption of surfactant on clay mineral reduced drastically by 40% and 75% in presence of Al₂O₃ and SiO₂ nanoparticles, respectively. The maximum adsorption of surfactant on the nanoparticles occurred at 0.3 wt % sodium dodecyl sulfate (SDS). The foam bulk and bubble scale stability results indicated that 1 wt % of SiO₂ and Al₂O₃ nanoparticles enhanced the stability of the foam in presence of oil and salts. There was a transition salt concentration beyond which the foam stability increased with increasing salt concentrations. The presence of Al₂O₃ and SiO₂ nanoparticles prevented the entering of emulsified oil into the foam lamellae and decreased the transition salt concentrations. From the results of the pore scale studies, the dominant mechanisms of foam propagation in water-wet system were lamellae division and bubble-to-multiple bubble lamellae division. The dominant mechanisms of residual oil mobilization and displacement by the foam in water-wet media were found to be direct displacement and emulsification of oil. The dominant mechanism of foam propagation and residual oil mobilization in oil-wet system was identified as the generation of pore spanning continuous gas foam. Inter-bubble trapping of oil and water, lamellae detaching and collapsing of SDS-foam were observed in presence of oil in both water-wet and oil-wet systems. Generally, the SiO₂-SDS and Al₂O₃-SDS foams propagated successfully in oil-filled water-wet and oil-wet systems. Bubble coalescence was prevented during film stretching. The results of the fluid diversion process indicated an effective diversion of fluid in layered macroscopic model with permeability ratio of 8:1 in presence of SiO₂ and Al₂O₃ nanoparticles. The outcomes of this research is a major breakthrough in prospective field applications of nanoparticles-surfactant foams in oil-filled water-wet and oil-wet porous media.
ABSTRAK

Busa zarah nano dan surfaktan mempunyai aplikasi meluas dalam perolehan minyak tertingkat. Kelebihan sinergi melalui penurunan tegangan permukaan oleh surfaktan dan jerapan zarah nano di permukaan gelembung boleh menghasilkan busa dengan kebolehbusaan yang tinggi dan kestabilan busa yang lebih lama dalam menghasilkan takungan minyak. Namun begitu, kesan zarah nano kepada kestabilan busa lebih lama dalam menghasilkan takungan minyak. Selain itu, tidak banyak kajian yang mempertimbangkan mekanisme skala-liang bagi proses aliran busa dalam media liang dan penurunan penjerapan surfaktan dengan kehadiran zarah nano. Oleh kerana penyelidikan yang terhad, kajian ini dijalankan untuk menentukan kesan zarah nano silika dioksida (SiO₂) dan alumina oksida (Al₂O₃) terhadap kestabilan busa pukal dan penjerapan surfaktan pada mineral lempung. Empat eksperimen utama yang dijalankan adalah kesan zarah nano terhadap jerapan surfaktan pada mineral lempung berkurang secara mendadak sebanyak 40% dan 75% dengan kehadiran zarah nano masing-masing SiO₂ dan Al₂O₃. Penjerapan maksimum surfaktan pada zarah nano berlaku pada 0.3 % berat sodium dodesil sulfat (SDS). Hasil daripada kestabilan busa pukal dan skala-gelembung menunjukkan peningkatan kestabilan busa pada 1% berat zarah nano SiO₂ dan Al₂O₃ dengan kehadiran minyak dan garam. Terdapat kepekatan garam peralihan yang melampaui kestabilan busa yang meningkat dengan peningkatan kepekatan garam. Kehadiran nano zarah Al₂O₃ dan SiO₂ menghalang kemasukan minyak yang diemulsi ke dalam lamela busa dan menurunkan kepekatan garam peralihan. Daripada hasil kajian skala-liang, mekanisme dominan pergerakan busa dalam sistem basah air adalah pembahagian lamela dan lamela gelembung-ke-multigelembung. Mekanisme dominan untuk pergerakan dan anjakan minyak baki oleh busa dalam sistem basah minyak dikenal pasti sebagai pembentukan liang yang merangkumi busa gas secara berterusan. Inter-gelembung memerangkap minyak dan air, lamela memisah dan meruntuhkan busa SDS yang dicerap dengan kehadiran minyak dalam sistem air-basah dan minyak-basah. Secara umum, pergerakan busa SDS-SiO₂ dan SDS-Al₂O₃ baik dalam sistem berisi minyak basah air dan minyak basah. Tautan gelembung dihalang semasa peregangan filem. Hasil proses lencongan bendalir menunjukkan pelencongan bendalir yang berkesan dalam model makro berlapis dengan nisbah ketertelapan 8:1 dengan kehadiran SiO₂ dan Al₂O₃. Hasil kajian ini merupakan satu kejayaan utama dalam aplikasi bidang prospektif busa zarah nano-surfaktan dalam media liang berisi minyak basah air dan minyak basah.
# TABLE OF CONTENT

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
<td></td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENT</td>
<td>vii</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
<td></td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xxvii</td>
<td></td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xxix</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Background of Study</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Problem Statement</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Objectives of the Work</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>Scope and Limitations of Study</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>Significance of Study</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>LITERATURE REVIEW</td>
<td>9</td>
</tr>
<tr>
<td>2.1</td>
<td>Brief overview of Gas Injection EOR</td>
<td>9</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Problems of Gas Injection EOR</td>
<td>10</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Solutions to the problems of Injection EOR</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>The Definitions of Foam</td>
<td>12</td>
</tr>
<tr>
<td>2.3</td>
<td>Mechanisms of Foam Generation in Porous Media</td>
<td>14</td>
</tr>
</tbody>
</table>
2.3.1 Snap-Off 14
2.3.2 Lamellae Division 15
2.3.3 Leave behind Mechanism 16

2.4 Mechanisms of Foam Coalescence in Porous Media 17

2.5 Foam as Mobility Control Agent in Porous Media 18

2.6 Mechanisms of Gas Mobility Control by Foam 21
2.6.1 Gas Trapping and Apparent Viscosity Increase 21
2.6.2 Fluid Diversion Mechanisms 22

