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**Application of Foam for Mobility Control in Enhanced Oil
Recovery (EOR) Process**

by

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ABSTRACT

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This thesis focuses on the application of foam for mobility control in enhanced oil recovery (EOR) process. The performance of foam and surfactants was evaluated by systematic laboratory study. This includes the screening and evaluation of surfactant formulations for foam EOR process and the investigation of foam for mobility control at reservoir conditions. The adsorption of cationic surfactants on natural minerals was discussed in a separate chapter, although it is one aspect for evaluating surfactant formulations. A numerical model was used to fit the foam strength for foam flooding at reservoir conditions.

The solubility, thermal and chemical stability and foaming ability of surfactant formulations were investigated in the screening and evaluation step. A qualified surfactant formulation for foam EOR should be soluble and stable from injection to reservoir conditions. The foaming ability of surfactant formulations needs to be verified in a porous media with crude oil. The bulk foam tests, *i.e.*, foam height, equilibrium foam volume and foam half-life, are not suggested to be used for evaluating foaming ability of surfactant formulations, because of the poor correlation with foam tests in porous media. The detrimental effect of oil, especially for light crude oil, for foam stability was demonstrated. Foam boosters,

e.g., betaine surfactants, can be used to stabilize the foam in the presence of crude oil.

The mobility control ability of foam was evaluated in Silurian dolomite cores at reservoir conditions after screening and evaluation step. The apparent viscosity of foam was used to describe the mobility control ability. The higher apparent viscosity indicates the stronger foam and better mobility control ability. The strength of foam depends on foam quality, salinity and temperature. The influence of each parameter was investigated and illustrated by controlled experiments. Ethomeen C12 in formation brine and CO₂ can generate strong foam at 120 °C and 3400 psi in a wide range of foam quality after the pressure gradient exceeded the minimum pressure gradient.

The adsorption of cationic surfactant on the pure carbonate minerals is low owing to the repulsion of the electrostatic force. However, the natural carbonate minerals contain negatively charged impurities, e.g., silica and clays. The adsorption of cationic surfactants on these impurities was significant. Multivalent cations, *i.e.*, Mg²⁺, Ca²⁺ and Al³⁺, can compete with cationic surfactants on the negatively charged binding sites to reduce the adsorption. The adsorption of Ethomeen C12 on silica was reduced from 5.33 mg/m² in DI water to 3.31 mg/m² in synthetic brine with 1.51×10⁻³ mol/L Al³⁺. The adsorption of Ethomeen C12 was measured at 2 atm CO₂ to keep the solution clear. The method of methylene blue (MB) two-phase titration was improved to determine the cationic surfactant concentrations in high salinity brine.

In summary, this study demonstrates the methodology to screen the surfactant formulations for the foam EOR process, elucidates the application of the foam for mobility control at reservoir conditions, improves the MB two-phase titration for cationic surfactant in high salinity brine and illuminates the reducing of the adsorption for cationic surfactants on natural carbonate minerals.

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Table of Contents

ABSTRACT	i
Acknowledgments	iv
Table of Contents	vi
List of Figures	ix
List of Tables	xvii
List of Equations	xviii
Chapter 1 Introduction	1
1.1 Enhanced Oil Recovery (EOR)	1
1.2 Foam Mobility Control for EOR Process	5
1.3 Screening and Evaluation of Surfactant Formulations for Foam EOR in Laboratory Scale	10
1.4 Adsorption of Surfactants	14
1.5 Thesis Structure	17
1.6 References	18
Chapter 2 Technical Background	27
2.1 Surfactant	27
2.1.1 Overview of Surfactants	27
2.1.3 Surfactants in Foam: Disjoining Pressure and Capillary Pressure	30
2.2.1 Darcy's Law and Mobility Ratio	32
2.2.2 Recovery Efficiency	34
2.2.3 Interfacial Tension (IFT) and Capillary Pressure	34
2.2.4 Wettability	37
2.3 Foam Flow in Porous Media	39
2.3.1 Foam Generation	39
2.3.2 Foam Coalescence	41
2.3.3 Foam Mobility Reduction	45

2.4 Determination of Surfactant Concentrations	47
2.4.1 Colorimetric Titration.....	47
2.4.2 Potentiometric Titration	50
2.4.3 High Performance Liquid Chromatography (HPLC)	50
2.5 References.....	52
Chapter 3 Screening of Surfactant Formulations for Foam EOR.....	55
3.1 Experimental.....	55
3.1.1 Materials	55
3.1.2 Solubility Test Procedure	59
3.1.3 Chemical and Thermal Stability Test Procedure	61
3.1.4 Foamability and Foam Stability in Bulk and Porous Media	62
3.2 Results and Discussions.....	68
3.2.1 Solubility of Surfactants.....	68
3.2.2 Chemical and Thermal Stability of Surfactants.....	77
3.2.3 The Comparison of Foam in Bulk and in Porous Media.....	88
3.2.4 The Influence of Crude Oil on Foam Stability	91
3.3 Conclusions	97
3.4 References.....	99
Chapter 4 Foam Mobility Control under Reservoir Conditions	101
4.1 Experimental.....	101
4.1.1 Materials	101
4.1.2 Apparatus for CO ₂ Foam Flooding at High Temperature and Pressure.....	102
4.1.3 Core Preparation and Characterization	114
4.1.4 Foam Flooding Procedures	118
4.1.5 A Local Equilibrium Foam Model (STARS Foam Model).....	120
4.2 Results and Discussions.....	122
4.2.1 The Influence of Foam Quality on Foam Strength	122
4.2.2 The Influence of Salinity in Brine on Foam Strength	126
4.2.3 The Influence of Elevated Temperature on Foam Strength	134
4.2.4 The pH in CO ₂ Foam Flooding Process	149
4.3 Conclusions	154

4.4 References.....	156
Chapter 5 Adsorption of Switchable Cationic Surfactants on Natural	
Carbonate Minerals	159
5.1 Experimental.....	159
5.1.1 Materials	159
5.1.2 The Improved MB Two-Phase Titration	163
5.1.3 Static Adsorption Measurement under 2 atm CO ₂	164
5.2 Results and Discussions.....	167
5.2.1 Spectrophotometric Parameters in MB Two Phase Titration	167
5.2.2 MB Two-Phase Titration with a Colorless End Point for Cationic Surfactants in DI Water.....	170
5.2.3 The Influence of Salinity on the MB Two-Phase Titration.....	173
5.2.4 MB Two-Phase Titration for Cationic Surfactants in High Salinity Brine	176
5.2.5 MB Two-Phase Titration for Switchable Cationic Surfactants.....	178
5.2.6 The Surface Charge and Zeta Potential of Carbonate Minerals.....	182
5.2.7 Adsorption of C12 on Pure and Natural Carbonates	189
5.2.8 The Influence of Cations on Adsorption.....	192
5.2.9 Adsorption of C12 on Formation Mineral.....	198
5.3 Conclusions	200
5.4 References.....	201
Chapter 6 Conclusions and Future Work	204
6.1 The Systematic Procedure to Screen the Surfactant Formulations for Foam EOR Process.....	204
6.1.1 The Investigation of Surfactant Formulations	204
6.1.2 The Pre-Screening for Foam Mobility Control	206
6.2 The Investigation of Foam Mobility Control at the Reservoir Conditions..	207
6.3 The Zeta Potential of Carbonate Minerals and Improved MB Two-Phase Titration	208
6.4 Future Work	210
6.5 References.....	212

List of Figures

Figure 1-1 Evolution of CO ₂ projects and oil price (Alvarado and Manrique, 2010)	3
Figure 1-2 The cross section of SAGD process (Gates, et al., 2007)	5
Figure 1-3 The pressure contour with gas and liquid rates (Cheng, et al., 2000)	8
Figure 2-1 Scheme for the formation of surfactant micelle in aqueous phase (Rangel-Yagui, et al., 2004)	29
Figure 2-2 Cartoon of disjoining and capillary pressure in foam plateau border. (http://www.maths.tcd.ie/~foams/PRESENTATIONS/Thursday12/Thursday12_Lecture1_Arnaud.pdf)	30
Figure 2-3 The schematic for the disjoining pressure as a function of film thickness (Bergeron, 1999)	31
Figure 2-4 The diagram of the interface between two condensed phase (Rosen, 2004)	35
Figure 2-5 The capillary desaturation curve (Lake, 1989; Camilleri, 1983)	37
Figure 2-6 Classification of wettability according to the water advancing contact angle (Morrow, 1990)	38
Figure 2-7 Interfacial tension balance based on Young's equation	38
Figure 2-8 Schematic of leave-behind mechanism (Chen, et al., 2005)	39
Figure 2-9 Schematic of snap-off mechanism (Falls, et al., 1988)	40
Figure 2-10 Schematic of lamella division mechanism (Falls, et al., 1988)	41
Figure 2-11 The process of an oil droplet entering, spreading and bridging across the foam film (Lobo and Wasan, 1993)	43
Figure 2-12 Diagram of pseudoemulsion film (Lobo and Wasan, 1993)	44
Figure 2-13 Schematic of Epton's Methylene Blue (MB) two-phase titration	49
Figure 2-14 The schematic of HPLC setup (Bian, 2009)	51
Figure 3-1 The structure of the anionic surfactants	57
Figure 3-2 The structure of cationic, zwitterionic and switchable cationic surfactants	58
Figure 3-3 Solubility test in capped bottle at room temperature and encased-glass-pipette at other temperatures. Left figure is 1% CTAB in DI water at 22 °C	

(the Krafft point is 27 °C), right figure is 1% C25 in synthetic formation brine at 130 °C (the cloud point is 70 °C).	60
Figure 3-4 The HPLC analysis results for CAB in pH=4.47 buffer (ammonium acetic – acetic acid). CAB degrades with aging time.	62
Figure 3-5 The schematic of bulk foam test apparatus.....	64
Figure 3-6 The schematic of the foam flooding in sandpack	65
Figure 3-7 Krafft phenomenon of 0.2% CTAB at room condition (22 °C). The solution in DI water becomes clear at around 27 °C	70
Figure 3-8 Krafft Phenomenon of 0.2% CPC at room condition (22 °C and 1 atm). The cloudy solution becomes clear at 40 °C.....	70
Figure 3-9 Krafft Temperature Test for 0.2% (wt) CPC in synthetic formation Brine. Original pH=6, and adjusted with HCl to pH=4.....	71
Figure 3-10 Cloud points of C25A, Upper: 1% C25A in DI water, Lower: 1% C25A in synthetic formation brine.....	72
Figure 3-11 Cloud points of 1% C12, Upper: C12 in DI Water, Lower: C12 in synthetic formation brine	73
Figure 3-12 Pictures of 1% C25A in synthetic formation brine with different pH. Left is at 90 °C, right is at 120 °C.	74
Figure 3-13 Cloud point test of 1% C25A in NaCl and CaCl ₂ solutions with the same ionic strength (2.05 mol/L) at pH≈9	75
Figure 3-14 Cloud point for C25A/CPC blends of 0.2% (wt) total activity at pH=6. The cloud point of the blend with 30% (wt) CPC is 126 °C	76
Figure 3-15 The comparison of 0.2% (wt) CTAB aged at 125 °C for 11 days and unaged sample at neutral pH. Upper: CTAB in DI water, Lower: CTAB in 3.5% (wt) NaCl solution. The characteristic peak of CTAB arrived at 19 min	77
Figure 3-16 0.2% (wt) CTAB in 1% (wt) Na ₂ CO ₃ solution. Left one was aged at 125 °C for 11 days, right one was at room temperature	78
Figure 3-17 The HPLC signals of 0.1% (wt) CAB in DI water at neutral pH. Sample was aged at 125 °C for 10 days	78
Figure 3-18 The HPLC signals of 0.1% (wt) CAB in 1.0% (wt) Na ₂ CO ₃ solution. Sample was aged at 125 °C for 40 hours and 8 days. (a) in full scale (b) in zoom scale for surfactant peaks part (the characteristic peak of CAB at 16.5 min) (c) in zoom scale for salinity peaks part.....	79

Figure 3-19 The HPLC signals of 0.1% (wt) CAB at pH=4.47. Sample was aged at 125 °C for 3 days and 8 days. (a) in full scale (b) in zoom scale for surfactant peaks part (the characteristic peak of CAB at 16.5 min) (c) in zoom scale for salinity peaks part.....	80
Figure 3-20 The HPLC signals of 0.1% (wt) CAB at pH=3.19. Sample was aged at 125 °C for 3 days and 8 days. (a) in full scale (b) in zoom scale for surfactant peaks part (the characteristic peak of CAB at 16.5 min) (c) in zoom scale for salinity peaks part.....	81
Figure 3-21 The comparison of aged and unaged 0.1% (wt) LB in DI water. Sample was aged at 125 °C for 24 days. (a) in full scale, (b) zoom in for surfactant peaks (at 8.1 and 10.9 min)	82
Figure 3-22 The comparison of aged and unaged 0.1% (wt) LB in 1.0% (wt) Na ₂ CO ₃ solution. (a) in full scale, (b) zoom in for surfactant peaks (at 8.1 and 10.9 min)	83
Figure 3-23 The comparison of aged and unaged 0.1% LB in pH=4.0 and 3.4 HCl solution.....	84
Figure 3-24 DSC analysis results for C12 in N ₂ atmosphere	85
Figure 3-25 TGA analysis of C12. Upper: in air atmosphere, Lower: in argon atmosphere.....	85
Figure 3-26 The HPLC results for 1% C12 in HCl acid solution at pH=4.0. Upper: in full scale, lower: in zoomed scale for salt peaks. The characteristic peaks of C12 are all peaks with retention time higher than 6 min	87
Figure 3-27 The equilibrium foam volume at various N ₂ flow rate	89
Figure 3-28 20/40 silica sandpack (U.S. Silica Company) in 1-D mode with intrinsic permeability $k = 144$ darcy	90
Figure 3-29 The foam apparent viscosity for various formulations, superficial velocity is 20 ft/day	90
Figure 3-30 Foam apparent viscosity of DowFax 8390 at various superficial velocities in 1-D silica sandpack (Ma, 2009, Jul.)	91
Figure 3-31 The foam apparent viscosity of 0.2% (wt) AOS in the presence and absence of crude oil.	92
Figure 3-32 The photos for sandpack in AOS foam flooding, at 0.1, 1.0, 2.1 and 3.0 total PV (sum of gas and surfactant solution)	93
Figure 3-33 The foam apparent viscosity of 0.5% (wt) N25-7EO or N67-9EO in the presence and absence of crude oil.....	93

Figure 3-34 The foam apparent viscosity of 0.2% AOS-CAB (weight ratio 1:1) in the presence and absence of crude oil	94
Figure 3-35 The photos of sandpack in AOS-CAB foam flooding, at 0.1, 1.0, 2.1, 3.0, 4.0, 5.1 and 5.4 total PV	94
Figure 3-36 The foam apparent viscosity of IOS-LB in the presence of crude oil, modified from Li and et al. (2012)	96
Figure 3-37 The foam apparent viscosity of S70-LB in the presence and absence of crude oil	97
Figure 3-38 The photos of sandpack in S70-LB foam flooding	97
Figure 4-1 The high temperature and high pressure setup for CO ₂ foam flooding	103
Figure 4-2 The pumps system and core holder module	103
Figure 4-3 The pressure transducer module	104
Figure 4-4 The back pressure regulators (BPR) module	104
Figure 4-5 The regular design of core holder, drawn by Maura Puerto.	111
Figure 4-6 The new design of core holder, designed by Maura Puerto	112
Figure 4-7 The pressure-enthalpy diagram of carbon dioxide. Temperature and pressure change across the relief valves	114
Figure 4-8 Covers of core samples for CO ₂ flooding. (a) Heated shrinkable Teflon, (b) aluminum foil and (c) Viton rubber sleeve. Red box indicates the hole caused by vugs on the core surface.....	115
Figure 4-9 The pressure gradient vs. superficial velocity of water	117
Figure 4-10 The pH of dolomite – water/brine system at room temperature with and without CO ₂ , calculated by Phreeqc software (version 3.0.2)	118
Figure 4-11 The apparent viscosity history for the water and C12 flooding. The apparent viscosity increased to the pressure transducer limit after 1% C12 in DI water solution was injected. 1% C12 in DI water was clear by purging CO ₂ to decrease pH	119
Figure 4-12 The apparent viscosity history for C12/DI and CO ₂ foam with various foam qualities at room temperature	123
Figure 4-13 The fitting results for C12/DI and CO ₂ foam at room temperature calculated by Local Equilibrium Foam Model. The parameters of (epdry, fmmob, fmdry) for simulated lines are (100, 379, 0.39), (200, 353, 0.39), (500, 333, 0.40) and (1000, 323, 0.40), respectively.	125

Figure 4-14 The apparent viscosity history for C12/synthetic formation brine and CO ₂ foam with various foam qualities at room temperature.....	127
Figure 4-15 The apparent viscosity history of C12/synthetic formation brine and CO ₂ foam flooding at 90% foam quality.....	128
Figure 4-16 The fitted results for C12/synthetic formation brine and CO ₂ foam at room temperature calculated by Local Equilibrium Foam Model	130
Figure 4-17 The comparison of foam apparent viscosity in DI water and synthetic formation brine at room temperature	131
Figure 4-18 Comparison of foam apparent viscosity in low salinity brine and in high salinity brine.....	132
Figure 4-19 The average apparent viscosity at steady state for glycidyl ether sulfonates GS surfactants	132
Figure 4-20 The foam strength history for C12/synthetic formation brine and CO ₂ co-injection at 4 ft/day and 120 °C for various foam qualities: from (1) to (5) are 30%, 50%, 60%, 70% and 80%, respectively. MPG means minimum pressure gradient	136
Figure 4-21 C12 in synthetic formation brine and CO ₂ foam strength history at 70% foam quality and 120 °C with 4 ft/day. The back pressure was manually changed down at 3 PV to increase the pressure gradient to minimum pressure gradient (MPG).....	137
Figure 4-22 C12/ synthetic formation brine and CO ₂ foam strength history at 80% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, no foam. Switch to 8 ft/day, foam is generated. Switch back to 4 ft/day, foam is still stable	138
Figure 4-23 C12/ synthetic formation brine and CO ₂ foam at 80% foam quality and 120 °C. Start at 16 ft/day, decrease to 4 ft/day before the pressure gradient reaches MPG, no foam. Switch to 16 ft/day again until the pressure gradient reaches MPG, decrease back to 4 ft/day, foam is generated	140
Figure 4-24 C12/ synthetic formation brine and CO ₂ foam strength and pressure gradient history at 80% foam quality and 120 °C. Start at 16 ft/day to reach the MPG and then switch back to 4 ft/day	141
Figure 4-25 The comparison of the foam strength at 20 and 120 °C for C12/ synthetic formation brine and CO ₂ co-injection foam.....	142
Figure 4-26 The C12/DI and CO ₂ co-injection foam flooding history at 120 °C. The upper one is 50% foam quality, the lower one is 70% foam quality.....	143

Figure 4-27 The apparent viscosity and pressure gradient history for co-injection of C12/DI and CO ₂ at 70% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, and increase to 8, 16, 32 ft/day	144
Figure 4-28 The comparison of foam apparent viscosity for C12/DI and CO ₂ co-injection at 4 ft/day at 20 and 120 °C	145
Figure 4-29 The apparent viscosity of CO ₂ foam for blend of C12 and CPC with weight ratio 1:1 and total activity 1.0% in DI water at room temperature and 4 ft/day	146
Figure 4-30 The foam apparent viscosity and pressure gradient history for the co-injection of blend of C12 and CPC in DI water and CO ₂ at 80% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, and then increase to 8 and 16 ft/day	146
Figure 4-31 The comparison of foam apparent viscosity at 20 and 120 °C for the co-injection of blend of C12 and CPC in DI water and CO ₂ with 80% foam quality at 4 ft/day	147
Figure 4-32 The Silurian dolomite core after C12/DI and blend of C12 and CPC in DI water flooding at 120 °C. The solid core was greatly dissolved by surfactant solution in DI water	148
Figure 4-33 The comparison of simulated and measured pH for DI and synthetic formation brine equilibrium with dolomite at 2 atm CO ₂	150
Figure 4-34 The color code of Bromocresol Green (BCG) in the absence of C12	151
Figure 4-35 The color code of Bromocresol Green (BCG) in the presence of C12/synthetic formation brine. The pH is measured value in bulk aqueous phase	152
Figure 4-36 The color change of BCG during synthetic formation brine flooding and brine alternating CO ₂ (WAG) flooding at 120 °C	153
Figure 4-37 BCG is green color during C12/synthetic formation brine and CO ₂ foam flooding. The pH=3.1-4.1	154
Figure 5-1 The molecular structure of Ethomeen C12	161
Figure 5-2 Analysis results of X-ray Photoelectron Spectroscopy (XPS) for mineral sands (Ma, 2013 b)	162
Figure 5-3 Energy dispersive spectroscopy scan of natural dolomite surface. The blue color is the carbonate surface background; other color spots are the silica and/or silicate impurity. The strength of silicon response increases from blue to red color	162

Figure 5-4 The cloud point of C12 at various pH. The pH is adjusted by HCl...	165
Figure 5-5 The equilibrium pH of minerals-water-CO ₂ system, calculated with PHREEQC software. Equilibrium temperature and CO ₂ pressure are in brackets.	165
Figure 5-6 The curves of light absorbance for MB active substance in DI water and chloroform.....	168
Figure 5-7 The light absorbance at $\lambda=655$ nm for various dilutions of MB solutions. DI indicates that the MB solution was diluted with DI water, and Brine indicates that the MB solution was diluted with synthetic brine.....	169
Figure 5-8 DTAB (4.012 mM) was titrated by SDS (4.009 mM). The corrected volume of the SDS titrant is determined by $V_{cor. tit.} = V_{titrant} - V_{blank}$...	171
Figure 5-9 A comparison of the titrated concentration and concentration calculated by mass of DTAB in DI water	172
Figure 5-10 The influence of salinity on the MB two-phase titration. 5.0 ml chloroform, 2.0 ml traditional MB solution and 1.0 ml aqueous phase (various) were added in each vial.....	174
Figure 5-11 The consumed SDS and SDES volumes in the blank tests at various salinities.....	175
Figure 5-12 Titration curve for DTAB in synthetic brine (4.022 mM) titrated with SDES in DI water (5.313 mM)	176
Figure 5-13 The comparison of the titrated concentration and concentration calculated by mass for DTAB in synthetic brine samples	177
Figure 5-14 The pH changed with added HCl volume	179
Figure 5-15 A comparison of the weighted and titrated concentration for C12 in DI water.	181
Figure 5-16 The results of HPLC analysis for 1% C12 in DI water. A surfactant column (Dionex Acclaim Surfactant, 4.6 × 250 mm, at 25 °C) and an evaporative light scattering detector (ELSD, at 60°C) were used. C18:1 and C18:2 indicate the degrees of unsaturation are 1 and 2, respectively	182
Figure 5-17 Zetapotential measurements in equilibrium solutions at various CO ₂ partial pressures. Purple asterisks and line display the linear relation between IEP and log ₁₀ (pCO ₂)), cited from Heberling, et al. (2011)	185
Figure 5-18 The Ca ²⁺ concentrations at zero zeta potential and 25 °C at various partial pressure of CO ₂	186

Figure 5-19 The adsorption curves of C12 in water and brine on both natural dolomite and pure calcite.....	191
Figure 5-20 The equilibrium adsorption of C12 in different solutions on carbonate minerals.....	191
Figure 5-21 The adsorption of C12 on natural dolomite, pure silica and kaolin in various solutions.....	193
Figure 5-22 The adsorption of C12 on the silica minerals with various Al^{3+} concentrations	196
Figure 5-23 The adsorption reduction per unit cation concentration	198
Figure 5-24 XPS results for potential minerals	199
Figure 5-25 C12 adsorption on the potential formation minerals	199

List of Tables

Table 2-1 Properties and major category for each type of surfactants	28
Table 3-1 The catalog of surfactants in Chapter 3.....	56
Table 3-2 Ions compositions of SME and synthetic formation brine	59
Table 3-3 1% C25A in NaCl and CaCl ₂ Solutions.....	75
Table 3-4 Surfactant peak areas of C12 in HPLC analysis.....	88
Table 4-1 The properties of water and CO ₂ at 72.5 °C and 3400 psi.....	108
Table 4-2 The properties of water at 72.5 °C.....	110
Table 4-3 The parameters of the core sample.....	117
Table 4-4 The parameters for local equilibrium foam model for C12/DI and CO ₂ foam at room temperature	124
Table 4-5 The parameters for local equilibrium foam model for C12/synthetic formation brine and CO ₂ foam at room temperature.....	130
Table 4-6 Parameters in local equilibrium foam model for C12/synthetic formation and CO ₂ foam at 120 °C	142
Table 5-1 The minerals used for adsorption measurement	161
Table 5-2 The results of DTAB in DI water titrated by SDES.....	172
Table 5-3 The results for DTAB in synthetic brine titrated by SDES.....	178
Table 5-4 The reactions and equilibrium constants of calcite-CO ₂ -H ₂ O system at 25 °C and low ionic strength (activity coefficient=1), (Ma, et al., 2013)	184
Table 5-5 The reactions and equilibrium constants of dolomite-CO ₂ -H ₂ O system at 25 °C and low ionic strength (activity coefficient=1) (Ma, et al. 2013; Hyeonga and Capuano, 2001).....	187
Table 5-6 Me ²⁺ activities and isoelectric concentrations during adsorption tests on carbonate minerals	188
Table 5-7 Cations concentration of various solutions	192
Table 5-8 Cations concentration in various solutions equilibrium with dolomite	194
Table 5-9 Cations concentration in various solutions equilibrium with kaolin ...	194

List of Equations

Equation 2-1 Balance of disjoining and capillary pressures in the Plateau border	30
Equation 2-2 Function of disjoining pressure	31
Equation 2-3 Single phase Darcy's law	32
Equation 2-4 Flow potential	32
Equation 2-5 Darcy's law for multiphase flow	33
Equation 2-6 Definition of mobility for a particular phase	33
Equation 2-7 Definition of mobility ratio	33
Equation 2-8 Function of overall, sweep and microscopic displacement efficiency	34
Equation 2-9 Definition of interfacial tension	35
Equation 2-10 Young-Laplace equation for capillary pressure	36
Equation 2-11 Definition of capillary number	36
Equation 2-12 Young's Equation for interfacial tension balance	39
Equation 2-13 Definition of (a) entering, (b) spreading, and (c) bridging coefficients	43
Equation 2-14 Definition of the film interfacial tension	44
Equation 2-15 Definition of the generalized entering coefficient	45
Equation 2-16 Gas relative permeability in foam for STARS foam model	46
Equation 2-17 Nernst Equation for the concentration of ionic surfactants	50
Equation 3-1 Formula for porosity of sandpack	65
Equation 3-2 1-D single-phase Darcy's law for horizontal flow	66
Equation 3-3 Formula for permeability calculation in 1-D sandpack	67
Equation 3-4 Formula for foam apparent viscosity in 1-D flow	68
Equation 3-5 Definition of degradation degree	86
Equation 4-1 LMTD (log-mean temperature difference) Equation for heat transfer	105
Equation 4-2 Formula of heat transfer rate	105

Equation 4-3 Formula of overall heat transfer coefficient	106
Equation 4-4 Overall heat transfer coefficient is assumed to equal to the heat transfer coefficients inside fluid.....	106
Equation 4-5 Definition of Nusselt number	107
Equation 4-6 Empirical correlation of Nusselt number for helical coils	107
Equation 4-7 Formula of total heat transfer area	107
Equation 4-8 Definition of log-mean temperature difference	108
Equation 4-9 Formula of foam apparent viscosity in core flooding	119
Equation 4-10 Formula of foam apparent viscosity in foam model	120
Equation 4-11 Formula of gas fraction.....	120
Equation 4-12 Sum of gas and water saturation is unity.....	120
Equation 4-13 Formula of Water permeability	121
Equation 4-14 Formula of gas (foam) permeability.....	121
Equation 4-15 Derivative of foam apparent viscosity to water saturation	121
Equation 5-1 Formula for sample concentration in MB two phase titration.....	164
Equation 5-2 Formula for adsorption calculation	166
Equation 5-3 The ratio of unreacted MB to total MB at the threshold point	169
Equation 5-4 Formula for sample concentration with titration slope	170
Equation 5-5 Formula for activity of surfactant	179
Equation 5-6 Calcium concentration in Calcite-H ₂ O-CO ₂ system	183
Equation 5-7 Carbonate concentration in Calcite-H ₂ O-CO ₂ system	184
Equation 5-8 Isoelectric calcium concentration in Calcite-H ₂ O-CO ₂ system.....	185
Equation 5-9 Isoelectric carbonate concentration in Calcite-H ₂ O-CO ₂ system .	185
Equation 5-10 Definition of adsorption reduction per unit cations concentration (AR)	196
Equation 5-11 Formula for adsorption reduction per unit magnesium concentration	197
Equation 5-12 Formula for adsorption reduction per unit calcium concentration	197
Equation 5-13 Formula for adsorption reduction per unit aluminum concentration	197

Chapter 1

Introduction

1.1 Enhanced Oil Recovery (EOR)

The traditional oil recovery process involves three steps: primary, secondary and tertiary process. The primary process mainly utilizes the natural energies from the expansion of water, crude oil, gas cap and dissolved gas in reservoirs to produce oil. After pressure depletion in reservoirs, water or immiscible gas is injected to maintain the pressure, called the secondary process. The average recovery efficiency is only one third of original oil in place (OOIP) after primary and secondary processes (Wardlaw, 1996), owing to the high interfacial tension and poor mobility control. Tertiary process, sometimes a synonym for enhanced oil recovery (EOR) process, uses miscible gases, chemicals, or thermal energies to overcome the problems of interfacial tension and/or mobility control to increase the oil recovery efficiency (Lake, 1989; Green and Willhite, 1998).

The major EOR techniques, *i.e.*, chemical EOR, miscible flooding and thermal methods, are briefly introduced below:

Chemical EOR methods utilize the surface active materials to reduce the interfacial tension (IFT) and polymers to control the mobility. The surface active

materials can be surfactants directly added in the injection solution, and/or be the soaps generated from the reaction of crude oil and the injected alkaline solution. Thus, chemical EOR methods include surfactant flooding (Bourrel and Schechter, 1988; Rosen, 2004; Hirasaki, et al., 2011), alkaline flooding (Mayer, et al., 1983; Pei, et al., 2012), polymer flooding (Needham and Doe, 1987) and their combination, e.g., alkaline-surfactant-polymer (ASP) flooding (Zerpa, et al., 2005 ;Liu and Zhang, 2008). Each chemical has distinct mechanism and limitation in chemical EOR process. The surfactants can reduce the IFT of water-oil and alter the wettability of the rocks (Hirasaki and Zhang, 2004). But, the high cost and retention, e.g., adsorption on the rocks, precipitation in high salinity brine and partition in the residual oil, of the surfactants restrict its application. The alkalis which are cost-effective chemicals can react with the acid components in the crude oil to generate soap for reducing the IFT of water-oil, and reduce adsorption of the injected surfactant (Nelson, et al., 1984; Liu and Zhang, 2008). If the soap number of the crude oil is high enough, the generated soap in alkaline flooding can reduce the IFT to a satisfactory level (Liu, 2007). Otherwise, the alkalis can still be used to reduce the surfactant adsorption (Nelson, et al., 1984). The high molecular weight of polymers can increase the viscosity of injected solutions to achieve a favorable mobility control. But the application of polymers is limited by the reservoir conditions. The high salinity and high temperature in reservoirs can result in the loss of polymer viscosity, because of the chemical and thermal degradation of high molecular weight polymer (Levitt and Pope,

2008). Foam generated by surfactants solution and injected gas, is an alternative method to polymers for mobility control in chemical EOR process (Li, et al., 2010).

In miscible flooding EOR processes, the displacing fluids are solvents or gases which are miscible with crude oil at reservoir conditions. The miscibility between displacing phase and oil results in the enhancement of microscopic displacement efficiency (Stalkup, 1983; Orr, 2007). The miscible gas flooding projects, especially for CO₂ flooding, keep growing from 1980, shown in Figure 1-1, due to the economically favorable CO₂ resources (Alvarado and Manrique, 2010). However, the miscible fluids tend to fingering through the residual oil, owing to the unfavorable mobility control (Stalkup, 1983; Orr, 2007). This problem can also be solved by foam EOR process, especially for CO₂ flooding process (Chen and et al., 2014).

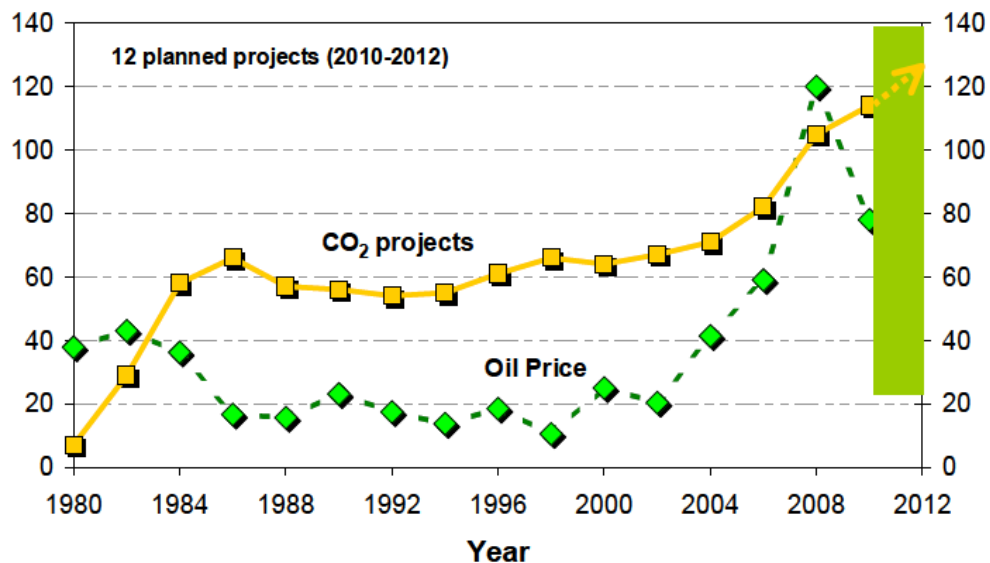


Figure 1-1 Evolution of CO₂ projects and oil price (Alvarado and Manrique, 2010)

Thermal methods, *i.e.*, well stimulation, in situ combustion method, steam flooding and steam-assisted gravity drainage (SAGD) method, are usually used to recover the heavy oils by elevating the temperature and reducing the viscosities of oils. Well stimulation is used for single well production (Green and Willhite, 1998). Steam is injected in the production well and is shut in for a while before producing (Bridges, et al., 1985). For in situ combustion processes, Air or oxygen can be injected in reservoirs and react with crude oil to increase the temperature. But the combustion front is hard to control. The horizontal well techniques can be used to improve in situ combustion processes (Greaves and Al-Shamali, 1996). For Steam flooding, the steam can be injected from the injection well, heat the reservoirs to reduce the viscosity of heavy oils and recover the oil from the production well. The electric heaters can be utilized to maintain the temperature near the wellbore region to reduce the heat loss of the steam (Sierra, et al., 2001). However, the density and viscosity of the steam are low relative to oil, which results in the poor vertically and horizontally volumetric sweep efficiency by gravity override and unfavorable mobility control. Thus, steam foam has been used to stabilize the front of steam drive (Hirasaki, 1989). The steam method can also be benefited from the horizontal well techniques. The technique which combines the steam and horizontal well is called steam-assisted gravity drainage (SAGD) method. Steam is injected in an upper horizontal well to heat the heavy oil. The heated oil drains to a lower horizontal well by gravity and is pumped out of the reservoirs (Butler, 1994), as shown in Figure 1-2. The steam chamber (Figure 1-2) is often partially developed due to

the heterogeneity of the formation, which detrimentally affects the recovery efficiency. Similar to the steam flooding, foam can be applied to control the mobility of steam and the development of the chamber in SAGD process (Chen, et al., 2010).

Although most EOR processes are conducted in tertiary process, some EOR techniques, *e.g.*, foam chemical EOR and miscible CO₂ flooding, can also be used as the secondary processes to maintain the reservoir pressure and simultaneously increase the oil recovery efficiency (Li, et al., 2012; Shedid, et al., 2007).

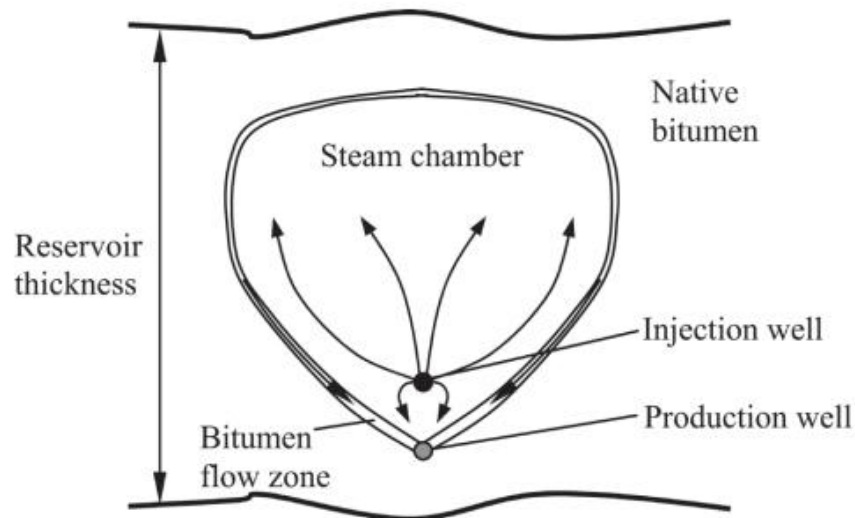


Figure 1-2 The cross section of SAGD process (Gates, et al., 2007)

1.2 Foam Mobility Control for EOR Process

The investigation and application of foam in EOR processes can date back to 1960s (Bernard and Jacobs, 1965). Foam is now widely applied in various EOR processes, *i.e.*, surfactant flooding (Li, et al., 2012), steam flooding (Hirasaki, 1989), gas flooding (Chen, et al., 2014), and SAGD method (Chen, et al., 2010).

Foam can effectively improve the sweep efficiency in EOR processes. The relatively high mobility of displacing fluids and the geological heterogeneity in reservoirs are two major reasons for poor sweep efficiency. In gas and steam flooding processes, the low density of displacing fluids can result in the gravity-override and accumulation of displacing fluids on the top of reservoirs, which also detrimentally affect the sweep efficiency (Green and Willhite, 1998). Two approaches with the application of foam were invented to solve above problems (Fussell, 1984). The simple one is to plug the swept zone or high permeability thief zone with foam and divert the fluids into the un-swept oil zone, called foam conformance method. In this method, the foam only exists near the wellbore region and cannot assist the flow diversion in the deep reservoirs. Thus, a more complicated foam method, called foam mobility control method, is applied to control the mobility of the entire reservoir. This method requires the foam can flow through the whole formation and stabilize for months or years to divert the displacing phase into the untouched zone and prevent the separation of lighter phases (Rossen, 1996). This thesis focuses on the latter method, *i.e.*, foam mobility control method.

The foam consists of liquid lamellae and the dispersed gas, which indicate that the foam mobility can be described by liquid and gas mobility separately. The viscosity and relative permeability of liquid are not directly affected by foam (Bernard and Jacobs, 1965; Sanchez and Hazlett, 1992). However, the foam can indirectly affect relative permeability of liquid by reducing liquid saturation. That's because that the relative permeability of liquid is a function of its saturation (Persoff, et al., 1991; Zhou and Rossen, 1995). The gas mobility is dominated by foam (Falls, et al., 1988). The foam can reduce the gas relative permeability and increase its apparent viscosity. Especially for the discontinuous-gas foam, the resistance of lamellae reduces the gas mobility by orders of magnitude (Hirasaki and Lawson, 1985).

The conditions for strong foam generation and foam stability in EOR processes are extensively investigated. One of the important findings is the minimum pressure gradient. Strong foam can only be generated as the pressure gradient is higher than minimum pressure gradient (Falls, et al., 1988; Rossen, 1996; Tanzil, et al., 2002; Kam and Rossen, 2003; Rossen and Bruining, 2007). The minimum pressure gradient is found to increase with decreasing of the permeability (Gauglitz, et al., 2002).

Another important finding for foam stability is the existence of limiting capillary pressure. In foam flooding, the water saturation is reduced by strong foam, which results in the increase of capillary pressure (Khatib, et al., 1988). If the final capillary pressure is lower than limiting capillary pressure, the foam flow falls in low-quality regime (Cheng, et al., 2000). The foam strength and pressure

gradient can increase with foam quality in the low-quality regime, as shown in Figure 1-3 (right lower part). After the foam quality is increased to transition foam quality (f_g^*), the foam strength and pressure gradient reach maximum, meanwhile the water saturation and capillary pressure is close to the critical water saturation and limiting capillary pressure (Ma, et al., 2013(a)). If the foam quality is continuously increased, the foam strength and pressure gradient will decrease to maintain the water saturation, consequently maintain the capillary pressure equal or lower than the limiting capillary pressure. The foam falls in the high-quality regime after foam quality is higher than transition foam quality (f_g^*), as shown in Figure 1-3 (left upper part). The pressure gradient and foam flow are dominated by yield stress and mobilization of foam bubbles in the low-quality regime, and by the limiting capillary pressure in the high-quality regime. This finding is significant to develop proper models under various injection stratifies (Rossen and Wang, 1999; Alvarez, et al., 2001; Ma, et al., 2013(a)).

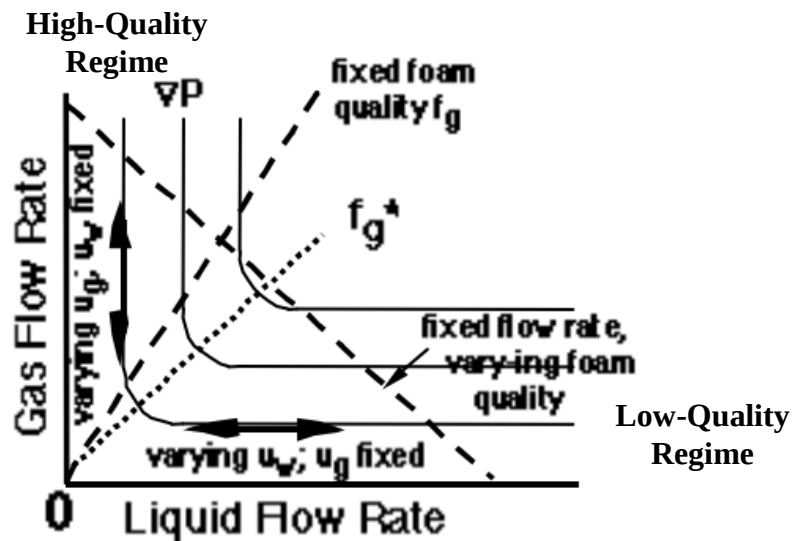


Figure 1-3 The pressure contour with gas and liquid rates (Cheng, et al., 2000)

The effects of oil and wettability on the foam stability are also important findings for the foam EOR. The crude oils, especially the lighter components, deleteriously affect the foam stability (Schramm and Novosad, 1992; Schramm, et al., 1993; Farajzadeh, et al., 2012). Some studies tried to illustrate the oil effects on foam stability with the entering and spreading coefficients (Lau and O'Brien, 1988; Kristiansen and Holt 1992), but other researchers argue this view with stable pseudoemulsion film, *i.e.*, an oil drop must overcome the disjoining pressure of pseudoemulsion film to enter the water-gas interface even with unfavorable entering coefficients ($E_{o/wg} > 0$) (Lobo and Wasan, 1993; Koczo, et al., 1992; Farajzadeh, et al., 2012). The experimental results which were contradictory to the entering and spreading coefficients theory have been reported by Manlowe and Radke (1990). The foam is expected to be unstable in not strongly water-wet formation due to the high-energy state of the lamella (Rossen, 1996). The alteration of wettability from oil-wet to water-wet may occur during surfactant foam flooding, because of the interfacial tension reduction and surfactant adsorption (Sanchez and Hazlett, 1992). Thus, the strength of foam generated in an initial oil-wet formation can be comparable to that in a water-wet formation with proper surfactants formulations (Suffridge, et al., 1989; Kuehne, et al., 1992).

The long-distance foam propagation and retention of surfactants are two major issues for the application of foam EOR in the field. The superficial velocities of injected fluids decrease in the deep reservoirs due to the radial flow from the injection well. The flow front of strong foam may be slower than the flow

front of gas at low superficial velocities, which may result in the gas leaking from the foam bank (Ashoori, et al., 2012). The surfactants can be retarded in foam process by adsorption on the rocks, partition into the oil and precipitation in formation brine at reservoir conditions. The retention of surfactants delays or restrains the foam generation and propagation, additionally increases the cost of EOR process (Patzek and Myhill, 1989; Ma, et al., 2013(b)).

Each reservoir has distinct conditions, thus suitable surfactant formulations and injection strategies should be designed by experimental and simulation results case by case.

1.3 Screening and Evaluation of Surfactant Formulations for Foam EOR in Laboratory Scale

Surfactant is commonly used for foam generation in EOR process (Li, et al., 2010). Many studies have focused on the screening and evaluation of surfactant formulations for foam EOR in laboratory scale (Li, et al., 2012; Chen, et al., 2014; Ma, et al., 2013(b)). However, most studies just focus on a specific topic, e.g., foamability, foam stability and adsorption. Few literatures proposed a systematic procedure for the screening and evaluation of surfactant formulations. A procedure which includes the solubility, thermal and chemical stability, foamability and foam stability, and adsorption of surfactants under reservoir conditions is illustrated in this thesis. Additionally, the IFT and partition coefficients of surfactants are also important parameters for foam EOR (Wang, et

al., 2001; Guo, et al., 2011; Patzek and Myhill, 1989; Ashoori, et al., 2010), but are not measured and optimized in this thesis.

It is necessary to maintain the solubility of surfactants at reservoir conditions for any flooding process. However, the harsh conditions of reservoirs, *i.e.*, high temperature, high salinity and extreme pH, will decrease the solubility of the surfactants. For example, sodium dodecylsulfonate surfactants can be salted out in high salinity brine, especially with high hardness (Somasundaran, et al., 1984). Regarding to the surfactant properties, the cloud point for nonionic surfactants and Krafft temperature for ionic surfactants may restrain their application at a particular temperature (Huibers, et al., 1997; Nasr-El-Din and Al-Ghamdi, 1996; Davey, et al., 1998). The solubility of switchable cationic surfactants depends on the pH, *i.e.*, surfactants are water soluble at low pH, but have poor solubility at neutral or high pH (Chen, et al., 2014). Thus, the solubility of surfactants should be tested at reservoir conditions prior to other evaluations. Glass pipette method can be used to monitor the solubility of surfactants in aqueous phase (Barnes, et al., 2008; Puerto, et al., 2012). A high pressure visual cell can be used to observe the solubility of surfactant in liquefied or supercritical gas, *e.g.*, CO₂ (Lemert, et al., 1990; Chen, et al., 2014).

The thermal and chemical stability of surfactants is another requisite condition due to the months or years traveling time of chemicals in reservoirs. Sulfate surfactants were found to be degraded at elevated temperature, especially at low pH (Talley, 1988). The carboxylate surfactants synthesized in University of Texas at Austin were reported to be used at high temperature and

salinity (Adkins, et al., 2012). Thermogravimetric analysis (TGA) is often used to characterize the thermal stability of chemicals (Cui, et al., 2008). However, the hydrolysis of surfactants in aqueous phase cannot be detected by TGA. Both Talley (1988) and Adkins (2012) utilized phase behavior experiments to investigate the stability of surfactants. In this thesis, the surfactants were aged at reservoir temperature and analyzed by high performance liquid chromatography (HPLC) to characterize the stability of the surfactants.

Foamability and foam stability are one of the most popular topics in the evaluation of surfactants for foam EOR. Two major experimental methods are used to screen the surfactant formulations: bulk foam test and porous media foam test. In bulk foam test, the column height and half-life of foam are common parameters (Bikerman, 1938; Iglesias, et al., 1995; Yu, et al., 2012). In porous media foam, the pressure gradient, apparent viscosity and mobility reduction factor (MRF) of foam are measured (Hirasaki and Lawson, 1985; Li, et al., 2012; Chen, et al., 2014; Simjoo, et al., 2013). However, the correlation between the bulk foam and porous media foam is poor, *i.e.*, the surfactants which generate good foam in bulk may not work in porous media, and vice versa (Cubillos, et al., 2012). That's because the foamability and foam stability depend on different mechanisms in bulk and porous media. For foam generation, two ways exist to generate bulk foam: forcibly injecting gas in liquid, and supersaturating gas in liquid under pressure then later releasing the pressure (Wilson, 1996). However, for foam generation in porous media, three major mechanics dominate the process: leave-behind, snap-off and lamella division (Falls, et al., 1988 ;Kovscek

and Radke, 1994). There are three mechanisms for the destruction of foam: gravity drainage, capillary pressure and gas diffusion (Narsimhan and Ruckenstein, 1986; Chambers and Radke, 1991). For bulk foam, the dominating factors are gravity drainage and gas diffusion (Rossen, 1996; Grassia and Neethling, 2005). But for foam in porous media, capillary pressure is more important (Khatib, et al., 1988). Thus, the foamability and foam stability were characterized in porous media for this thesis. Fast screening procedure with sandpack at atmosphere conditions, and foam evaluation in Silurian dolomite core at reservoir conditions are discussed separately.

Adsorption of surfactants is an important parameter to determine the foam propagation and the economic cost (Ma, et al., 2013(b)). Static and dynamic adsorption tests are two major methods. In static adsorption test, the surfactant solution is mixed with adsorbent minerals. After reaching the equilibrium, the adsorption can be calculated by the initial and finally equilibrium concentration based on mass balance (Ma, et al., 2013(b)). In dynamic adsorption test, the surfactant solution is injected through the porous media. The concentration of surfactant in the effluent is analyzed, until reaching the injected concentration. The adsorption can be calculated from the surfactant breakthrough curves (Trogus, et al., 1977). In the reservoir flooding, the typical flow rate of surfactant solution is 1 ft/day, which indicates the local equilibrium can be assumed to be established during flooding process. Thus, the dynamic adsorption results in low flow rate can be predicted by the static adsorption isotherm curve (Trogus, et al., 1977; Zhang, et al., 2006). The surfactant selection based on the adsorption is

discussed in the next section 1.4. In this thesis, the static adsorption tests were conducted for the evaluation of surfactant formulations.

Low IFT is required for immiscible foam flooding, e.g., N₂ foam flooding, to achieve the high capillary number, consequently, the high microscopic displacement efficiency (Wang, et al., 2001; Guo, et al., 2011; Lake, 1989). The surfactant formulations for low IFT can be determined by glass pipette method (Barnes, et al., 2008; Puerto, et al., 2012) and direct measurement with spinning drop and pendant drop apparatus (Handy, et al., 1983; Song and Springer, 1996). The partition of surfactants from water to oil should be small to reduce the retention of surfactants in foam EOR (Patzek and Myhill, 1989; Ashoori, et al., 2010). The preferential partition of surfactant from water to supercritical CO₂ can enhance the foam generation and propagation in CO₂ foam flooding (Ren, et al., 2013). The partition coefficients between phases can be measured by bottle mixing method (Chen, et al., 2014). The measurement and discussion of IFT and partition for surfactant candidates were not included in this thesis.

1.4 Adsorption of Surfactants

Surfactant is one of common foaming agents in foam EOR process, (Farajzadeh, et al., 2010; Li, et al., 2012; Chen, et al., 2014). The adsorption of surfactants on the formation minerals detrimentally affects the foam generation and propagation (Tsau and Heller, 1992; Liu, et al., 2005). Extra surfactants have to be injected to compensate the surfactants adsorption on the rocks, which results in the increase of the cost for foam EOR process. Thus, the surfactant

formulation with low adsorption should be designed (Ma, et al., 2013b), or the adsorption of surfactant should be reduced to an acceptable level by various methods (Tabatabal, et al., 1993; Novosad, 1984; Shamsijazeyi, et al., 2013).

The electrostatic force is a determining factor for the surfactants adsorption (Zhang and Somasundaran, 2006), which indicates the electrokinetics properties, *i.e.*, the surface charge and the zeta potential, are the important parameters for selecting surfactants. The surface charge can't be directly measured. Generally, the sign of the surface charge was consistent with that of zeta potential, which is a measurable electrostatic parameter. For silica (SiO_2) minerals, the surface charge was generally negative at pH higher than 4 (Kosmulski, 2003; Mannhardt, et al., 1993), which indicates that anionic surfactants were usually used in sandstone formations because of the low adsorption compared to cationic surfactants (Thibaut, et al., 2000; Ma, et al., 2013). For clay minerals, *e.g.*, kaolinite, the surface bears both positive and negative charges because of the structure's heterogeneity (Tombácz and Szekeres, 2006), which results in the capacity to adsorb both anionic and cationic surfactants (Sánchez-Martín, et al., 2008). However, the net surface charge of clay is negative in a wide pH range, thus the adsorption of cationic surfactants on clays is higher than that of anionic surfactant (Alkan, et al., 2005). Generally, the surface charge of carbonate minerals is positive at neutral or lower pH (Somasundaran and Agar, 1967; Pokrovsky, et al., 1999). But the concentrations of potential determining ions (PDI), *i.e.*, CO_3^{2-} and Me^{2+} (Ca^{2+} and Mg^{2+}), change the surface charge at a given pH (Heberling, et al., 2011). The

higher concentrations of Me^{2+} leads to a more positive surface charge, and the higher concentration of CO_3^{2-} leads to a more negative surface charge (Foxall, et al., 1979). The surface charge of carbonate was changed to negative from positive at neutral pH in the presence of carbonate/bicarbonate ions (Hirasaki and Zhang, 2004). Thus, the surface charge and zeta potential should be analyzed for designing the suitable surfactant formulation.

The electrostatic force doesn't dominate the adsorption of the nonionic surfactants. The hydrogen bond between the hydroxyl groups on mineral surfaces and ethoxylated (EO) or/and propoxylated (PO) groups in the surfactant is more important for the nonionic surfactant adsorption. The hydrogen bond results in the fairly high adsorption of nonionic surfactants on silica and clay minerals compared to the low adsorption on carbonate minerals (Trogus, et al., 1977; Lawson, 1978; Zhang, et al., 2006). But the sparing solubility of ethoxylated nonionic surfactants at elevated temperature limits the application in the hot carbonate reservoirs.

The cationic surfactant adsorption can be reduced by adding multivalent ions. Tabatabai et al. (1993) found the adsorption of cationic surfactants on carbonate minerals can be reduced by adding multivalent cations, *i.e.*, Mg^{2+} and Ca^{2+} . This adsorption reduction was attributed to the increase of the surface charge. Similar results were observed by us for the adsorption of cationic surfactants on natural carbonate minerals. A different mechanism for the surfactant reduction was proposed in this thesis. The competition of multivalent cations and monovalent surfactant reduces the surfactant adsorption on negative

binding sites. This mechanism is supported by our test results on silica (SiO_2), on which the Ca^{2+} and Mg^{2+} are not the lattice ions. The injection of sacrificial agents, e.g., polyacrylate and lignosulfonates, is another method to reduce the adsorption of surfactants by covering the binding sites on the minerals with cheaper chemicals (Novosad, 1984; Shamsijazeyi, 2013).

1.5 Thesis Structure

The thesis is organized as follows:

Chapter 1 briefly introduces the background and issues to be solved in foam EOR.

Chapter 2 describes the techniques and theories used in this thesis.

Chapter 3 presents a procedure to screen the surfactant formulations, and compare the foam in bulk and porous media to find out the reliable screening method. The detrimental influence of oil on foam stability is demonstrated. Betaine was utilized as a foam booster to stabilize foam in the presence of oil.

Chapter 4 presents the results of foam evaluation under reservoir conditions. The influence of parameters, *i.e.*, foam quality, temperature, and salinity, on foam strength is studied.

Chapter 5 introduces an improved colorimetric titration method and illustrates the adsorption of cationic surfactant on various minerals. The reason

for the high adsorption on natural carbonate minerals is explored, and a method for adsorption reduction is introduced.

Chapter 6 concludes the findings and suggests the future work.

1.6 References

- Adkins, S., Arachchilage, G. P., Solairaj, S., Lu, J., Weerasooriya, U., & Pope, G. A. (2012). Development of Thermally and Chemically Stable Large-Hydrophobe Alkoxy Carboxylate Surfactants. *SPE Improved Oil Recovery Symposium*. Tulsa, Oklahoma. SPE-154256-MS.
- Alkan, M., Demirbaş , Ö., & Doğan, M. (2005). Electrokinetic properties of kaolinite in mono- and multivalent electrolyte solutions. *Microporous and Mesoporous Materials*, 83(1-3), 51–59.
- Alvarado, V., & Manrique, E. (2010). Enhanced Oil Recovery: An Update Review. *Energies*, 3(9), 1529-1575.
- Alvarez, J. M., Rivas, H. J., & Rossen, W. R. (2001). Unified Model for Steady-State Foam Behavior at High and Low Foam Qualities. *SPE Journal*, 6(03), 325 - 333. SPE-74141-PA.
- Ashoori, E., Heijden, T. V., & Rossen, W. R. (2010). Fractional-Flow Theory of Foam Displacements With Oil. *SPE Journal*, 15(02), 260 - 273. SPE-121579-PA
- Ashoori, E., Marchesin , D., & Rossen, W. R. (2012). Multiple Foam States and Long-Distance Foam Propagation in Porous Media. *SPE Journal*, 17(04), 1,231 - 1,245. SPE 154024-PA.
- Barnes, J. R., Smit, J. P., Smit, J. R., Shpakoff, G., Raney, K. H., & Puerto, M. C. (2008). Development of Surfactants for Chemical Flooding at Difficult Reservoir Conditions. *SPE Symposium on Improved Oil Recovery*. Tulsa, Oklahoma. SPE 113313-MS
- Bernard, G. G., & Jacobs, W. L. (1965). Effect of Foam on Trapped Gas Saturation and on Permeability of Porous Media to Water. *SPE Journal*, 5(04), 295-300. SPE-1204-PA.
- Bikerman, J. J. (1938). The Unit of Foaminess. *Transactions of the Faraday Society*, 34, 634-638.

Bourrel, M., & Schechter, R. S. (1988). Microemulsions and related systems: formulation, solvency, and physical properties. M. Dekker.

Bridges, J. E., Sresty, G. C., & Taflove, A. (1985). *Patent No. US4524827 A*. US.

Butler, R. M. (1994). Steam-assisted Gravity Drainage: Concept, Development, Performance And Future. *Journal of Canadian Petroleum Technology*, 32(02).

Chambers, K. T., & Radke, C. J. (1991). Capillary phenomena in foam flow through porous media. In N. R. Morrow (Ed.), *Interfacial phenomena in petroleum recovery* (pp. 191-255).

Chen, Q., Gerritsen, M. G., & Kovscek, A. R. (2010). Improving Steam-Assisted Gravity Drainage Using Mobility Control Foams: Foam Assisted-SAGD (FA-SAGD). *SPE Improved Oil Recovery Symposium*. Tulsa, Oklahoma: Society of Petroleum Engineers. SPE-129847-MS.

Chen, Y., Elhag, A. S., Poon, B. M., Cui, L., Ma, K., Liao, S. Y., Reddy, P. P., Worthen, A. J., Hirasaki G. J., Nguyen, Q. P., Biswal, S. L. and Johnston, K. P. (2014). Switchable Nonionic to Cationic Ethoxylated Amine Surfactants for CO₂ Enhanced Oil Recovery in High-Temperature, High-Salinity Carbonate Reservoirs. *SPE Journal*, 19 (02), 249 - 259. SPE-154222-PA

Cheng, L., Reme, A. B., Shan, D., Coombe, D. A., & Rossen, W. R. (2000). Simulating Foam Processes at High and Low Foam Qualities. *SPE/DOE Improved Oil Recovery Symposium*. Tulsa, Oklahoma. SPE-59287-MS.

Cubillos, H., Montes, J., Prieto, C., & Romero, P. (2012). Assessment of Foam for GOR Control to Optimize Miscible Gas Injection Recovery. *SPE Improved Oil Recovery Symposium*. Tulsa, Oklahoma. SPE-152113-MS.

Cui, L., Khramov, D. M., Bielawski, C. W., Hunter, D. L., Yoon, P. J., & Paul, D. R. (2008). Effect of organoclay purity and degradation on nanocomposite performance, Part 1: Surfactant degradation. *Polymer*, 49(17), 3751–3761.

Davey, T. W., Ducker, W. A., Hayman, A. R., & Simpson, J. (1998). Krafft Temperature Depression in Quaternary Ammonium Bromide Surfactants. *Langmuir*, 14(12), 3210–3213.

Falls, A. H., Hirasaki, G. J., Patzek, T. W., Gauglitz, D. A., Miller, D. D., & Ratulowski, T. (1988). Development of a Mechanistic Foam Simulator: The Population Balance and Generation by Snap-Off. *SPE Reservoir Engineering*, 3(03), 884-892. SPE-14961-PA.

Farajzadeh, R., Andrianov, A., & Zitha, P. (2010). Investigation of Immiscible and Miscible Foam for Enhancing Oil Recovery. *Ind. Eng. Chem. Res.*, 1910-1919.

Farajzadeh, R., Andrianov, A., Krastev, R., Hirasaki, G. J., & Rossen, W. R., 2012. Foam–oil interaction in porous media: Implications for foam assisted enhanced oil recovery. *Advances in colloid and interface science*, 183, 1-13.

Foxall, T., Peterson, G., Rendall, H., & Smith, A. (1979). Charge determination at calcium salt/aqueous solution interface. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 75, 1034-1039.

Fussell, L. T. (1984). Sweep Improvement Scoping Studies. *SPE Annual Technical Conference and Exhibition*. Houston, TX: Society of Petroleum Engineers. SPE-13168-MS.

Gates, I. D., Kenny, J., Hernandez-Hdez, I. L., & Bunio, G. L. (2007). Steam Injection Strategy and Energetics of Steam-Assisted Gravity Drainage. *SPE Reservoir Evaluation & Engineering*, 10(01), 19 - 34. SPE-97742-PA

Gauglitz, P. A., Friedmann, F., Kam, S. I., & Rossen, W. R. (2002). Foam generation in homogeneous porous media. *Chemical Engineering Science*, 57(19), 4037–4052.

Grassia, P., & Neethling, S. J. (2005). Quasi-one-dimensional and two-dimensional drainage of foam. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 263(1-3), 165–177.

Greaves, M., & Al-Shamali, O. (1996). In Situ Combustion Isc Process Using Horizontal Wells. *Journal of Canadian Petroleum Technology*, 35(04).

Green, D. W., & Willhite, G. P. (1998). *Enhanced oil recovery*. Richardson, TX: Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers.

Guo, H., Faber, M. J., Buijse, M. A., & Zitha, P. L. (2011). A Novel Alkaline-Surfactant-Foam EOR Process. *SPE Enhanced Oil Recovery Conference*. Kuala Lumpur, Malaysia. SPE-145043-MS.

Handy, L. L., El-Gassier, M., & Ershaghi, I. (1983). A Modified Spinning Drop Method for High-Temperature Applications. *SPE Journal*, 23(01), 155 - 156. SPE-9003-PA

Heberling, F., Trainor, T., Lützenkirchen, J., Eng, P., Denecke, M., & Bosbach, D. (2011). Structure and reactivity of the calcite–water interface. *Journal of Colloid and Interface Science*, 342(2), 843-857.

Hirasaki, G., Miller, C. A., & Puerto, M. (2011). Recent advances in surfactant EOR. *SPE Journal*, 16(04), 889-907. SPE-115386-PA.

Hirasaki, G. J., & Lawson, J. B. (1985). Mechanisms of Foam Flow in Porous Media: Apparent Viscosity in Smooth Capillaries. *SPE Journal*, 25(02), 176-190. SPE-12129-PA

Hirasaki, G. J., & Zhang, D. L. (2004). Surface chemistry of oil recovery from fractured, oil-wet, carbonate formations. *SPE Journal*, 9(2), 151-162. SPE-88365-PA

- Hiraski, G. J. (1989). The Steam-Foam Process. *Journal of Petroleum Technology*, 41(05), 449 - 456. SPE-19505-PA.
- Iglesias, E., Anderrez, J., Forgiarini, A., & Salager, J. L. (1995). A new method to estimate the stability of short-life foams. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 98(1), 167-174.
- Kam, S. I., & Rossen, W. R. (2003). A Model for Foam Generation in Homogeneous Media. *SPE Journal*, 8(04), 417 - 425. SPE-87334-PA.
- Khatib, Z. I., Hirasaki, G. J., & Falls, A. H. (1988). Effects of Capillary Pressure on Coalescence and Phase Mobilities in Foams Flowing Through Porous Media. *SPE Reservoir Engineering*, 3(03), 919 - 926. SPE-15442-PA.
- Koczko, K., Lobo, L. A., & Wasan, D. T. (1992). Effect of oil on foam stability: Aqueous foams stabilized by emulsions. *Journal of Colloid and Interface Science*, 150(2), 492-506.
- Kosmulski, M. (2003). A literature survey of the differences between the reported isoelectric points and their discussion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 222(1-3), 113-118.
- Kovscek, A. R., & Radke, C. J. (1994). Fundamentals of foam transport in porous-media. *ACS Advances in Chemistry Series*, 242, pp. 115-163. American Chemical Society.
- Kristiansen, T. S., & Holt, T. (1992). Properties of Flowing Foam in Porous Media Containing Oil. *SPE/DOE Enhanced Oil Recovery Symposium*. Tulsa, Oklahoma. SPE-24182-MS.
- Kuehne, D. L., Frazier, R. H., Cantor, J., & Horn, W. (1992). Evaluation of Surfactants for CO₂ Mobility Control in Dolomite Reservoirs. *SPE/DOE Enhanced Oil Recovery Symposium*,. Tulsa, Oklahoma. SPE-24177-MS.
- Lake, L. W. (1989). *Enhanced oil recovery*. Englewood Cliffs, N.J.: Prentice Hall Incorporated.
- Lau, H. C., & O'Brien, S. M. (1988). Effects of Spreading and Nonspreading Oils on Foam Propagation Through Porous Media. *SPE Reservoir Engineering*, 3(03), 893 - 896. SPE-15668-PA.
- Lawson, J. B. (1978). The Adsorption Of Non-Ionic And Anionic Surfactants On Sandstone And Carbonate. *SPE Symposium on Improved Methods of Oil Recovery*. Tulsa, Oklahoma. SPE-7052-MS.
- Lemert, R. M., Fuller, R. A., & Johnston, K. P. (1990). Reverse micelles in supercritical fluids. 3. Amino acid solubilization in ethane and propane. *Journal of Physical Chemistry*, 94(15), 6021-6028.

Levitt, D., & Pope, G. A. (2008). Selection and screening of polymers for enhanced-oil recovery. In *SPE Symposium on Improved Oil Recovery*. Society of Petroleum Engineers, Tulsa, Oklahoma. SPE-113845-MS.

Li, R. F., Hirasaki, G. J., Miller, C. A., & Masalmeh, S. (2012). Wettability Alteration and Foam Mobility Control in a Layered 2-D Heterogeneous System. *SPE Journal*, 17 (04), 1207-1220. SPE-141462-PA.

Li, R. F., Yan, W., Liu, S., Hirasaki, G. J., & Miller, C. A. (2010). Foam Mobility Control for Surfactant EOR. *SPE Journal*, 15 (04), 928-942. SPE-113910-PA.

Liu, S. (2007). Alkaline Surfactant Polymer Enhanced Oil Recovery Process. PhD thesis, Rice University, Houston, TX, December 2007.

Liu, S., Zhang, D. L., Yan, W., Puerto, M., Hirasaki, G. J. & Miller, C. A. (2008). Favorable Attributes of Alkaline-Surfactant-Polymer Flooding. *SPE Journal*, 13(1), 5-16. SPE-99744-PA.

Liu, Y., Grigg, R., & Bai, B. (2005). Salinity, pH , and Surfactant Concentration Effects on CO₂-Foam. *SPE International Symposium on Oilfield Chemistry*. The Woodlands, Texas: Society of Petroleum Engineers. SPE-93095-MS.

Lobo, L., & Wasan, D. T. (1993). Mechanisms of aqueous foam stability in the presence of emulsified non-aqueous-phase liquids: structure and stability of the pseudoemulsion film. *Langmuir*, 9(7), 1668-1677.

Ma, K., Lopez-Salinas, J. L., Puerto, M. C., Miller, C. A., Biswal, S. L., & Hirasaki, G. J. (2013(a)). Estimation of Parameters for the Simulation of Foam Flow through Porous Media. Part 1: The Dry-Out Effect. *Energy Fuels*, 27(5), 2363–2375.

Ma, K., Cui, L., Dong, Y., Wang, T., Da, C., Hirasaki, G., et al. (2013(b)). Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. *J Colloid Interface Sci*, 408, 164–172.

Manlowe, D. J., & Radke, C. J. (1990). A Pore-Level Investigation of Foam/Oil Interactions in Porous Media. *SPE Reservoir Engineering*, 5(04), 495 - 502. SPE-18069-PA.

Mannhardt, K., Schramm, L., & Novosad, J. (1993). Effect of Rock Type and Brine Composition on Adsorption of Two Foam-Forming Surfactants. *SPE Advanced Technology Series*, 1(1), 212-218. SPE-20463-PA.

Mayer, E. H., Berg, R. L., Carmichael, J. D., & Weinbrandt, R. M., (1983). Alkaline injection for enhanced oil recovery-A status report. *Journal of Petroleum Technology*, 35(01), 209-221.

Narsimhan, G., & Ruckenstein, E. (1986). Hydrodynamics, enrichment, and collapse in foams. *Langmuir*, 2(2), 230-238.

- Nasr-El-Din, H. A., & Al-Ghamdi, A. M. (1996). Effect of Acids and Stimulation Additives on the Cloud Point of Nonionic Surfactants. *SPE Formation Damage Control Symposium*. Lafayette, Louisiana. SPE-31106-MS.
- Needham, R. B., & Doe, P. H. (1987). Polymer Flooding Review. *Journal of Petroleum Technology*, 39(12), 1,503 - 1,507.
- Nelson, R. C., Lawson, J. B., Thigpen, D. R., & Stegemeier, G. L. (1984). Cosurfactant-enhanced alkaline flooding. In *SPE Enhanced Oil Recovery Symposium*. SPE-12672-MS.
- Novosad, J. (1984). Laboratory Evaluation Of Lignosulfonates As Sacrificial Adsorbates In Surfactant Flooding. *Petroleum Society of Canada*, 23(03).
- Orr, F. M. (2007). *Theory of Gas Injection Processes*. Holte, Denmark: Tie-Line Publications.
- Patzek, T. W., & Myhill, N. A. (1989). Simulation of the Bishop Steam Foam Pilot. *SPE California Regional Meeting*. Bakersfield, California. SPE-18786-MS.
- Pei, H., Zhang, G., Ge, J., Jin, L., & Ding, L. (2012). Study on the variation of dynamic interfacial tension in the process of alkaline flooding for heavy oil. *Fuel*, 372-378.
- Persoff, P., Radke, C. J., Pruess, K., Benson, S. M., & Witherspoon, P. A. (1991). A Laboratory Investigation of Foam Flow in Sandstone at Elevated Pressure. *SPE Reservoir Engineering*, 6(03), 365-372. SPE-18781-PA.
- Pokrovsky, O., Schott, J., & Thomas, F. (1999). Dolomite surface speciation and reactivity in aquatic systems. *Geochimica et Cosmochimica Acta*, 63(19-20), 3133–3143.
- Puerto, M. C., Miller, C. A., Hirasaki, G. J., & Barnes, J. R. (2012). Surfactant Systems for EOR in High-Temperature, High-salinity Environments. *SPE Journal*, 17(01), 11 - 19. SPE-129675-PA.
- Ren, G., Zhang, H., & Nguyen, Q. (2013). Effect of Surfactant Partitioning on Mobility Control During Carbon-Dioxide Flooding. *SPE Journal*, 18(04), 752 - 765. SPE-145102-PA.
- Rosen, M. J., 2004. *Surfactants and Interfacial Phenomena*. Third Edition ed. s.l.:Wiley-Interscience.
- Rossen, W. R. (1996). Foams in Enhanced Oil Recovery. In R. K. Prud'homme, & S. A. Khan, *Foams: Theory, Measurements, and Applications* (p. 413). US: Marcel Dekker, Inc.
- Rossen, W. R., & Bruining, J. (2007). Foam Displacements with Multiple Steady States. *SPE Journal*, 12(01), 5 - 18. SPE-89397-PA

- Rossen, W. R., & Wang, M. W. (1999). Modeling Foams for Acid Diversion. *SPE Journal*, 4(02), 92 - 100. SPE-56396-PA.
- Sanchez, J. M., & Hazlett, R. D. (1992). Foam Flow Through an Oil-Wet Porous Medium: A Laboratory Study. *SPE Reservoir Engineering*, 7(01), 91-97. SPE-19687-PA.
- Sánchez-Martín, M., Dorado, M., del Hoyo, C., & Rodríguez-Cruz, M. (2008). Influence of clay mineral structure and surfactant nature on the adsorption capacity of surfactants by clays. *Journal of Hazardous Materials*, 150(1), 115-123.
- Schramm, L. L., & Novosad, J. J. (1992). The destabilization of foams for improved oil recovery by crude oils: Effect of the nature of the oil. *Journal of Petroleum Science and Engineering*, 7(1-2), 77–90.
- Schramm, L. L., Turta, A. T., & Novosad, J. J. (1993). Microvisual and Coreflood Studies of Foam Interactions With a Light Crude Oil. *SPE Reservoir Engineering*, 8(03), 201 - 206. MS-20197-PA.
- Shamsijazeyi, H., Hirasaki, G. J., & Verduzco, R. (2013). Sacrificial Agent for Reducing Adsorption of Anionic Surfactants. *SPE International Symposium on Oilfield Chemistry*. Woodlands, Texas. SPE-164061-MS
- Shedid, S., Zekri, A., & Almehaideb, R. (2007). Laboratory Investigation of Influences of Initial Oil Saturation and Oil Viscosity on Oil Recovery by CO₂ Miscible Flooding. *EUROPEC/EAGE Conference and Exhibition*. London, U.K.: Society of Petroleum Engineers. SPE-106958-MS
- Sierra, R., Tripathy, B., Bridges, J. E., & Farouq Ali, S. M. (2001). Promising Progress in Field Application of Reservoir Electrical Heating Methods. *SPE International Thermal Operations and Heavy Oil Symposium*,. Porlamar, Margarita Island, Venezuela: Society of Petroleum Engineers. SPE-69709-MS
- Simjoo, M., Dong, Y., Andrianov, A., Talanana, M., & Zitha, P. L. (2013). Novel Insight Into Foam Mobility Control. *SPE Journal*, 18(03), 416 - 427. SPE-163092-PA
- Somasundaran, P., & Agar, G. (1967). The zero point of charge of calcite. *Journal of Colloid and Interface Science*, 24(4), 433–440.
- Somasundaran, P., Ananthapadmanabhan, K. P., Celik, M. S., & Manev, E. D. (1984). A Thermodynamic Model of Redissolution of Calcium Sulfonate Precipitates in NaCl Solutions. *SPE Journal*, 24(06), 667 - 676. SPE-10598-PA
- Song, B., & Springer, J. (1996). Determination of Interfacial Tension from the Profile of a Pendant Drop Using Computer-Aided Image Processing: 1. Theoretical. *Journal of Colloid and Interface Science*, 184(1), 64–76.
- Stalkup, F. I. (1983). *Miscible Displacement*. New York; Dallas: SPE Monograph Series.

- Suffridge, F. E., Raterman, K. T., & Russell, G. C. (1989). Foam Performance Under Reservoir Conditions. *SPE Annual Technical Conference and Exhibition*. San Antonio, Texas. SPE-19691-MS
- Tabatabal, A., Gonzalez, M. V., Harwell, J. H., & Scamehorn, J. F. (1993). Reducing Surfactant Adsorption in Carbonate Reservoirs. *SPE Reservoir Engineering*, 8(2), 117 - 122. SPE-24105-PA.
- Talley, L. D. (1988). Hydrolytic Stability of Alkylethoxy Sulfates. *SPE Reservoir Engineering*, 3(01), 235 - 242. SPE-14912-PA.
- Tanzil, D., Hirasaki, G. J., & Miller, C. A. (2002). Conditions for Foam Generation in Homogeneous Porous Media. *Society of Petroleum Engineers*. Tulsa, Oklahoma. SPE-75176-MS.
- Tombácz, E., & Szekeres, M. (2006). Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. *Applied Clay Science*, 34(1-4), 105-124.
- Trogus, F. J., Sophany, T., Schechter, R. S., & Wade, W. H. (1977). Static and Dynamic Adsorption of Anionic and Nonionic Surfactants. *SPE Journal*, 17(05), 337 - 344. SPE-6004-PA.
- Tsau, J., & Heller, J. (1992). Evaluation of Surfactants for CO₂-Foam Mobility Control. *Permian Basin Oil and Gas Recovery Conference*. Midland, Texas: Society of Petroleum Engineers. SPE-24013-MS
- Wang, D., Cheng, J., Yang, Z., Qun, L., Wu, W., & Yu, H. (2001). Successful Field Test of the First Ultra-Low Interfacial Tension Foam Flood. *SPE Asia Pacific Improved Oil Recovery Conference*. Kuala Lumpur, Malaysia. SPE-72147-MS.
- Wardlaw, N. C. (1996). Factors Affecting Oil Recovery from Carbonate Reservoirs and Prediction of Recovery. In G. V. Chilingarian, S. J. Mazzullo, & H. H. Rieke, *Carbonate Reservoir Characterization: A Geologic- Engineering Analysis, Part II* (p. 867). Elsevier.
- Wilson, A. J. (1996). Experimental Techniques for the Characterization of Foams. In R. K. Prud'homme, & S. A. Khan (Eds.), *Foams: Theory, Measurements, and Application* (pp. 243-272). Marchel Dekker, Inc.
- Yu, J., Liu, N., Li, L., & Lee, R. (2012). Generation of Nanoparticle-Stabilized Supercritical CO₂ Foams. *Carbon Management Technology Conference*. Orlando, Florida.
- Zerpa, L. E., Queipo, N. V., Pintos, S., & Salager, J. L. (2005). An optimization methodology of alkaline–surfactant–polymer flooding processes using field scale numerical simulation and multiple surrogates. *Journal of Petroleum Science and Engineering*, 47(3), 197-208.

Zhang, D. L., Liu, S., Puerto, M. C., Miller, C. A., & Hirasaki, G. J. (2006). Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering*, 52(1-4), 213–226.

Zhang, R., & Somasundaran, P. (2006). Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. *Advances in Colloid and Interface Science*, 123-126, 213–229.

Zhou, Z., & Rossen, W. R. (1995). Applying Fractional-Flow Theory to Foam Processes at the "Limiting Capillary Pressure". *SPE Advanced Technology Series*, 3(01), 154-162. SPE-24180-PA.

Chapter 2

Technical Background

2.1 Surfactant

2.1.1 Overview of Surfactants

Surfactants that are one type of surface-active substances consist of a polar/hydrophilic head and apolar/hydrophobic tail. The amphiphilic nature of surfactants indicates their tendency to favor both water and non-aqueous phase and concentrate at interfaces (Fainerman, et al., 2011). The surfactants are classified into anionic, cationic, nonionic, zwitterionic and “switchable” surfactants based on the types of polar head. Anionic and cationic surfactants carry negative and positive charge, respectively. Nonionic surfactants are not charged. Zwitterionic surfactants carry both negative and positive charge. **Switchable surfactants change the electric charge with pH, i.e.,** ethoxylated amine is nonionic at high pH and cationic at low pH. The ethoxylated amine is called switchable surfactant rather than amphoteric surfactant. That’s because that amphoteric surfactants, *e.g.*, amino acids, can react with both acid and base, and change from cationic through zwitterionic to anionic surfactant with pH from low to high (Holmberg, et al., 2003). But the ethoxylated amine can only react with acid and change from cationic to nonionic surfactant with pH from low to high. The electric charge of amino acid, betaine and carboxylic surfactant also

changes with pH. But usually, amino acid and betaine are classified as zwitterionic surfactants and carboxylic is classified as anionic surfactant. The properties and major category for each type of surfactants are listed in Table 2-1.

Table 2-1 Properties and major category for each type of surfactants

Type	Charge on the polar head	Category
Anionic	Negative	carboxylates, sulfonates, sulphates and phosphates
Cationic	Positive	quaternary ammonium salts and pyridinium
Nonionic	No charge	ethoxylated alcohol/ glycols, and glucoside
Zwitterionic	Negative and Positive	amino acid, betaine and sultaine
Switchable	Switchable	primary, secondary, and tertiary amines, ethoxylated amine and amine oxide

2.1.2 Surfactants in Aqueous Solution: CMC, Krafft and Cloud Point

At low concentrations, the surfactant molecules disperse in water as monomers; the interfacial tension (IFT) between water and oil phase decreases with increasing surfactant concentrations. After the concentration is increased to a particular value, called critical micelle concentration (CMC), the surfactant

molecules form micelles in aqueous phase, as shown in Figure 2-1, and the IFT reaches nearly a constant value above the CMC for a pure surfactant.

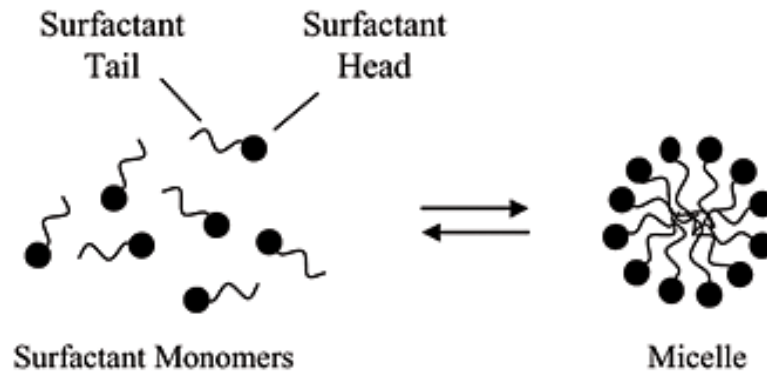


Figure 2-1 Scheme for the formation of surfactant micelle in aqueous phase (Rangel-Yagui, et al., 2004)

However, for some ionic surfactants, their solubility in aqueous phase is lower than the CMC below a particular temperature, termed Krafft point (T_k). At the Krafft point temperature, surfactant crystals will separate from aqueous phase if temperature falls below T_k because of the limited solubility of the crystal compared to the high solubility of micelles (Schramm and Marangoni, 2000). Nonionic surfactants don't have the Krafft point limit, but have the cloud point temperature (T_c), above which the solution becomes turbid. If the temperature is higher than T_c , the solution separates into surfactant-lean aqueous phase and surfactant-rich phase. This is due to the reduction of the hydration of polyoxyethylene groups in surfactants with increase in temperature. Thus, the Krafft point of ionic surfactants and the cloud point of nonionic surfactants should

be checked under injection and reservoir conditions to maintain solubility of surfactants during injection and flooding process.

2.1.3 Surfactants in Foam: Disjoining Pressure and Capillary Pressure

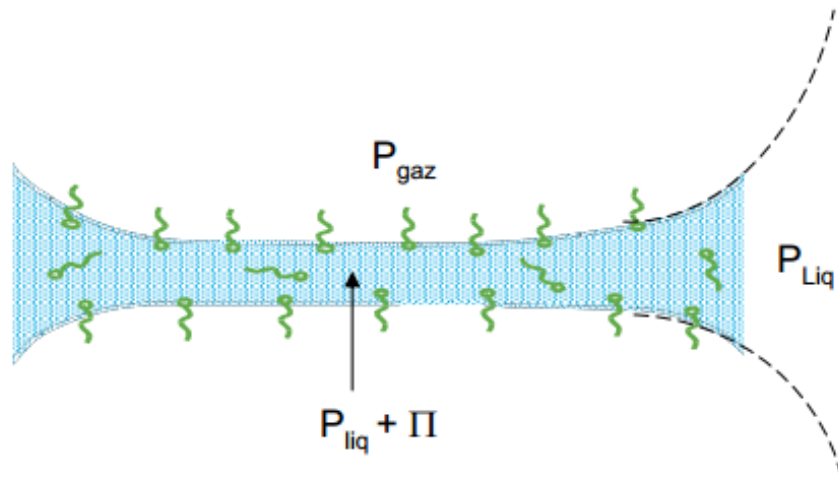


Figure 2-2 Cartoon of disjoining and capillary pressure in foam plateau border.