2.7 Experimental Study of foam for EOR Applications 24
2.7.1 Bulk Foam Stability Experiments 25
2.7.2 Macroscopic Studies 26
2.7.3 Microscopic Studies 27

2.8 Critical Parameters that Influences Foam Performance in Porous media 33
2.8.1 Influence of Foam Texture and Pore geometry 33
2.8.2 Influence of Foam-Oil Interaction In Porous Media 34
2.8.3 Influence of Porous media Wettability 39
2.8.4 Influence of Foaming Agents and Stabilizers 43

2.9 Influence of Nanoparticles on Foam Stability 45
2.9.1 Mechanisms of foam Stabilization by nanoparticles 46
2.9.2 Influence of Critical parameters on Nanoparticles-SDS foam performance 47
3 RESEARCH METHODOLOGY 61

3.1 Overview and Research Strategy 61

3.2 Materials 62
3.2.1 The Foaming agents 63
3.2.2 The Stabilizing Agents 63
3.2.3 The Fluid Systems 64
3.2.4 Clay Mineral 67
3.2.5 Porous Media Characterization 68

3.3 Experimental Procedures 73
3.3.1 Preparations of surfactants and Nanoparticles-surfactant solutions 73
3.3.2 Surface and interfacial Tension Measurements 74
3.3.3 Characterization of the Nanoparticles 76
3.3.4 Adsorption on Kaolinite Experiments 77
3.3.5 CO\textsubscript{2} Static and Bubble Scale Stability and Liquid Drainage Experiments 80
3.3.6 Foam Flow Dynamics in 2D Hele-Shaw Cell 84
3.3.7 Bulk Foam Apparent Viscosity Investigation 85
3.3.8 Pore Scale Visualization Study in Etched Glass Micromodel 86
3.3.9 Foam Fluid Diverting Experiments In a Layered Macroscopic Model 89
3.3.10 Porous Media Basic Properties Determination 90

4 RESULTS AND DISCUSSIONS 93

4.1 Introduction 93
4.2.1 Extent of Surfactant Adsorption on Nanoparticles 93
4.2.2  Surfactants Adsorption at Different Nanoparticles Concentrations 95

4.3  Nanoparticles Characterizations 96

4.4  Solid Particle Wettability Determination 98

4.5  Mechanisms of SDS-Foam Improvement by Nanoparticles 101

  4.5.1  Foam Apparent Viscosity Determination in Hele-Shaw Cell 101

  4.5.2  Films Strength and Bubbles Morphology 104

  4.5.3  Nanoparticles Adsorption and Accumulation at Foam Lamellae 112

4.6  Main Experiments 115

  4.6.1  Surfactant Adsorption on Kaolinite in Presence of Salts 115

  4.6.2  Adsorption Isotherm Models 118

  4.6.3  Influence of SiO$_2$ and Al$_2$O$_3$ nanoparticles on the SDS Adsorption 121

  4.6.4  Equilibrium Adsorption Models for the Experimental Data 124

4.7  Bulk and Bubble –Scale Foam Stability Experiments 127

  4.7.1  Influence of Al$_2$O$_3$ Nanoparticles Concentration 127

  4.7.2  Influence of Hydrophilic SiO$_2$ Nanoparticles Concentration 128

  4.7.3  Influence of Modified SiO$_2$ Nanoparticles Concentration 130

  4.7.4  Evidence of Nanoparticles Agglomeration from Static Stability 132
4.7.5 Evidence of Agglomeration From The Bubble-Scale Experiments

4.8 Effects of Oil Presence on Foam Stability
4.8.1 Foam Static Stability Improvement by Nanoparticles in Presence of Oil
4.8.2 Foam Stability Improvement from the Bubble Size Distribution
4.8.3 Mechanisms of Foam Stability Improvement by Nanoparticles in Presence of Oil

4.9 Influence of Salinity on Foam Stability
4.9.1 Influence of Surfactant and Salts Concentration On SDS-Foam Generation
4.9.2 Effects Of Surfactant and NaCl Salts Concentration on SDS-Foam Stability
4.9.3 Influence of CaCl₂ Concentration on SDS-Foam Stability
4.9.4 Effects of AlCl₃ Concentration on SDS-Foam Stability
4.9.5 Influence of SiO₂ and Al₂O₃ Nanoparticles on SDS-Foam Stability in Presence of Salts
4.9.6 Mechanisms of Foam Stability Improvement by Nanoparticles in Presence of Salts

4.10 Foam Flow Dynamics in 2D Hele–Shaw cell

4.11 Pore-Scale Visualization Experiments in Micromodels
4.11.1 Fluid Distributions in Water-Wet and Oil-Wet System
4.11.2 Configuration and Distribution of Connate Water Saturation in Water-Wet and Oil-Wet Micromodels