(http://www.maths.tcd.ie/~foams/PRESENTATIONS/Thursday12/Thursday12_Lecture1_Arnaud.pdf)

The disjoining and capillary pressures are balanced in a quasi-static state of foam expressed in Figure 2-2 and Equation 2-1 (Khatib, et al., 1988).

$$\Pi(h) = P_{gas} - P_{liq} = P_c = 2\sigma H$$

Equation 2-1 Balance of disjoining and capillary pressures in the Plateau border

where, $\Pi(h)$ is the disjoining pressure and is a function of the film thickness, h ; P_{gas} and P_{liq} are the gas and liquid pressure, respectively; P_c is the capillary

pressure; σ is the surface tension of liquid; H is the mean curvature in the plateau border .

The disjoining pressure usually consists of two repulsive pressures: long-range electrostatic (Π_{dl}) and short-range steric pressures (Π_{steric}), and an attractive pressure: short-range van der Waals pressure (Π_{van}) as explicated in Figure 2-3 and Equation 2-2:

$$\Pi(h) = \Pi_{dl} + \Pi_{van} + \Pi_{steric}$$

Equation 2-2 Function of disjoining pressure

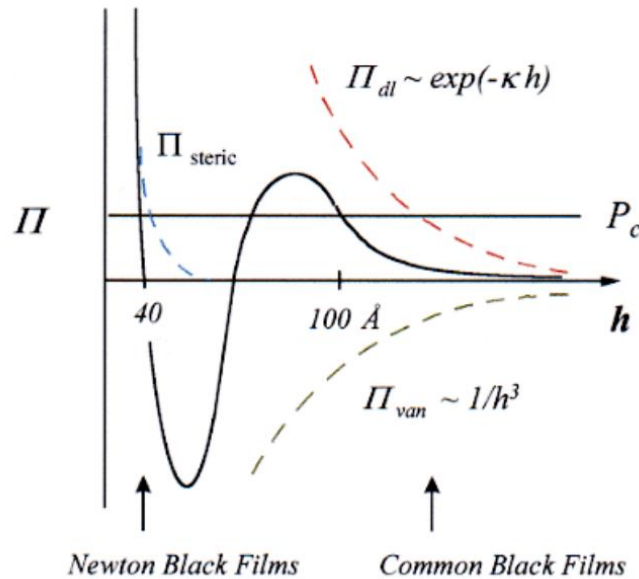


Figure 2-3 The schematic for the disjoining pressure as a function of film thickness (Bergeron, 1999)

During the drainage process, the film thickness is reduced, which results in a change in $\Pi(h)$. If $\Pi(h)$ becomes equal to P_c , the drainage will stop and an equilibrium film thickness reached. If the maximum $\Pi(h)$ is lower than P_c

throughout the drainage process, the film will rupture. A higher maximum value of $\Pi(h)$ and lower P_c are favorable for the foam stability. Surfactants can reduce the P_c by decreasing the surface tension σ and enhance $\Pi(h)$ by increasing Π_{elec} and possibly Π_{steric} . Thus, some surfactants can be good foam stabilizers.

2.2 Fundamentals of Flow in Porous Media

2.2.1 Darcy's Law and Mobility Ratio

Darcy's law originally developed by Henry Darcy in 1856 describes viscous flow through porous media at low Reynolds number (Simmons, 2008).

For single phase flow, Darcy's law is expressed in Equation 2-3:

$$\vec{u} = -\frac{k}{\mu} \nabla \Phi$$

Equation 2-3 Single phase Darcy's law

where $\vec{u}$ is the superficial velocity; k is the permeability of porous media; μ is the viscosity of fluid; $\nabla \Phi$ is the flow potential gradient, and Φ is defined in Equation 2-4:

$$\Phi = p - g \int_{D_0}^D \rho dD$$

Equation 2-4 Flow potential

where p is the pressure; g is acceleration of gravity; ρ is the density of the fluid; D is the height of fluid level, D_0 is the reference height.

For multiphase flow, Darcy's law can be explicated in Equation 2-5:

$$\vec{u}_j = -\lambda_j \nabla \Phi_j$$

Equation 2-5 Darcy's law for multiphase flow

where subscript j indicates the phase index; λ_j is the mobility of phase j , defined in Equation 2-6:

$$\lambda_j = \frac{k \cdot k_{rj}(S_j)}{\mu_j}$$

Equation 2-6 Definition of mobility for a particular phase

where $k_{rj}(S_j)$ is the relative permeability of phase j , which is a function of saturation (S_j) of phase j in two phases flow. In three phases flow, k_{rj} is the function of saturations for two phases.

Mobility ratio (M) is the ratio of the invading phase mobility ($\sum \lambda_i$) to the displaced phase mobility ($\sum \lambda_d$) which is the sum of mobility for all the phases at initial conditions, explicit in Equation 2-7:

$$M = \frac{\sum \lambda_i}{\sum \lambda_d}$$

Equation 2-7 Definition of mobility ratio

where subscripts i and d stand for invading phase and displaced phase, respectively.

$M > 1$ indicates an unfavorable mobility control and bypass/fingering of invading phase through displaced phase is possible. In conventional oil recovery processes, water is the invading phase and oil is the displaced phase. Thus, unit ($M = 1$) or favorable mobility ($M < 1$) is desirable for high sweep efficiency (Lake, 1989).

2.2.2 Recovery Efficiency

The overall oil recovery efficiency (E_R) is the product of sweep efficiency (E_V) and microscopic displacement efficiency (E_D), explicit in Equation 2-8

$$E_R = E_V \cdot E_D$$

Equation 2-8 Function of overall, sweep and microscopic displacement efficiency

The E_V is the ratio of swept pore volume to the total pore volume. The E_D is the ratio of displaced oil to initial oil volume in the swept region. The ideal oil recovery process requires both E_V and E_D , and consequently E_R , to reach 1.0 (Wardlaw, 1996). The E_V can be enhanced by control of mobility ratio (M), and the E_D can be improved by increasing the capillary number through decreasing the interfacial tension (IFT).

2.2.3 Interfacial Tension (IFT) and Capillary Pressure

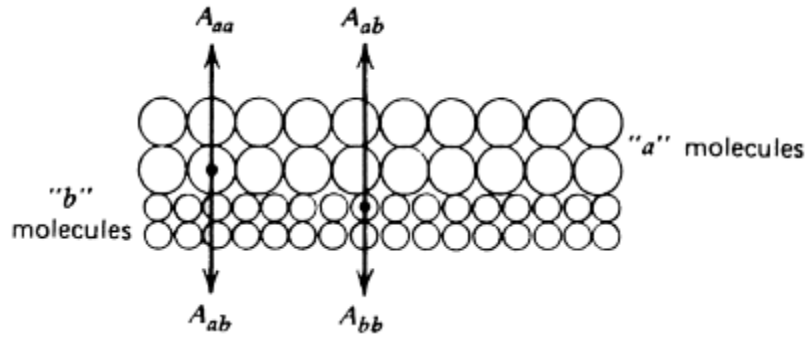


Figure 2-4 The diagram of the interface between two condensed phase (Rosen, 2004)

The molecules on the interface between two condensed phases are subjected to anisotropic tensile stresses, owing to distinct attractions from different molecular pairs, as shown in Figure 2-4. The interfacial free energy per unit area caused by the anisotropy on the interface is quantitatively characterized by interfacial tension (IFT, σ), defined in Equation 2-9:

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{T,P,N}$$

Equation 2-9 Definition of interfacial tension

where G is Gibbs free energy; A is surface area; T, P, N are temperature, pressure and amount of substance, respectively.

Capillary pressure (P_c) is the pressure difference across the curved interface of two immiscible fluids, as described by Young-Laplace Equation (Equation 2-10):

$$P_c = 2H\sigma$$

Equation 2-10 Young-Laplace equation for capillary pressure

where P_c is the pressure difference across the interface; H is the mean curvature; and σ is the interfacial or surface tension.

The high interfacial tension is detrimental to E_D . Higher interfacial tension results in the lower E_D by decreasing the capillary number (N_{vc} , Equation 2-11), as demonstrated in Figure 2-5.

$$N_{vc} = \frac{u\mu}{\sigma}$$

Equation 2-11 Definition of capillary number

where u and μ are the superficial velocity and viscosity of invading phase, respectively; σ is the interfacial tension between invading and displaced phases.

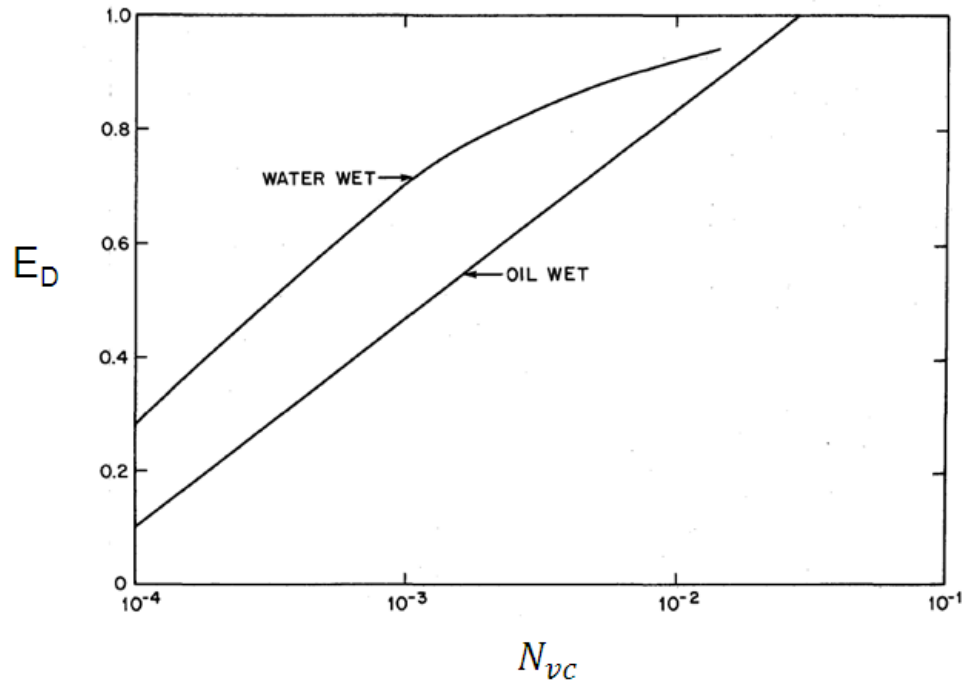


Figure 2-5 The capillary desaturation curve (Paul, et al., 1982)

The high interfacial tension is also detrimental to E_V of a non-wetting invading phase. That's because that the high capillary entry pressure prevents the non-wetting phase flowing into the lower-permeability zone.

Thus, surface-active chemicals, e.g., surfactants, are used to reduce the IFT, consequently increase the capillary number, decrease the capillary entry pressure, and enhance the oil recovery.

2.2.4 Wettability

Wettability in this thesis refers to the preference of a liquid to spread on or stick to the solid surface in the presence of another immiscible fluid. When two immiscible phases contact a solid surface simultaneously, the phase that is

attached to solid more strongly is called wetting phase, and the other one is non-wetting phase. In oil recovery processes, the formations are generally divided into water-wet, oil-wet and intermediate-wet, based on the contact angles, illustrated in Figure 2-6.

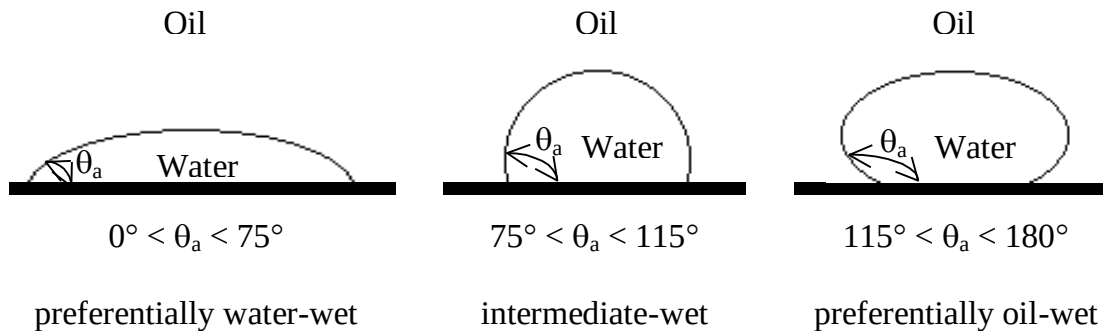


Figure 2-6 Classification of wettability according to the water advancing contact angle (Morrow, 1990)

The equilibrium contact angle is determined by Young's Equation, demonstrated in Figure 2-7 and Equation 2-12:

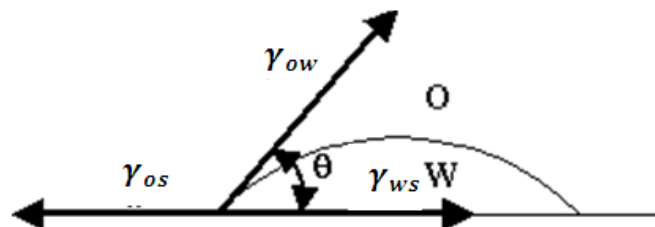


Figure 2-7 Interfacial tension balance based on Young's equation

$$\gamma_{ow} \cos \theta = \gamma_{os} - \gamma_{ws}$$

Equation 2-12 Young's Equation for interfacial tension balance

where θ is the equilibrium contact angle; the subscripts o , w and s represent oil, water and solid, respectively.

2.3 Foam Flow in Porous Media

2.3.1 Foam Generation

There are three main mechanisms for foam generation in porous media:

Leave-Behind Mechanism. Leave-behind only occurs in the drainage process. The lamellae are left behind in the throats between adjacent pore bodies, after gas flows through a porous medium that is initially saturated with liquid, illustrated in Figure 2-8. Foams created only by leave-behind mechanism are considered as weak or ineffective foam, because the lamellae are parallel to the gas flow direction and provide little resistance.

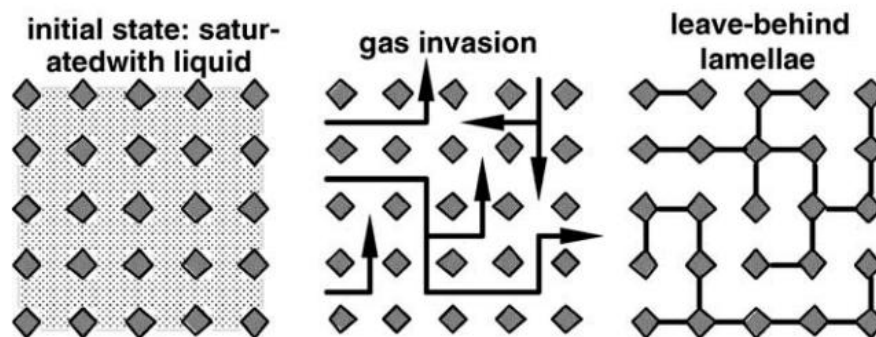


Figure 2-8 Schematic of leave-behind mechanism (Chen, et al., 2005)

Snap-Off Mechanism. Snap-off occurs in multiphase flow in porous media. The capillary pressure plays an important role. The capillary pressure in the pore neck is greater than that in pore body. If the gas pressure gradient is negligible, the liquid pressure in pore neck will be smaller than in that in pore body, which results in the liquid flows and accumulates in the pore neck, as shown in Figure 2-9. A liquid film is created after the liquid collars bring across the pore neck. A permeability change, especially flow from low to high permeability region, is favorable for foam generation by snap-off (Tanzil, et al., 2002).

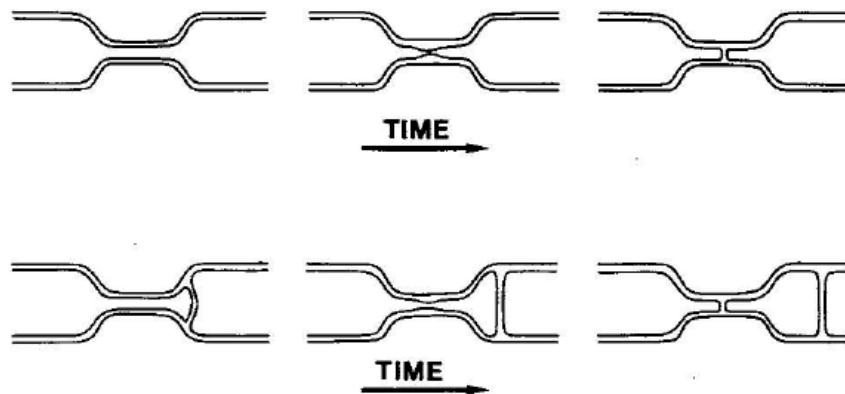


Figure 2-9 Schematic of snap-off mechanism (Falls, et al., 1988)

Lamella Division Mechanism. Lamella division occurs as lamellae move through a porous medium. When a lamella encounters a branch point, it splits into two lamellae, as illustrated in Figure 2-10 (right). There are two requirements for this mechanism: the high enough pressure gradient to mobilize the multiple bubble trains in branches and the large bubble size compared to the pore bodies (Falls, et al., 1988; Kavscek and Radke, 1994). If the stationary lamellae in one

branch can't be mobilized, the bubble only flows through the other branch and the foam texture is unchanged, as demonstrated in Figure 2-10 (left). If the bubble size is small compared to the pore size, the small bubble will flow through one or the other branch without dividing.

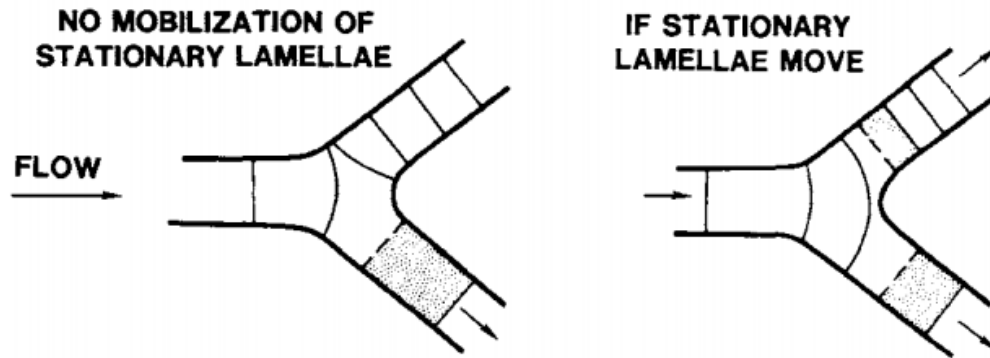


Figure 2-10 Schematic of lamella division mechanism (Falls, et al., 1988)

2.3.2 Foam Coalescence

Gravity drainage, capillary suction coalescence and gas diffusion are major mechanisms for foam coalescence. But capillary pressure is the dominating factor for foam coalescence in porous media, because of the geometry of pores and foam bubbles (Falls, et al., 1988; Khatib, et al., 1988; Chambers and Radke, 1991).

Limiting Capillary Pressure

Limiting capillary pressure (P_c^*) is an important concept to characterize the influence of capillary pressure ($P_c(S_w)$) on foam stability. $P_c(S_w)$ is a decreasing

function of water saturation (S_w). The foam coalescence is slow at $P_c(S_w) < P_c^*$. This can result in the rate of foam generation higher than that of coalescence at low capillary pressure (or high water saturation). S_w decreases with generation and accumulation of foam, which results in the increase of $P_c(S_w)$. The foam coalescence suddenly increases as capillary pressure approaches the limiting capillary pressure or as $P_c(S_w) = P_c^*$. This results in that a rate of coalescence equals to that of generation and steady-state is reached. In the case at $P_c(S_w) > P_c^*$, coalescence or weak foam dominates the foam process until the S_w increases back to reduce the $P_c(S_w)$ to below P_c^* .

Effect of Oil

Besides the above mechanisms, the effect of oil on foam stability is another dominating factor for foam coalescence in petroleum industry.

The deleterious effect of crude oil on foam stability has been recognized since 1960s (Bernard and Jacobs, 1965). Two plausible explanations for the oil effect are introduced below:

Entering, Spreading and Bridging Coefficients. The entering (E), spreading (S) and bridging coefficients (B) of oil droplets are defined in Equation 2-13 (a-c) (Lobo and Wasan, 1993; Garrett, 1980; Farajzadeh, et al., 2012):

$$E_{o/wg} = \sigma_{ow} + \sigma_{gw} - \sigma_{og} \quad (a)$$

$$S_{o/wg} = \sigma_{gw} - \sigma_{ow} - \sigma_{og} \quad (b)$$

$$B_{o/wg} = \sigma_{ow}^2 + \sigma_{gw}^2 - \sigma_{og}^2 \quad (c)$$

Equation 2-13 Definition of (a) entering, (b) spreading, and (c) bridging coefficients

where σ is interfacial tension; the subscripts o , w and g refer to oil, water and gas, respectively.

An oil droplet tends to enter gas/water interface if $E_{o/wg} > 0$, as demonstrated in the change from Figure 2-11 (a) to (b). The entered oil droplet tends to spread on the interface if $S_{o/wg} > 0$, as demonstrated in Figure 2-11 (c), which results in the replacement of stable gas/water interface by unstable gas/oil interface and rupture of the lamella (Lobo and Wasan, 1993).

The entered oil droplet can stay as a lens rather than spreading on the surface and doesn't rupture the film (Figure 2-11 b) if $S_{o/wg} < 0$. However, as the film continues to drain, the oil lens will bridge across the opposite surface and rupture the films if $B_{o/wg} > 0$, as demonstrated in Figure 2-11 (d) (Garrett, 1980).

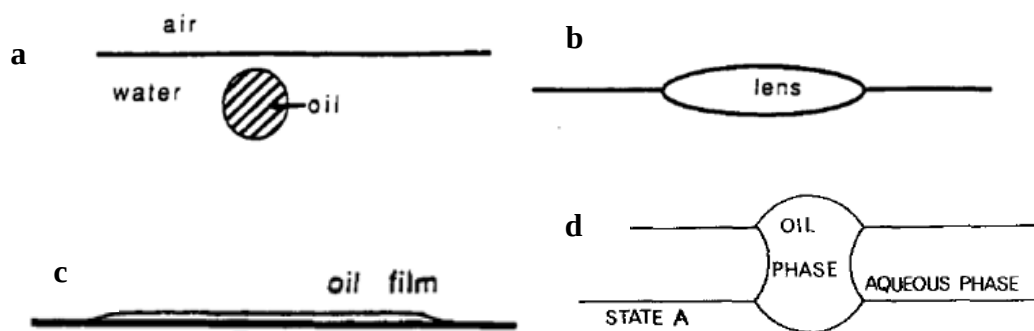


Figure 2-11 The process of an oil droplet entering, spreading and bridging across the foam film (Lobo and Wasan, 1993)

Pseudoemulsion-Film. The pseudoemulsion-film is the aqueous film that forms as oil drop approaches air-water interface (Nikolov et al., 1986), illustrated in Figure 2-12.

The stability of pseudoemulsion-film governs the stability of foam in the presence of oil or in the case of oil-wet substrate. The film interfacial tension (σ_f) is defined in Equation 2-14.

$$\sigma_f = \sigma_{ow} + \sigma_{gw} + \int_{\Pi(h_\infty)=0}^{\Pi=\Pi(h_0)} h d\Pi$$

Equation 2-14 Definition of the film interfacial tension

where h is the thickness of pseudoemulsion-film; h_0 is the thickness at equilibrium.

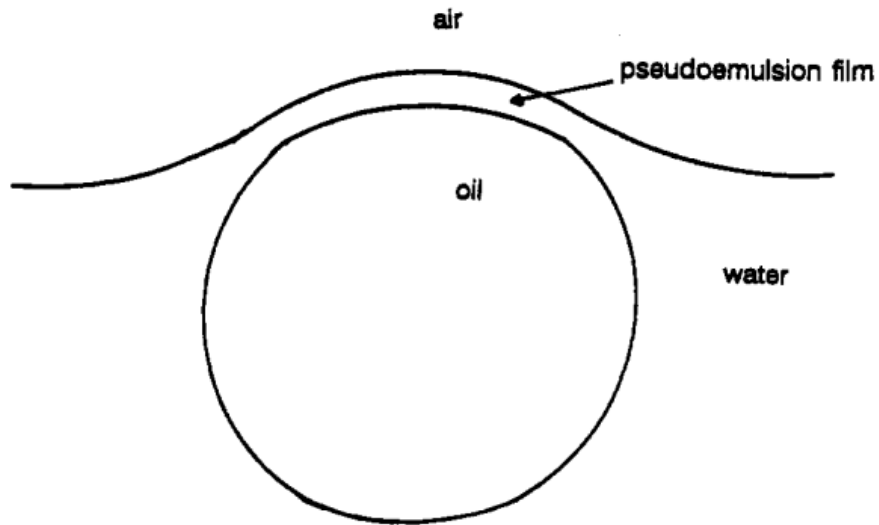


Figure 2-12 Diagram of pseudoemulsion film (Lobo and Wasan, 1993)

Entering coefficient and pseudoemulsion film mechanisms can be combined in a generalized entering coefficient ($E_{o/wg}^g$), expressed in Equation 2-15 (Bergeron, et al., 1993).

$$E_{o/wg}^g = \sigma_{ow} + \sigma_{gw} - \sigma_f = - \int_{\Pi(h_\infty)=0}^{\Pi=\Pi(h_0)} h d\Pi$$

Equation 2-15 Definition of the generalized entering coefficient

Thus, $E_{o/wg}^g$ only depends on the property of pseudoemulsion-film.

$E_{o/wg}^g$ is a sufficient rather than necessary condition for the pseudoemulsion film stability, *i.e.*, the pseudoemulsion film is thermodynamically stable if $E_{o/wg}^g < 0$, and may or may not be stable if $E_{o/wg}^g > 0$.

2.3.3 Foam Mobility Reduction

In foam flooding processes, liquid phase is wetting phase compared to gas phase. Most of liquid flows next to the solid walls of pores, or occupies the smaller pores where no gas exists. Thus, the liquid mobility isn't directly affected by foam and is still a function of liquid saturation (Bernard and Jacobs, 1965; Falls, et al., 1988; Sanchez and Hazlett, 1992). Foam directly reduces the gas mobility by decreasing gas relative permeability and increasing gas apparent viscosity.

Reduction of Gas Relative Permeability

Falls, et al., (1988) assumed that gas relative permeability was proportional to the area which gas flows through. Thus, the gas permeability is reduced by stationary lamellae, as demonstrated in Figure 2-10 (left).

STARS foam model (2007 version) utilized an empirical equation (Equation 2-16) for gas relative permeability to describe the mobility reduction by foam (Ma, et al., 2013a).

$$k_{rg}^f = k_{rg}^{nf} \times FM$$

Equation 2-16 Gas relative permeability in foam for STARS foam model

where k_{rg}^f and k_{rg}^{nf} indicate the gas relative permeability in the presence and absence of foam; FM is the foam mobility reduction factor which is described by seven functions (Ma, et al., 2013a).

In this empirical foam model, the gas viscosity is assumed to be a constant, and the reduction of foam mobility is assumed to be resulted from the decrease of relative gas permeability (Equation 2-16).

Increase of Gas Apparent Viscosity

The apparent viscosity of gas phase in foam is results from two factors: (1) the flow resistance of liquid slug between gas bubbles, (2) the deformation of gas-liquid interface through viscous and capillary forces and/or capillary constrictions, and (3) the surface tension gradient which occurs when the surfactant concentration in bubble front is less than that in the back of bubble (Hirasaki and Lawson, 1985; Falls, et al., 1989).

The foam texture (bubble size) is the key factor for the apparent viscosity of gas phase (Hirasaki and Lawson, 1985; Falls, et al., 1986). The finer foam texture indicates the higher bubble density and larger number of bubbles delivered through the porous media, consequently, results in the higher apparent viscosity of gas phase. The influence of foam texture on foam mobility is described by Population-Balance model proposed by Falls, et al. (1988).

2.4 Determination of Surfactant Concentrations

The methods for quantitative analysis of surfactants mainly include acid-base titration, colorimetric titration, potentiometric titration, chromatographic analysis, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy (Cullum, 1994). Three methods: colorimetric titration, potentiometric titration and chromatographic titration were used in this thesis and are introduced below:

2.4.1 Colorimetric Titration

A dye is used as a color indicator to imply the stoichiometric end point in colorimetric titration process. Two-phase colorimetric titration is a widely used method to determine the concentrations of ionic and nonionic surfactants.

For ionic surfactant titration, a charged dye is added with surfactant sample in an aqueous buffer and chloroform two-phase system. The titrant surfactant solution carries the opposite charge to surfactant in sample solution. The ion pairs of anionic and cationic surfactants are preferentially soluble in

chloroform phase. The transfer of the charged dye, *i.e.*, the color, from one phase to the other phase indicates the end point. Methylene blue (MB) two-phase titration is one of widely used colorimetric methods, proposed by Epton (1947). The MB, a positively charged cationic blue dye, is used as a color indicator for the anionic surfactant titration with cationic titrant, as illustrated in Figure 2-13 (A). One of the disadvantages of Epton's method is the untitrated anionic surfactant in MB and anionic ion pairs, which results in the underestimation for the concentrations of anionic surfactants. Cullum (1960) proposed to extend MB two-phase titration for determining cationic surfactant concentration (Figure 2-13 B) and used colorless end point to replace the equally blue Epton's end point, as shown in Figure 2-13 (C). But the colorless end point is hard to determine by visual check.

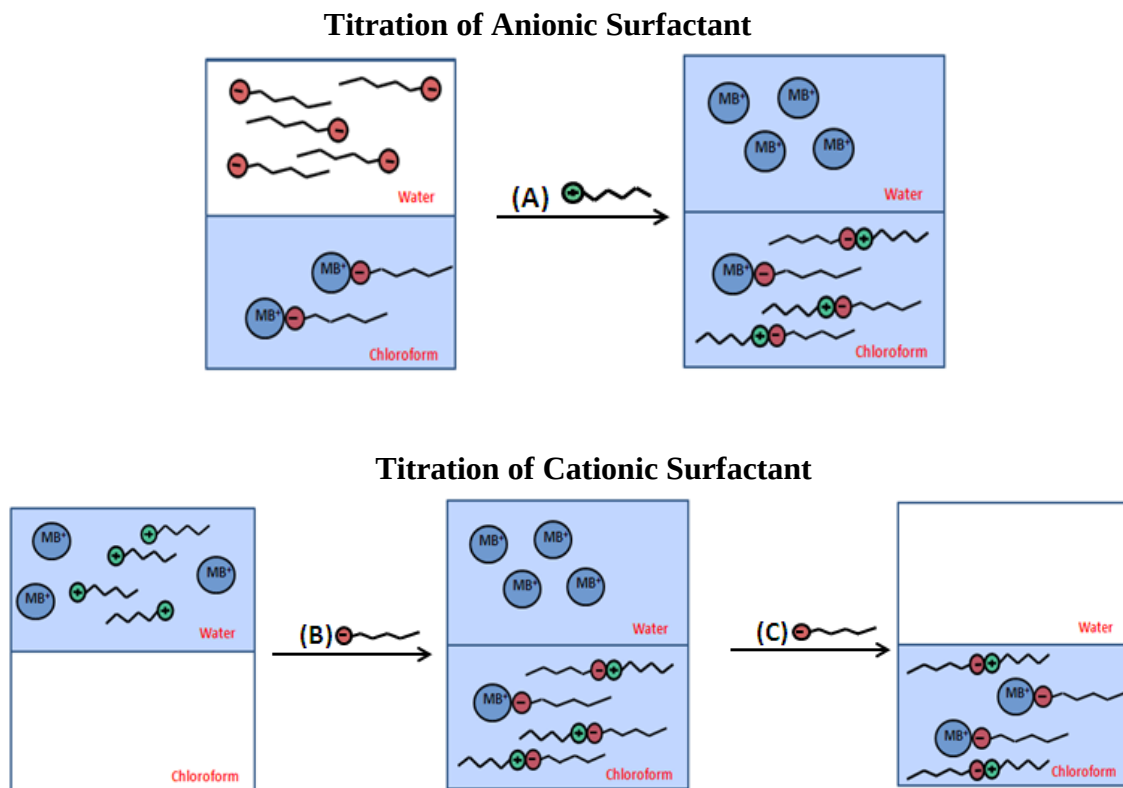


Figure 2-13 Schematic of Epton's Methylene Blue (MB) two-phase titration

The interference of inorganic ions, *e.g.*, Cl^- , restrains the application of MB two-phase titration in high salinity brine (Longwell and Maniece, 1955; George and White, 1999). An improved method with colorless end point, new MB solution and lauryl ether sulfate titrant is introduced in Chapter 5 and is used to determine the surfactant concentrations of some ionic surfactants in this thesis.

For nonionic surfactants, Tsubouchi and Tanaka (1984) proposed to add sodium tetraphenylborate to form water-insoluble complex with ethoxylated nonionic surfactant, extract the complex into organic solvent and titrate with ammonium surfactant in the presence of color indicator, *i.e.*, Victoria Blue B. The end point is reached when the color changes from blue to red in organic phase.

The method is limited for the surfactants with 8-40 ethoxylate (EO) units and sometimes is not 1:1 stoichiometric ratio. Thus, the calibration curve with a pure sample should be plotted.

2.4.2 Potentiometric Titration

Potentiometric methods utilize electrodes to measure the change in electric potential during titration with a titrant surfactant of opposite charge to that of the surfactant being determined. The electrode measures the electrochemical activity of ionic surfactants based on Nernst equation (Equation 2-17)

$$E = E^0 + 0.059\log(a)$$

Equation 2-17 Nernst Equation for the concentration of ionic surfactants

where E is the electric potential; E^0 is the reference electric potential, usually measured by a reference electrode; a is the activity of surfactants.

The potentiometric titration is a fast and efficient method, especially when equipped with an automatic titrator. But the method requires the carbon number of the hydrophobic chain higher than 10 (Bian, 2009), and is not sufficiently efficient for switchable cationic surfactant in high salinity brine.

2.4.3 High Performance Liquid Chromatography (HPLC)

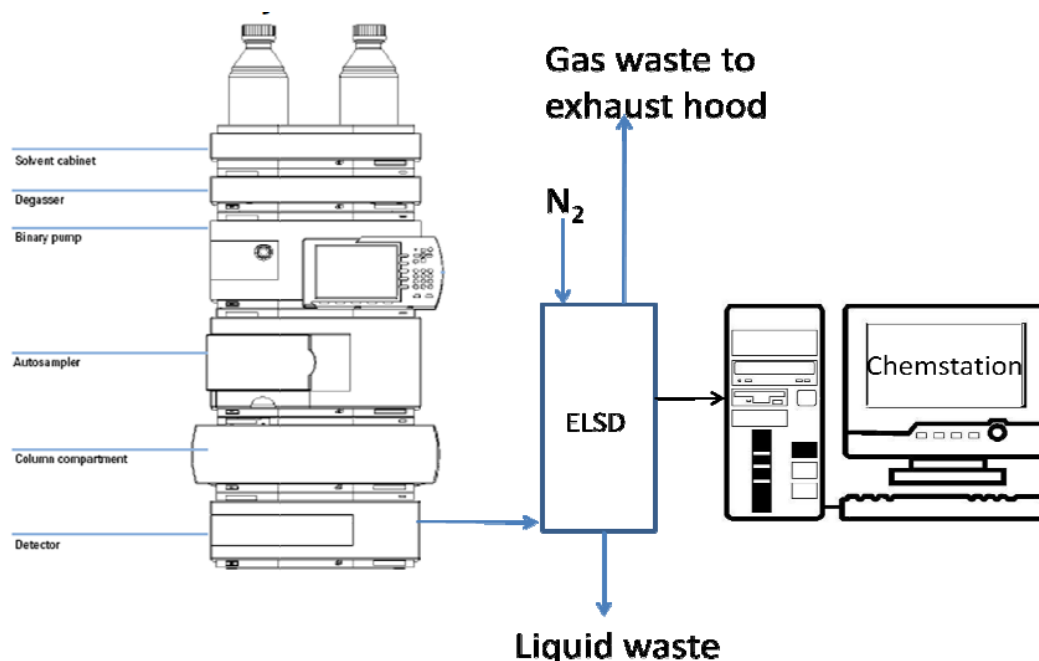


Figure 2-14 The schematic of HPLC setup (Bian, 2009)

Chromatography is a separation method to distinguish the components in a mixture of surfactants. Samples are injected with mobile phase through a separation column, and the effluent is analyzed by a detector in high performance liquid chromatography (HPLC) shown in Figure 2-14 (Bian, 2009). An evaporative light scattering detector (ELSD) equipped in our HPLC setup, is a universal detector for all the dissolved solid matter in the solutions.

HPLC can determine the concentrations of each component or total surfactant in solution by the peak areas or heights. Therefore, a concentration index (calibration curve) with peak areas/heights of standard solutions with known concentrations should be plotted. HPLC is a universal method for all kinds of surfactants, but is also a tedious and time consuming method because of the

long precondition and separation time for a single sample. Frequent recalibration may be needed if there is change in the detector response.

2.5 References

Bergeron, V., Fagan, M. E. & Radke, C. J., 1993. Generalized entering coefficients: a criterion for foam stability against oil in porous media. *Langmuir*, 9(7), pp. 1704-1713.

Bergeron, V., 1999. Forces and structure in thin liquid soap films. *Journal of Physics: Condensed Matter*, 11(19), R215.

Bernard, G. G. & Jacobs, W. L., 1965. Effect of Foam on Trapped Gas Saturation and on Permeability of Porous Media to Water. *SPE Journal*, 5(04), pp. 295-300. SPE-1204-PA.

Bian, Y., 2009. Manual for Surfactant Titration. *Internal Manual, Rice Univeristy, Dr. Hirasaki's Lab*.

Chambers, K. T. & Radke, C. J., 1991. Capillary phenomena in foam flow through porous media. In: N. R. Morrow, ed. *Interfacial phenomena in petroleum recovery*. s.l.:s.n., pp. 191-255.

Chen, M., Yortsos, Y. C. & Rossen, W. R., 2005. Insights on foam generation in porous media from pore-network studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 256(2-3), p. 181–189.

Cullum, D. C., 1960. *Determination of Cationic Surfactants by Anionic Detergents..* Cologne, s.n., pp. 42-45.

Cullum, D. C., 1994. *Introduction to Surfactant Analysis*. First edition ed. s.l.:Chapman & Hall.

Epton, S., 1947. A RAPID METHOD OF ANALYSIS FOR CERTAIN SURFACE-ACTIVE AGENTS. *NATURE* , 160(4075), pp. 795-796 .

Falls, A. H., Hirasaki, G. J., Patzek, T. W., Gauglitz, D. A., Miller, D. D., & Ratulowski, T. (1988). Development of a Mechanistic Foam Simulator: The Population Balance and Generation by Snap-Off. *SPE Reservoir Engineering*, 3(03), 884-892. SPE-14961-PA.

Falls, A. H., Musters, J. J., & Ratulowski, J. (1989). The apparent viscosity of foams in homogeneous bead packs. *SPE Reservoir Engineering*, 4(02), 155-164. SPE-16048-PA.

- Fainerman, V. B., Mobius, D. & Miller, R., 2001. *Surfactants: Chemistry, Interfacial Properties, Applications*. First Edition ed. s.l.:Elsevier.
- Garrett, P. R., 1980. Preliminary considerations concerning the stability of a liquid heterogeneity in a plane-parallel liquid film. *Journal of Colloid and Interface Science*, 76(2), pp. 587-590.
- George, A. & White, G., 1999. Optimization of the methylene blue assay for anionic surfactants added to estuarine and marine water. *Environmental toxicology and chemistry*, 18(10), pp. 2232-2236.
- Hirasaki, G. J., & Lawson, J. B. (1985). Mechanisms of Foam Flow in Porous Media: Apparent Viscosity in Smooth Capillaries. *Society of Petroleum Engineers Journal*, 25(02), 176-190. SPE-12129-PA.
- Holmberg, K., Jönsson, B., Kronberg, B., & Lindman, B. (2003). *Surfactants and polymers in aqueous solution*. John Wiley & Sons, Ltd.
- Khatib, Z. I., Hirasaki, G. J. & Falls, A. H., 1988. Effects of Capillary Pressure on Coalescence and Phase Mobilities in Foams Flowing Through Porous Media. *SPE Reservoir Engineering*, 3(03), pp. 919 - 926. SPE-15442-PA
- Kovscek, A. R. & Radke, C. J., 1994. Fundamentals of Foam Transport in Porous Media. In: L. L. Schramm, ed. *Foams: Fundamentals and Applications in the Petroleum Industry*. s.l.:American Chemical Society, p. 115–163.
- Lake, L. W., 1989. *Enhanced oil recovery*. Englewood Cliffs, N.J.: Prentice Hall Incorporated.
- Lobo, L. & Wasan, D. T., 1993. Mechanisms of aqueous foam stability in the presence of emulsified non-aqueous-phase liquids: structure and stability of the pseudoemulsion film. *Langmuir*, 9(7), pp. 1668-1677.
- Longwell, J. & Maniece, W., 1955. Determination of anionic detergents in sewage, sewage effluents and river waters. *Analyst*, 80(948), pp. 167-171.
- Ma, K., Lopez-Salinas, J. L., Puerto, M. C., Miller, C. A., Biswal, S. L., & Hirasaki, G. J. (2013(a)). Estimation of Parameters for the Simulation of Foam Flow through Porous Media. Part 1: The Dry-Out Effect. *Energy Fuels*, 27(5), 2363–2375.
- Morrow, N. R., 1990. Wettability and Its Effect on Oil Recovery. *Journal of Petroleum Technology*, 42(12), pp. 1,476 - 1,484.
- Nikolov, A. D., Wasan, D. T., Huang, D. W. & Edwards, D. A., 1986. The Effect of Oil on Foam Stability: Mechanisms and Implications for Oil Displacement by Foam in Porous Media. *SPE Annual Technical Conference and Exhibition*, New Orleans, Louisiana. SPE-15443-MS

- Paul, G. W., Lake, L. W., Pope, G. A., & Young, G. B. (1982). A simplified predictive model for micellar-polymer flooding. In *SPE California Regional Meeting*. SPE-10733-MS.
- Rangel-Yagui, C. O., Pessoa-Jr, A. & Blankschtein, D., 2004. Two-phase aqueous micellar systems - an alternative method for protein purification. *Brazilian Journal of Chemical Engineering*, Volume 4, p. 21.
- Rosen, M. J., 2004. *Surfactants and Interfacial Phenomena*. Third Edition ed. s.l.:Wiley-Interscience.
- Rossen, W. R., 1996. Foams in Enhanced Oil Recovery. In: *Foams: Theory, Measurements, and Applications*. US: Marcel Dekker, Inc., p. 413.
- Ross, S., 1949. The Inhibition of Foaming. II. A Mechanism for the Rupture of Liquid Films by Anti-foaming Agents. *The Journal of Physical and Colloid Chemistry*, 54(3), pp. 429-436.
- Sanchez, J. M., & Hazlett, R. D. (1992). Foam Flow Through an Oil-Wet Porous Medium: A Laboratory Study. *SPE Reservoir Engineering*, 7(01), 91-97. SPE-19687-PA
- Schramm, L. L. & Marangoni, D. G., 2000. Surfactants and Their Solutions: Basic Principles. In: L. L. Schramm, ed. *Surfactants: Fundamentals and Applications in the Petroleum Industry*. s.l.:Cambridge University Press, pp. 3-51.
- Simmons, C. T., 2008. Henry Darcy (1803–1858): Immortalised by his scientific legacy. *Hydrogeology Journal*, 16(6), pp. 1023-1038.
- Stubenrauch, C. & Klitzing, R. v., 2003. Disjoining pressure in thin liquid foam and emulsion films—new concepts and perspectives. *Journal of Physics: Condensed Matter*, 15(27).
- Talley, L. D., 1988. Hydrolytic Stability of Alkylethoxy Sulfates. *SPE Reservoir Engineering*, 3(01), pp. 235 - 242. SPE-14912-PA
- Tanzil, D., Hirasaki, G. J. & Miller, C. A., 2002. Conditions for Foam Generation in Homogeneous Porous Media. *SPE/DOE Improved Oil Recovery Symposium*, Tulsa, Oklahoma. SPE-75176-MS
- Tsubouchi, M. & Tanaka, Y., 1984. Determination of poly(oxyethylene) non-ionic surfactants by two-phase titration. *Talanta*, 31(8), p. 633–634.
- Wardlaw, N. C., 1996. Factors Affecting Oil Recovery from Carbonate Reservoirs and Prediction of Recovery. In: *Carbonate Reservoir Characterization: A Geologic- Engineering Analysis, Part II*. s.l.:Elsevier, p. 867.