4.11.3 Residual Oil Saturation to Waterflood in Water-wet System

4.11.4 Residual Oil Saturation to Waterflood in Oil-wet System

4.11.5 Gas Injection into the Water-Wet Etched Glass Micromodel Experiments

4.11.6 Gas Injection into the Oil-Wet Etched Glass Micromodel Experiments

4.11.7 Mechanisms of Foam Generation Propagation and Residual Oil Mobilization

4.11.8 Foam Flow Process in Oil-Wet System

4.11.9 Mechanisms of Oil Mobilization by Foam in Oil-Wet System

4.11.10 Influence of Nanoparticles on Foam Performance in Oil-Wet System

4.11.11 Foam-Oil Interaction in Etched Glass Micromodels

4.12 Fluid Diversion Mechanisms

4.12.1 Fluid Diversion Performance of Foam in the Absence of Oil

4.12.2 Fluid Diversion Process in Presence of Crude Oil

5 CONCLUSIONS AND RECOMMENDATIONS 215

5.1 Conclusions 215

5.2 Recommendations 217

REFERENCES 218

Appendices A-C 241-251
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Summary of the previous research on experimental study of foam</td>
<td>31</td>
</tr>
<tr>
<td>2.2</td>
<td>Foam stability prediction by L, E and S</td>
<td>36</td>
</tr>
<tr>
<td>2.3</td>
<td>Summary of the previous research about the effect of oil on foam stability</td>
<td>37</td>
</tr>
<tr>
<td>2.4</td>
<td>Summary of the previous research about the influence of critical parameters on nanoparticles-surfactant foam performance</td>
<td>59</td>
</tr>
<tr>
<td>3.1</td>
<td>Properties of the nanoparticles used in this study</td>
<td>64</td>
</tr>
<tr>
<td>3.2</td>
<td>Properties of the model oils used in this study</td>
<td>65</td>
</tr>
<tr>
<td>3.3</td>
<td>Properties of crude oil used in the experiments</td>
<td>66</td>
</tr>
<tr>
<td>3.4</td>
<td>Basic properties of the Hele-Shaw cell used in the study</td>
<td>69</td>
</tr>
<tr>
<td>3.5</td>
<td>Basic properties of the etched glass micromodels</td>
<td>71</td>
</tr>
<tr>
<td>3.6</td>
<td>Basic properties of the visual layered macroscopic model</td>
<td>72</td>
</tr>
<tr>
<td>3.7</td>
<td>Formulae and description of parameters for Temkin adsorption isotherm, Langmuir adsorption isotherm and Freundlich adsorption isotherm.</td>
<td>79</td>
</tr>
<tr>
<td>4.1</td>
<td>Summary of the basic measurement experiments</td>
<td>100</td>
</tr>
<tr>
<td>4.2</td>
<td>Static analysis of the foam morphology through IMAGE J</td>
<td>111</td>
</tr>
<tr>
<td>4.3</td>
<td>Average particle diameter for Al₂O₃ nanoparticles in Al₂O₃/SDS dispersions</td>
<td>135</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.4</td>
<td>Entering, spreading coefficients and lamella number for paraffin oil</td>
<td>149</td>
</tr>
<tr>
<td>4.5</td>
<td>Influence of NaCl, CaCl$_2$ and AlCl$_3$ salts on foam generation</td>
<td>151</td>
</tr>
<tr>
<td>4.6</td>
<td>Summary of gas injection experiments, foam generation, propagation and oil mobilization mechanisms in water-wet system</td>
<td>187</td>
</tr>
<tr>
<td>4.7</td>
<td>The summary of foam performance in oil-wet micromodel</td>
<td>200</td>
</tr>
<tr>
<td>4.8</td>
<td>Influence of oil on the performance of SDS-foam and nanoparticles-SDS foam.</td>
<td>204</td>
</tr>
<tr>
<td>FIGURE NO.</td>
<td>TITLE</td>
<td>PAGE</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.1</td>
<td>(a) Ideal flow of CO$_2$ from Injection well (I) to production well (P) and (b) Viscous fingering of CO$_2$ with large volume of un-swept oil</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>Problems of gas Injection EOR in form of (a) Poor area sweep (b) Gas Channelling and (c) Gravity Overrides</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Sketch of (a) continuous gas foam and (b) discontinuous gas foam</td>
<td>13</td>
</tr>
<tr>
<td>2.4</td>
<td>Schematics of snap-off-mechanism showing (a) first stage (b) second stage (c) third stage</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematics of lamellae division mechanism showing (a) mobilized lamellae at branching point and (b) splitting of lamellae into two</td>
<td>16</td>
</tr>
<tr>
<td>2.6</td>
<td>Schematics of leave behind mechanism showing (a) two gas fingers at pore throats and (b) draining of liquid lenses to lamellae</td>
<td>17</td>
</tr>
<tr>
<td>2.7</td>
<td>Gravity override when (a) only CO$_2$ gas (blue) was injected and (b) prevention of gravity override by foam</td>
<td>20</td>
</tr>
<tr>
<td>2.8</td>
<td>Prevention of viscous fingering by injection of CO$_2$ foam</td>
<td>20</td>
</tr>
<tr>
<td>2.9</td>
<td>Comparison of (a) SAG with (b) waterflooding in sandpack with 19:1 permeability ratio</td>
<td>23</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>2.10</td>
<td>Comparison of sweep efficiency of SAG, WAG and waterflooding</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>Side view of a glass-bead Hele Shaw micromodel</td>
<td></td>
</tr>
<tr>
<td>2.12</td>
<td>Heterogeneous layered micromodel with permeability contrast of 4</td>
<td></td>
</tr>
<tr>
<td>2.13</td>
<td>Diagrams showing the different interface</td>
<td></td>
</tr>
<tr>
<td>2.14</td>
<td>Side view of pore level diagram of water-wet, mixed-wet and oil-wet porous media</td>
<td></td>
</tr>
<tr>
<td>2.15</td>
<td>Mechanisms of oil droplet mobilization by SDS-foam and SiO$_2$/SDS foam</td>
<td></td>
</tr>
<tr>
<td>2.16</td>
<td>Effect of SDS/SiO$_2$ concentration ratio on foam generation and stability</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Overview of the overall research strategy</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Magnified section of (a) circular shaped grain design micromodels and (b) diamond shaped grain design micromodels used in this study</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic diagram of the 2D layered macroscopic model</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Schematic of the experimental set-up for the bulk foam stability</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>Krüss foam analyser (DFA100) used to investigate foam bubble-scale stability and drainage</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Leica EZ4 HD stereo microscope used for lamellae thickness and foam morphology determination</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>Set-up of the 2D Hele-Shaw Cell used for foam flow dynamics</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>Experimental set-up for the pore scale visualization experiments in etched glass micromodels</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>Experiments to determine the fluid diverting performance of foam</td>
<td></td>
</tr>
<tr>
<td>3.10</td>
<td>Procedures for wettability alterations of the micromodels</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Adsorption index versus surfactant concentration for different nanoparticles</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Adsorption index versus surfactant concentration for different SiO$_2$ concentration</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Scanning electron microscope image of modified SiO$_2$ nanoparticles</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Scanning electron microscope (SEM) images of (a) SiO$_2$ nanoparticles and (b) Al$_2$O$_3$ nanoparticles</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Transmission electron microscope (SEM) images of (a) SiO$_2$ nanoparticles and (b) Al$_2$O$_3$ nanoparticles</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>Images for contact angle measurement for (a) hydrophilic Al$_2$O$_3$ nanoparticles (b) hydrophilic SiO$_2$ nanoparticles and (c) modified SiO$_2$ nanoparticles</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>Foam apparent viscosity at 50 % foam quality and different flowrates</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>Foam apparent viscosity at 75 % foam quality and different flowrates</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Lamellae thickness and bubble diameter of the SDS-stabilized foam (a) immediately after generation and (b) 60 minutes after generation</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>Morphology of the bubble size distribution of the SDS-foam</td>
<td></td>
</tr>
<tr>
<td>4.11</td>
<td>Histogram of bubble size distribution of SDS stabilized foam</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.12</td>
<td>Lamellae thickness of the hydrophilic SiO$_2$-SDS 60 minutes after generation</td>
<td></td>
</tr>
<tr>
<td>4.13</td>
<td>Morphology of the bubble size distribution of the SiO$_2$/SDS foam</td>
<td></td>
</tr>
<tr>
<td>4.14</td>
<td>Histogram of bubble size distribution of SiO$_2$/SDS stabilized foam</td>
<td></td>
</tr>
<tr>
<td>4.15</td>
<td>Lamellae thickness of the modified SiO$_2$/SDS foam</td>
<td></td>
</tr>
<tr>
<td>4.16</td>
<td>Morphology of the bubble size distribution of the modified SiO$_2$/SDS foam</td>
<td></td>
</tr>
<tr>
<td>4.17</td>
<td>Histogram of bubble size distribution of modified SiO$_2$/SDS bubbles</td>
<td></td>
</tr>
<tr>
<td>4.18</td>
<td>Lamellae thickness and bubble diameter of the Al$_2$O$_3$-SDS foam</td>
<td></td>
</tr>
<tr>
<td>4.19</td>
<td>Histogram of bubble size distribution of Al$_2$O$_3$/SDS stabilized bubbles</td>
<td></td>
</tr>
<tr>
<td>4.20</td>
<td>Image of Al$_2$O$_3$/SDS foam showing nanoparticles accumulation at the thin films</td>
<td></td>
</tr>
<tr>
<td>4.21</td>
<td>Time of liquid drainage from the modified SiO$_2$/SDS foam as a function of nanoparticles concentration</td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>Effect of NaCl concentration on the adsorption of SDS onto kaolinite</td>
<td></td>
</tr>
<tr>
<td>4.23</td>
<td>Effect of CaCl$_2$ on the adsorption of SDS onto kaolinite</td>
<td></td>
</tr>
<tr>
<td>4.24</td>
<td>Effect of AlCl$_3$ on the adsorption of SDS onto kaolinite</td>
<td></td>
</tr>
<tr>
<td>4.25</td>
<td>Langmuir Equation fitting for adsorption isotherm at NaCl concentration</td>
<td></td>
</tr>
<tr>
<td>4.26</td>
<td>Langmuir equation fitting for adsorption isotherm of SDS at different CaCl$_2$ concentration</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.27</td>
<td>Langmuir equation fitting for adsorption isotherm of SDS at different AlCl$_3$ concentration</td>
<td></td>
</tr>
<tr>
<td>4.28</td>
<td>Surface tension trends of different concentration of SDS in absence and presence of 1 wt% SiO$_2$ and Al$_2$O$_3$ nanoparticles</td>
<td></td>
</tr>
<tr>
<td>4.29</td>
<td>Adsorption isotherms of SDS in absence and presence of 1 wt% SiO$_2$ and Al$_2$O$_3$ nanoparticles (Results of two-phase titration experiments).</td>
<td></td>
</tr>
<tr>
<td>4.30</td>
<td>Langmuir isotherm model fit for the adsorption of SDS, SiO$_2$/SDS and Al$_2$O$_3$/SDS mixtures onto kaolinite</td>
<td></td>
</tr>
<tr>
<td>4.31</td>
<td>Freundlich isotherm model fit for the adsorption of SDS, SiO$_2$/SDS and Al$_2$O$_3$/SDS mixtures onto kaolinite</td>
<td></td>
</tr>
<tr>
<td>4.32</td>
<td>Temkin isotherm model fit for the adsorption of SDS, SiO$_2$/SDS and Al$_2$O$_3$/SDS mixtures onto kaolinite</td>
<td></td>
</tr>
<tr>
<td>4.33</td>
<td>Influence of Al$_2$O$_3$ nanoparticles concentration on Al$_2$O$_3$/SDS Foam</td>
<td></td>
</tr>
<tr>
<td>4.34</td>
<td>Influence of hydrophilic SiO$_2$ nanoparticles on SiO$_2$/SDS foam</td>
<td></td>
</tr>
<tr>
<td>4.35</td>
<td>Normalized foam height of hydrophilic SiO$_2$/SDS CO$_2$ foam showing 1 wt % as optimum concentrations for maximum foam stability</td>
<td></td>
</tr>
<tr>
<td>4.36</td>
<td>Influence of nanoparticles concentration on modified SiO$_2$/SDS foam</td>
<td></td>
</tr>
<tr>
<td>4.37</td>
<td>Normalized foam height of modified SiO$_2$/SDS CO$_2$ foam showing that foam stability increases with increasing nanoparticles concentration</td>
<td></td>
</tr>
<tr>
<td>4.38</td>
<td>Images of Al$_2$O$_3$/SDS CO$_2$ foam with (a) 1 wt % Al$_2$O$_3$ concentration (b) 2 wt % Al$_2$O$_3$ concentration</td>
<td></td>
</tr>
</tbody>
</table>
4.39 Influence of particle agglomeration on the bubble size distribution of (a) Al\textsubscript{2}O\textsubscript{3}/SDS foam (b) hydrophilic SiO\textsubscript{2}/SDS foam and (c) modified SiO\textsubscript{2}/SDS foam.