Chapter 3

Screening of Surfactant Formulations for Foam EOR

The solubility, chemical and thermal stability, fomability and foam stability of surfactant formulations for foam mobility control were investigated in this chapter. A qualified surfactant formulation should be clear solution and chemically and thermally stable under injection and reservoir conditions, and can provide mobility control in the presence of crude oil.

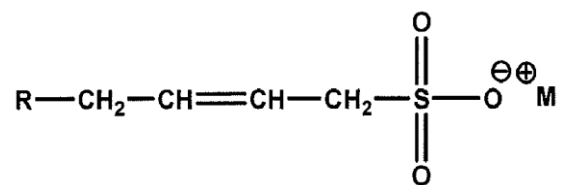
3.1 Experimental

3.1.1 Materials

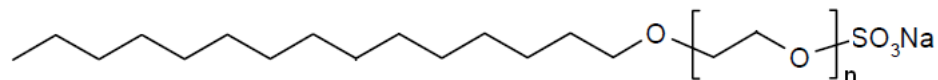
Four families of anionic surfactants, two families of cationic surfactants, two zwitterionic surfactants and two switchable cationic surfactants were used in this chapter, as listed in Table 3-1. All the information of surfactant structures, *i.e.*, carbon number, EO number and functional group, is shown in Figure 3-1and Figure 3-2.

Table 3-1 The catalog of surfactants in Chapter 3

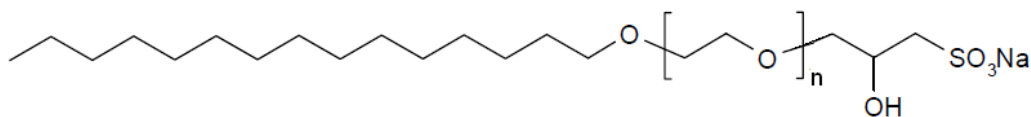
Type	Family	Name and Abbreviation	Source
Anionic Surfactant	Alpha-Olefin Sulfonate	AOS 16-18 (AOS)	Stepan Co.
	Alkyl Ether Sulfonate	Avanel S70 (S70)	BASF Co.
	Alkyl Glycidyl Ether Sulfonates	N25-7EO	Shell, Enordet, CO72
		N67-9EO	Shell, Enordet, A092
	Alkyldiphenyloxide Disulfonate	DowFax 8390	Dow
Cationic Surfactants	Quaternary Ammonium	hexadecyl-trimethyl ammonium bromide (CTAB)	ACROS Organics
	Pyridinium	hexadecyl-pyridinium chloride (CPC)	Sigma-Aldrich Co.
Zwitterionic Surfactants	Betaine	cocamidopropyl betaine (CAB)	Rhodia Co
		lauryl betaine (LB)	
Switchable Cationic Surfactants	Ethoxylated Amine	Ethomeen C12	AkzoNobel Co.
		Ethomeen C25A	



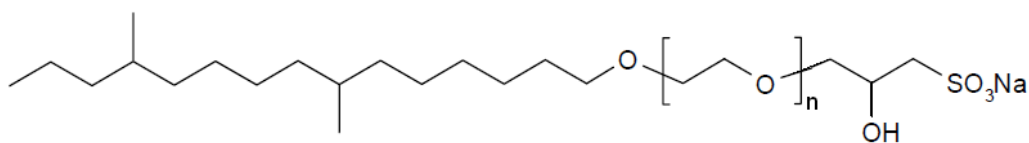
AOS 16-18 ($\text{R}=\text{C}_n\text{H}_{2n+1}$, $n=12-14$, $\text{M}=\text{Na}$)



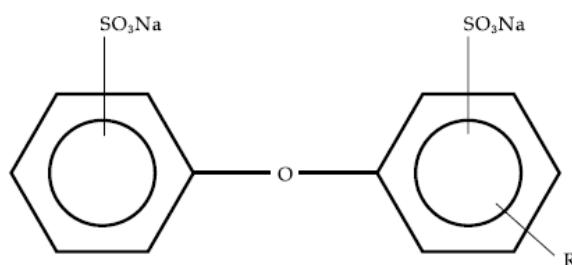
Avenel S70 ($\text{C}=12-15$, $n=7$)



N25-7EO ($\text{C } 12-15$, 80% linear and 20% branches, $n=7$)



N67-9EO ($\text{C } 16-17$, methyl branches, $n=9$)



DowFax 8390 (R is C_{16} α -olefin)

Figure 3-1 The structure of the anionic surfactants

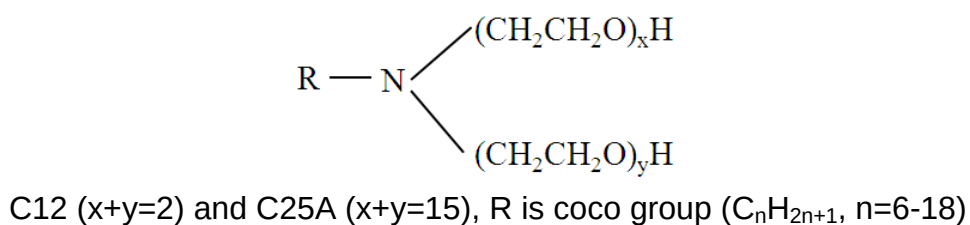
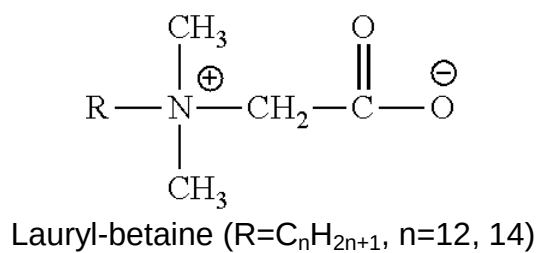
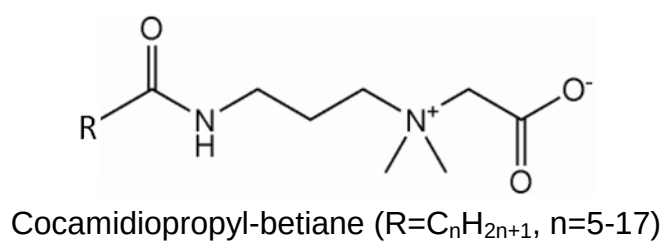
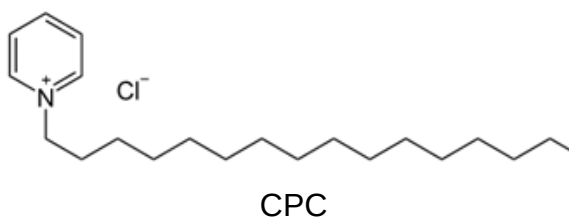
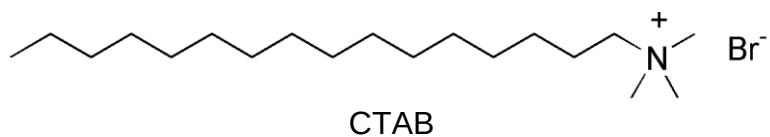


Figure 3-2 The structure of cationic, zwitterionic and switchable cationic surfactants

The inorganic salts used were of ACS or higher grade, and all solutions were prepared in deionized water (DI water, 18.2 MΩ).

Two synthetic brines were prepared. One is SME brine with 18.7% total dissolved solid (TDS), which contains 127.00 g/L NaCl (catalog # 3624-01, Avantor Performance Materials), 53.29 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (catalog # 223506, Sigma-Aldrich Co.), 22.67 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (catalog # M33, Fisher Scientific Co.) and 0.69 g/L Na_2SO_4 (catalog # 239313, Sigma-Aldrich Co.). The other one is synthetic formation brine with 182.31 g/L NaCl, 77.25 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 25.62 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 22.0% TDS. The ions compositions in SME and synthetic formation brine are demonstrated in Table 3-2.

Table 3-2 Ions compositions of SME and synthetic formation brine

Brine Name	Na^+ (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)
SME	50,185	14,528	2,710	110,643	467
Synthetic Formation Brine	71,720	21,060	3,063	156,777	0

Sandpack was used to evaluate the foam mobility control in this chapter. The sandpack consisted of 20/40 mesh silica sand (Ottawa silica sand, US Silica).

3.1.2 Solubility Test Procedure

The precipitation or phase separation was visually checked in the solubility tests. At room temperature, the solubility of surfactant solution was checked in a

capped bottle (22.0 ml capacity, catalog # 71000-180, VWR International Co.), as shown in Figure 3-3 (left). At other temperatures, the solubility was tested in a sealed glass pipette (5 ml glass pipet, catalog # 13-678-31H, from Fisher Sci.), called encased-glass-pipette method (Barnes, et al., 2008; Puerto, et al., 2012). This method was originally designed for micro-emulsion phase behavior tests. The glass pipette was cut and filled with tested sample, and then was heat-sealed and immersed in the safety bottle which was filled with the mineral oil which has high boiling point (Figure 3-3, right). The tested samples were heated or cooled to the target temperature in oil bath and were observed for the cloudy phenomena.



Capped Bottle



Encased-Glass-Pipette

Figure 3-3 Solubility test in capped bottle at room temperature and encased-glass-pipette at other temperatures. Left figure is 1% CTAB in DI water at 22 °C (the Krafft point is 27 °C), right figure is 1% C25 in synthetic formation brine at 130 °C (the cloud point is 70 °C).

The photos were shot in a black box. The front side of the box was open for photography. The bottom of the box was translucent for the light source which consisted of the fluorescent lamps. Other sides of the box were black background. The sample was located in the center of the box bottom.

3.1.3 Chemical and Thermal Stability Test Procedure

Surfactant solutions were sealed in capped bottles (2 ml, catalog # 5182-0553, from Agilent Tech.), and were placed in a pressure vessel. The pressure inside the vessel was maintained above the boiling pressure of water by N₂. The samples in the vessel were aged at 125 °C for a particular period.

The aged samples were analyzed by high performance liquid chromatography (HPLC) equipped with reverse-phase column (Dionex Acclaim Surfactant column, 4.6 × 250 mm, at 25 °C) and evaporative light scattering detector (ELSD, at 60 °C). The aqueous mobile phase is sodium acetate (100 mM) –acetic acid (20 mM) buffer at pH=5.5 and the organic mobile phase is Acetonitrile (ACN). The total flow rate of mobile phase is 1 ml/min. The decrease of area or height of surfactant peaks indicated the surfactant degradation under tested conditions, as demonstrated in Figure 3-4.

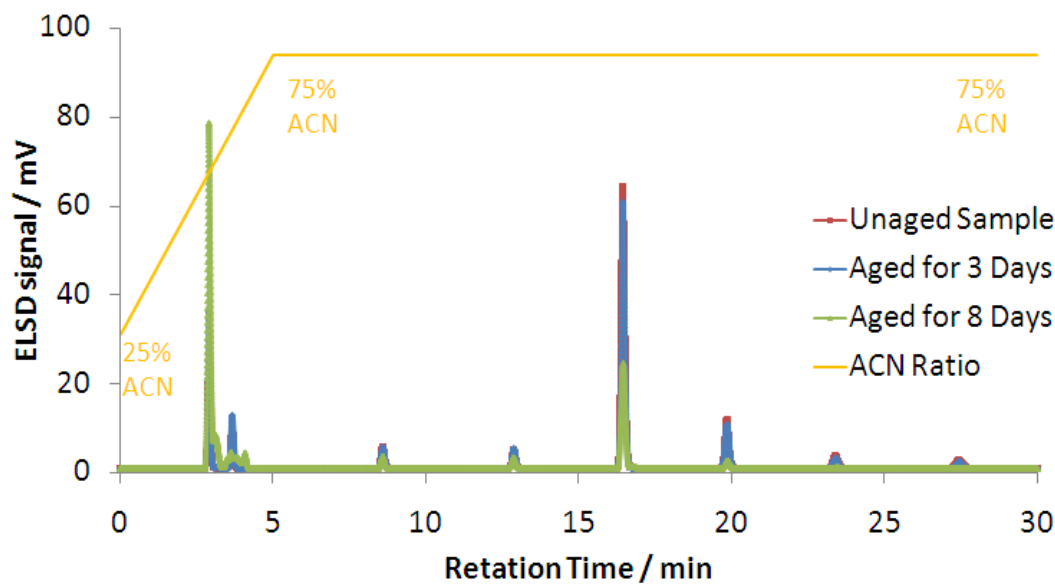


Figure 3-4 The HPLC analysis results for CAB in pH=4.47 buffer (ammonium acetic – acetic acid). CAB degrades with aging time.

This method should be improved to eliminate the oxygen effect, because of the anaerobic environment in the reservoirs. The sample can be sealed in a cramp neck bottle (catalog # 548-0611, from VWR Co.) with aluminium cap (catalog # 548-0062, from VWR Co.) in glove box which is full of N₂ or other inert gas. And oxygen scavengers, *e.g.*, sodium sulfite (Na₂SO₃) and sodium thiosulfate (Na₂S₂O₃), should be added into the brine before the surfactant is added (Wellington, 1983).

3.1.4 Foamability and Foam Stability in Bulk and Porous Media

Bulk and porous media foam tests are two popular methods to evaluate foamability and foam stability of surfactant formulations.

In bulk foam tests, the foam decay with elapsed time only describes the foam stability, and the equilibrium foam volume quantitatively reveals the balance of foam formation and foam collapse. In foam EOR, foam is generated and coalesced simultaneously in situ (Falls, et al., 1988). Thus, the dynamic equilibrium foam volume which combines the foamability and foam stability was chosen for bulk foam test method. The apparatus is schematized in Figure 3-5. A 100 ml glass graduated cylinder (I.D.=2.0 cm) was used to measure the foam column. The glass graduated cylinder was double-end opened. The bottom of the graduated cylinder was plugged by a rubber stopper, and the top was open to the atmosphere. Surfactant solution was injected by a needle syringe through the stopper, and the gas was injected through a glass frit (145-174 μm , catalog # Z408700, from Aldrich Co.). The liquid level of excess surfactant solution was maintained at zero mark, so the foam column can be directly read from graduated cylinder. The gas, *i.e.*, N_2 , flow rate was controlled in the range of 0-20 ml/min at tested conditions by a mass flow controller. The equilibrium foam volume at a particular N_2 flow rate was recorded. The higher equilibrium foam volume indicates the better foamability and foam stability of the surfactant formulation.

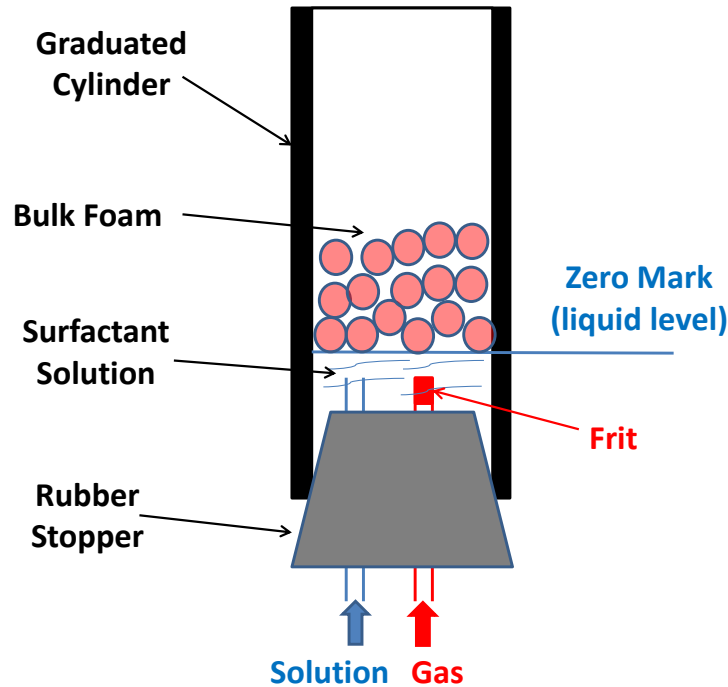


Figure 3-5 The schematic of bulk foam test apparatus

Sandpack and core are common porous media methods for foam evaluation. The characteristics, *i.e.*, permeability, formation and heterogeneity, of a sandpack can be controlled by selecting the sands with a particular size distribution. Core samples which come from outcrop or reservoirs have poor reproducibility of characteristics, but are close to the real flooding condition. Thus, the sandpack was used for screening of surfactant formulations at controlled conditions in this chapter, and the cores were used to test the foam mobility control under reservoir conditions in Chapter 4. The apparatus for foam flooding in sandpack is schematized in Figure 3-6. The 1-D sandpack was prepared in a glass column (Ace Glass Co.) with 1 foot long and 1 inch inner diameter. The 20/40 mesh silica sand (Ottawa silica sand, US Silica) was tightly packed into the

glass column by continuously tapping the glass wall. The metal screens of 100-mesh were placed at each end to retain the sand in the pack and to distribute fluids. The whole system was sealed with rubber stoppers and flanges. Pressure transducer (UPC608, Validyne Corp.) which was calibrated before measurement was connected at the inlet to record the pressure drop of the system. The fluids were injected into sandpack by syringe pumps (Harvard Apparatus), which can control the superficial velocities of fluids in the system.

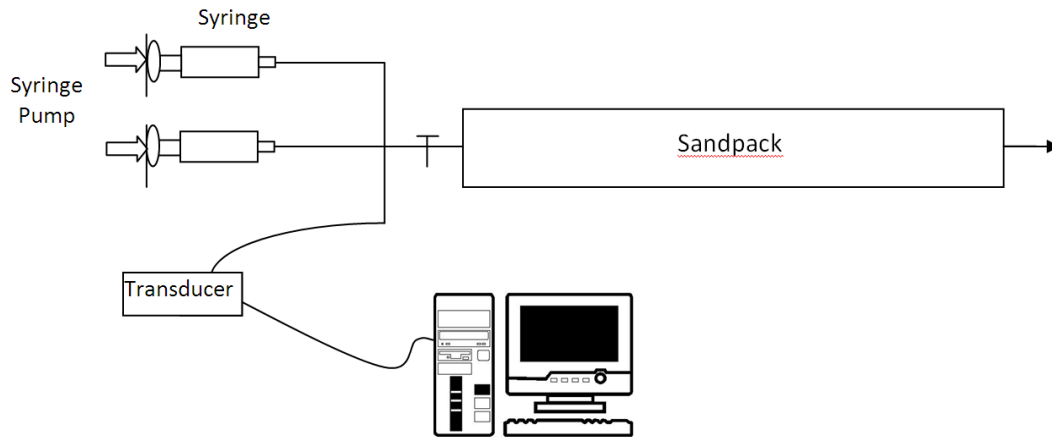


Figure 3-6 The schematic of the foam flooding in sandpack

The porosity (ϕ) of the sandpack was calculated by following Equation 3-1:

$$\phi = \frac{PV}{\pi(\frac{D}{2})^2 L}$$

Equation 3-1 Formula for porosity of sandpack

where PV is pore volume of the sandpack, mL; D is the diameter of the sandpack, here D is a constant which is the inner diameter of glass column, D

=1.00 inch= 2.54 cm; L is the length of the sandpack, which can be directly measured by a ruler; PV was measured by following procedure:

1st step: CO₂ was injected into 1-D column for 40 minutes at 2.5 psig to purge all air out of the sandpack.

2nd step: 300 ml (about 5 PV) distilled water was injected into column. Because CO₂ can dissolve into water, the sandpack was fully saturated by water. The pore volume equaled to the volume difference between injected water (300 mL) and produced water. The dead volume in the connections was measured to correct the pore volume.

Permeability of a sandpack was calculated from 1-D single-phase Darcy's law. The gravity term was neglected because of horizontal flow, and the Darcy's law is expressed in Equation 3-2:

$$u = -\frac{k \Delta P}{\mu L}$$

Equation 3-2 1-D single-phase Darcy's law for horizontal flow

where ΔP is pressure drop through the sandpack. $\Delta P = P(outlet) - P(inlet)$. Because the outlet was directly exposed to atmosphere, $P(outlet)$ equaled to atmosphere pressure, which results in that ΔP equals to the negative of the inlet gage pressure ($-P_g(inlet)$). Thus, the Equation 3-3 was used to calculate the permeability:

$$k = \frac{u \cdot \mu \cdot L}{P_g(inlet)}$$

Equation 3-3 Formula for permeability calculation in 1-D sandpack

Water is usually used to measure permeability. The procedures are shown as following:

1st step: the sandpack was fully saturated with water.

2nd step: water was injected through sandpack at a particular flow rate.

The pressure drop was recorded after reaching the steady state.

3rd step: repeat the 2nd step at various injection flow rates, and plot $\vec{u}$ versus $\frac{P_g(inlet)}{L}$. The slop was $\frac{k}{\mu}$. Because the water viscosity is 1.003 cp at 20 °C, the permeability of the sandpack can be obtained.

The effect of residual oil on foam strength and mobility control ability was studied. Crude oil flooding and water flooding were done sequentially before foam evaluation. 2 PV crude oil were injected into sandpack vertically from top to bottom at 5.0 ft/day in oil flooding process. The volume of the displaced water, V_{dw} , was recorded to calculate the initial oil saturation, $S_{io} = \frac{PV - V_{dw}}{PV}$. The column stood for 12 hours, and then water was injected into column from bottom to top at 5.0 ft/day until water cut reached 100%. The injection direction of water and oil was determined by gravity effect in the flooding process. The volume of displaced oil, V_{do} , was measured to calculate the residual oil saturation

$$S_{ro} = \frac{V_{dw} - V_{do}}{PV}.$$

Foam strength and mobility control ability were described in terms of foam apparent viscosity (μ_{app}), which is a normalized pressure gradient to the reciprocal of permeability and total superficial velocity (the sum of gas and liquid superficial velocity) calculated based on Darcy's law, as expressed in Equation 3-4. The higher μ_{app} indicates the stronger foam and better mobility control.

$$\mu_{app} = -\frac{k}{u_{total}} \nabla P = \frac{k}{u_{total}} \frac{P_g(inlet)}{L}$$

Equation 3-4 Formula for foam apparent viscosity in 1-D flow

In this chapter, foams were generated by water or surfactant alternating gas (WAG/SAG) injection. The superficial velocities of both aqueous solutions and gas were 20.0 ft/day, if not specified. The aqueous solution slug was 0.1 PV, and the gas slug was 0.2 PV, which indicates the gas fraction (f_g) was 2/3. The aqueous solution slug was injected as the first slug.

3.2 Results and Discussions

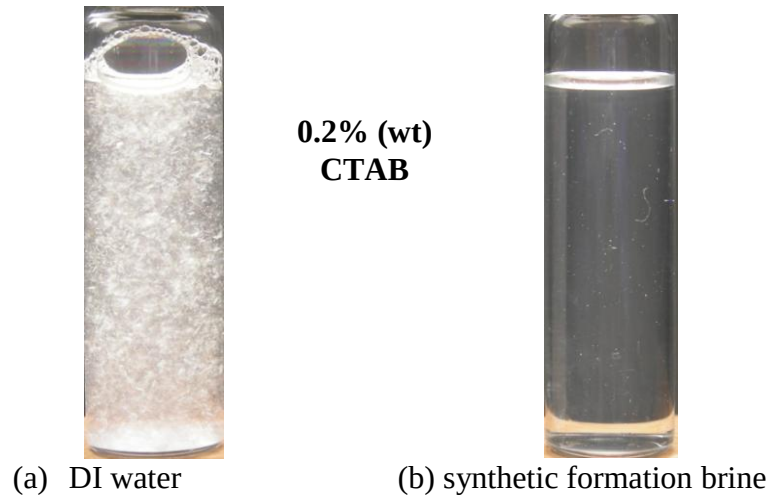
3.2.1 Solubility of Surfactants

The solubility of surfactants depends on the brine compositions and pH. For example, the sodium dodecyl sulfate (SDS) is clear in DI water, but is cloudy

and precipitated in the presence of high concentration Ca^{2+} (Sammalkorpi, et al., 2009).

The Krafft points (T_K) of ionic surfactants are affected by the competition of “salting-in” and “salting-out” effects of the electrolyte (de Lima and de Oliveira, 2010; Chu and Feng, 2012). Some salts can enhance the hydration of the surfactant head group to increase the surfactant solubility, called “salting-in” effect. Some salts can decrease the Debye length, consequently decrease the electric repulsion of surfactant head group to depress the surfactant solubility, called “salting-out” effect (Lin, et al., 2005). The Krafft point (T_K) of CTAB in DI water (around 27 °C) is slightly higher than room temperature (22 °C), but in synthetic formation brine it is lower than room temperature, as shown in Figure 3-7, because the “salting-in” effect dominated this process. However, CPC is clear in DI water but is cloudy in synthetic formation brine at room temperature, as shown in Figure 3-8. The T_K of CPC in synthetic formation brine was increased to 40 °C, as demonstrated in Figure 3-9, owing to the “salting-out” effect of the increased salinity.

Thus, the Krafft points of ionic surfactant candidates should be checked in reservoir and injected brine for screening purpose.



**Figure 3-7 Krafft phenomenon of 0.2% CTAB at room condition (22 °C).
The solution in DI water becomes clear at around 27 °C**

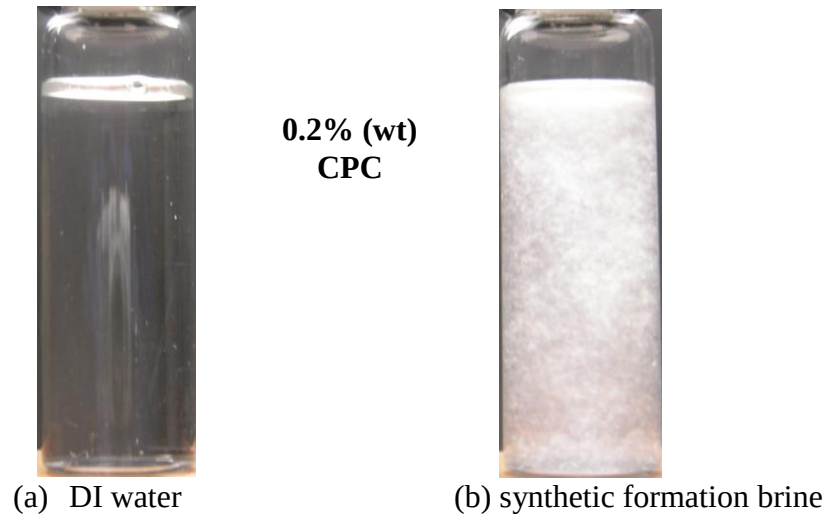


Figure 3-8 Krafft Phenomenon of 0.2% CPC at room condition (22 °C and 1 atm). The cloudy solution becomes clear at 40 °C.

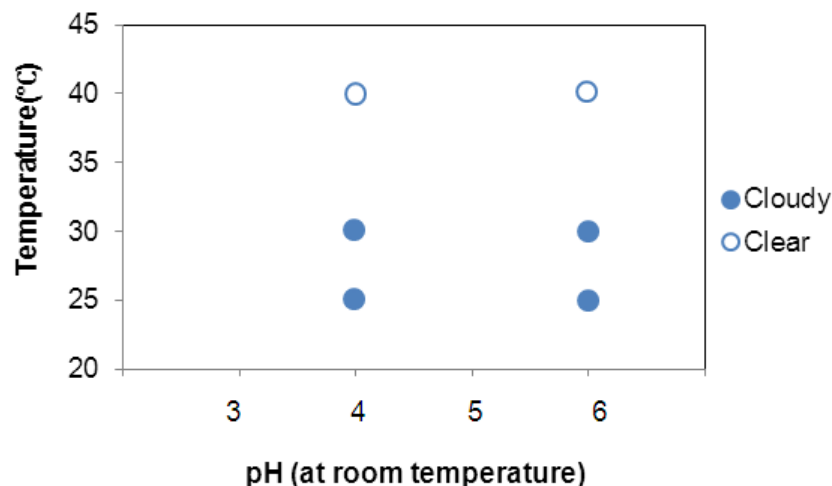


Figure 3-9 Krafft Temperature Test for 0.2% (wt) CPC in synthetic formation brine. Original pH=6, and adjusted with HCl to pH=4

The switchable cationic surfactants are nonionic surfactants at high pH, but are protonated to cationic surfactants at low pH. Thus, the cloud points of the switchable cationic surfactants should be checked at various pH. Figure 3-10 and Figure 3-11 show the cloud point test results for C25A and C12 in DI water and synthetic formation brine, respectively. The original pHs of both C25A and C12 solutions were higher than 9, as demonstrated in figures. Hydrochloric acid (HCl) was used to adjust the pH to 4 and 6. Pictures for the cloud point tubing tests of 1% C25A in synthetic formation brine are shown in Figure 3-12 as an example to illustrate the visual check for the cloud point.

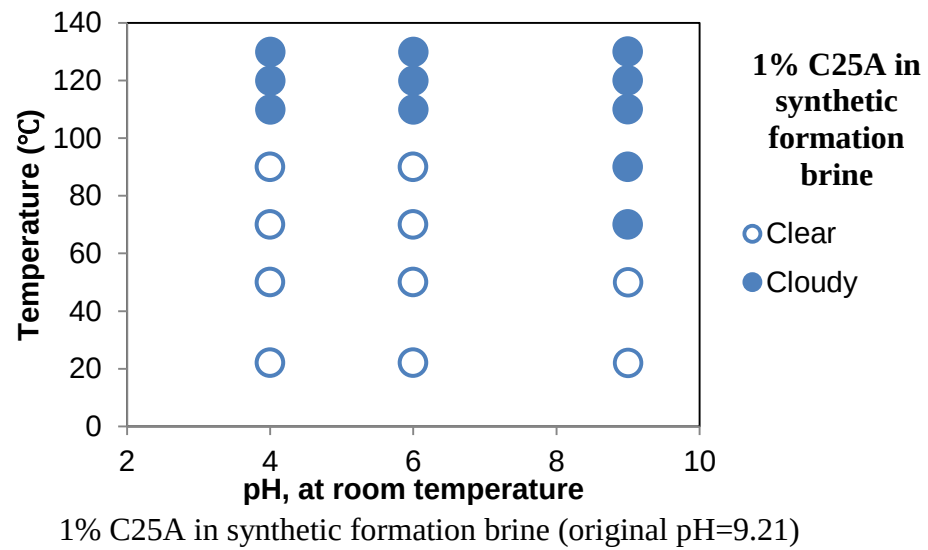
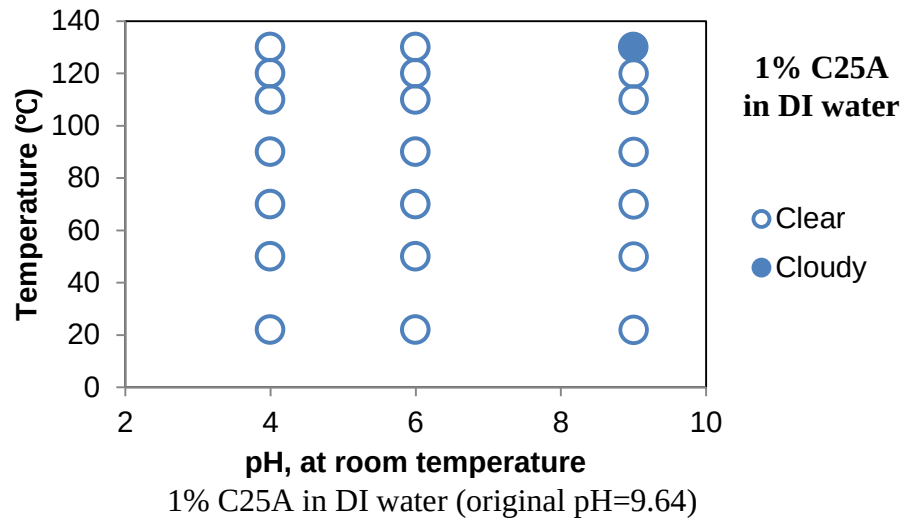


Figure 3-10 Cloud points of C25A, Upper: 1% C25A in DI water, Lower: 1% C25A in synthetic formation brine

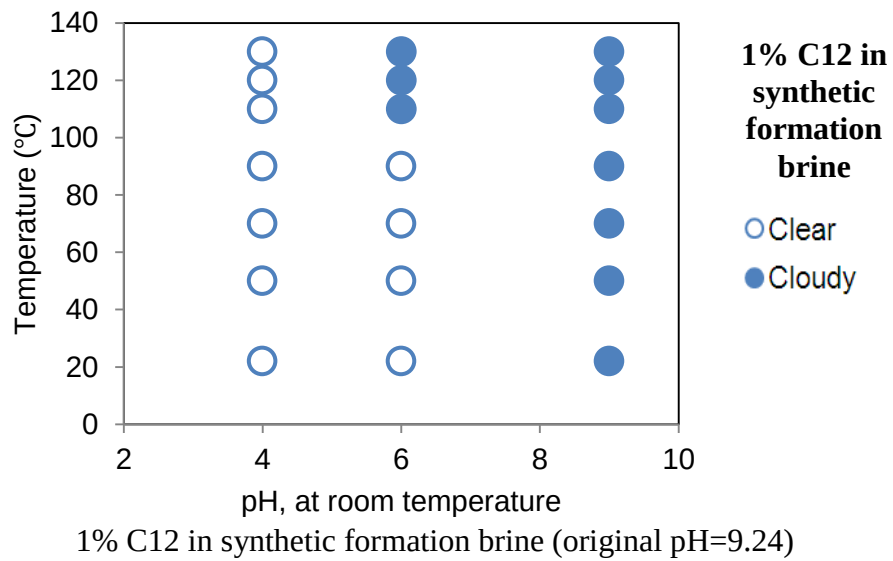
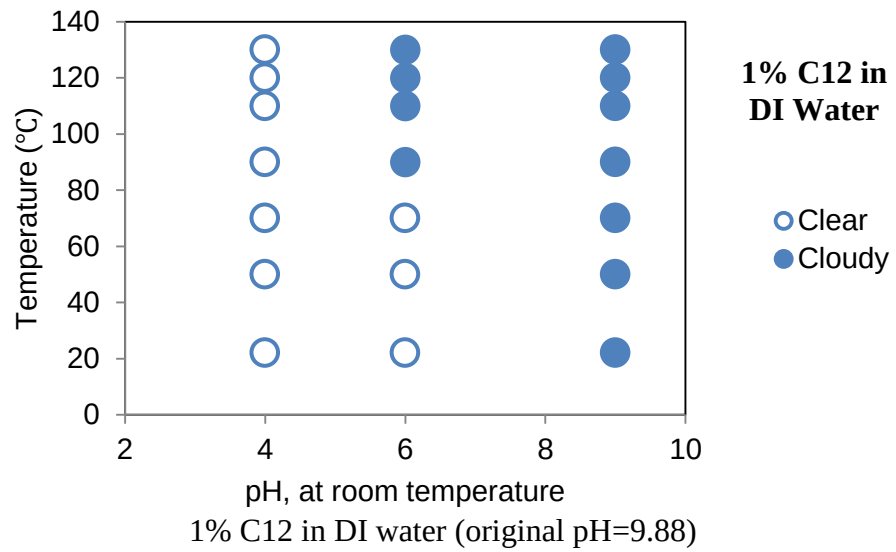


Figure 3-11 Cloud points of 1% C12, Upper: C12 in DI Water, Lower: C12 in synthetic formation brine

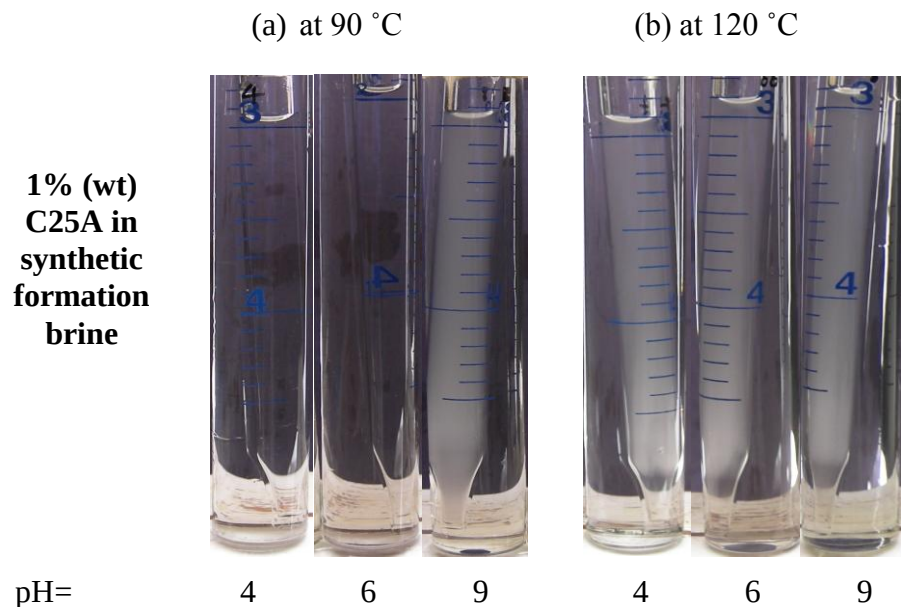


Figure 3-12 Pictures of 1% C25A in synthetic formation brine with different pH. Left is at 90 °C, right is at 120 °C.

The long EO groups in C25A were responsible for the high solubility in DI water, and limited solubility in synthetic formation brine at high temperature ($T > 110$ °C), because of the “salting-out” effect on long EO groups by electrolyte (Li, et al., 2009; Curbelo, et al., 2013) and steric blocking of EO groups to the protonated amine (Yaseen, et al., 2013). With short EO groups, the solubility of C12 was sparing at the original high pH. The electrolyte effect and steric blocking of EO groups were greatly reduced, which results in high cloud points of C12 at pH=4 in both DI water and high electrolyte solution. Thus, the switchable surfactants with high EO number should be used for the reservoirs with low temperature and high pH, the ones with low EO number should be used for the process at high temperature and low pH, e.g., CO₂ flooding in hot reservoirs.

Table 3-3 1% C25A in NaCl and CaCl₂ Solutions

pH at room temperature	Solvent	Cl ⁻ Concentration (mol/L)	Ionic Strength (mol/L)
9.98	120 g/L NaCl	2.05	2.05
9.62	75.97 g/L CaCl ₂	1.38	2.05

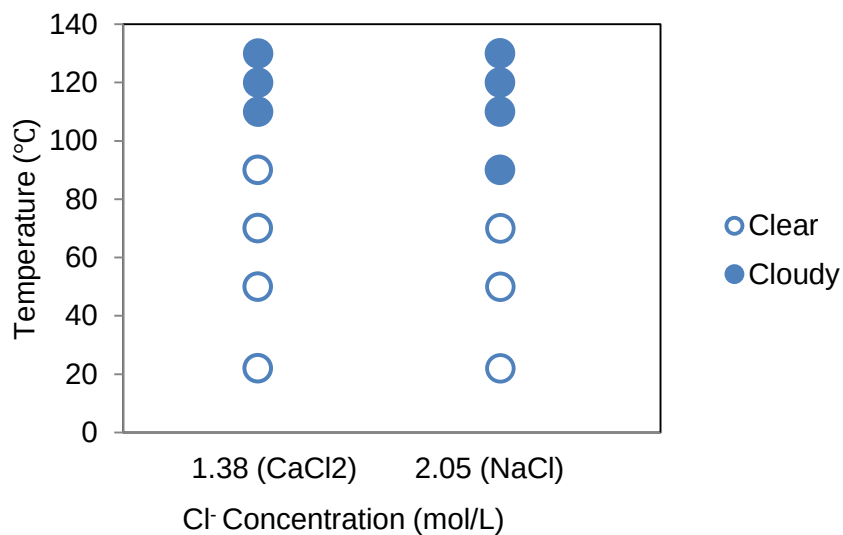


Figure 3-13 Cloud point test of 1% C25A in NaCl and CaCl₂ solutions with the same ionic strength (2.05 mol/L) at pH≈9

The “salting-out” effect of electrolyte was determined by Cl⁻ concentration rather than the ionic strength for cloud point of C25A and C12. NaCl and CaCl₂ solutions with the same ionic strength were prepared as listed in Table 3-3. The

cloud point of C25A was lower in NaCl than in CaCl_2 solution because of higher Cl^- concentration, as shown in Figure 3-13, which indicates the brine composition is more important than ionic strength for cloud points of surfactants.

Mixing ionic and nonionic surfactants is an effective method to depress the Krafft point of ionic surfactant and enhance the cloud point of nonionic surfactant. Figure 3-14 is the solubility test results for the blend of CPC and C25A in synthetic formation brine at 0.2% (wt) total activity and pH 6, adjusted by HCl. The Krafft point of the blend is higher than room temperature (22 °C) from 50% to 100% (wt) CPC, and the cloud point of the blend is lower than 120 °C from 0% to 20% (wt) CPC, as shown in Figure 3-14. At 40%(wt) of CPC, the surfactants blend was clear in the temperature range from room temperature (22 °C) to 130 °C. Thus, proper additives can be added to maintain the clear solution under injection to reservoir conditions.

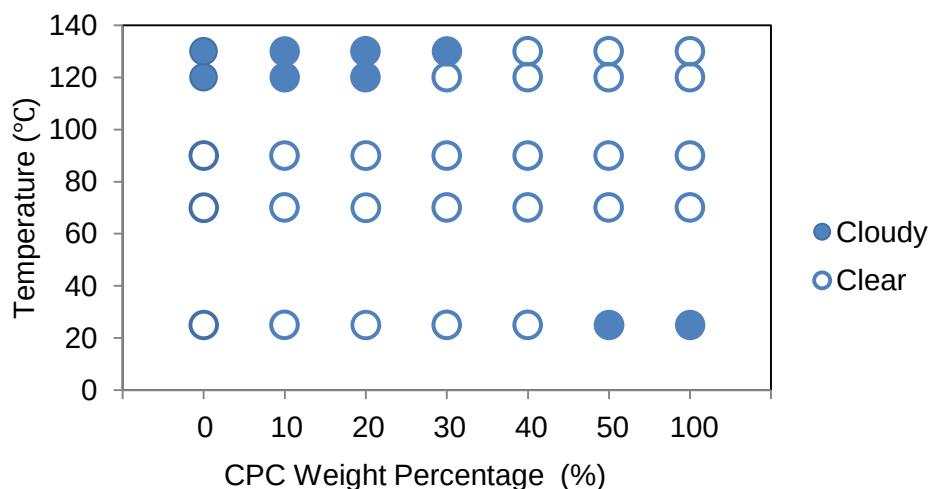


Figure 3-14 Cloud point for C25A/CPC blends of 0.2% (wt) total activity at pH=6. The cloud point of the blend with 30% (wt) CPC is 126 °C

3.2.2 Chemical and Thermal Stability of Surfactants

The chemical and thermal stability of surfactants depends on the brine composition, pH and temperature. CTAB was stable in DI water and 3.5% (wt) NaCl solution at neutral pH, as illustrated by HPLC results in Figure 3-15, but precipitated in 1% (wt) Na₂CO₃ solution at 125 °C, as shown in Figure 3-16.

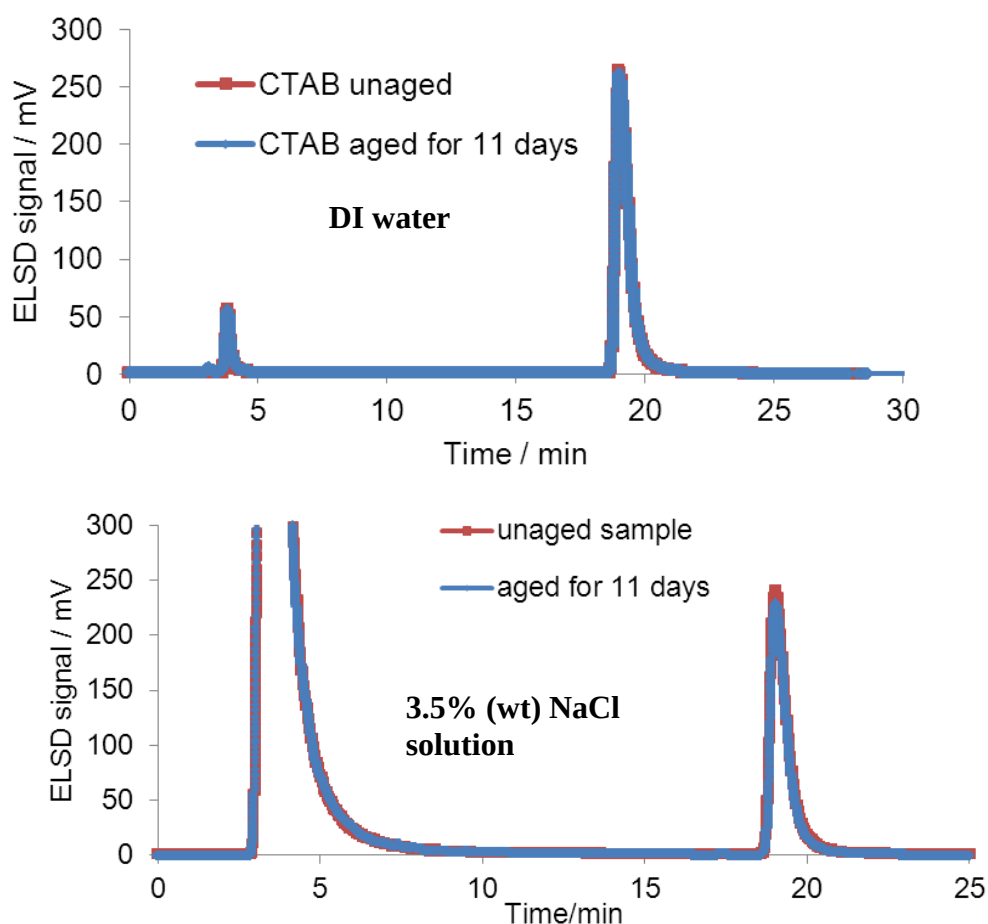


Figure 3-15 The comparison of 0.2% (wt) CTAB aged at 125 °C for 11 days and unaged sample at neutral pH. Upper: CTAB in DI water, Lower: CTAB in 3.5% (wt) NaCl solution. The characteristic peak of CTAB arrived at 19 min



Figure 3-16 0.2% (wt) CTAB in 1% (wt) Na_2CO_3 solution. Left one was aged at 125 °C for 11 days, right one was at room temperature

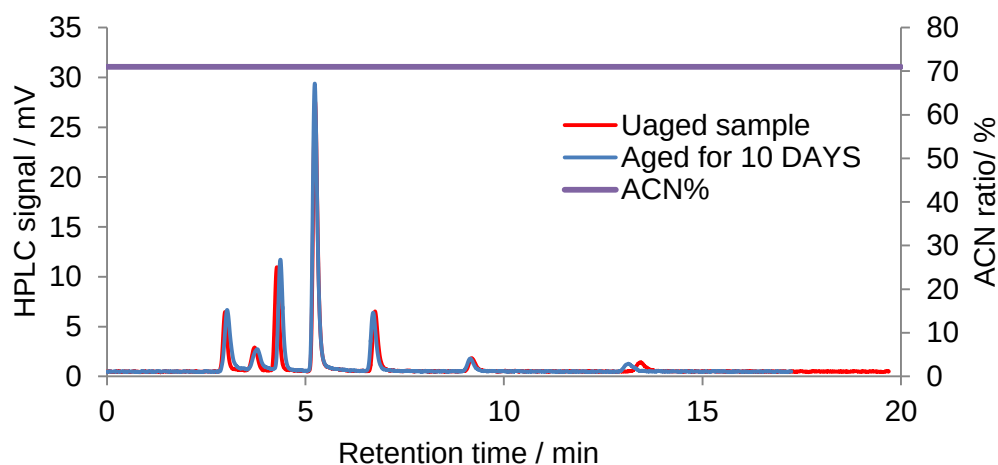


Figure 3-17 The HPLC signals of 0.1% (wt) CAB in DI water at neutral pH. Sample was aged at 125 °C for 10 days

CAB was stable at neutral pH for 10 days (Figure 3-17), but degraded at high and low pH (Figure 3-18, Figure 3-19 and Figure 3-20) at 125 °C, owing to the hydrolysis of amide group at extreme pHs. The speed of hydrolysis was fast in basic solution (Figure 3-18 (b)), was slow in acidic solution (Figure 3-19 (b)),

and increased with decreasing pH (Figure 3-20 (b)). The pH was adjusted by HCl.

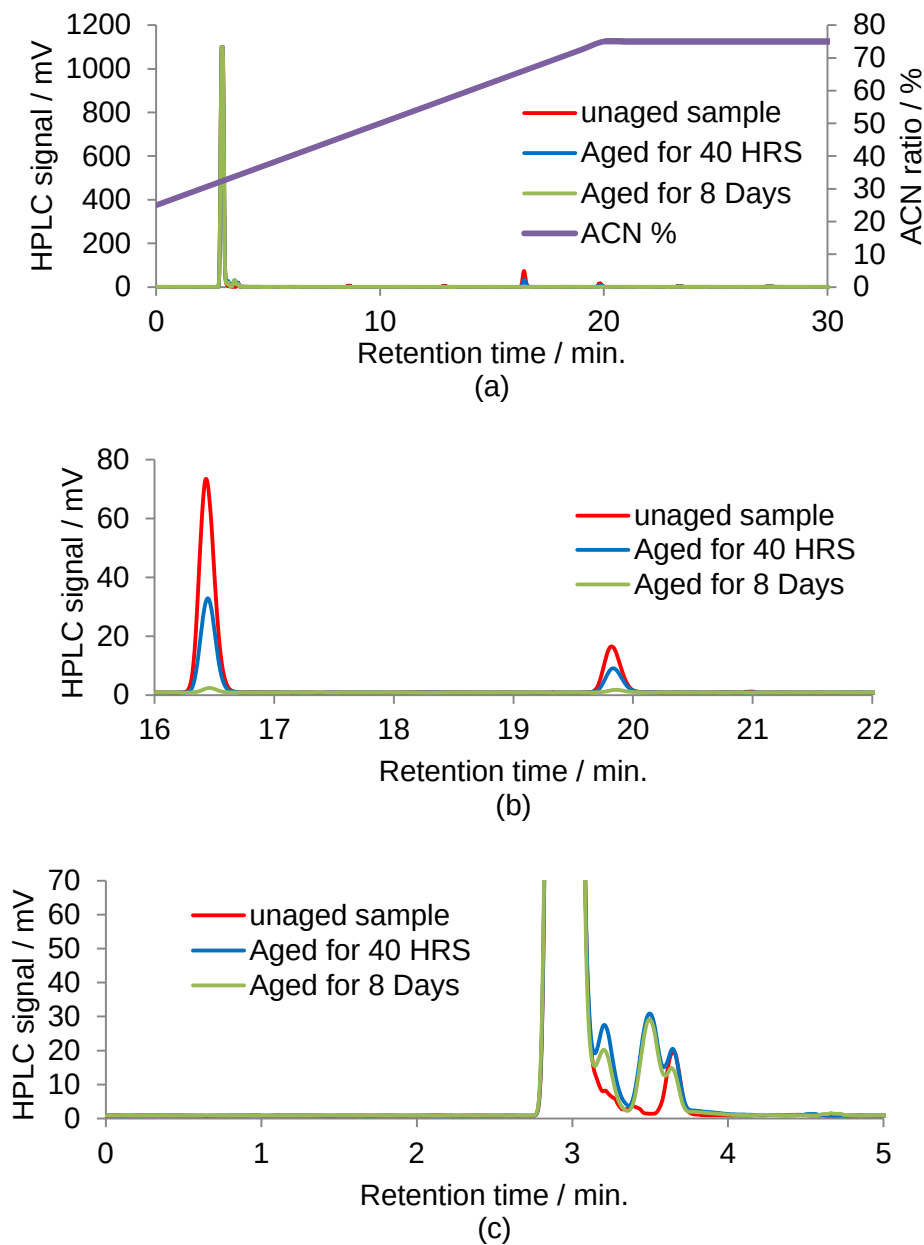


Figure 3-18 The HPLC signals of 0.1% (wt) CAB in 1.0% (wt) Na_2CO_3 solution. Sample was aged at 125 °C for 40 hours and 8 days. (a) in full scale (b) in zoom scale for surfactant peaks part (the characteristic peak of CAB at 16.5 min) (c) in zoom scale for salinity peaks part

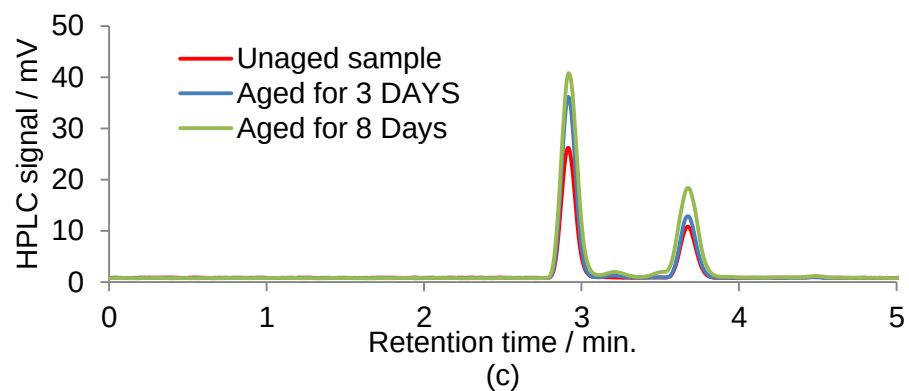
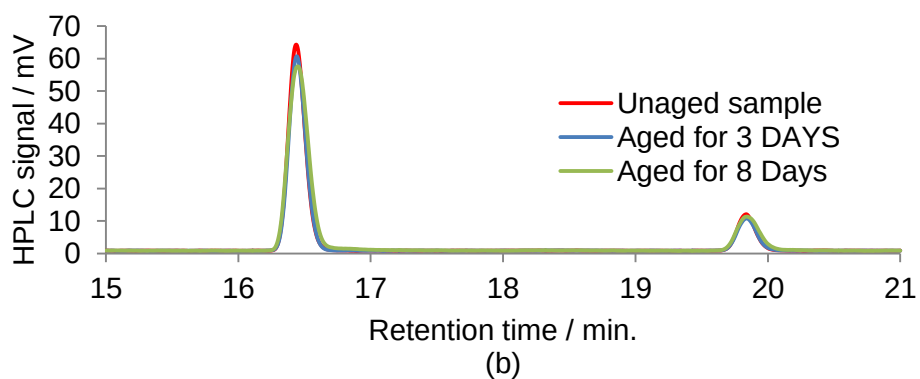
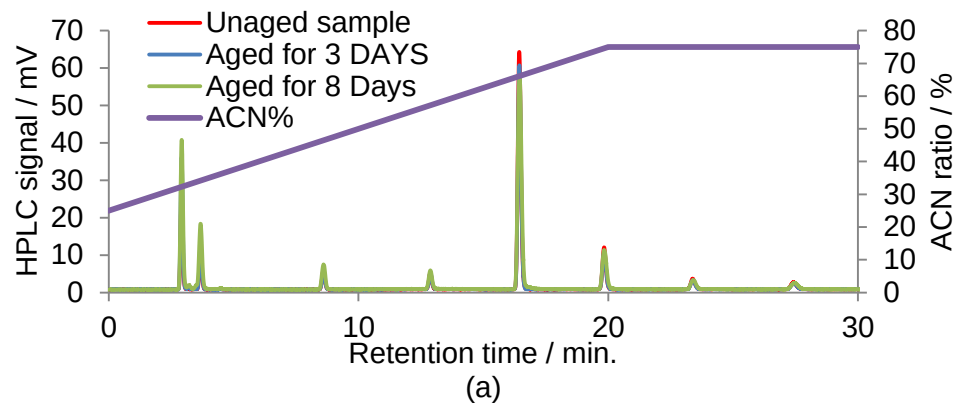


Figure 3-19 The HPLC signals of 0.1% (wt) CAB at pH=4.47. Sample was aged at 125 °C for 3 days and 8 days. (a) in full scale (b) in zoom scale for surfactant peaks part (the characteristic peak of CAB at 16.5 min) (c) in zoom scale for salinity peaks part

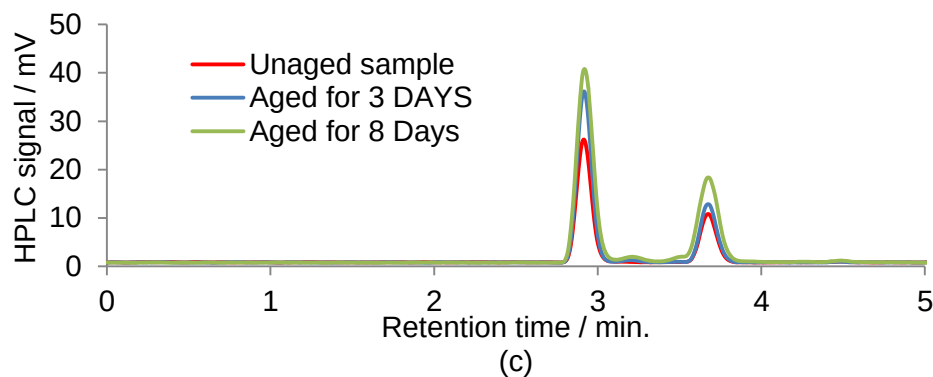
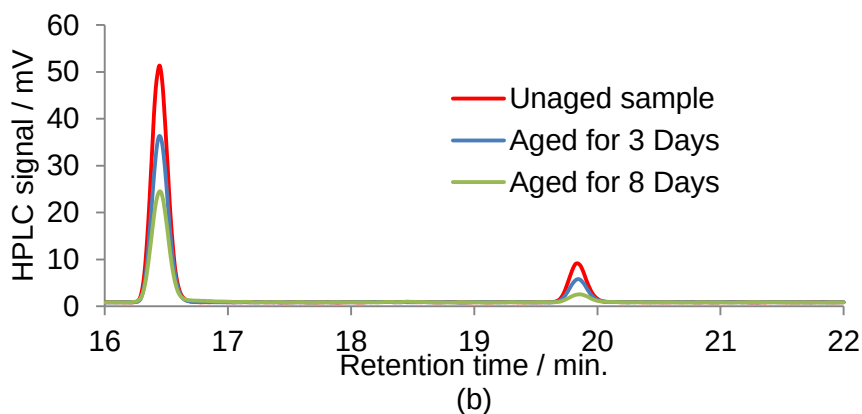
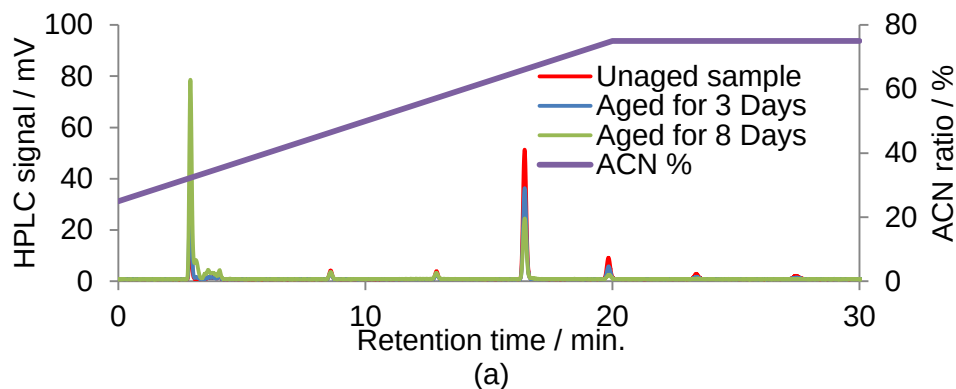


Figure 3-20 The HPLC signals of 0.1% (wt) CAB at pH=3.19. Sample was aged at 125 °C for 3 days and 8 days. (a) in full scale (b) in zoom scale for surfactant peaks part (the characteristic peak of CAB at 16.5 min) (c) in zoom scale for salinity peaks part.

The salt peaks in short retention time region in Figure 3-18 (c) – Figure 3-20 (c) increase with aging time, which indicates CAB was hydrolyzed into more hydrophilic and polar molecules.

Betaine group was stable at elevated temperature at various pH. LB was aged at 125 °C for 24 days in DI water (Figure 3-21), 1.0% (wt) Na₂CO₃ solution (Figure 3-22) and HCl acid solutions at pH= 4.0 and 3.4 (Figure 3-23). Obvious degradation is not observed. The ACN% for HPLC analysis of LB changed from 50% to 80% in 10 minutes and remained at 80% to the end.

Thus, LB can be used at extreme pH and elevated temperature, but CAB will degrade under such conditions.

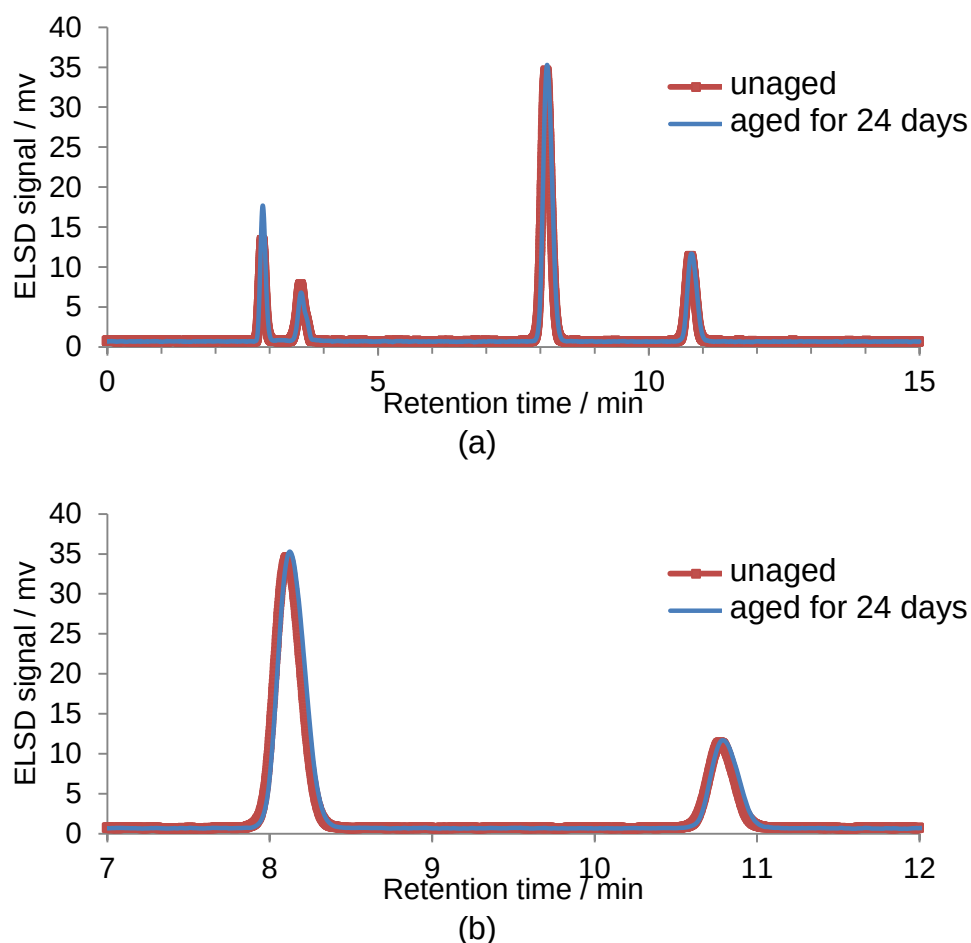


Figure 3-21 The comparison of aged and unaged 0.1% (wt) LB in DI water. Sample was aged at 125 °C for 24 days. (a) in full scale, (b) zoom in for surfactant peaks (at 8.1 and 10.9 min)

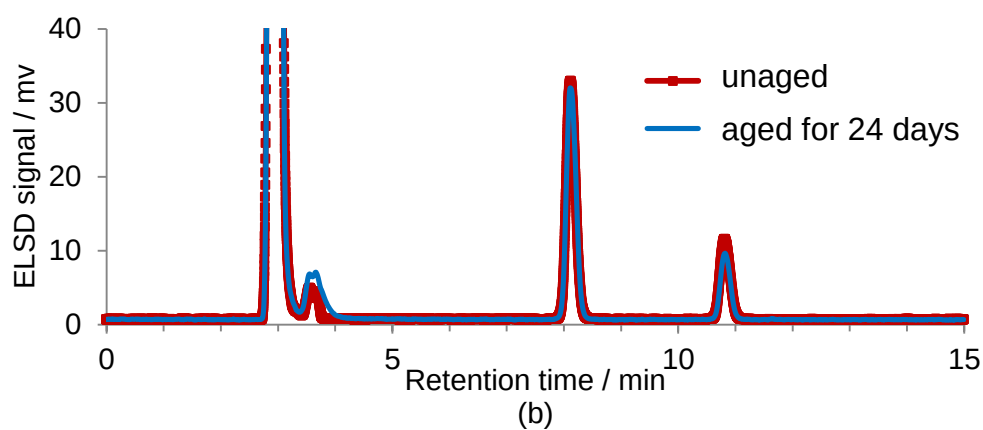
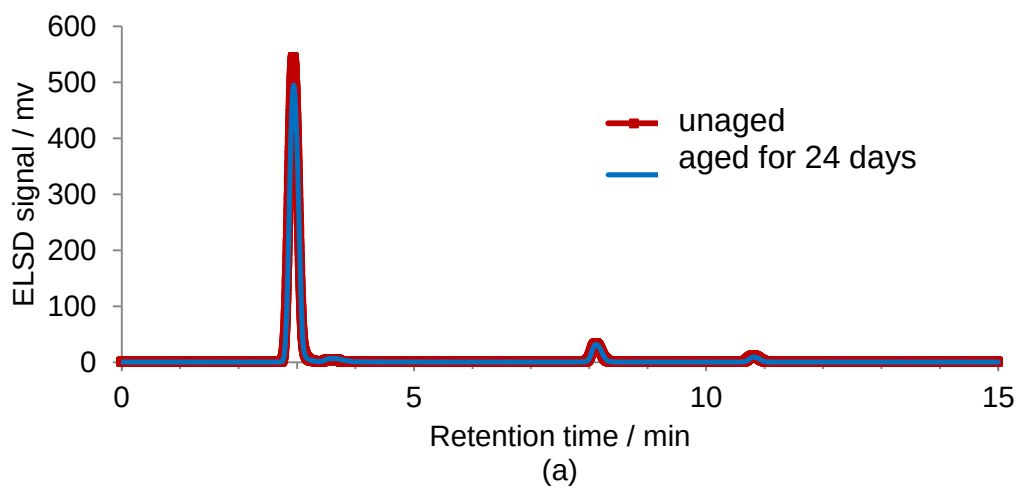


Figure 3-22 The comparison of aged and unaged 0.1% (wt) LB in 1.0% (wt) Na_2CO_3 solution. (a) in full scale, (b) zoom in for surfactant peaks (at 8.1 and 10.9 min)

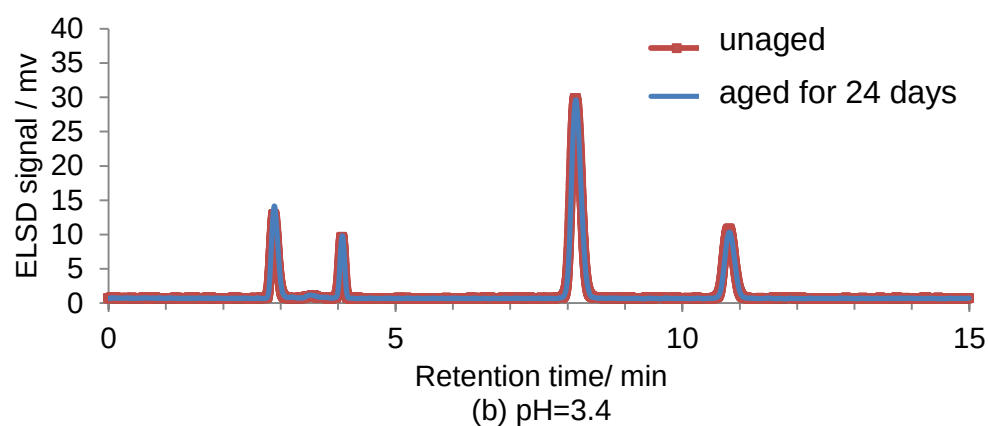
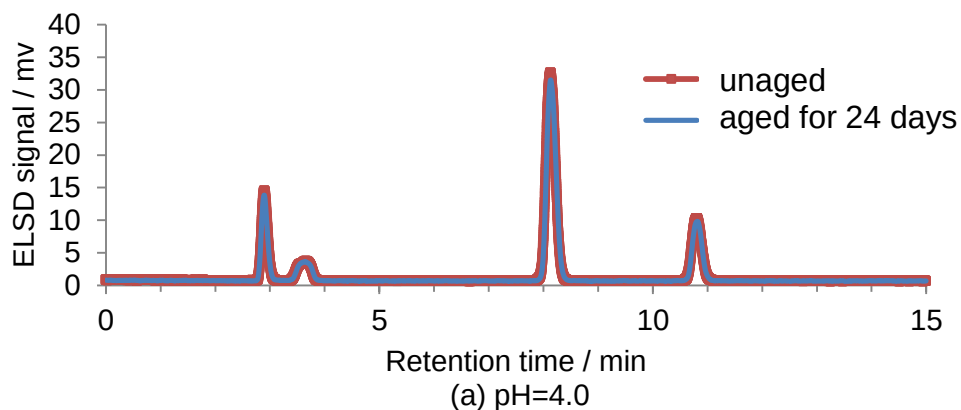


Figure 3-23 The comparison of aged and unaged 0.1% LB in pH=4.0 and 3.4 HCl solution.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) are common methods to analyze the thermal stability of chemicals. The DSC and TGA analysis results for C12 are shown in Figure 3-24 and Figure 3-25. All the analyses give consistent results: the surfactant is stable at $T < 150$ °C; the slow degradation of C12 began at 150 °C, and was accelerated at 200 °C. The influence of oxygen in air is negligible as indicated in Figure 3-25.

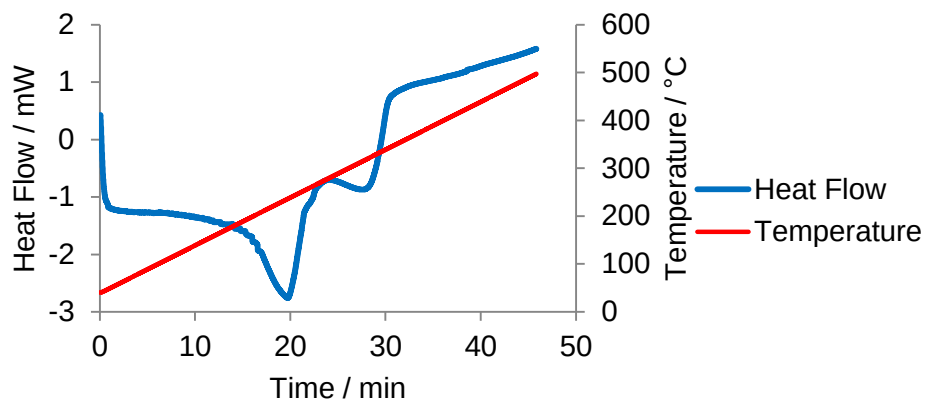


Figure 3-24 DSC analysis results for C12 in N₂ atmosphere

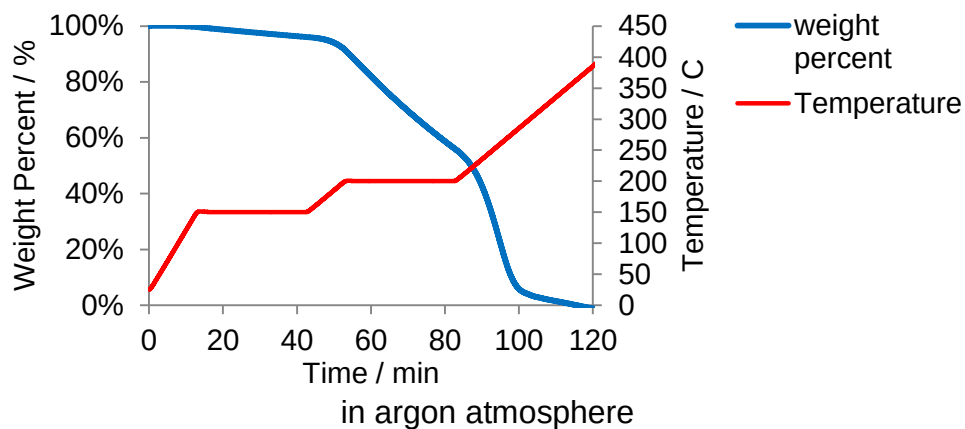
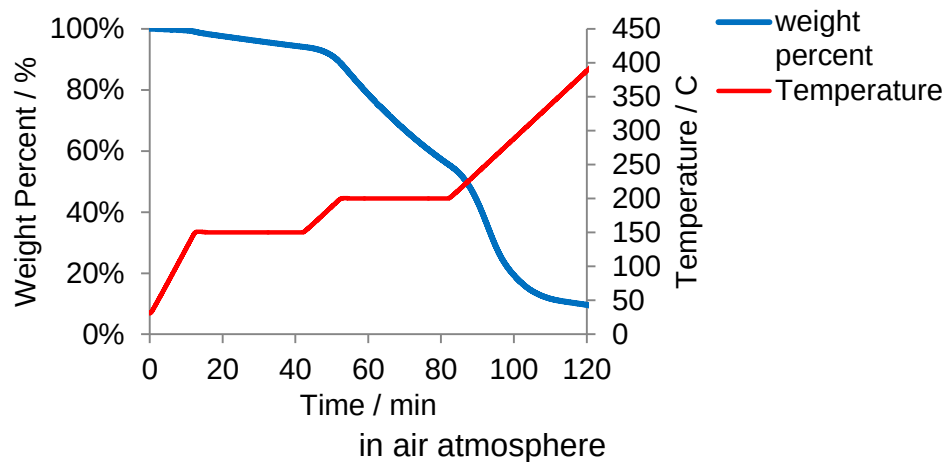


Figure 3-25 TGA analysis of C12. Upper: in air atmosphere, Lower: in argon atmosphere

However, the DSC and TGA results can not reflect the chemical stability in solution, especially at extreme pH. C12 which is a good CO₂ foaming agent was aged at typical reservoir temperature and pH in CO₂ flooding, *i.e.*, 125 °C and pH=4 (Chen, et al., 2014). The HPLC analysis result of the aged sample is shown in Figure 3-26. The peak areas for surfactant characteristic peaks (retention time > 6 mins) decreased (in Table 3-3), for polar and hydrophilic salt peaks increased for the aged sample (in Figure 3-26, Lower), which indicates the C12 is partially degraded under tested conditions. Because the HPLC peak area is proportional to surfactant concentration, the degradation degree (DD) is calculated as following Equation 3-5:

$$DD = \frac{\text{Area of unaged sample} - \text{Area of aged sample}}{\text{Area of unaged sample}}$$

Equation 3-5 Definition of degradation degree

The total degradation degree is 6.0% after aged for 11 days, as listed in Table 3-4. Notice, the oxygen was not eliminated from the surfactant sample as stated in Section 3.1.3.

Thus, the chemical and thermal stability of surfactant should be tested in solution under reservoir temperature and pH, with exclusion of oxygen for foam EOR process.

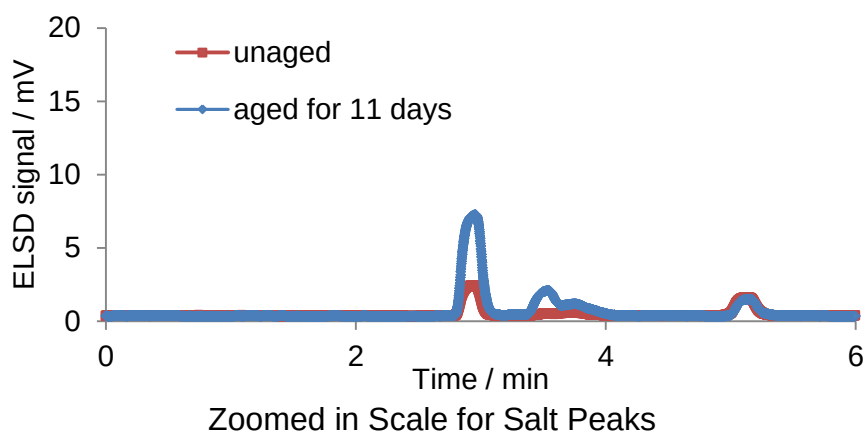
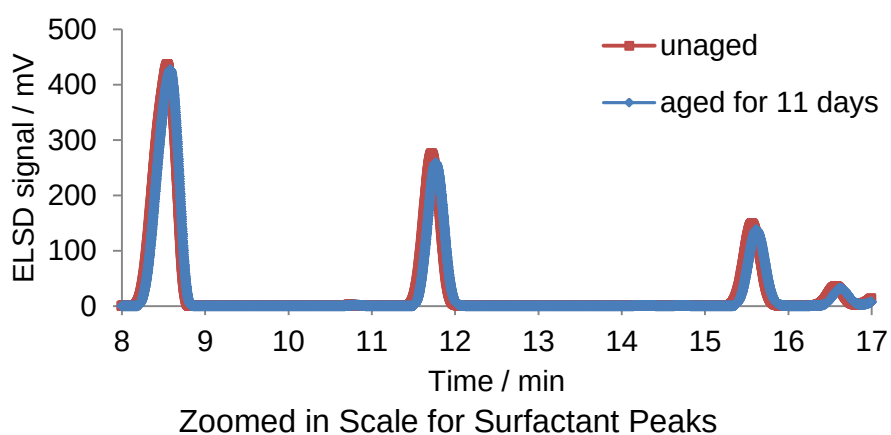
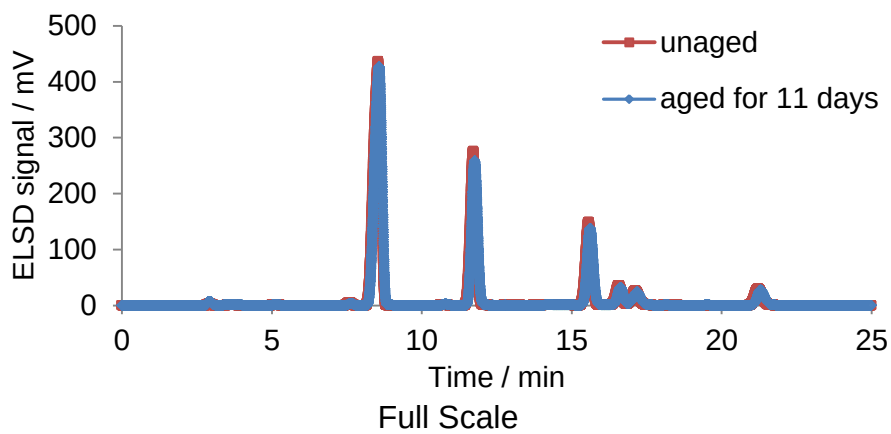


Figure 3-26 The HPLC results for 1% C12 in HCl acid solution at pH=4.0. Upper: in full scale, lower: in zoomed scale for salt peaks. The characteristic peaks of C12 are all peaks with retention time higher than 6 min

Table 3-4 Surfactant peak areas of C12 in HPLC analysis

Time (min)	Peaks Areas of Unaged Sample (A_{unaged})	Peaks Areas of Aged Sample (A_{aged})	Degradation Degree: $DD=(A_{\text{unaged}}-A_{\text{aged}})/A_{\text{unaged}}$
8.5	7843	7521	4.1%
11.7	3895	3615	7.2%
15.6	2178	1963	9.9%
16.6	500	459	8.0%
17.1	450	428	4.9%
21.2	525	480	8.7%
Sum	15391	14466	6.0%

3.2.3 The Comparison of Foam in Bulk and in Porous Media

Four surfactant solutions were used to evaluate the foamability and foam stability in bulk tests and porous media tests: DowFax 8390 in 2% (wt) NaCl solution, AOS 16-18 in 2% (wt) NaCl and 1% (wt) Na_2CO_3 solution, CAB in 3.5% (wt) NaCl and 1% (wt) Na_2CO_3 solution, and AOS-CAB blend with weight ratio 1:1 in 3.5% (wt) NaCl and 1% (wt) Na_2CO_3 solution. The total surfactant activity for all the solutions was 0.2% (wt). The equilibrium foam volumes with various N_2 flow rates are shown in Figure 3-27. The foam volume exceeded the capacity of graduated cylinder (100 ml) at 6 ml/min of N_2 for AOS, CAB and their blend. The bulk foam test results indicate that (1) the best foaming agent was the blend of

AOS-CAB, (2) AOS 16-18 and CAB had similar ability to generate foam, (3) DowFax 8390 was not as good as other formulations, but still generated significant volume foam at high N₂ flow rate.

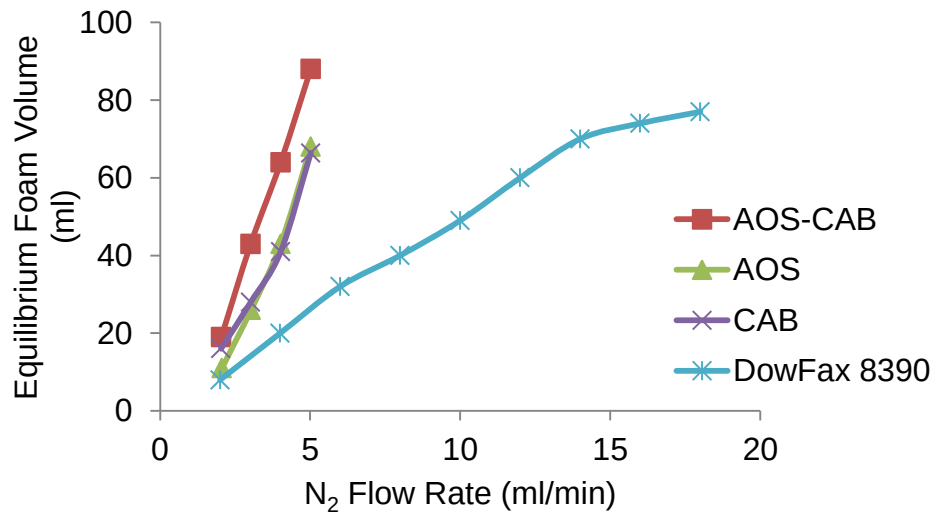


Figure 3-27 The equilibrium foam volume at various N₂ flow rate

The surfactant formulations were also evaluated in a silica sandpack, of which the permeability was 144 darcy (Figure 3-28). The sandpack was prepared by virgin silica sand (mesh 20-40 from US Silica) for each surfactant formulation. The results of foam evaluation in porous media (Figure 3-29) are not completely consistent with the results in bulk foam tests. In Figure 3-29, AOS-CAB has the highest foam apparent viscosity (μ_{app}), which indicates this formulation was the best foaming agent and was consistent with bulk foam test; the μ_{app} of AOS was order of magnitude higher than that of CAB, and the μ_{app} of CAB and DowFax 8390 was comparable to water alternating gas (WAG), which indicates CAB and

DowFax 8390 can't generate strong foam in porous media, and are contrary to the bulk foam test results.