4.40 Influence of nanoparticles on foam stability in presence of oil

4.41 The normalized height of SiO\textsubscript{2}/SDS CO\textsubscript{2}-foams in the presence of oil

4.42 The normalized height of CO\textsubscript{2}-foams in the presence of crude oil

4.43 Bubble size distribution of (a) SDS foam (b) Al\textsubscript{2}O\textsubscript{3}-SDS foam (c) Modified SiO\textsubscript{2}-SDS foam and (d) Hydrophilic SiO\textsubscript{2}-SDS foam in presence of decane

4.44 Entering and spreading of oil at the lamellae of (a) Al\textsubscript{2}O\textsubscript{3}/SDS foam and (b) SDS-foam

4.45 Bubble-scale dynamics of (a) Al\textsubscript{2}O\textsubscript{3}/SDS foam and (b) SDS-foam in presence of decane oil

4.46 Bubble-scale dynamics of (a) Al\textsubscript{2}O\textsubscript{3}/SDS foam and (b) SDS foam in presence of crude oil

4.47 Histograms of the bubble size distribution for foam in presence of oil

4.48 Rate of liquid drainage from foam in presence of (a) Paraffin oil (b) Crude oil (c) Decane oil and (d) Hexadecane oil

4.49 Change in foam height with respect to time for SDS-foam in the absence of salt

4.50 Change in foam height with respect to time for SDS-foam (with 1 wt % NaCl concentration)

4.51 Change in foam height with respect to time for SDS in presence of 0.1 wt% CaCl\textsubscript{2}

4.52 Change in foam height with respect to time for SDS foam in presence of 0.5 wt% CaCl\textsubscript{2}
4.53 Change in foam height with respect to time for SDS foam in presence of 0.025 wt% AlCl$_3$ 155
4.54 Foam half-life as a function of surfactant concentrations 156
4.55 Foam half-life as a function of NaCl concentrations 158
4.56 Influence of nanoparticle on foam stability (0 wt % NaCl) 159
4.57 Influence of nanoparticle on foam stability (0.25 wt % NaCl) 159
4.58 Foam half-life as a function of different CaCl$_2$ concentrations 161
4.59 Foam half-life as a function of different AlCl$_3$ concentrations 161
4.60 Effect of different NaCl concentration on the surface tension of SDS, SiO$_2$-SDS and Al$_2$O$_3$-SDS mixtures 162
4.61 Aggregate size and zeta potential of the nanoparticles in nanoparticles-surfactant solutions as function of NaCl concentrations 163
4.62 Bubble size distribution of SDS-stabilized CO$_2$ foams (a) immediately after generation and (b) after 60 minutes in the 2D Hele-Shaw cell 165
4.63 Bubble size distribution of Al$_2$O$_3$/SDS-stabilized CO$_2$ foams (a) immediately after generation and (b) after 60 minutes in 2D Hele-Shaw Cell 166
4.64 Bubble size distribution of the (a) Hydrophilic SiO$_2$/SDS CO$_2$ foams and (b) modified SiO$_2$/SDS CO$_2$ foam in 2D Hele-Shaw cell after 60 minutes 167
4.65 Magnified images of the (a) SDS-stabilized CO$_2$ foam and the (b) modified SiO$_2$/SDS CO$_2$ foam showing the thickness of the foam lamellae in the 2D Hele-Shaw Cell 168
4.66 Fluid distributions in water-wet micromodels (a) Circular shaped system and (b) Diamond shaped system (red color indicates oil and blue color indicates water).

4.67 Fluid distributions in oil-wet micromodels (a) Circular shaped system and (b) diamond shaped system (red color indicates oil and blue color indicates water)

4.68 Connate water saturation in the water-wet system in form of (a) thin films on the grain surfaces (b) dense water films in pore throat (c) dense water films in pore body and (d) connate water in entire pore body and pore throat (red color indicates oil and blue color indicates water)

4.69 Connate water saturation in the oil-wet system in form of (a) evenly distributed layer in the middle of the larger pores (b) isolated water droplets and globules that are surrounded by thick continuous oil films (c) uniformly distributed or in form of trapped water globules and (d) isolated water droplets, thick and thin strip, or occupied the middle of the larger pore (red colour indicates oil and blue colour indicates water)

4.70 Residual oil saturation to waterflood in water-wet micromodel showing (a) spontaneous imbibition of water (b) growth and gradual thickening of water layers (c) oil filaments becomes thinner and water filament become thicker and (d) discrete oil ganglia from oil-snap off (Red colour indicates oil and blue colour indicates water).

4.71 Residual oil saturation to waterflood in oil-wet micromodel in form of (a) continuous oil filaments on the pore surface (b) the residual oil
clusters trapped in smaller pore bodies for the circular shaped model (c) the residual oil clusters trapped in smaller pore bodies for the diamond shaped model (d) High residual oil saturation and earlier water breakthrough in a diamond shaped model (e) High residual oil saturation and earlier water breakthrough in a circular shaped model.

4.72 Gas Injection into the water-wet system showing (a) direct displacement of oil by gas (b) gas fingering through the oil.

4.73 Gas Injection into the oil-wet system showing (a) direct displacement of oil by gas (b) gas fingering through the oil.

4.74 Foam regeneration by the occurrence of lamellae division mechanism in (a) circular shaped micromodel and (b) diamond shaped micromodel (c) Magnified pore body and throat showing lamellae division and leave behind mechanisms.

4.75 Bubble-to-multiple-bubble lamellae division in (a) Circular shaped micromodel and (b) diamond shaped micromodel (c) at pore throat and pore body

4.76 Mechanism of direct displacement of oil by foam showing (a) Foam behind an oil bank in the micromodel and (b) 100% microscopic displacement efficiency by the foam.

4.77 Mechanism of the emulsification of oil showing oil within the foam system and at pleateau borders in (a) circular shaped micromodel and (b) diamond shaped micromodel.
4.78 Direct displacement mechanisms in SDS-Stabilized foam showing (a) trapping of oil in form of oil filament and macro-emulsions and (b) oil trapped between bubbles at pore body and pore throat.

4.79 Direct displacement mechanisms of (a) hydrophilic SiO\(_2\)/SDS foam showing almost 100% microscopic efficiency and (b) Al\(_2\)O\(_3\)/SDS foam with some trapped oil.

4.80 Oil mobilization and displacement process through the oil emulsification mechanism by (a) SDS-stabilized foam and (b) modified SiO\(_2\)/SDS foam.

4.81 Foam flow process in circular shaped etched glass micromodel showing (a) Almost 100% sweep by the Al\(_2\)O\(_3\)/SDS foam and (b) trapped oil by the pore walls of the micromodel during SDS-stabilized foam.

4.82 Foam flow process showing (a) 100% sweep during hydrophilic SiO\(_2\)/SDS foam flow and (b) trapped oil at the pore walls during SDS-stabilized foam flow process in a diamond shaped micromodel.

4.83 Foam propagation in oil-wet system as (a) isolated trapped bubbles (b) isolated and pore spanning bubbles in form of continuous gas foam.

4.84 Propagation and mobilization of oil by SDS-stabilized foam in oil-wet porous medium.

4.85 Pore spanning continuous SiO\(_2\)/SDS foam in (a) circular shaped micromodel and (b) diamond shaped micromodel.

4.86 Image of oil-wet etched glass micromodel after (a) Al\(_2\)O\(_3\)/SDS foam flooding and (b) SiO\(_2\)/SDS foam flooding.
4.87 SDS-stabilized foam interaction with (a) Paraffin oil in etched glass micromodel (b) Crude oil in etched glass micromodel.

4.88 Successful propagation of Al₂O₃/SDS foam in presence of crude oil resisting entering and spreading of oil at foam lamellae.

4.89 Foam image showing high microscopic displacement efficiency of (a) SiO₂/SDS foam (b) Al₂O₃/SDS foam in presence of paraffin oil.

4.90 Mobilization and recovery of oil from the dead end pores by (a) SDS-stabilized foam (b) hydrophilic SiO₂/SDS foam (c) modified SiO₂/SDS foam and (d) Al₂O₃/SDS foam.

4.91 The layer model when the high and low permeability layer was filled with the injected brine (water is coloured blue for visual observation).

4.92 The layer model when 8 PV of brine was injected. The upper permeability layer was filled while cross flow of fluid into low permeability layer was observed (the water is coloured blue for visual observation).

4.93 Injection of SDS-foam and brine into model showing fluid (brine) diversion process by the foam. The foam is white while the water is coloured blue for visual observation.

4.94 Injection of Al₂O₃/SDS foam and brine into model showing fluid (brine) diversion process by the foam. The foam is white while the water is coloured blue for visual observation.
4.95 Injection of hydrophilic SiO$_2$/SDS foam followed by the injection of brine into model showing fluid diversion process. Foam is white while the water is coloured blue.

4.96 Injection of modified SiO$_2$/SDS foam followed by the injection of brine into model showing fluid diversion process.

4.97 Crude oil saturated high and lower permeability layer of the macroscopic layered model

4.98 Waterflooding of the model resulted in recovery of oil from the upper permeability layer only. The oil is brown and the water blue.

4.99 The diversion of injected water towards the oil by SDS-foam.

4.100 SiO$_2$/SDS foam flooding after the water-flooding of the macroscopic model. The oil is dark brown, the foam is white while the water is colored blue for visual observation.
LIST OF SYMBOLS

\( \gamma_{\alpha\beta} \) - Interfacial tension

\( \Delta P \) - The differential pressure

\( \theta \) - The particle contact angle at the interface

\( \lambda \) - Conductivity coefficient

\( \mu \) - Viscosity coefficient

\( \sigma \) - Surface tension coefficient

\( c_e \) - The equilibrium concentration.

\( c_o \) - The initial concentration of surfactant

\( K_f \) - The Freundlich adsorption capacity and intensity

\( K_L \) - The Langmuir equilibrium constant

\( K_r \) - Relative permeability

\( r_{\text{max}} \) - Maximum amount of surfactant

\( b \) - The gap thickness of the 2D Hele-shaw cell

\( W_r \) - The energy required to remove the particle from the interface

\( L \) - The length of cell

\( M \) - Mobility ratio

\( R \) - Radius of the particle

\( \Gamma \) - The amount of adsorbate adsorbed

\( S \) - Surfactant solution

\( U \) - The velocity of the foam

\( \text{Al} \) - Adsorption index
$NP$ - Nanoparticles dispersion
$NPS$ - Nanoparticles/surfactant mixtures
$\mu_{f_{app}}$ - Foam apparent viscosity
LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Basic Properties Measurements</td>
<td>241</td>
</tr>
<tr>
<td>B</td>
<td>Summary of Adsorption Isotherm Parameters of SDS at Different Salinities Conditions</td>
<td>248</td>
</tr>
<tr>
<td>C</td>
<td>List of Publications</td>
<td>250</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil recovery from the petroleum reservoirs can be achieved by primary, secondary and tertiary oil recovery methods. Primary and secondary recovery methods depending on the reservoir characteristics, can only recover about 30 to 40% of the original oil in place (Xing, 2012). Hence, the remaining oil in the petroleum reservoir remains the target of any enhanced oil recovery (EOR) operations such as gas injection, chemical injection, microbial enhanced oil recovery and thermal oil recovery. During enhanced oil recovery process, there is an improvement in the oil displacement and volumetric sweep efficiencies. This can be achieved through reduction of oil viscosity, capillary forces, interfacial tension and the development of a favorable mobility ratio between the displacing and the displaced fluid (Simjoo, 2012). This results in the eventual mobilization and the production of a substantial portion of the trapped residual oil in the reservoir at minimum cost (Payatakes, 1982).

Gas injection with about 39% contributions to world’s EOR (Oil & Gas Journal, 2010) remains one of the most commonly used and generally accepted EOR methods. In gas injection, hydrocarbon and non-hydrocarbon gases like methane, air, carbon dioxide, natural gas and nitrogen are injected into the reservoirs for the recovery of residual oil (Liu et al., 2011). Gas injection can either be miscible or an immiscible gas flooding. In miscible gas flooding, the gas is injected either at
minimum miscibility pressure (MMP) or beyond. Oil recovery is enhanced by the reduction of viscosity and interfacial tension as the injected gas mixes completely with the oil. In immiscible flooding, the injected gas does not mix with the reservoir oil. Reservoir pressure is maintained as the gas injection takes place below the minimum miscibility pressure (MMP) (Shokrollahi et al., 2013). However, any gas enhanced oil recovery process suffers from poor macroscopic sweep efficiency because of gas higher mobility and lower density compared to oil or water (Rossen et al., 2010). Gas segregation, gravity override, viscous fingering and channeling through the high permeability streaks are the major challenges of gas injection EOR process (Andrianov et al., 2012).