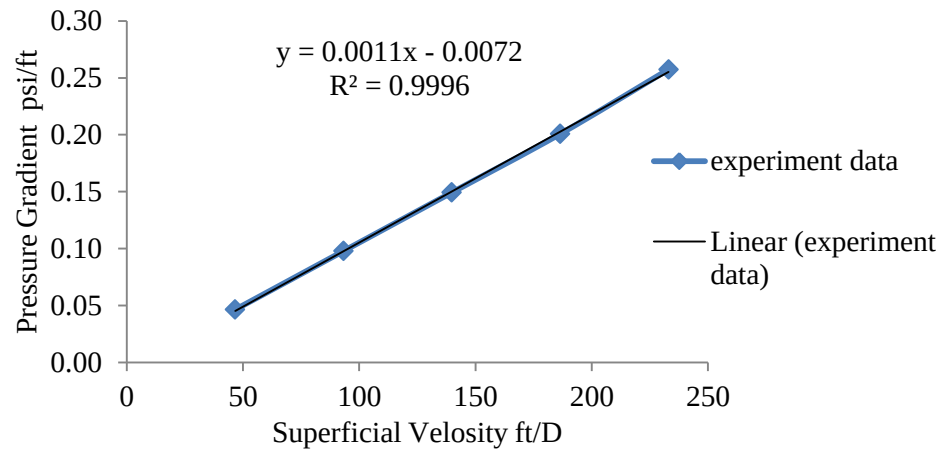


Figure 3-28 20/40 silica sandpack (U.S. Silica Company) in 1-D mode with intrinsic permeability $k = 144$ darcy

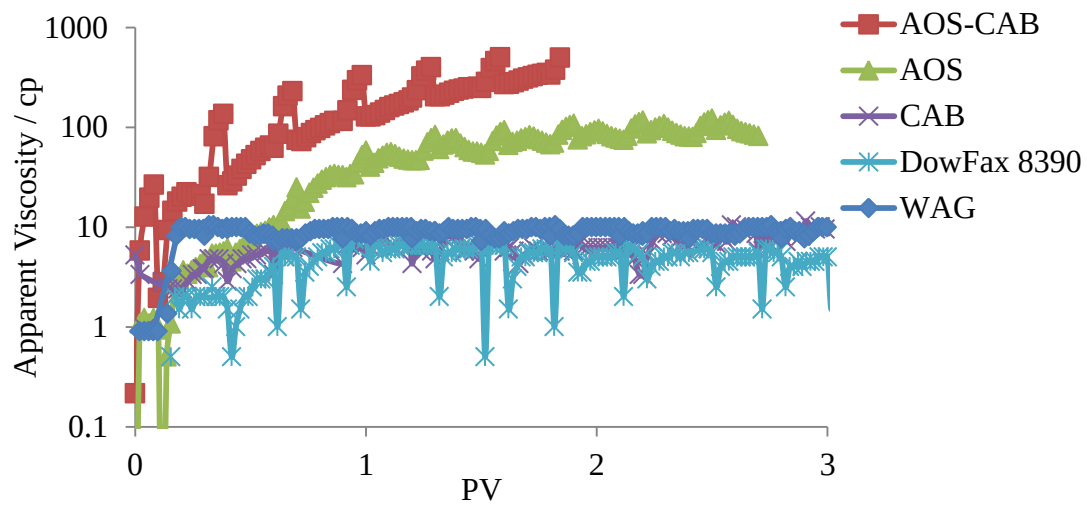


Figure 3-29 The foam apparent viscosity for various formulations, superficial velocity is 20 ft/day

The inner diameter (I.D.) of the graduated cylinder in bulk tests was 2.0 cm, so the superficial velocity of N_2 increased from 15.0 to 300.8 ft/day with flow

rate increasing from 1.0 to 20.0 ml/min. The equilibrium foam volume of DowFax 8390 increased with superficial velocity and reached a significant value at 200 ft/day (13.3 ml/min) in bulk foam test, as shown in Figure 3-27. However, in porous media tests, the μ_{app} of DowFax 8390 was as low as WAG from 20 to 200 ft/day (Ma, 2009, Jul.), as shown in Figure 3-30, which indicates the strong foam wasn't generated in sandpack for DowFax 8390 solutions.

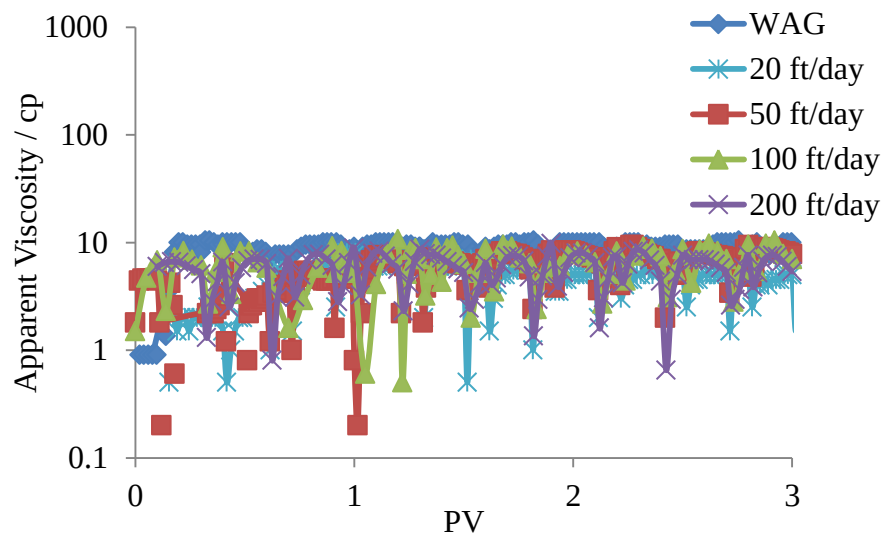


Figure 3-30 Foam apparent viscosity of DowFax 8390 at various superficial velocities in 1-D silica sandpack (Ma, 2009, Jul.)

The poor correlation between bulk foam and porous media foam comes from the different dominating factor for foam generation and destruction. Thus, the foam evaluation for EOR process is suggested to be conducted in porous media rather than in bulk foam tests.

3.2.4 The Influence of Crude Oil on Foam Stability

The detrimental effect of crude oil, especially for light oil, on foam stability

has been widely disclosed, as discussed in Section 2.3.2. Suitable formulations which can tolerate crude oil should be designed for foam EOR process.

0.2% (wt) AOS 16-18 in 2% (wt) NaCl and 1% (wt) Na₂CO₃ has been demonstrated to be a good foaming agent in silica sandpack in the absence of crude oil in section 3.2.3. But AOS 16-18 can't generate strong foam in the presence of 20.4% residual oil; the foam apparent viscosity is comparable to WAG, as shown in Figure 3-31. The residual oil can't be recovered by AOS foam, as shown in the photographs in Figure 3-32. Similar for 0.5% (wt) N25-7EO or N67-9EO glycidyl sulfonate (GS) in 3.5% (wt) NaCl and 1.0% (wt) Na₂CO₃, the strong foams were generated in the absence of crude oil, but the foam strength was as low as in WAG in the presence of oil, as shown in Figure 3-33.

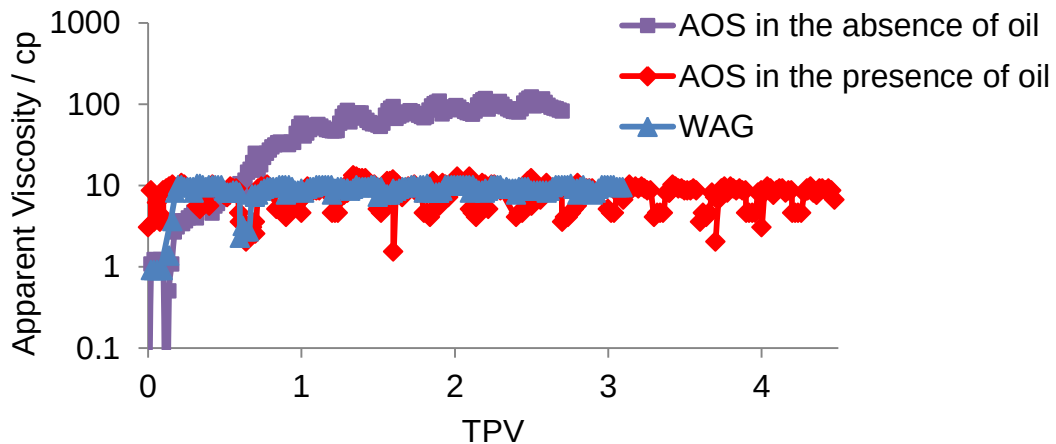


Figure 3-31 The foam apparent viscosity of 0.2% (wt) AOS in the presence and absence of crude oil.



Figure 3-32 The photos for sandpack in AOS foam flooding, at 0.1, 1.0, 2.1 and 3.0 total PV (sum of gas and surfactant solution)

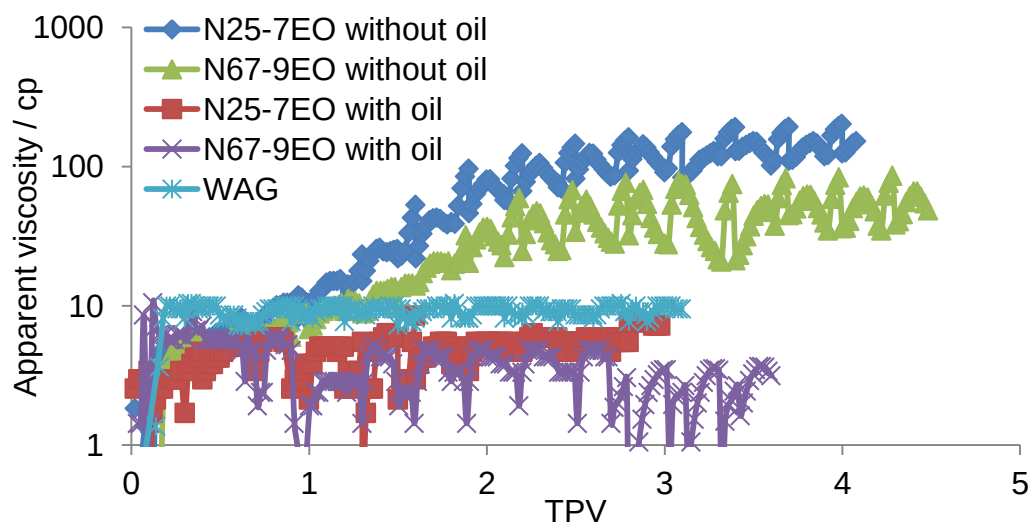


Figure 3-33 The foam apparent viscosity of 0.5% (wt) N25-7EO or N67-9EO in the presence and absence of crude oil

The foam strength of AOS-CAB blend (0.2% (wt) total activity, weight ratio 1:1) in 3.5% NaCl and 1% Na₂CO₃ was reduced by residual oil, but still

generated strong foam as shown in Figure 3-34. The oil recovery efficiency reached 100% after 5.4 TPV, as shown in Figure 3-35.

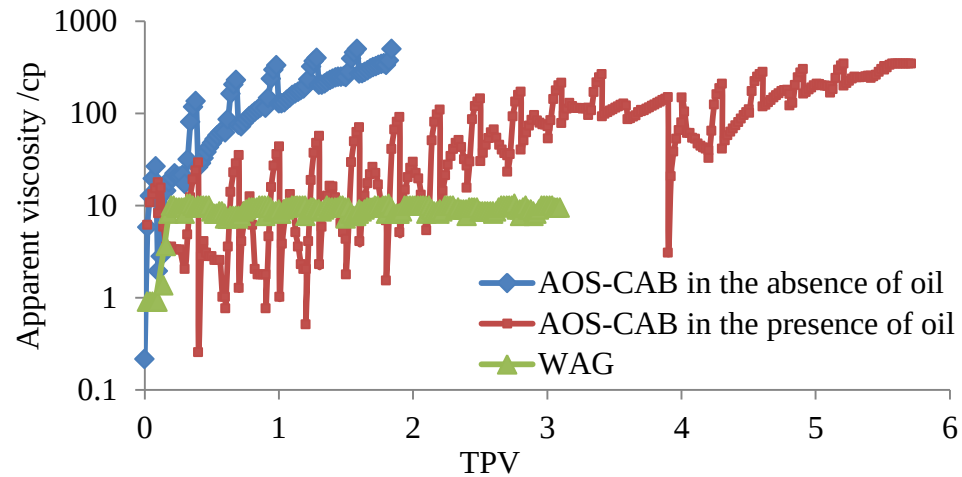


Figure 3-34 The foam apparent viscosity of 0.2% AOS-CAB (weight ratio 1:1) in the presence and absence of crude oil



Figure 3-35 The photos of sandpack in AOS-CAB foam flooding, at 0.1, 1.0, 2.1, 3.0, 4.0, 5.1 and 5.4 total PV

The detrimental influence of oil on foam was confirmed in various surfactant formulations foam flooding. However, AOS-CAB blend still generated strong foam in the presence of oil. That's because that betaine is a foam booster which can enhance the foamability in the absence of oil and stabilize the foam in the presence of oil (Basheva, et al., 2000).

The packing density of surfactants on the water-air interface was increased by mixing anionic surfactants and betaine (Wang, et al., 2010), which resulted in the enhancement of foamability of surfactant formulation in the absence of oil. The electric attraction between anionic surfactant and cationic center in betaine functional group enhances the packing density on the air-water interface (Li, et al., 1998; Wang, et al., 2013). Simultaneously, the interaction of hydrophobic tails of anionic surfactant and betaine is also favorable to increase the packing density, especially when the tails have the similar structure and length (Li, et al., 1998).

Betaine can stabilize the foam in the presence of oil due to two possible reasons. (1) The water/gas interfacial tension (σ_{gw}) was reduced by adding betaine because of the increase of surfactant density on water-gas interface (Wang, et al., 2010). The lower σ_{gw} is favorable to the negative $E_{o/wg}$, $S_{o/wg}$ and $B_{o/wg}$ and thermodynamic stability of foam in the presence of oil (Farajzadeh, et al., 2012). (2) The pseudo-emulsion film between oil droplets and water-gas interface is more stable in betaine solution-oil-gas system, as reported in literatures (Bergeron, et al., 1993; Vikingstad, et al., 2006). The stable pseudo-emulsion film can stabilize the foam by stopping the oil droplets entering the

water-gas interface.

LB has been investigated as an alternative foam booster (Li, et al., 2012), because the thermal stability of CAB at extreme pH was poor, as discussed in Section 3.2.2. A blend of IOS 15-18 and LB with 0.55% total activity and weight ratio 10:1 generated strong foam in the presence of the same crude oil as used in this chapter, as demonstrated in Figure 3-36.

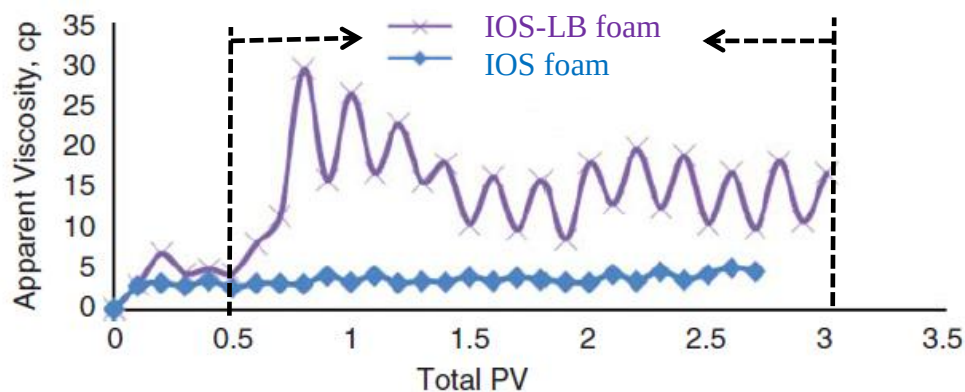


Figure 3-36 The foam apparent viscosity of IOS-LB in the presence of crude oil, modified from Li and et al. (2012)

However, not all the formulations with betaine can generate strong foam in the presence of crude oil. The blend of Avel S70 and LB at 0.5% (wt) total activity and 1:1 weight ratio in DI water failed to generate strong foam in the presence of oil, as shown in Figure 3-37. Residual oil was not recovered as shown in Figure 3-38.

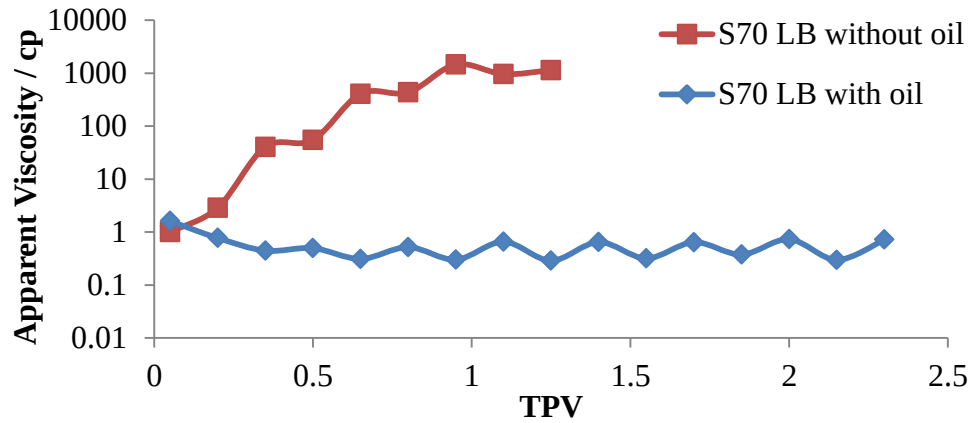


Figure 3-37 The foam apparent viscosity of S70-LB in the presence and absence of crude oil



Figure 3-38 The photos of sandpack in S70-LB foam flooding

Thus, the surfactant formulations should be designed and evaluated in the presence of oil, especially for light crude oil.

3.3 Conclusions

Solubility, chemical and thermal stability, foamability and foam stability were evaluated to screen the surfactant formulations for foam EOR process.

The Krafft points of ionic surfactants and cloud points of nonionic surfactants are affected by the brine compositions and pH. Clear solutions should be maintained under reservoir temperature, salinity and pH for foam EOR process.

Some surfactants will hydrolyze or precipitate at reservoir conditions. DSC and TGA can't determine the chemical and thermal stability of surfactants under reservoir conditions because of lack of water. Thus, bottle test with surfactants dissolved in brine and aged at reservoir temperature and pH is proposed to use check the thermal and chemical stability of surfactant formulations.

Foamability and foam stability were evaluated in bulk and porous media. The poor correlation between them indicates the foamability and foam stability should be investigated in porous media for EOR process rather than as bulk foam. Foam evaluation in sandpacks in a visual glass column is a fast and reproducible method to screen the surfactant formulations at controlled conditions.

CAB is not a good foaming agent, but is a good foam booster. The formulation of AOS-CAB can generate strong foam in the presence of light crude oil, although the foam is not as strong as in the absence of oil. CAB will degrade at extreme pHs and elevated temperature, which restrains the application of CAB for CO₂ or ASP flooding in hot reservoirs. LB is an alternative as foam booster under such extreme conditions.

3.4 References

- Barnes, J. R., Smit, J. P., Smit, J. R., Shpakoff, G., Raney, K. H., & Puerto, M. C. (2008). Development of Surfactants for Chemical Flooding at Difficult Reservoir Conditions. *SPE Symposium on Improved Oil Recovery*. Tulsa, Oklahoma. SPE-113313-MS
- Basheva, E. S., Ganchev, D., Denkov, N. D., Kasuga, K., Satoh, N., & Tsujii, K. (2000). Role of Betaine as Foam Booster in the Presence of Silicone Oil Drops. *Langmuir*, 16(3), 1000–1013.
- Bergeron, V., Fagan, M. E., & Radke, C. J. (1993). Generalized entering coefficients: a criterion for foam stability against oil in porous media. *Langmuir*, 9(7), 1704-1713.
- Chen, Y., Elhag, A. S., Poon, B. M., Cui, L., Ma, K., Liao, S. Y., Reddy, P. P., Worthen, A. J., Hirasaki G. J., Nguyen, Q. P., Biswal, S. L. and Johnston, K. P. (2014). Switchable Nonionic to Cationic Ethoxylated Amine Surfactants for CO₂ Enhanced Oil Recovery in High-Temperature, High-Salinity Carbonate Reservoirs. *SPE Journal*, 19 (02), 249 - 259. SPE-154222-PA
- Chu, Z., & Feng, Y. (2012). Empirical Correlations between Krafft Temperature and Tail Length for Amidosulfobetaine Surfactants in the Presence of Inorganic Salt. *Langmuir*, 28(2), 1175–1181.
- Curbelo, F., Garnica, A., & Neto, E. (2013). Salinity Effect in Cloud Point Phenomena by Nonionic Surfactants Used in Enhanced Oil Recovery Tests. *Petroleum Science and Technology*, 31(15), 1544-1552.
- de Lima, S. V., & de Oliveira, H. P. (2010). Melting point of ionic ternary systems (surfactant/salt/water) probed by electrical impedance spectroscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 364(1-3), 132–137.
- Falls, A. H., Hirasaki, G. J., Patzek, T. W., Gauglitz, D. A., Miller, D. D., & Ratulowski, T. (1988). Development of a Mechanistic Foam Simulator: The Population Balance and Generation by Snap-Off. *SPE Reservoir Engineering*, 3(03), 884-892. SPE-14961-PA
- Farajzadeh, R., Andrianov, A., Krastev, R., Hirasaki, G. J., & Rossen, W. R. (2012). Foam–oil interaction in porous media: Implications for foam assisted enhanced oil recovery. *Advances in colloid and interface science*, 183, 1-13.
- Joye, J., Hirasaki, G. J., & Miller, C. A. (1994). Asymmetric Drainage in Foam Films. *Langmuir*, 10(9), 3174-3179.
- Li, F., Li, G. Z., & Chen, J. B. (1998). Synergism in mixed zwitterionic–anionic surfactant solutions and the aggregation numbers of the mixed micelles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 145(1), 167-174.

- Li, J., Bai, D., & Chen, B. (2009). Effects of additives on the cloud points of selected nonionic linear ethoxylated alcohol surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 346(1-3), 237–243.
- Li, R. F., Hirasaki, G. J., Miller, C. A., & Masalmeh, S. (2012). Wettability Alteration and Foam Mobility Control in a Layered 2-D Heterogeneous System. *SPE Journal*, 17 (04), 1207-1220. SPE-141462-PA.
- Lin, B., McCormick, A. V., Davis, H. T., & Strey, R. (2005). Solubility of sodium soaps in aqueous salt solutions. *Journal of colloid and interface science*, 291(2), 543-549.
- Ma, K. (2009 July 03). Weekly report 02 Kun Ma surfactant DOWFAX 8390 foam evaluation 2. *Internal Report in Dr. Hirasaki's group*.
- Ma, K. (2009, Oct.). Weekly report 07 Kun Ma AOS1618 foam evaluation in CTAB-treated Silica sand F42. *Internal Reports in Dr. Hirasaki's Lab*.
- Puerto, M. C., Miller, C. A., Hirasaki, G. J., & Barnes, J. R. (2012). Surfactant Systems for EOR in High-Temperature, High-Salinity Environments. *SPE Journal*, 17(01), 11 - 19.
- Sammalkorpi, M., Karttunen, M., & Haataja, M. (2009). Ionic surfactant aggregates in saline solutions: sodium dodecyl sulfate (SDS) in the presence of excess sodium chloride (NaCl) or calcium chloride (CaCl₂). *The Journal of Physical Chemistry B*, 113(17), 5863-5870.
- Vikingstad, A. K., Aarra, M. G., & Skauge, A. (2006). Effect of surfactant structure on foam–oil interactions: comparing fluorinated surfactant and alpha olefin sulfonate in static foam tests. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 279(1), 105-112.
- Wang, X., Wang, R., Zheng, Y., Sun, L., Yu, L., Jiao, J., et al. (2013). Interaction between Zwitterionic Surface Activity Ionic Liquid and Anionic Surfactant: Na⁺-Driven Wormlike Micelles. *The Journal of Physical Chemistry B*, 117(6), 1886-1895.
- Wang, Z. Y., Zhang, S. F., Fang, Y., & Qi, L. Y. (2010). Synergistic behavior between zwitterionic surfactant α -decylbetaine and anionic surfactant sodium dodecyl sulfate. *Journal of surfactants and detergents*, 13(4), 381-385.
- Wellington, S. L. (1983). Biopolymer solution viscosity stabilization: polymer degradation and antioxidant use. *SPE Journal*, 23(6), 901-912. SPE-9296-PA
- Yaseen, Z., Aslam, J., Dar, A. A., & Kabir-ud-Din. (2013). Effect of Temperature on the Supramolecular Behavior of Antidepressant Drug Amitriptyline Hydrochloride in the Presence of Nonionic Surfactants (Tweens and Brij)s as Pharmaceutical Excipients. *Z. Phys. Chem.*, 227(4), 459–479.

Chapter 4

Foam Mobility Control under Reservoir Conditions

The application of CO₂ foam for mobility control was investigated under reservoir conditions. The CO₂ foam was generated in situ in dolomite cores. The influence of salinity and temperature on foam mobility control was compared with controlled experiments. The experimental results were well fitted by a local equilibrium foam dry-out model.

4.1 Experimental

4.1.1 Materials

The switchable cationic surfactant, *i.e.*, Ethomeen C12 (C12, from AkzoNobel Co.), was used as CO₂ foaming agent in this chapter. The solution was cloudy after C12 was added to brine or DI water. CO₂ was purged on top of the solution to decrease the pH until the solution became clear.

Hexadecyl-pyridinium chloride (CPC, from Sigma-Aldrich Co.) can be added in C12 solution to obtain a clear surfactant solution at original pH, as discussed in Chapter 3. The cloud point of the blend of CPC and C12 in DI water with weight ratio 1:1 was higher than 120 °C at original pH.

A Silurian dolomite core was used as porous media in foam mobility control process. The characterization of the core, *i.e.*, diameter, length, porosity and permeability, is discussed in section 4.1.3.

The inorganic salts used were of ACS or higher grade, and all solutions were prepared in deionized water (DI water, 18.2 MΩ).

The synthetic formation brine consists of 182.31 g/L NaCl, 77.25 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 25.62 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ with 22.0% TDS.

Bromocresol Green (BCG, from Sigma-Aldrich Co., ACS reagent) solution was used as a pH indicator. The solution was prepared with 0.1 g BCG dissolving in 14.3 ml 0.01 M NaOH and 235.7 ml water.

4.1.2 Apparatus for CO₂ Foam Flooding at High Temperature and Pressure

The foam was evaluated in a high pressure core flooding system of which all the wetting materials at elevated temperature were made of special materials, *i.e.*, Hastelloy alloy. The core flooding system with special design can tolerate extremely harsh conditions, *i.e.*, 5000 psi, 120 °C, 22% TDS and low pH (pH ≈ 4), and stably control the system pressure with two-stage relief valves system for multiphase flow.

The schematic of whole core flooding system is demonstrated in Figure 4-1. The details for each part are illustrated in Figure 4-2 to Figure 4-4.

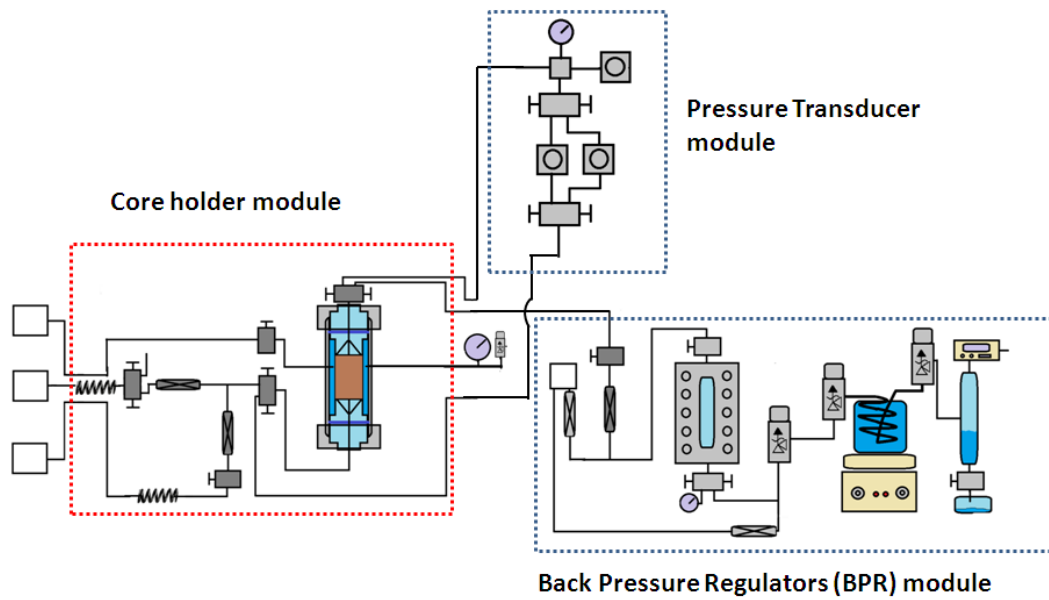


Figure 4-1 The high temperature and high pressure setup for CO₂ foam flooding

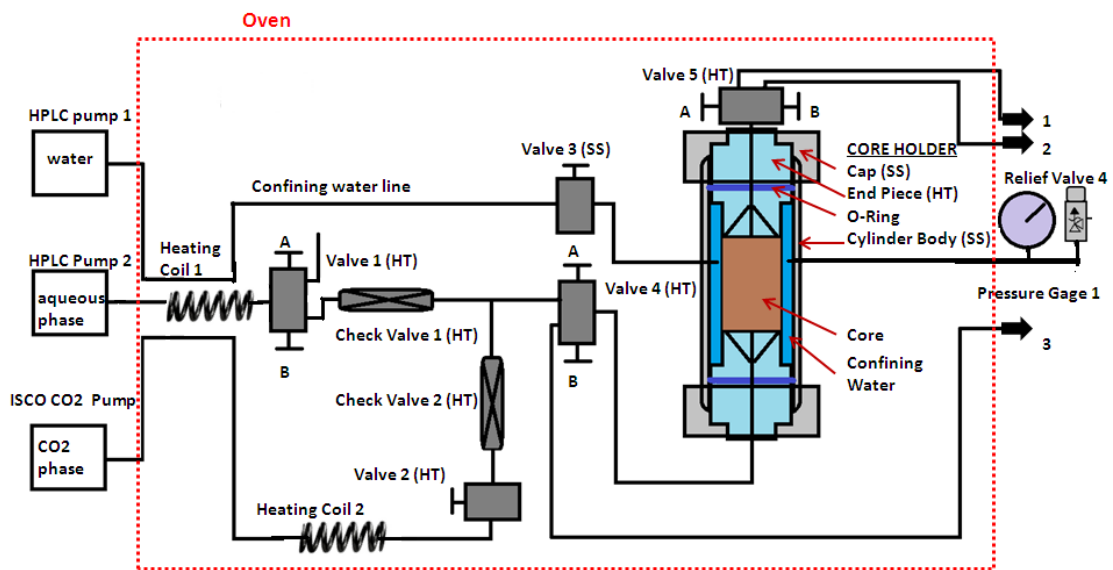


Figure 4-2 The pumps system and core holder module

Note: Red dot box indicates the oven, HT indicates Hastelloy alloy, SS indicates stainless steel 316

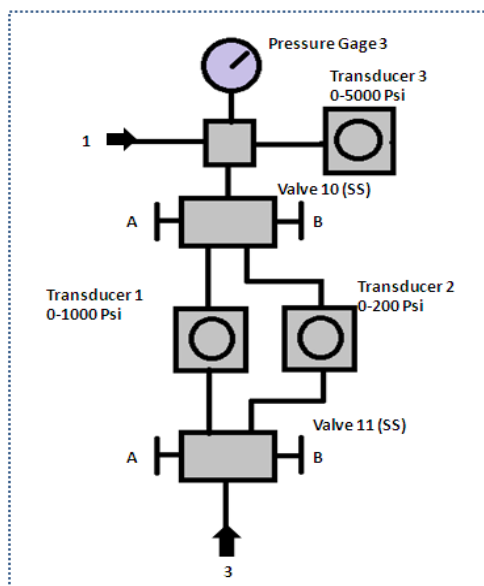


Figure 4-3 The pressure transducer module

Note: HT indicates Hastelloy alloy, SS indicates stainless steel 316

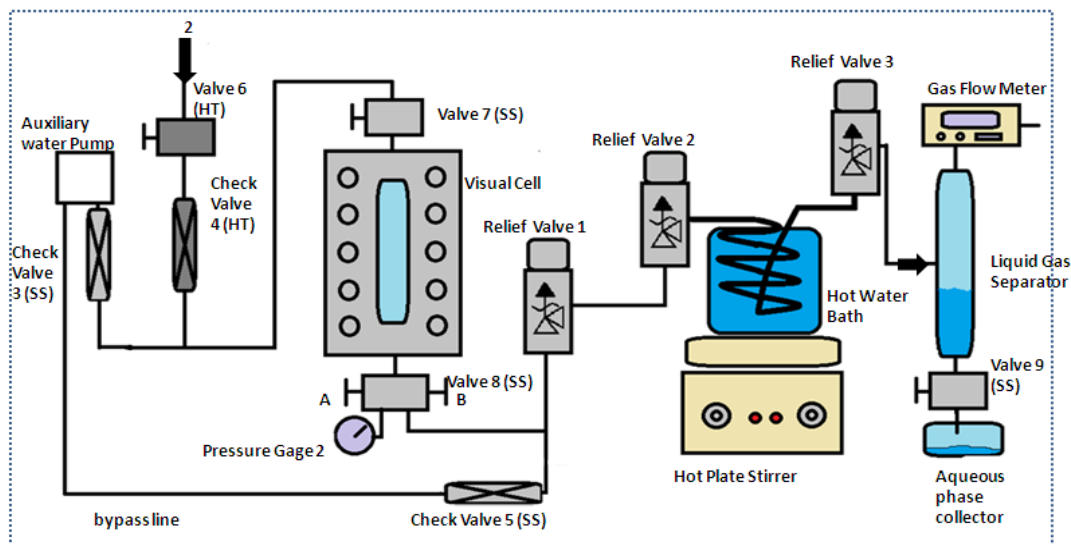


Figure 4-4 The back pressure regulators (BPR) module

Note: HT indicates Hastelloy alloy, SS indicates stainless steel 316

Pumps System and Core Holder Module

The high pressure CO₂ was injected by ISCO dual pumps system (E260, from Teledyne ISCO Inc.). CO₂ in the pumps was compressed to the system pressure and was naturally cooled to room temperature before injection. The aqueous solution and confining water were injected by HPLC pumps (Lab Alliance Series III). A check valve was installed in the CO₂ and aqueous solution lines, respectively. A purge bypass line is designed in aqueous solution line (Valve 1 (A)) for the switch of the injected solutions. For example, if the injected solution was switched from brine to surfactant solution, Valve 1 (B) was shut off and Valve 1 (A) was turned on, and then flushed the pump and line with 30 mL surfactant solutions.

Heating Coil

The aqueous solutions and CO₂ were heated from room temperature (25 °C) to reservoir temperature (120 °C) by heating coil 1 and 2 in Figure 4-2. The length of the heating coil is determined by LMTD (log-mean temperature difference) method, as shown in Equation 4-1.

$$Q = UA\Delta T_{lm}$$

Equation 4-1 LMTD (log-mean temperature difference) Equation for heat transfer

Q is the heat transfer rate, calculated by Equation 4-2:

$$Q = q\rho c_p(T_{outlet} - T_{inlet})$$

Equation 4-2 Formula of heat transfer rate

where q is the volumetric flow rate, ρ is the density of fluid, c_p is the specific heat capacity at constant pressure, T_{outlet} and T_{inlet} are the fluid temperature at inlet and outlet, respectively.

U is the overall heat transfer coefficient, defined as in Equation 4-3:

$$UA = \frac{1}{\frac{1}{h_i A_i} + \frac{\ln\left(\frac{r_o}{r_i}\right)}{2\pi k L} + \frac{1}{h_o A_o}}$$

Equation 4-3 Formula of overall heat transfer coefficient

where A is the total heat transfer area on one side of a tube, h is the heat transfer coefficient, k is the thermal conductivity of fluid, L is the length of a tube, r is the radius of a tube. The subscripts i and o represent inside and outside of the tube. Because the thermal conductivity (k) of the metal is much higher than those of fluids and the air in oven was in forced convection flow, the overall heat transfer coefficient was assumed to equal to the heat transfer coefficients inside fluid, as shown in Equation 4-4.

$$U = h_i$$

Equation 4-4 Overall heat transfer coefficient is assumed to equal to the heat transfer coefficients inside fluid

For the single phase forced convection flow, the heat transfer coefficient (h) is calculated from Nusselt number (Nu), as defined in Equation 4-5:

$$Nu = \frac{hL}{k}$$

Equation 4-5 Definition of Nusselt number

The Nu of helical coils at constant temperature boundary condition can be calculated based on following empirical correlation Equation 4-6 (Kakaç and Liu, 2002):

$$Nu = \left[\left(3.657 + \frac{4.343}{x_1} \right)^3 + 1.158 \left(\frac{De}{x_2} \right)^{\frac{3}{2}} \right]^{\frac{1}{3}}$$

Equation 4-6 Empirical correlation of Nusselt number for helical coils

where $x_1 = \left(1.0 + \frac{957}{De^2 Pr} \right)^2$, $x_2 = 1.0 + \frac{0.477}{Pr}$, and Dean number (De) is defined as:

$De = Re \left(\frac{a}{R} \right)^{\frac{1}{2}}$, Prandtl number (Pr) is defined as: $Pr = \frac{c_p \mu}{k}$, where Re is Reynolds number, a is the radius of tube which is the same as r_i in Equation 4-3, R is the radius of helical coils, μ is the viscosity of fluid.

A is the total heat transfer area, which can be calculated as Equation 4-7: Because the inside fluid dominated the heat transfer rate ($U = h_i$), the inside heat transfer area was used to estimate the total heat transfer area, as expressed in Equation 4-7:

$$A = A_i = 2\pi r_i L$$

Equation 4-7 Formula of total heat transfer area

ΔT_{lm} is the log-mean temperature difference, which is defined in Equation 4-8:

$$\Delta T_{lm} = \frac{(T_{h,inlet} - T_{c,intlet}) - (T_{h,outlet} - T_{c,outlet})}{\ln\left(\frac{T_{h,inlet} - T_{c,intlet}}{T_{h,outlet} - T_{c,outlet}}\right)}$$

Equation 4-8 Definition of log-mean temperature difference

where $T_{h,inlet}$ and $T_{c,intlet}$ are the hot and cold fluid temperature at inlet of the heating coil, respectively; $T_{h,outlet}$ and $T_{c,outlet}$ are the hot and cold fluid temperature at outlet of the heating coil, respectively. Because the heating coils were in a forced convection air oven, $T_{h,inlet}$ and $T_{h,outlet}$ were the temperature in the oven. Here, we set the oven temperature at 120.05 °C, which is very close to reservoir temperature 120.00 °C. So, $T_{h,inlet} = T_{h,outlet} = 120.05$ °C, $T_{c,intlet} = 25.00$ °C and $T_{c,outlet} = 120.00$ °C.

The properties of fluids at average bulk temperature (72.5 °C) and 3400 psi were used for calculation, as listed in Table 4-1.

Table 4-1 The properties of water and CO₂ at 72.5 °C and 3400 psi

	Density (kg/m ³)	Viscosity (Pa s)	Specific Heat Capacity (J/ (kg K))	Thermal Conductivity (W/ (K m))
Water	9.86×10 ²	3.91×10 ⁻⁴	4.14×10 ³	6.77×10 ⁻¹
CO ₂	6.89×10 ²	5.82×10 ⁻⁵	2.33×10 ³	7.75×10 ⁻²

Note: the properties of water were calculated by online peach software

(http://www.peacesoftware.de/einigewerte/einigewerte_e.html)

The properties of CO₂ were calculated by interpolation based on reference data (Angus, et al., 1976)

The highest possible superficial velocity in 1.5 inch diameter core is 10 ft/day, which implies the highest volumetric flow rate (q) is 2.41 ml/min. The inner diameter of the tubing (r_i or a) is $\frac{1}{16}$ inch. The diameter of the helical coil (R) is 5×10^{-2} m. The lengths of the heating coils for water and CO_2 can be obtained, respectively, by substituting above parameters into Equation 4-1 to Equation 4-8, which are 1.00×10^{-1} m for water and 6.23×10^{-2} m for CO_2 . The safety factor was 10. Thus, the coil lengths in our apparatus were 1.00 m for water and 6.23×10^{-1} m for CO_2 .

The designed heating coil was verified by water at 100 psi. The properties of water at 72.5 °C and 100 psi are close to those at 3400 psi, as demonstrated in Table 4-2. DI Water was injected at room temperature through the oven (set at 120 °C) with 100 psi back pressure. An online thermocouple was used to monitor the temperature at the outlet of heating coil. The measured temperature was approximately $120 \pm 1^\circ\text{C}$ at flow rates from 0.24 – 4.85 ml/min (1 to 20 ft/day for 1.5 in. diameter core)

Table 4-2 The properties of water at 72.5 °C

Pressure/ psi	Density (kg/m ³)	Viscosity (Pa s)	Specific Heat Capacity (J/ (kg K))	Thermal Conductivity (W/ (K m))
100	9.77×10^2	3.91×10^{-4}	4.19×10^3	6.65×10^{-1}
3400	9.86×10^2	3.91×10^{-4}	4.14×10^3	6.77×10^{-1}

Note: the properties of water were calculated by online peach software

(http://www.peacesoftware.de/einigewerte/einigewerte_e.html)

Core Holder

The core holder was designed to automatically fit various lengths of cores without any spacer.

The regular core holders have fixed the length between inlet and outlet end pieces, as shown in Figure 4-5. Therefore, the length of the core samples should be carefully cut to fit the strict length. If the core is short, spacers need to be added.

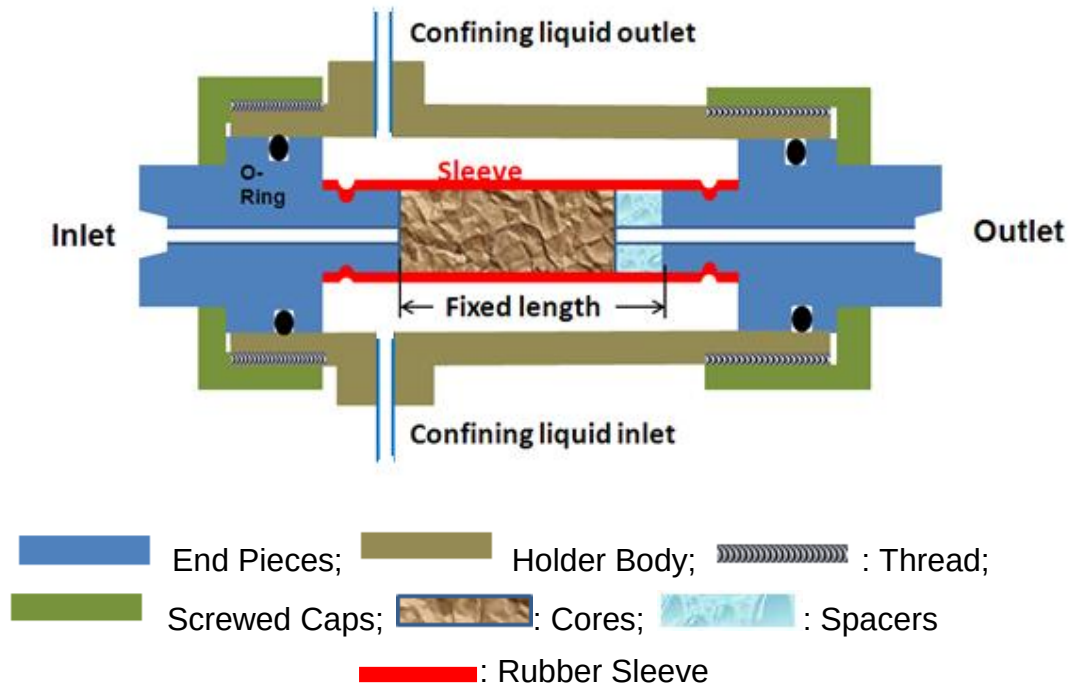


Figure 4-5 The regular design of core holder, drawn by Maura Puerto.

For the specially designed core holder by Maura Puerto in Rice University, extra threads were added on end piece and cap at the outlet, as shown in Figure 4-6, which results in the adjustable length between end pieces. Two core holders with different length were designed. The shorter one was used for 3-6 inches cores, the longer one was used for 8-12 inches cores.

The Hastelloy alloy end pieces are wetting materials contacted by corrosive fluids in core flooding process. The other metal parts are made from stainless steel 316. The o-ring is made from Viton with 44 mm inner diameter and 4 mm thickness. A Viton rubber sleeve (1.5 in. inner diameter, 0.125 in. thickness and 70 durometer hardness, from Warco Biltrite Co.) was used to cover the core sample. This holder can work at 5000 psi, 120 °C, pH=4 and 22% TDS brine.

The confining pressure was usually 1000 psi higher than system pressure. If the pressure drop is higher than 1000 psi, higher confining pressure is required.

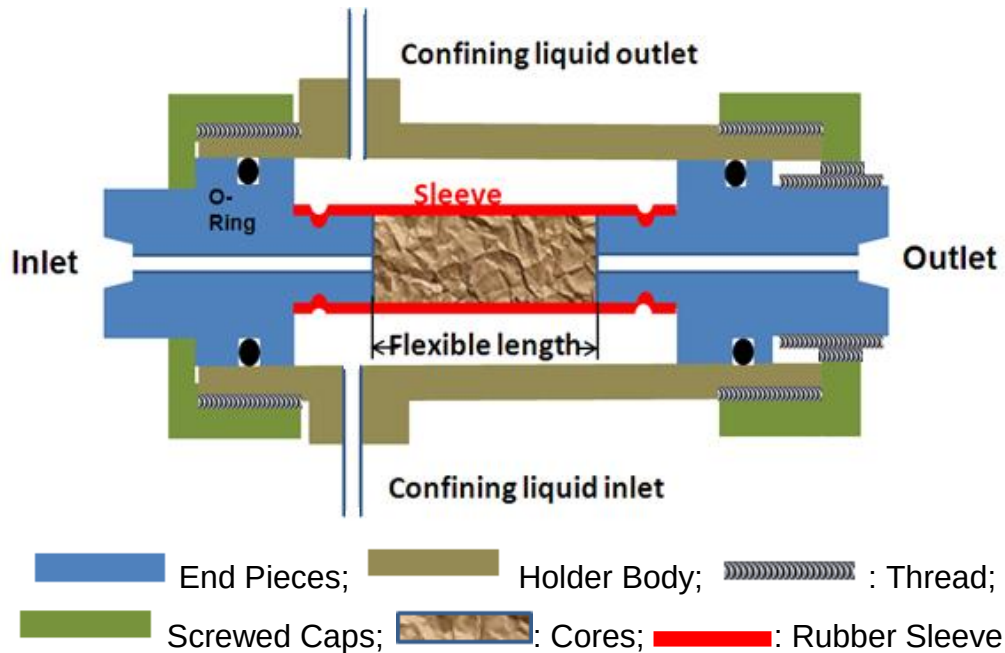


Figure 4-6 The new design of core holder, designed by Maura Puerto

Pressure Transducer Module

The pressure drop across the core was measured by two parallel transducers (Validyne, DP 303) with different ranges (transducer 1 and 2 in Figure 4-3). The transducer was chosen based on the permeability of core, flow rates and apparent viscosity of foam. If the pressure drop is less than 100 psi, transducer 2 with 0-200 psi range should be used. If the pressure drop exceeds 200 psi, the transducer 2 should be isolated by shutting off Valve 10 (B) and 11 (B), and transducer 1 with 0-1000 psi range should be used. The outlet pressure of core holder was measured by transducer 3 as the system pressure.

Back Pressure Regulators (BPR) Module

A visual cell was equipped in the effluent line out of the core holder (Figure 4-4).

The system pressure was reduced to atmosphere by three stages relief valves (Relief valve 1, 2 and 3, from Swagelok with catalog # SS-4R3A-KZ). The first relief valve was set at reservoir pressure. The second relief valve was set 400-500 psi lower than the first one to assist the first relief valve to stably maintain the system pressure. The third relief valve was set at 1200 psi. A heating tape and water bath were installed between the second and third relief valve to maintain the temperature in the tubing above 82 °C (Figure 4-4). Thus, the CO₂ phase transition zone and the plug problem in tubing caused by frozen ice and CO₂ hydrate can be avoided, as illustrated by pressure-enthalpy diagram in Figure 4-7 (Energy Institute, 2010). The stable back pressure can be maintained by continuous injection of water from an auxiliary pump in Figure 4-4 (proposed by Maura Puerto and José Luis López Salinas), because the constant injection of incompressible fluid can prevent the completely shut-down and reopen of relief valves. This results in the stable control of back pressure. The flow rate of the auxiliary pump can be lower to 1ml/min for non-condensable gas, *i.e.*, N₂, but the high flow rate, *e.g.*, 6 ml/min, is required for condensable gas, *i.e.*, CO₂, especially when the relief valves are full of CO₂. That's because that the high flow rate of water can prevent the CO₂ hydrate plugging the throat of relief valves. Multi relief valves are required even for incompressible fluid, *e.g.*, water, at high pressure. The pressure oscillation was up to 100 psi for water with single

relief valve at 3400 psi back pressure, because of the dramatic change of back pressure to atmosphere pressure.

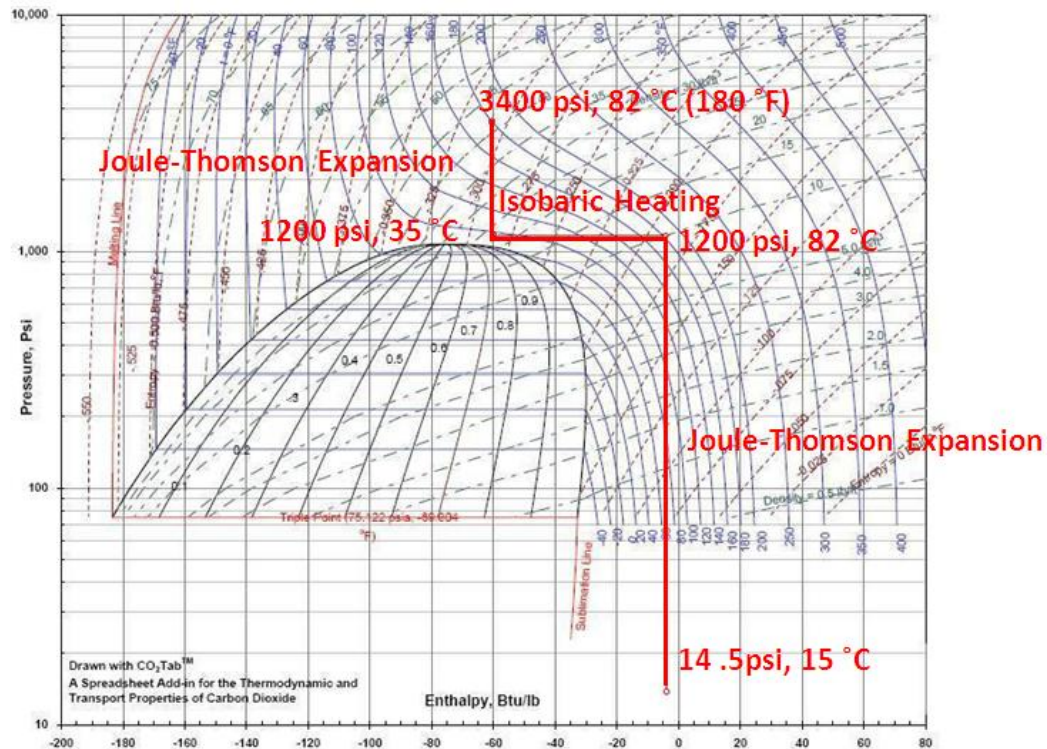


Figure 4-7 The pressure-enthalpy diagram of carbon dioxide. Temperature and pressure change across the relief valves

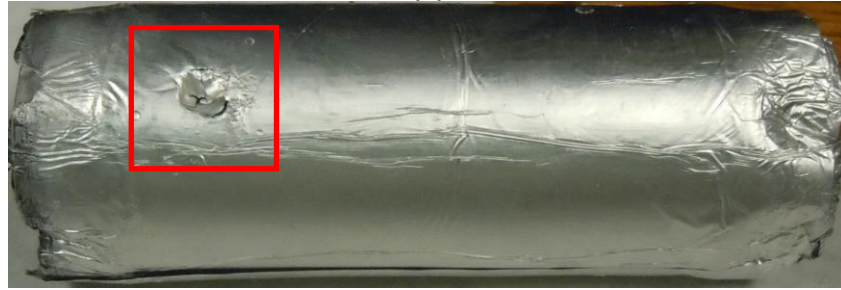
A gas/liquid separator was proposed to be installed at the outlet of the system to record the gas and liquid flow rates. However, the separator was not installed in the present work.

4.1.3 Core Preparation and Characterization

Core Preparation



(a)



(b)



(c)

Figure 4-8 Covers of core samples for CO₂ flooding. (a) Heated shrinkable Teflon, (b) aluminum foil and (c) Viton rubber sleeve. Red box indicates the hole caused by vugs on the core surface

Because the supercritical CO₂ is permeable to Teflon heating shrinking tube (catalog # 8703K892, from McMaster-Carr Co.) and can dissolve into the rubber sleeve, aluminum foil (thickness = 16 micrometer, from Walmart Co.) was used to cover the core and hold the CO₂ (Figure 4-8 (b)). The aluminum can react with aqueous solution in core flooding process, so the following procedure was designed. The core was covered by one layer of Teflon heating shrinking tube, and then was wrapped by one layer of aluminum foil, finally was covered by

another layer of shrinking tube to tightly hold aluminum foil in between. After that, the core was inserted into a rubber sleeve, installed in the core holder and tightened by wires (from McMaster-Carr Co., with catalog #: 2001T56), as shown in Figure 4-8 (c).

The vugs on the core surface should be filled by Teflon tape or plumber's putty. Otherwise, the rubber sleeves and other covers would be penetrated by high pressure confining liquid, as demonstrated in Figure 4-8 (red box).

Pore Volume

The pore volume of the core was measured by the following procedure.

1000 psi confining pressure was applied in the core holder. CO₂ at 20 psi (gauge pressure) was injected into core for half of hour to purge out air. The core was vacuumed by oil pump. Sometimes the system can't be completely vacuumed owing to the pump capacity. But in most cases the pressure can be reduced to lower than -28 inches of mercury (gauge pressure). The residual gas was CO₂ which is soluble in water. DI water in a graduated cylinder was connected to the vacuumed core and was spontaneously sucked in. The volume change of the water in the graduated cylinder is the pore volume of the core plus the dead volume of the connections. The dead volume can be measured directly before or after the PV measurement. The pore volume and geometry of the core are shown in Table 4-3.

Table 4-3 The parameters of the core sample

Diameter / in.	Length / cm	Pore Volume / ml	Porosity / %
1.5	7.6	13.0	15.0

Permeability

The pressure drops at various flow rates were measured, and then the permeability was calculated based on Darcy's law. Initially, it took more than 10 PV to reach the stable pressure drop. That may be because of the slow migration of the tiny particles in the core. The permeability of the core was 737 md, as shown in Figure 4-9.

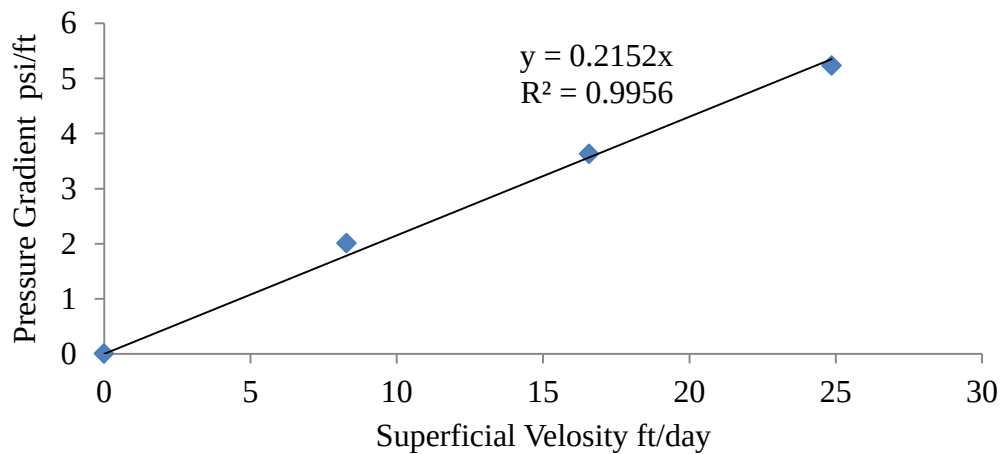


Figure 4-9 The pressure gradient vs. superficial velocity of water

4.1.4 Foam Flooding Procedures

The solubility of C12 has been discussed in Chapter 3. C12 was cloudy at high pH (pH>9) even at room temperature, and was clear at pH around 4 which is the typical pH in CO₂ flooding up to 130 °C. The pH of dolomite - water system was 9.9 calculated by PHREEQC software, as shown in Figure 4-10. Thus, C12 will precipitate and plug the core even at room temperature in the absence of CO₂ as demonstrated in Figure 4-11, where the clear C12 (1% wt) solution was injected in the core which was fully saturated by water, and pressure increased to the limit of the pressure transducer after 0.4 PV of C12. Thus, a slug of CO₂ had to be injected first to acidify the system to pH around 4 before C12 solution was injected.

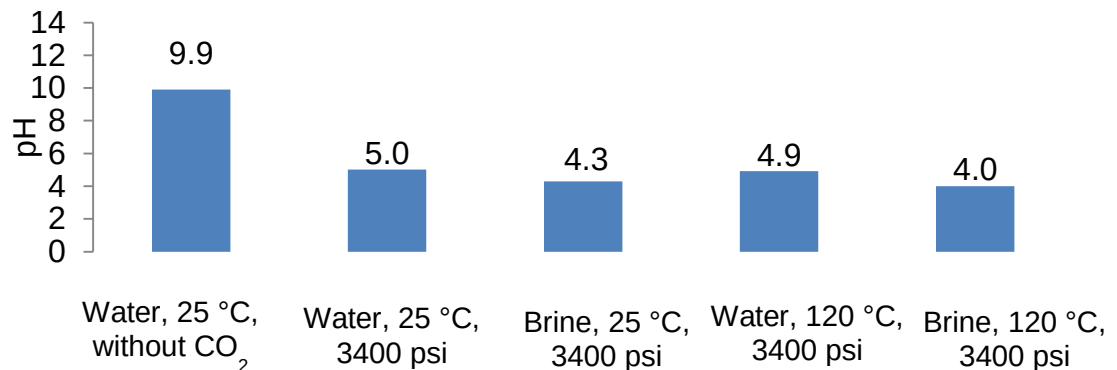


Figure 4-10 The pH of dolomite – water/brine system at room temperature with and without CO₂, calculated by Phreeqc software (version 3.0.2)

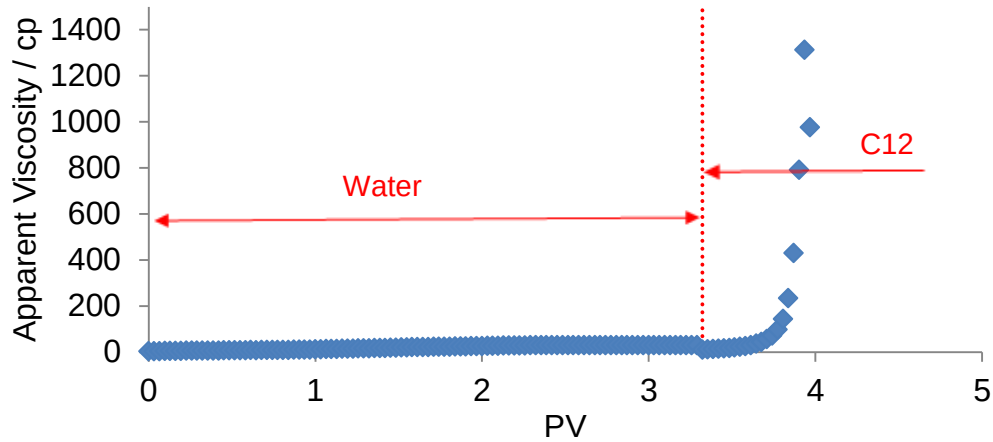


Figure 4-11 The apparent viscosity history for the water and C12 flooding. The apparent viscosity increased to the pressure transducer limit after 1% C12 in DI water solution was injected. 1% C12 in DI water was clear by purging CO₂ to decrease pH

Water alternating CO₂ (WAG) was injected before C12 and CO₂ co-injection. Each cycle of the WAG was 0.5 PV. The gas volumetric fraction of WAG was equal to the foam quality of C12 and CO₂ co-injection. For example, if C12 and CO₂ foam with 50% foam quality was designed to be evaluated at 4 ft/day (total superficial velocity), initially 0.25 PV CO₂ alternating 0.25 PV brine was injected for 4 PV at 4 ft/day, and then 2 ft/day CO₂ and 2 ft/day C12 solution were co-injected to reach the steady state.

The foam strength is described by apparent viscosity, which is the pressure drop across the core normalized by superficial velocity and the reciprocal of permeability, as shown in Equation 4-9:

$$\mu_{app} = \frac{k}{u_t} \cdot \frac{(-\Delta p - zfp)}{L}$$

Equation 4-9 Formula of foam apparent viscosity in core flooding

where μ_{app} is foam apparent viscosity, k is the core permeability, u_t is the total superficial velocity, L is core length, Δp is the pressure drop, zfp is the zero flowrate pressure which came from the static potential of the fluids. The higher apparent viscosity indicates the stronger foam.

The flow rates of water and CO₂ at room temperature were converted to those at elevated temperature based on the density changes. The superficial velocities reported in this chapter are the real velocities at tested conditions.

4.1.5 A Local Equilibrium Foam Model (STARS Foam Model)

The foam model was described by Ma et al. (2013 b), as expressed in following Equation 4-10 to Equation 4-14.

$$\mu_{foam,app} = \frac{-k\nabla p}{\frac{-kk_{rw}\nabla p}{\mu_w} + \frac{-kk_{rg}^f\nabla p}{\mu_g}} = \frac{1}{\frac{k_{rw}(S_w)}{\mu_w} + \frac{k_{rg}^f(S_g)}{\mu_g}}$$

Equation 4-10 Formula of foam apparent viscosity in foam model

$$f_g = \frac{u_g}{u_w + u_g} = \frac{1}{1 + \frac{k_{rw}(S_w)}{\mu_w} \cdot \frac{\mu_g}{k_{rg}^f(S_g)}}$$

Equation 4-11 Formula of gas fraction

$$S_w + S_g = 1$$

Equation 4-12 Sum of gas and water saturation is unity

$$k_{rw} = k_{rw}^0 \left(\frac{S_w - S_{wc}}{1 - S_{gr} - S_{wc}} \right)^{n_w}$$

Equation 4-13 Formula of Water permeability

$$k_{rg}^f = k_{rg}^0 \left(1 - \frac{S_w - S_{wc}}{1 - S_{gr} - S_{wc}} \right)^{n_g} \cdot \frac{1}{1 + fmmob \times \left\{ 0.5 + \frac{\arctan[epdry(S_w - fmdry)]}{\pi} \right\}}$$

Equation 4-14 Formula of gas (foam) permeability

For a given $epdry$, $fmmob$ and $fmdry$ can be determined by zero derivative of following Equation 4-15 at the maximum $\mu_{foam,app}$ and corresponding S_w . Ma, et al. (2013a) proposed an alternative method to search $fmmob$ and $fmdry$ by using the golden section search method (the command “fminbnd” in MATLAB).

$$\begin{aligned} & \left. \frac{d\mu_{foam,app}}{dS_w} \right|_{S_w=S_w^*} \\ &= \{ \{ k_{rw}^0 \cdot n_w \cdot [-(S_w^* - S_{wc}) / (S_{gr} + S_{wc} - 1)]^{n_w-1} \} / [\mu_w \cdot (S_{gr} + S_{wc} - 1)] - \{ k_{rg}^0 \cdot n_g \cdot [(S_w^* - S_{wc}) / (S_{gr} + S_{wc} - 1) + 1]^{n_g-1} \} / \{ \mu_g \cdot \{ fmmob \cdot \arctan[epdry \cdot (S_w^* - fmdry)] / \pi + 1/2 \} + 1 \} \cdot (S_{gr} + S_{wc} - 1) \} + \{ epdry \cdot fmmob \cdot k_{rg}^0 \cdot [(S_w^* - S_{wc}) / (S_{gr} + S_{wc} - 1) + 1]^{n_g} \} / \{ \pi \cdot \mu_g \cdot \{ fmmob \cdot \arctan[epdry \cdot (S_w^* - fmdry)] / \pi + 1/2 \} + 1 \}^2 \cdot [epdry^2 \cdot (S_w^* - fmdry)^2 + 1] \} \} / \{ \{ k_{rw}^0 \cdot [-(S_w^* - S_{wc}) / (S_{gr} + S_{wc} - 1)]^{n_w} \} / \mu_w + \{ k_{rg}^0 \cdot [(S_w^* - S_{wc}) / (S_{gr} + S_{wc} - 1) + 1]^{n_g} \} / \{ \mu_g \cdot \{ fmmob \cdot \arctan[epdry \cdot (S_w^* - fmdry)] / \pi + 1/2 \} + 1 \} \}^2 \} \\ &= 0 \end{aligned}$$

Equation 4-15 Derivative of foam apparent viscosity to water saturation

The apparent viscosity at other water saturations was calculated based on Equation 4-10 to Equation 4-14 with the parameters: ep_{dry} , $fmmob$ and $fmdry$.

4.2 Results and Discussions

4.2.1 The Influence of Foam Quality on Foam Strength

1% C12 in DI water and CO₂ were co-injected into cores following WAG at various foam qualities and room temperature. The equilibrium pH is 5.0, as demonstrated in Figure 4-10. Thus, the surfactant solution should be clear at room temperature in the core. The apparent viscosity histories are shown in Figure 4-12.

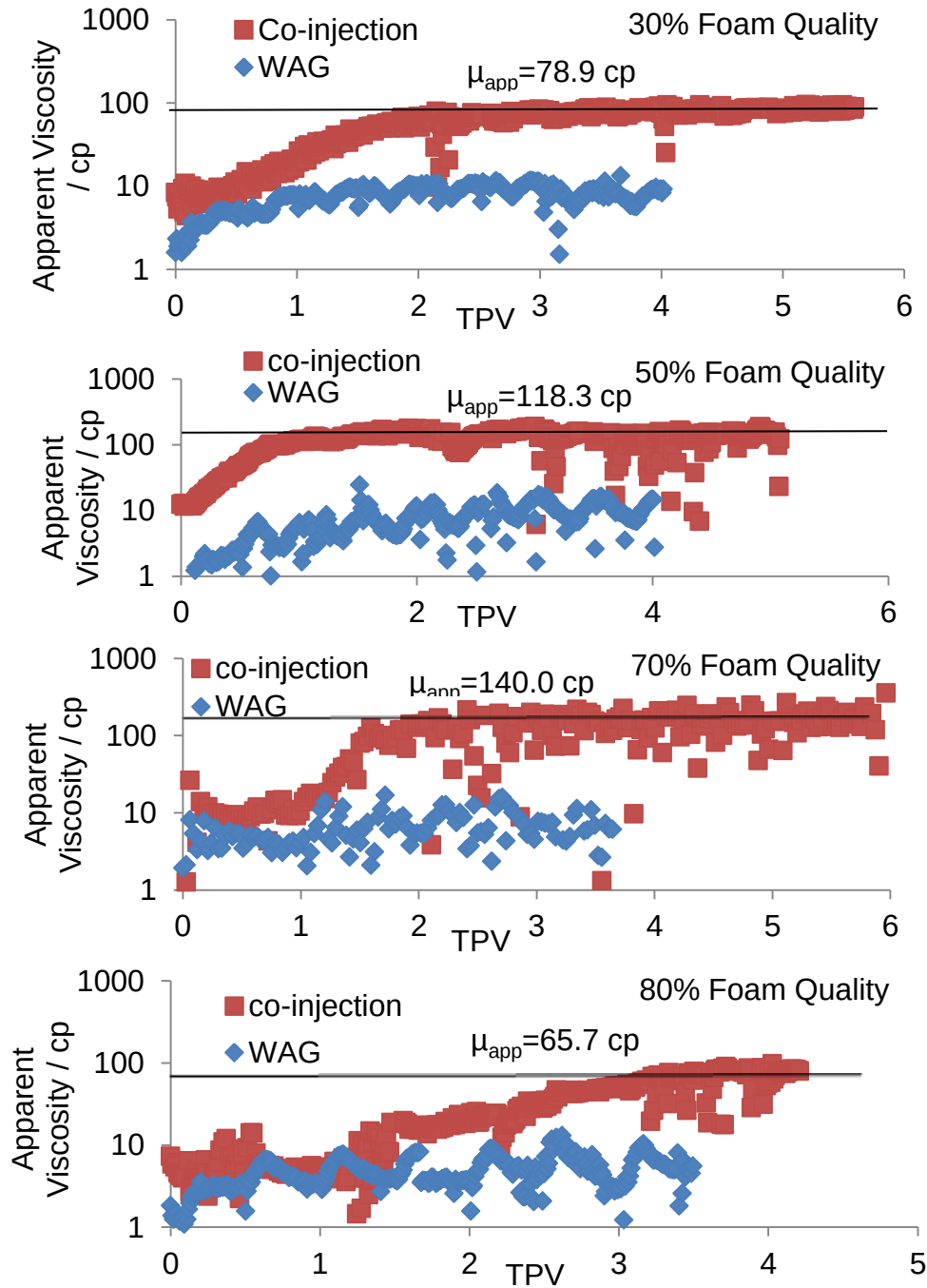


Figure 4-12 The apparent viscosity history for C12/DI and CO₂ foam with various foam qualities at room temperature

The average value on the plateau is taken as the apparent viscosity at steady state. The local equilibrium foam model was used to fit the experimental

data. The parameters are listed in Table 4-4. The relative permeability curves described by the parameters in Table 4-4 are for drainage process in carbonate cores (Bennion and Bachu, 2008). The relative permeability of brine at the end point (k_{rw}^0) equals to 1 and the residual gas saturation (S_{gr}) equals to 0, because of the 100% brine saturation at the initial condition of drainage process. The k_{rw}^0 and S_{gr} in foam process were assumed to be equal to those in drainage process for this foam model. Similar assumption for k_{rw}^0 and S_{gr} was also made in the literature (Ma, et al., 2013a). However, the k_{rw}^0 and S_{gr} in foam process may not be the same as those in drainage process. The investigation for the influence of trapped gas on the local equilibrium foam model is beyond the scope in this thesis.

Table 4-4 The parameters for local equilibrium foam model for C12/DI and CO₂ foam at room temperature

Parameters	Value
k_{rw}^0	1
k_{rg}^0	0.1768
S_{wc}	0.33
S_{gr}	0
n^w	2.8
n^g	1.1
μ_w	1.0 cp
μ_g	0.1025 cp

*Relative permeability parameters are cited from Bennion and Bachu (2008) for Nisku #1 carbonate rock

The fitting results are close to the experimental data except that at 80% foam quality in a wide range of ep_{dry} , as shown in Figure 4-13. The unique ep_{dry} should be determined by a transient experiment, *i.e.*, continuous gas injection (Ma, et al., 2013a). But we didn't attempt to investigate the transient foam in this thesis. The ep_{dry} with which the simulated line passed the most experimental data, *i.e.*, the residual sum of squares deviation (RSS) was minimum (Ma, et al., 2013a), was chosen as the parameter for the steady state simulation. For C12/DI water and CO₂ foam at room temperature, the parameters of (ep_{dry} , f_{mob} , f_{mdry}) were chosen as (100, 379, 0.39) respectively.

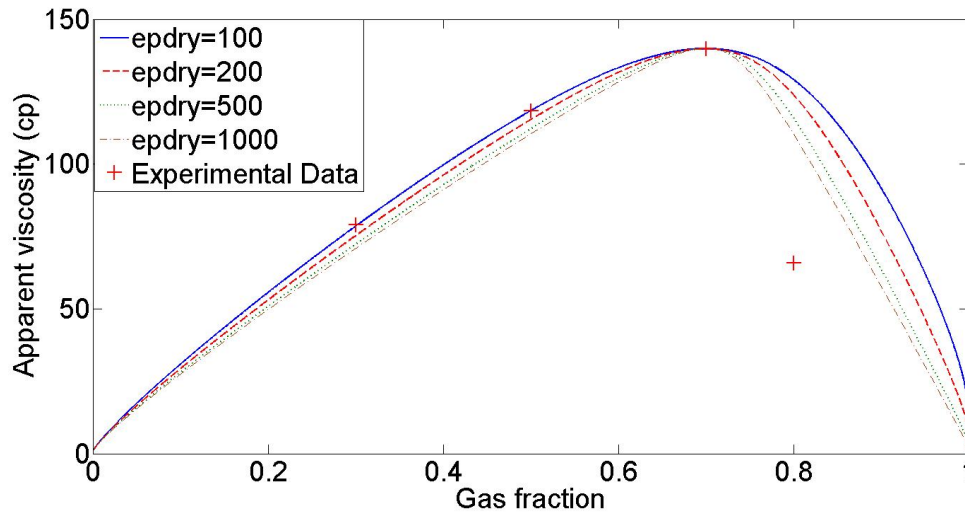


Figure 4-13 The fitting results for C12/DI and CO₂ foam at room temperature calculated by Local Equilibrium Foam Model. The parameters of (ep_{dry} , f_{mob} , f_{mdry}) for simulated lines are (100, 379, 0.39), (200, 353, 0.39), (500, 333, 0.40) and (1000, 323, 0.40), respectively.

The fitting result is higher than experimental value at 80% foam quality. That's probably because the apparent viscosity didn't reach the steady state within 4 PV at 80% foam quality, as shown in Figure 4-12 at 80% foam quality.

The change of foam apparent viscosity with foam quality, *i.e.*, gas fraction in Figure 4-13, is consistent with the literature (Cheng, et al., 2000; Rossen and Wang, 1999; Vassenden and Holt, 2000, Ma, et al., 2013 (a)). The apparent viscosity increased with gas fraction in “low quality” regime as demonstrated at gas fraction from zero to 70% in Figure 4-13, because of the constant bubble size and decrease of water saturation with increasing gas fraction. The maximum foam apparent viscosity reached at transition foam quality, as shown at 70% gas fraction in Figure 4-13. After the gas fraction was increased higher than transition foam quality, the limiting capillary pressure dominated the “high quality” regime. In this “high quality” regime, the foam strength is a decreasing function of foam quality, as observed at foam quality higher than 70% in Figure 4-13.

4.2.2 The Influence of Salinity in Brine on Foam Strength

The Influence of Salinity on C12 and CO₂ Foam

The core was saturated with synthetic formation brine by injecting at 4 ft/day for 4PV. The synthetic formation brine alternating CO₂ (WAG) was injected, and then followed by 1% C12 in synthetic formation brine and CO₂ co-injected at room temperature. The equilibrium pH is 4.3, as shown in Figure 4-10. Thus, the surfactant solution should be clear in the core. The apparent viscosity histories from 30% to 80% foam qualities are shown in Figure 4-14.

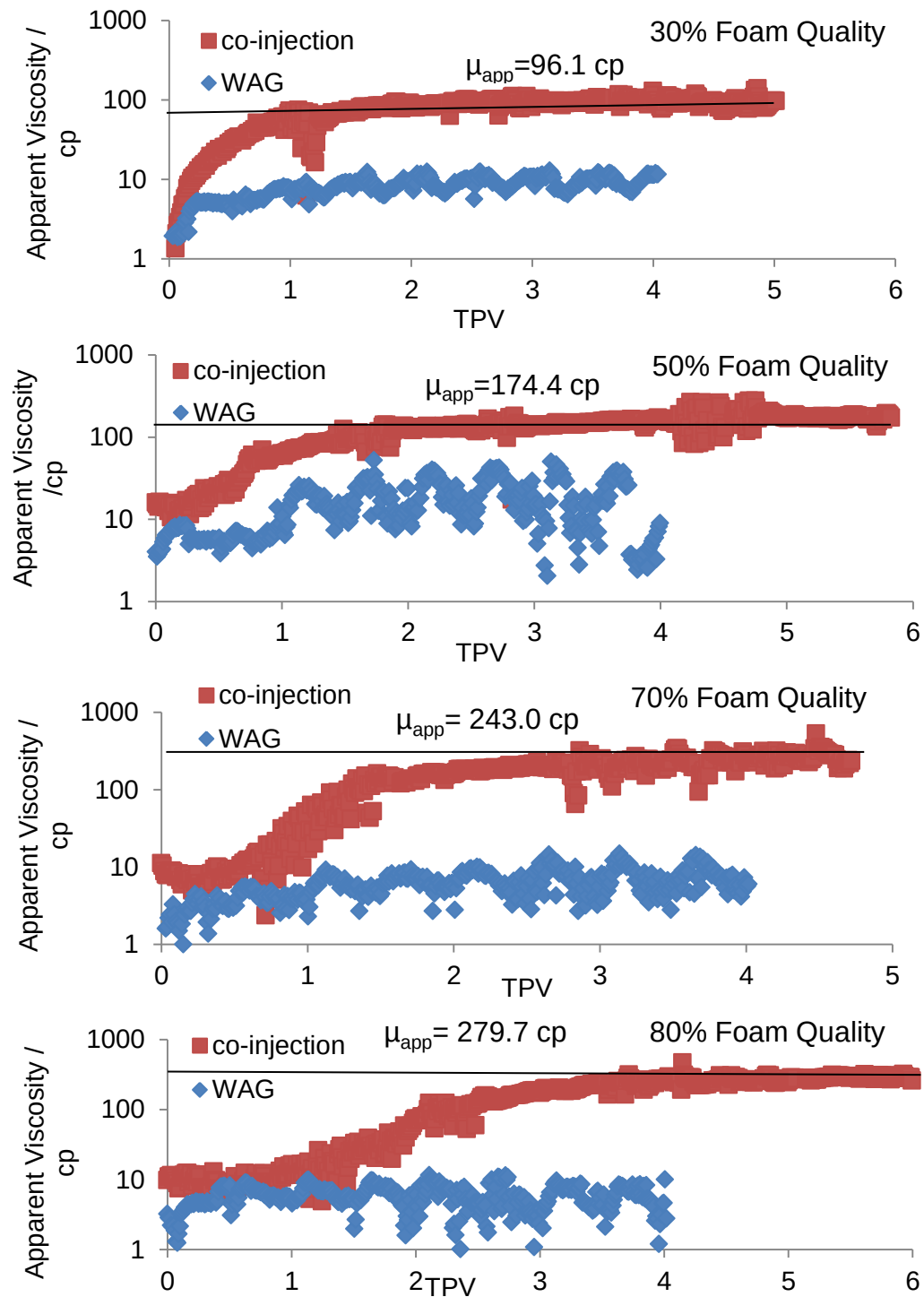


Figure 4-14 The apparent viscosity history for C12/synthetic formation brine and CO₂ foam with various foam qualities at room temperature

The salinity of synthetic formation brine was high. The salt was probably precipitated and plugged the core at high foam quality (90%) due to the evaporation of water to the “dry” CO₂ phase which was not equilibrium with water before co-injection (Muller, et al., 2009; Hurter, et al., 2007), as shown in Figure 4-15.

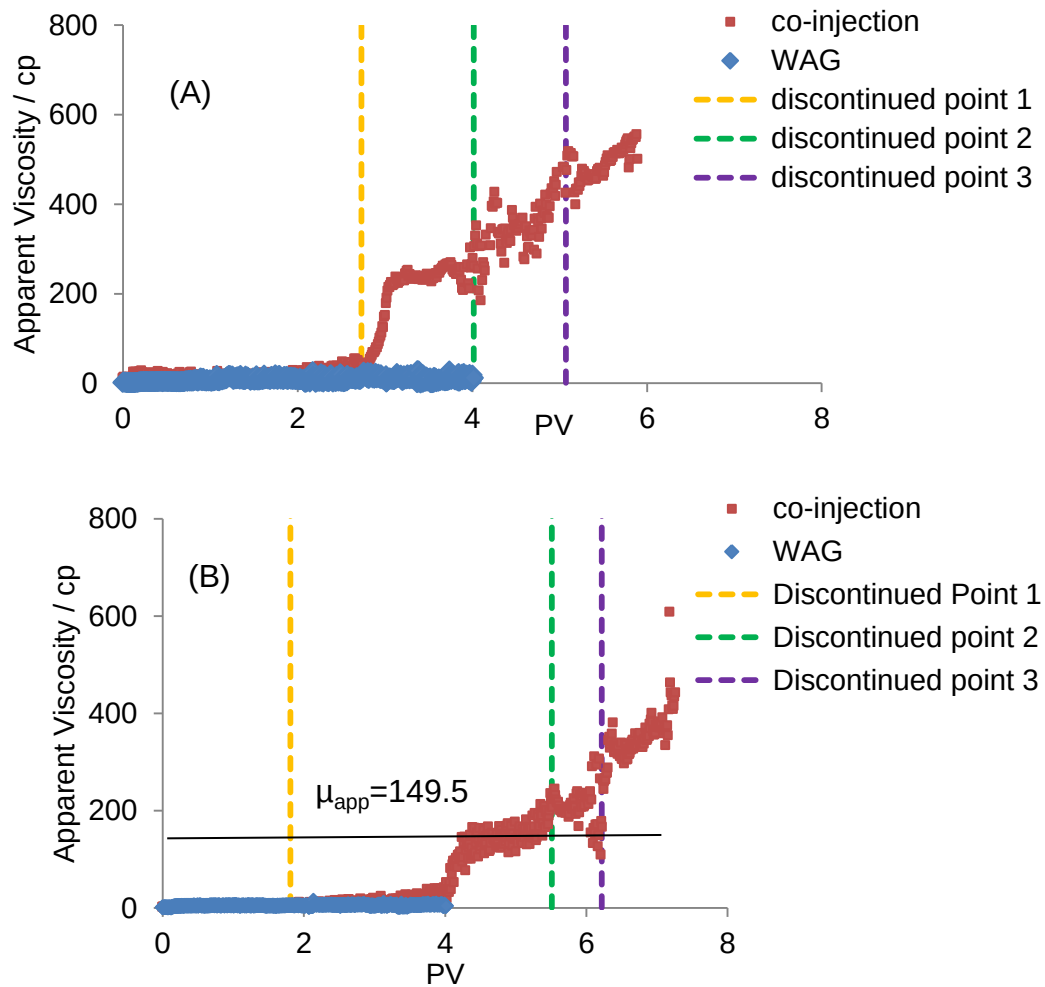


Figure 4-15 The apparent viscosity history of C12/synthetic formation brine and CO₂ foam flooding at 90% foam quality

The “Discontinued Point” in Figure 4-15 means the surfactant solution and CO₂ were stopped injecting for some reasons. As shown in Figure 4-15 (A), the apparent viscosity increased immediately after the 1st discontinued point at around 3 PV. The apparent viscosity increased again after the 2nd discontinued points, even though the apparent viscosity had reached a steady state before 2nd discontinued point. These increases of pressure after discontinued points are probably caused by the precipitation of salt, *i.e.*, the water evaporated in the presence of high fraction of CO₂ during discontinued points. This resulted in the salt concentration being higher than the saturation point.