In order to control the injected gas mobility and improve the poor volumetric efficiency during gas injection EOR, injection of gas slugs and water alternatively known as water-alternating gas (WAG process) has been used for several decades. The synergistic blend of the improved macroscopic sweep of waterflooding and the enhanced microscopic displacement efficiency of gas injection is exploited during WAG process (Sagir et al., 2014). However, as WAG process continues, large volume of oil is considerably trapped by excess production of water that prevents the injected gas from contacting the resident oil in the reservoir. Moreover at some distances away from the wellbore, the process may lead to a poor gravity segregation control due to the large density contrast between the injected gases and the trapped oil (Sohrabi et al., 2001). Consequently, vertical sweep efficiency and total oil recovery are drastically reduced as the process ultimately suffers from viscous instabilities and gravity segregation (Khalil and Asghari, 2006; Farajzadeh et al., 2009).

Due to the inadequacy of WAG, foam, a dispersion of gas in liquid, such that the liquid phase is continuous and some part of the gas phase is made discontinuous by a thin liquid film called lamellae (Falls et al., 1988) emerged in 1958 as a promising solution for controlling gas mobility. Foam controls gas mobility by increasing the apparent viscosity of the displacing fluid and reducing the relative permeability of the gas phase. In heterogeneous porous media, foam helps to divert the injected fluid from the high permeability regions to the low permeability un-swept areas by lowering the
gas mobility in the high permeability zones (Kovscek and Bertin, 2002; Skauge et al., 2002; Blaker et al., 2002). Results of previous studies show that foams apparent viscosities can be up to 1,000 times higher than that of their constituent phases (Zhu et al., 2004; Liu et al., 2005). Foam flooding are also more efficient than WAG process, waterflooding and gas flooding in reducing viscous fingering and improving sweep efficiency (Hirasaki and Lawson, 1985; Liu et al., 2005).

Nevertheless, foams are thermodynamically unstable and require surface active agents for their continuous generation and stability. For effective foam applications in enhanced oil recovery process, the foam have to remain stable and be able to propagate in the reservoir in the presence of resident reservoir brines and oils and at high temperatures (Zhu et al., 2004). Stable foams generation has been achieved using surfactants, polymer and proteins as the conventional foaming and stabilizing agents for several decades (Romero et al., 2002; Murray and Ettelaie, 2004; Romero-Zerón et al., 2010). It has been demonstrated experimentally that gaseous bubbles can be prevented from coalescing by the adsorption of surfactant, polymers and protein molecules at the gas–liquid interface of the foam (Rossen, 1996; Bournival et al., 2014; Zhang et al., 2015).

However, surfactant-stabilized foams, polymer enhanced foams and protein foams are unable to maintain their stability for a long time at reservoir conditions of high salinity, temperatures, and in the presence of oil in porous media. This is due to their high propensity to degrade and their low adhesion energy at the foam interface. Low adhesion of the stabilizing agents at foam lamellae promotes easy desorption and rapid film thinning of foam films (Carrier and Colin, 2003; Adkins et al., 2007; Fameau and Salonen, 2014). The film thinning increases and the foam becomes drier as a result of liquid drainage from the foam films (Fameau and Salonen, 2014). The thinning of the foam films eventually results in foam coalescence, that is, the breaking of smaller unstable bubbles to form bigger bubbles (Carrier and Colin, 2003; Fameau and Salonen, 2014). For surfactant-stabilized foam, the rate of surfactants adsorption on rock surfaces can also be very high thereby reducing the amount of surfactant molecules available for stabilizing the gas-liquid interface of the foam.
Recently, there is an emerging interest in foam stabilized by a mixture of nanoparticles and surfactant. The synergistic advantage of interfacial tension and capillary forces reduction by the surfactant and nanoparticles adsorption at the foam lamellae is exploited for producing foam with high foamability and long time stability (Osei-Bonsu et al., 2015). Results of some previous studies showed that nanoparticles-surfactant foams demonstrated high static and dynamic stability (Hunter, 2008; Cui et al., 2010; Sun et al., 2014; Singh and Mohanty, 2015). This has been attributed to the remarkable stability of the foam films due to the irreversible adsorption and aggregation of nanoparticles at the thin liquid films of the foam. Nanoparticles as the stabilizing components of the foam are solids; therefore, foams stabilized by nanoparticles–surfactant mixtures are more resistant to high salinity, temperatures, and the presence of resident reservoir brines and oils (Adkins et al., 2007). The rate of surfactant adsorption on reservoir rock surfaces and clay minerals is also reduced in presence of nanoparticles (Ahmadi and Shadizadeh, 2013).

1.2 Problem Statement

The performance of foam also depends on the adsorption properties of the foaming agents in presence of resident reservoir brine in porous media. Inorganic salt influences the adsorption of surfactant molecules on clay minerals and at gas-liquid interface of surfactant-stabilized foam. The higher the adsorption of surfactant on clay minerals, the less the available surfactant molecules on the gas-liquid interface of the foam. Effects of different parameters on surfactant adsorption from solution onto reservoir rocks and clay minerals have been investigated in literatures (Zhang and Somasundaran, 2006; Sánchez-Martín et al., 2008; Gogoi, 2009; Muherei et al., 2009; Lv et al., 2011; Amirianshoja et al., 2013; Bera et al., 2013). The results show that surfactants adsorption increases with increasing adsorbent dose, decreasing temperature and NaCl concentration due to their influence on the screening of the electrostatic charge (Behera et al., 2014). However, these previous studies focused only on surfactant adsorption onto reservoir rocks and clay minerals. There is still paucity of information on the influence of electrolyte on the competitive and
co-operative adsorption of surfactant and nanoparticles onto reservoir clay. It is essential to gather information regarding the effect of salts on the adsorption of these foaming/stabilizing agents in order to optimize their performance for foam generation.

Another major concern for ensuring effective foam application in EOR is the stability of foam in the presence of oil. Jensen and Friedmann (1987) discovered from their studies that residual oil saturation of 15% and above in the reservoir will drastically affect foam propagation and performance. Foam stability in the presence of oil depends on aqueous phase composition, type of foaming and/or stabilizing agent, and oil type (Osei-Bonsu et al., 2015). Generally, it has been reported from previous studies that oil has a destabilizing effect on the static and dynamic stability of foam (Vikingstad et al., 2005; Simjoo et al., 2013b; Duan et al., 2014; Osei-Bonsu et al., 2015; Farzaneh and Sohrabi, 2015). Results of these studies further showed that small-chain hydrocarbons with lower density and viscosity are more detrimental to the longevity of foams than long-chain hydrocarbons. Although the influence of oil on the stability of surfactant-stabilized foam has been widely investigated, few studies on the effects of oil on bulk stability of foams stabilized by nanoparticles–surfactant mixtures have been carried out. Thus, the role of nanoparticles on the static stability of surfactant foam in the presence of oil is yet to be well understood.

Porous media wettability is another critical parameter that influence foam stability and performance through their influence on fluid distribution and foam flow characteristics in porous media (Kulkarni and Rao, 2005; Talebian et al., 2013). Results of previous experimental studies suggested divided opinions among researchers on the influence of porous media wettability on foam performance in porous media. Some researchers reported that the ideal reservoir rock wettability for optimum foam performance in porous media is water-wet (Kristiansen and Holt, 1992; Rossen, 1996). Others asserted that foam can be generated and propagated in an oil-wet porous media due to wettability alteration of hydrophobic porous medium to hydrophilic porous medium (Sanchez and Hazlett, 1992; Schramm and Mannhardt, 1996; Mannhardt, 1999). Few other researchers reported optimum foam generation, propagation and stability in oil-wet porous media due to lower surfactants adsorption in the oil-wet porous medium (Lescure and Claridge, 1986; Haugen et al., 2012;
Romero-Zeron and Kantzas, 2007). These results are still contradictory and inconclusive and further studies will be required to obtained consistent results.

Meanwhile, most of the recent studies of nanoparticles-surfactant foams has been focused on either the bulk foam stability static experiments or the macroscopic studies (Yu et al., 2012a; Worthen et al., 2013c; Singh and Mohanty, 2015; Farhadi et al., 2016). The dominant mechanisms controlling the foam generation, propagation and stability in porous media especially in the presence of resident reservoir oils and brines are largely unknown due to limited studies. Knowledge of nanoparticles-surfactant foam propagation and stability in porous media at pore scale is vital for successful field design, application and implementation of nanoparticles-surfactant foam EOR.

1.3 Objectives of Study

The aim of this research is to determine the influence of silicon oxide (SiO2) and aluminum oxide (Al2O3) nanoparticles on the static and dynamic stability of sodium dodecyl sulfate (SDS) foams and to carry out a pore scale mechanistic study of the nanoparticles-surfactant stabilized foam flow process in water-wet and oil-wet porous media. Thus the specific objectives of this study are as follows:

I. To evaluate the influence of SiO2 and Al2O3 nanoparticles on the adsorption of SDS surfactant by kaolinite at different salinities
II. To determine the effect of nanoparticles concentration, salinity and oil presence on bulk and bubble scale stability of nanoparticles-surfactant foams
III. To determine the mechanisms of nanoparticles-surfactant foam flow process at pore scale in water-wet and oil-wet porous media.
IV. To investigate the role of nanoparticles on the process of fluid diversion by nanoparticles-surfactant foam in heterogeneous porous media.
1.4 Scope and Limitations of Study

This research comprises four main experiments which are surfactant adsorption experiments using two-phase titration method, bulk and bubble scale stability experiments conducted using foam column, dynamic foam analyzer and the 2D Hele-Shaw cell, pore scale visualization studies in the water-wet and oil-wet etched glass micromodels and fluid diversion experiments in unconsolidated visual layered glass bead packed macroscopic models. Some preliminary experiments were conducted in order to support and explain the observations and the results of the main experiments. These includes: surface tension measurements, determination of surfactant adsorption extent on the nanoparticles, determination of particle shape and wettability, determination of foam apparent viscosity in 2D Hele-Shaw cell, determination of foam lamellae thickness and morphology under the Leica EZ4 HD microscope.

The foam was pre-generated before injection into the porous media in all experiments in this study and all experiments were conducted at room temperature and pressure. The foam quality is limited to from 50% to 90%. The porosity of the etched glass micromodels ranges from 29% to 40% and the permeability ranges from 0.741 to 1.359 Darcy. The flowrate of 0.5 ml/hr (0.00833 ml/min) was used in the pore scale visualization experiments. It was difficult to generate foam at lower flowrate than that in this study. The dead end pores investigation experiments were limited to the water-wet system. Influence of pore geometry in terms of aspect ratio and coordination number on the foam performance was not very significant due to the presence of dead end pores. It was difficult to determine any reasonable oil recovery at the production outlet from the diamond shaped micromodels due to its low pore volume (0.47 ml). The permeability contrast of the layered model is 8:1 while the porosity ranges from 30% to 45%. The flowrate of fluid diversion experiments could not translate into 2 ft/day at flow rate of 3 ml/min-6 ml/min. The contact angle of nanoparticles was measured in the absence of oil. Three major salts, NaCl, CaCl$_2$ and AlCl$_3$ were used in this research. These salts represent the major monovalent, divalent and trivalent cations, and the major anion found in reservoir brines.
1.5 Significance of Study

A micro-scale understanding of influence of nanoparticles on conventional foam stability and the displacement behaviours of nanoparticles-surfactant stabilized CO$_2$ foam in oil and water-wet porous media has been provided from the results of these experiments. This will provide the basic guidelines for further research, future field design and implementation of nanoparticles-surfactant CO$_2$ foam enhanced oil recovery (EOR) process.
REFERENCES