In Figure 4-15 (B), the apparent viscosity remained the same after the 1st discontinued point around 2PV, which indicates the salt didn’t precipitate. That’s because the CO₂ fraction was low in the presence of weak foam at 2 PV. The evaporation of water was not as intense as at other discontinued points. With development of strong foam, the CO₂ fraction was increased, which results in the salt precipitating and immediate increase of foam apparent viscosity at the 2nd and 3rd discontinued point in Figure 4-15. The average of plateau value before 2nd discontinued point in Figure 4-15 was taken as the apparent viscosity at steady state for 90% foam quality.

Thus, in the field application, the CO₂ should be saturated with water before injection to prevent the salt precipitation near the well bore zone (Muller, et al., 2009).

The experimental data were fitted by local equilibrium foam model. The parameters are shown in Table 4-5. Figure 4-16 demonstrates that the model fits the experimental data well.

Table 4-5 The parameters for local equilibrium foam model for C12/synthetic formation brine and CO₂ foam at room temperature

Parameters	Value
k_{rw}^0	1
k_{rg}^0	0.1768
S_{wc}	0.33
S_{gr}	0
n^w	2.8
n^g	1.1
μ_w	1.0 cp
μ_g	0.1025 cp
epdry	10000
fmmob	563
fmdry	0.38

*Relative permeability parameters are cited from Bennion and Bachu (2008) for Nisku #1 carbonate rock.

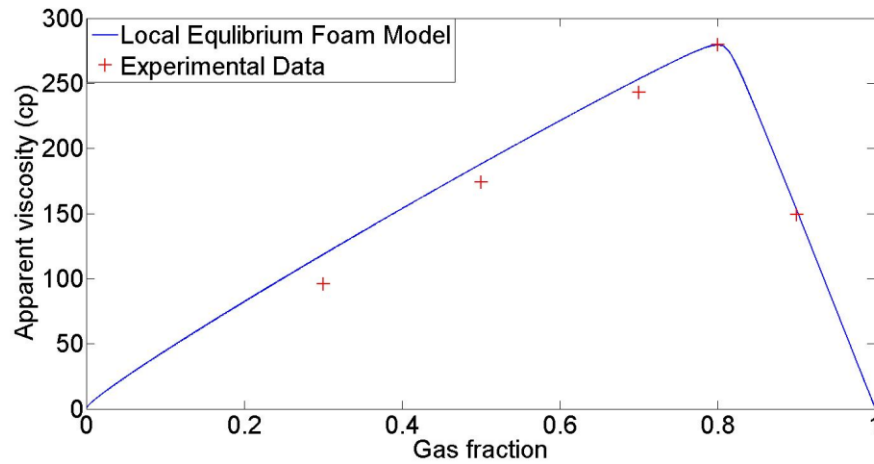


Figure 4-16 The fitted results for C12/brine and CO₂ foam at room temperature calculated by Local Equilibrium Foam Model

The comparison of CO₂ foam in DI water and synthetic formation brine at room temperature is shown in Figure 4-17. The foam apparent viscosity in synthetic formation brine is higher than in DI water, which is consistent with the observation made by Chen, et al. (2014).

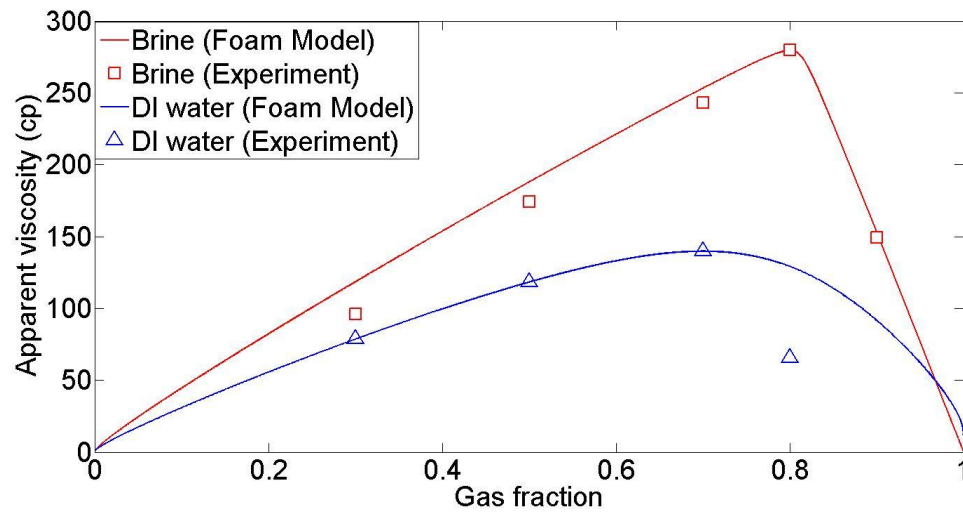


Figure 4-17 The comparison of foam apparent viscosity in DI water and synthetic formation brine at room temperature

The Influence of Salinity on Glycidyl Sulfonates and N₂ Foam

The high salinity brine was favorable for C12 and CO₂ foam, but was not favorable for alkyl glycidyl ether sulfonates, *i.e.*, N25-7EO GS and N67-9EO GS.

The surfactant was dissolved in two brines: low salinity brine which contains 3.5% (wt) NaCl and 1.0% (wt) Na₂CO₃, and high salinity SME brine which contains 127.00 g/L NaCl, 53.29 g/L CaCl₂·2H₂O, 22.67 g/L MgCl₂·6H₂O and 0.69 g/L Na₂SO₄. The total content of active surfactant was 0.5% (wt). The foam was generated in a silica sandpack by SAG (surfactant alternating gas) at

2/3 foam quality and 20 ft/day superficial velocity as described in Chapter 3. The apparent viscosity history and the average viscosity at steady state are shown in Figure 4-18 and Figure 4-19.

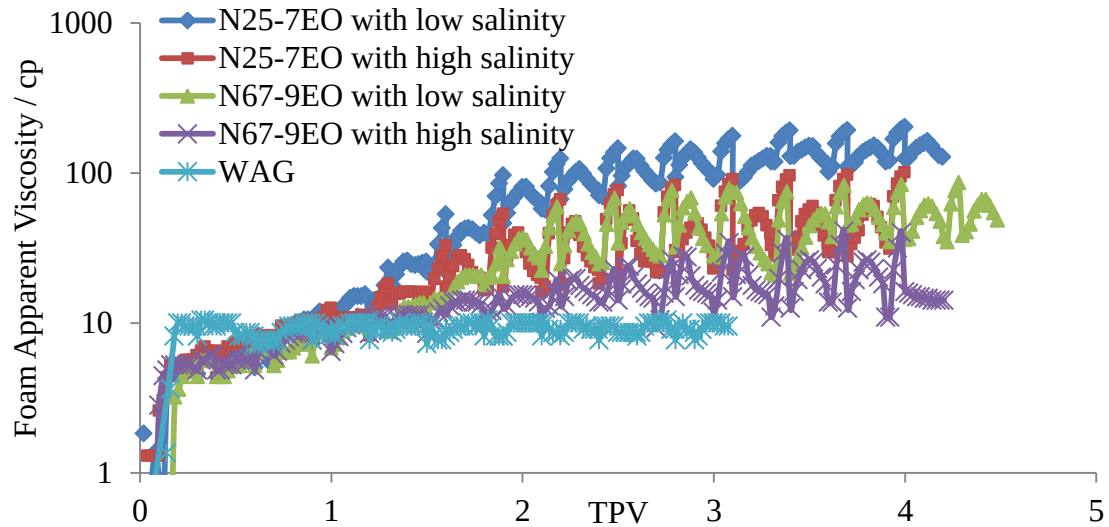


Figure 4-18 Comparison of foam apparent viscosity in low salinity brine and in high salinity brine

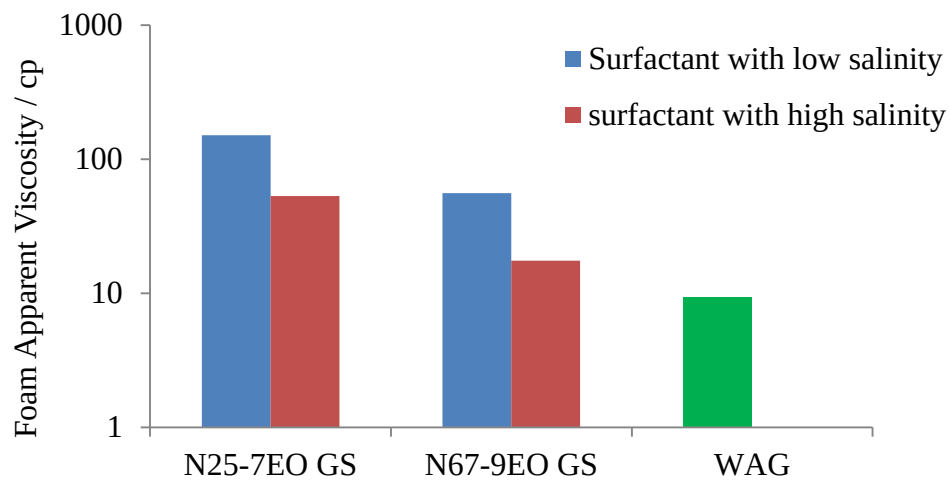


Figure 4-19 The average apparent viscosity at steady state for glycidyl ether sulfonates GS surfactants

The Comparison and Discussion

The high salinity in brine is favorable for C12 and CO₂ foam strength, but is detrimental for glycidyl sulfonates and N₂ foam strength. That's because that the influence of salinity on foam stability is controlled by two competitive mechanisms, *i.e.*, foam stabilization and destabilization by electrolyte. The counter-ions in brine can decrease the repulsion of head groups in surfactants, which results in a more tightly packing of surfactant molecules in the water-gas interface. A higher packing density of surfactant leads to a higher surface viscosity and more stable foam (Joye, et al., 1994; Aronson, et al., 1994; Pandey, et al., 2003). Simultaneously, the addition of the electrolyte depresses the electrostatic repulsion (Π_{elec}) of double layers in film plateau and destabilizes the foam (Bergeron and Radke, 1992; Bhakta and Ruckenstein, 1996).

The disjoining pressure can be utilized to explain the electrolyte influence caused by above two competitive factors (Aronson, et al., 1994; Bhakta and Ruckenstein, 1996). With increasing salinity, the disjoining pressure initially increases to reach a maximum at an optimal salinity and then decreases, which results in the same change of foam stability. The disjoining pressure also depends on the nature of surfactants. For alkyl glycidyl sulfonates and N₂ foam, the salinity in SME brine has far exceeded the optimal value at which the disjoining pressure reached the maximum, which resulted in the deleterious influence on foam stability. For C12 and CO₂ foam, the salinity in synthetic formation brine may have been around the optimal value, which resulted in the enhancement of the foam stability and strength. A systematic investigation with a

wide range of salinity needs to be done to find out the influence of salinity on the foam stability and strength.

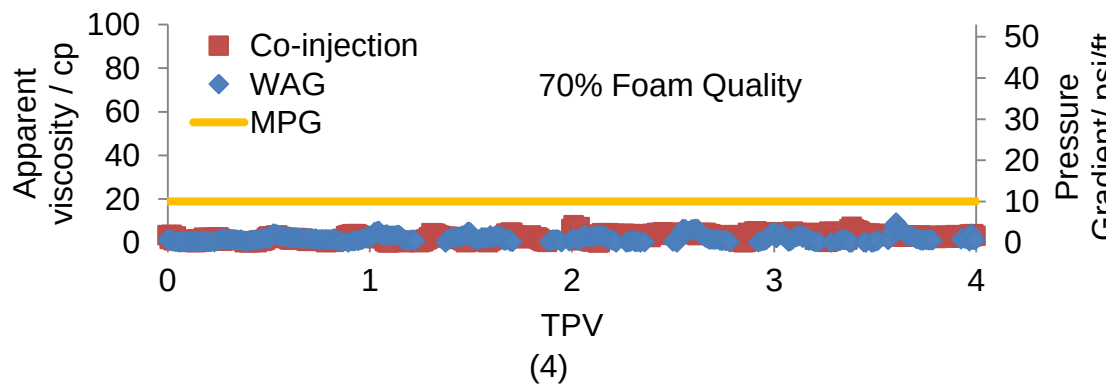
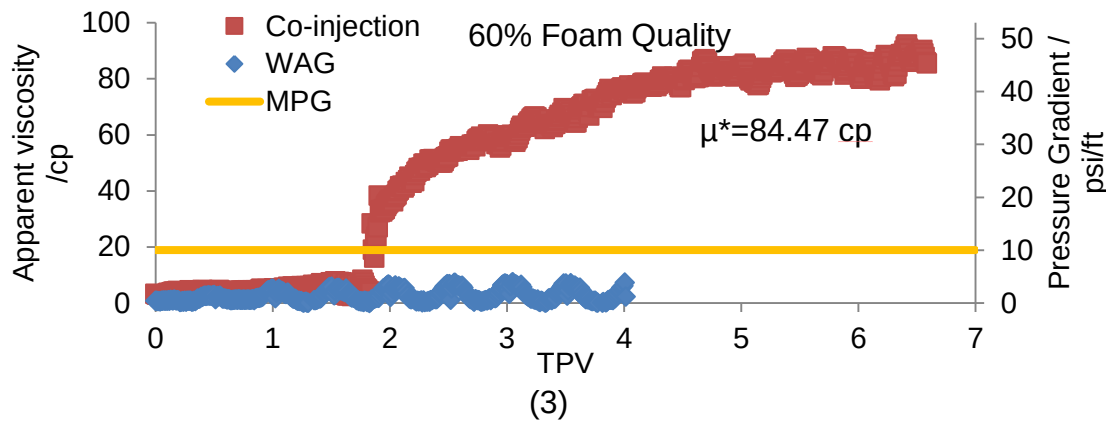
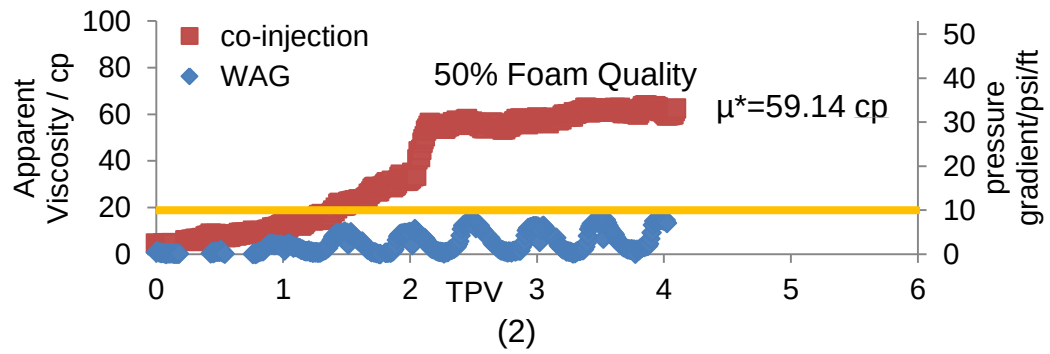
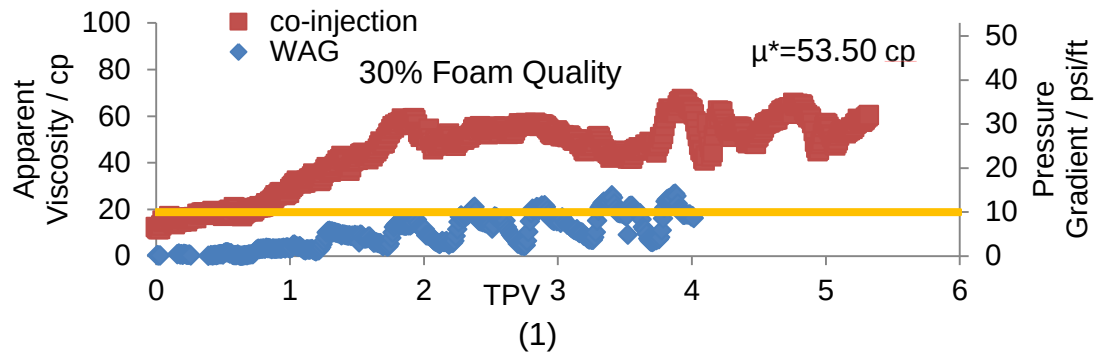
4.2.3 The Influence of Elevated Temperature on Foam Strength

The C12 and CO₂ foam was evaluated at 120 °C in synthetic formation brine and DI water, respectively. The injection strategy was the same as at room temperature. The moderately strong foam was generated with C12 in synthetic formation brine at 120 °C. The minimum pressure gradient (MPG) was observed in this foam process. However, only weak foam was generated with C12 in DI water at 120 °C. The obvious dissolution of dolomite core was observed in this foam flooding.

C12/Synthetic Formation Brine and CO₂ Foam at 120 °C

The equilibrium pH is 4.0, as shown in Figure 4-10. Thus the surfactant solution should be clear at 3400 psi and 120 °C in the core. The foam viscosities are shown in Figure 4-20.

Foam can be generated at 4 ft/day for 30%, 50% and 60% foam quality (Figure 4-20 (1), (2) and (3)), but cannot for 70% and 80% foam quality (Figure 4-20 (4) and (5)). Notice the foam pressure history at low foam quality. The strong foam was generated after the pressure gradient higher than 10 psi/ft. Thus, minimum pressure gradient (MPG) at 10 psi/ft was required to generate strong foam.



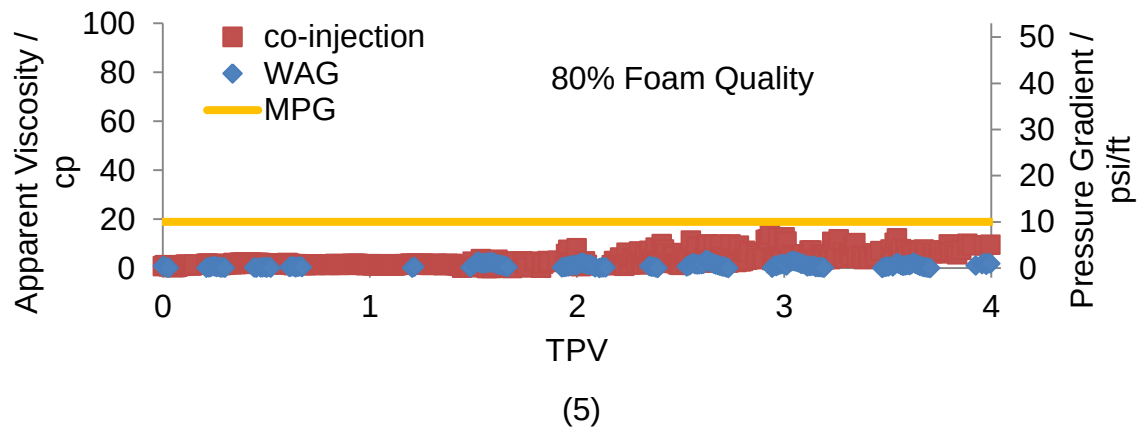


Figure 4-20 The foam strength history for C12/synthetic formation brine and CO₂ co-injection at 4 ft/day and 120 °C for various foam qualities: from (1) to (5) are 30%, 50%, 60%, 70% and 80%, respectively. MPG means minimum pressure gradient

The Minimum Pressure Gradient (MPG) and Minimum Superficial Velocity (MSV)

The back pressure regulator was manually changed down to reduce the outlet pressure and blow the pressure gradient higher than MPG in a short time interval (less than 0.1 PV) for 70% foam quality case. The strong foam was generated immediately, as demonstrated in Figure 4-21. The strong foam after the manual reduction of back pressure indicates the existence of the MPG.

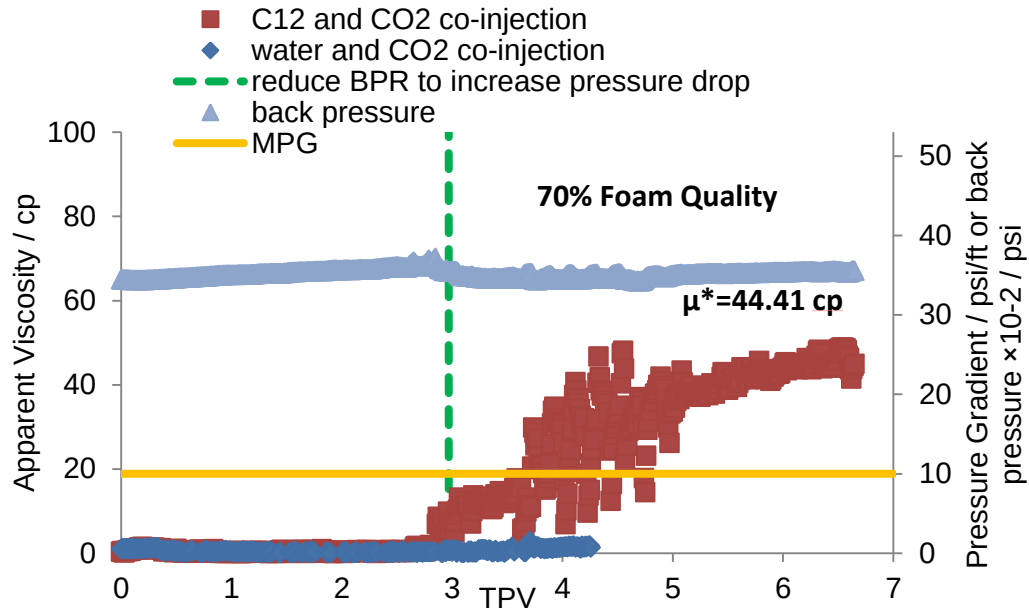


Figure 4-21 C12 in synthetic formation brine and CO₂ foam strength history at 70% foam quality and 120 °C with 4 ft/day. The back pressure was manually changed down at 3 PV to increase the pressure gradient to minimum pressure gradient (MPG)

The pressure gradient can be enhanced at higher superficial velocity. In Figure 4-22, initially the strong foam wasn't generated at 4 ft/day at 80% foam quality, because the pressure gradient was lower than MPG. After the superficial velocity was switched to 8 ft/day, strong foam was generated readily. If the flow rate was switched back to 4 ft/day, strong foam kept generating because of the high pressure gradient in the presence of foam. Note, the steady foam apparent viscosity at 4 ft/day was higher than that at 8 ft/day, but the pressure gradient was in an opposite situation, owing to the shear thinning property of foam.

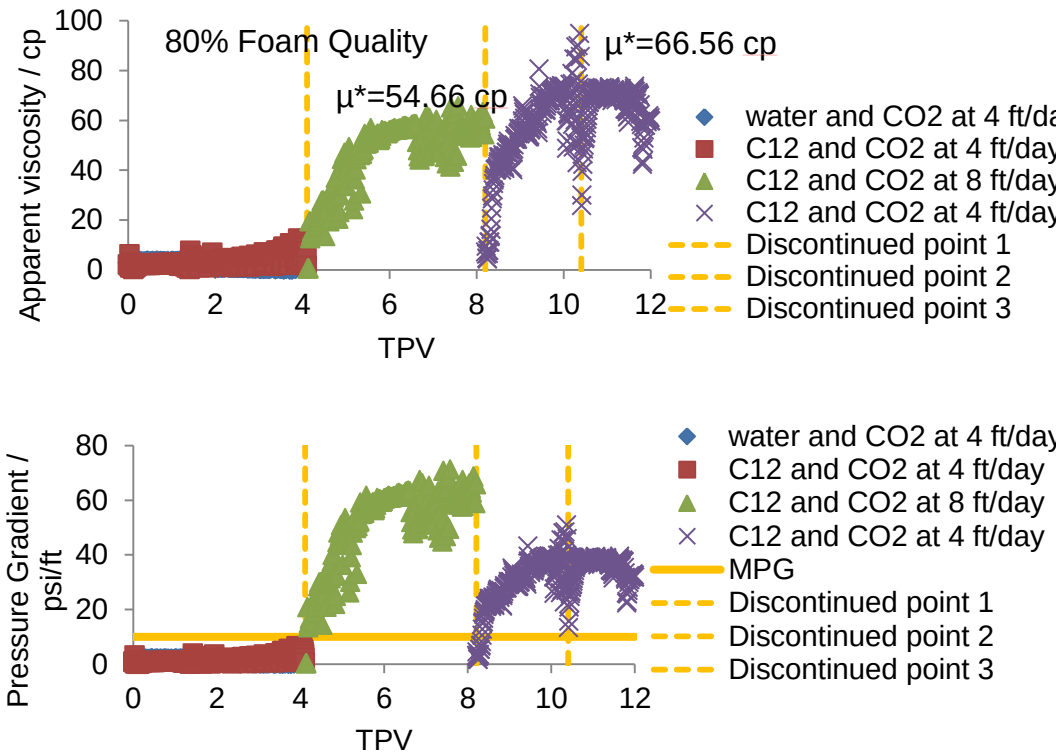


Figure 4-22 C12/brine and CO₂ foam strength history at 80% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, no foam. Switch to 8 ft/day, foam is generated. Switch back to 4 ft/day, foam is still stable

Ransohoff and Radke (1988) reported the existence of minimum superficial velocity (MSV), which indicates the strong foam wasn't generated unless the superficial velocity was higher than MSV. If MSV existed for C12/Brine and CO₂ foam, it should be somewhere between 4 and 8 ft/day, as demonstrated in Figure 4-22. The high pressure gradient and foam apparent viscosity at 4 ft/day after 8 PV in Figure 4-22 can be attributed to the residual foam at 8 ft/day.

The following experiment was designed to determine which one is the dominant factor, minimum pressure gradient (MPG) or minimum superficial velocity (MSV), for C12/brine and CO₂ foam at reservoir conditions. Initially,

C12/brine and CO₂ were co-injected at high superficial velocity (16 ft/day). The velocity was switched to 4 ft/day before the pressure gradient reached the MPG (10 psi/ft). The foam wasn't generated at 4 ft/day for 1 PV injection, as demonstrated in Figure 4-23, which indicates the foam generation was not initiated by high superficial velocity.

And then, the injection was switched back to 16 ft/day and stopped at the pressure gradient that just reached MPG (Figure 4-23, lower), which indicates the foam just started to be generated, but the volume of generated foam can be assumed to be negligible. Finally, the injection velocity was set at 4 ft/day, and the moderately strong foam (30-40 cp) was readily generated within 1 PV. After another 2 PV, the strong foam (71.19 cp) was developed (Figure 4-23, upper). If the MSV dominated the foam generation, the foam generation at 4 ft/day should be stopped and the pressure gradient should be reduced back, because of the lack of residual foam at 16 ft/day. However, the continuous generation of foam at 4 ft/day after the MPG had been exceeded indicates that the dominant factor for C12/brine and CO₂ foam generation was MPG rather than MSV.

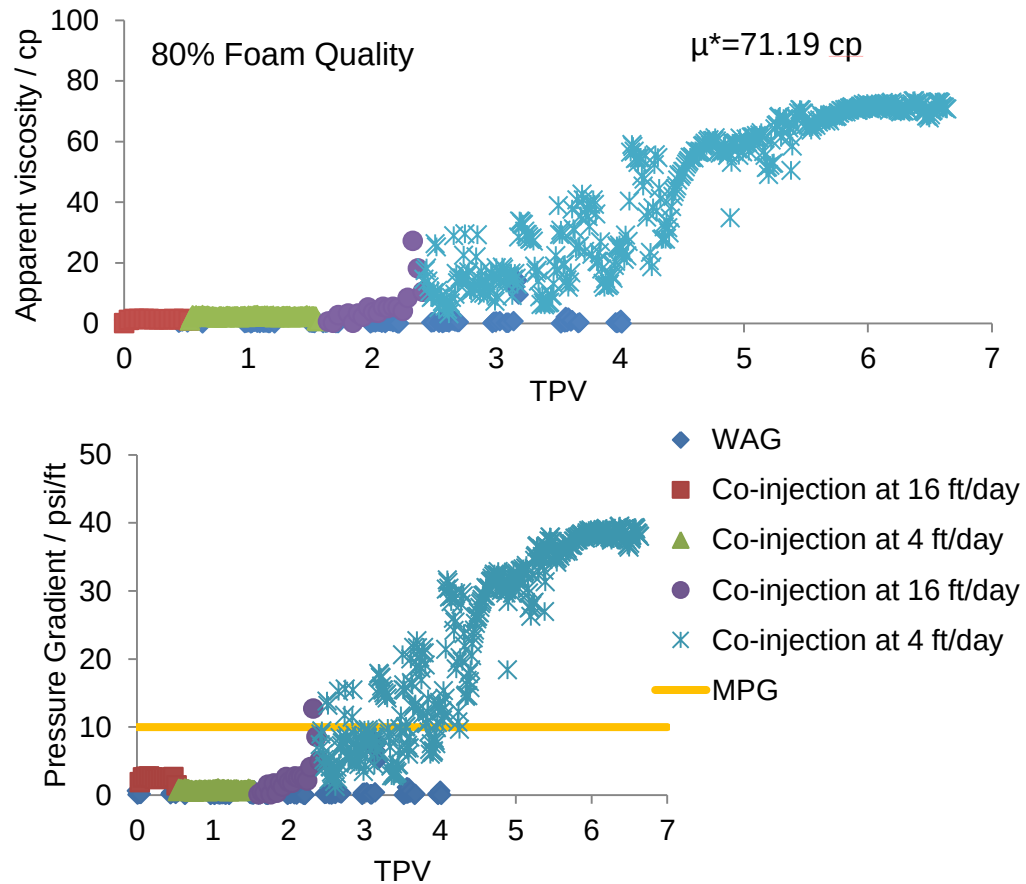


Figure 4-23 C12/Brine and CO₂ foam at 80% foam quality and 120 °C. Start at 16 ft/day, decrease to 4 ft/day before the pressure gradient reaches MPG, no foam. Switch to 16 ft/day again until the pressure gradient reaches MPG, decrease back to 4 ft/day, foam is generated

Thus, for the field application, the initially higher injection velocity is required to reach the pressure gradient to MPG, and then the velocity can be switched to a lower value to generate stronger foam, because of the shear-thinning property of foam, as demonstrated in Figure 4-24.

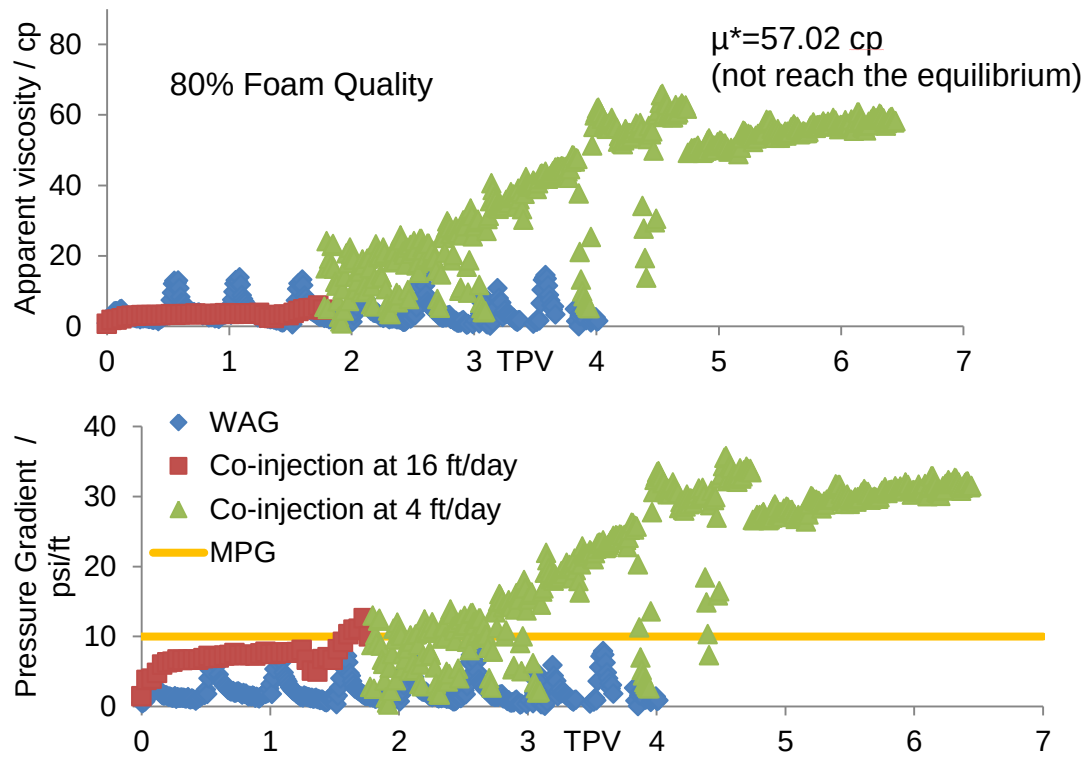


Figure 4-24 C12/brine and CO₂ foam strength and pressure gradient history at 80% foam quality and 120 °C. Start at 16 ft/day to reach the MPG and then switch back to 4 ft/day

The local equilibrium foam model was used to fit the experimental data. The parameters are shown in Table 4-6. The comparison of the strength of C12/brine and CO₂ foam at 20 °C and 120 °C is shown in Figure 4-25. The foam strength was largely reduced at elevated temperature, and the transition foam quality shifted from 80% at 20 °C to 60% at 120 °C. However, the viscosities in a wide range of foam qualities were close at 120 °C, which indicates the influence of limiting capillary pressure on foam stability at 120 °C was not as significant as that at 20 °C. The relatively steady viscosity of C12/brine and CO₂ foam in various gas fractions can be achieved at 120 °C.

Table 4-6 Parameters in local equilibrium foam model for C12/brine and CO₂ foam at 120 °C

Parameters	Value
k_{rw}^0	1
k_{rg}^0	0.1768
S_{wc}	0.33
S_{gr}	0
n^w	2.8
n^g	1.1
μ_w	0.2381 cp
μ_g	3.935×10^{-2} cp
epdry	10000
fmmob	588
fmdry	0.39

*Relative permeability parameters are cited from Bennion and Bachu (2008).

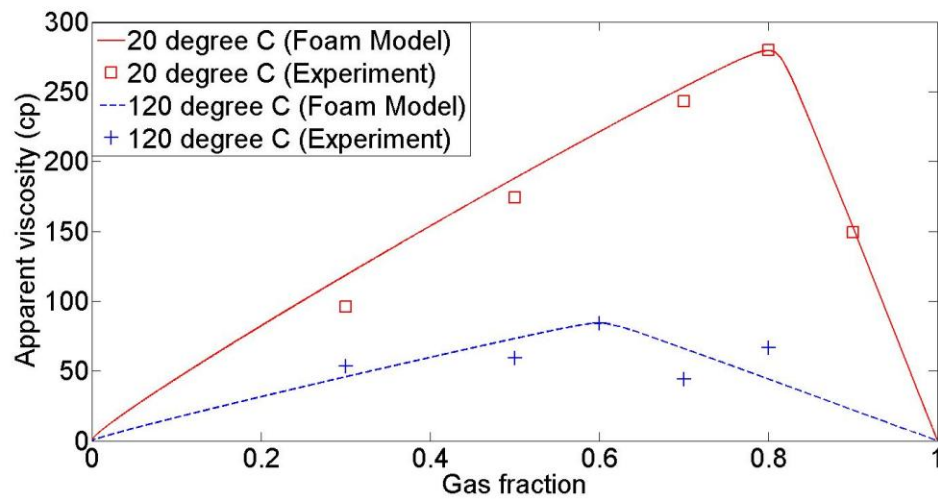


Figure 4-25 The comparison of the foam strength at 20 and 120 °C for C12/brine and CO₂ co-injection foam

C12/DI Water and CO₂ Foam at 120 °C

1% C12 in DI water and CO₂ were co-injected at 4 ft/day with similar procedure for C12/brine and CO₂. Weak foam was generated at low foam quality (50%), as demonstrated in Figure 4-26. The apparent viscosity and pressure gradient at 70% foam quality were as low as those for WAG, which indicates no foam was generated at 70% foam quality.

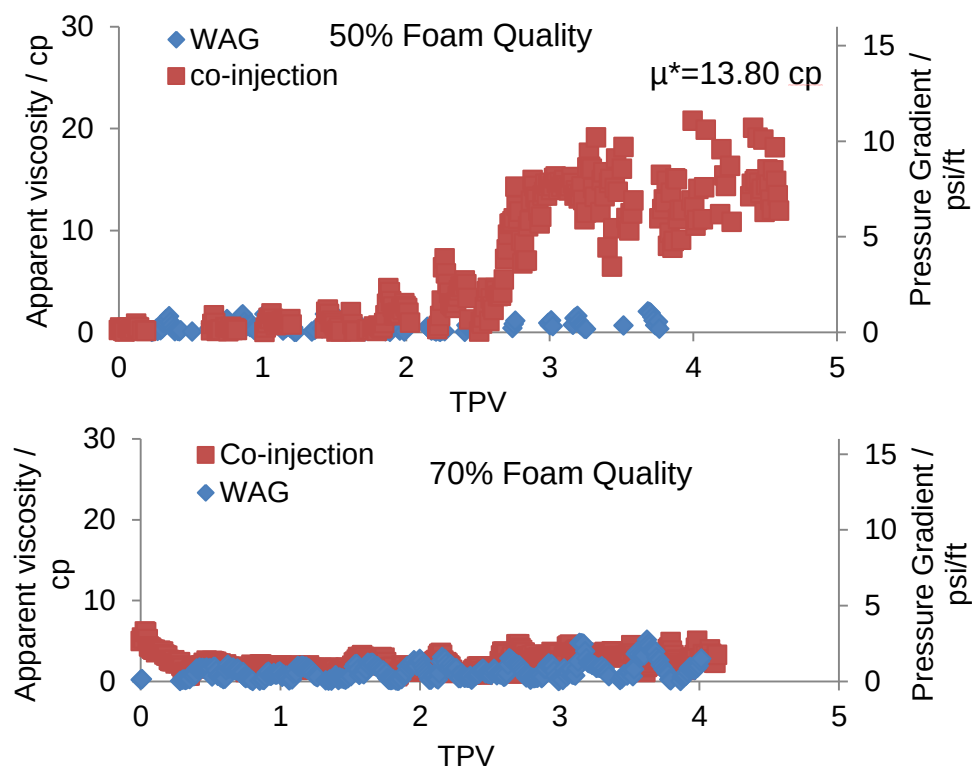


Figure 4-26 The C12/DI and CO₂ co-injection foam flooding history at 120 °C. The upper one is 50% foam quality, the lower one is 70% foam quality

Higher superficial velocities were tried. The pressure gradient at 32 ft/day was increased to 10 psi/ft. But, the foam still wasn't generated, as shown in Figure 4-27.

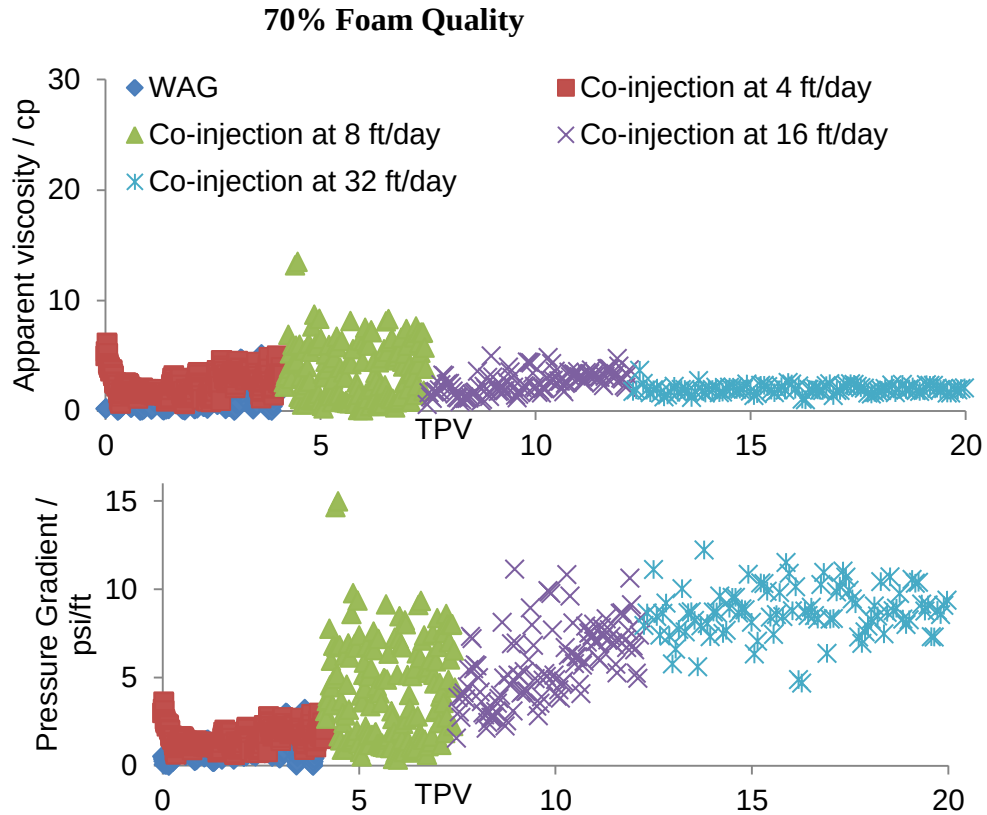


Figure 4-27 The apparent viscosity and pressure gradient history for co-injection of C12/DI and CO₂ at 70% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, and increase to 8, 16, 32 ft/day

The comparison of apparent viscosity for C12/DI and CO₂ foam at 20 and 120 °C is shown in Figure 4-28. Strong foam of C12/DI and CO₂ was not generated at elevated temperature.

The equilibrium pH of DI water-dolomite at 120 °C and 3400 psi is 4.9, as shown in Figure 4-10. The limited pH for C12 solubility at 120 °C is somewhere between 4 and 6, as demonstrated in Figure 3-11. The equilibrium pH (4.9) may approach to the limited pH, which may result in the poor foam performance at the elevated temperature. Notice, C12/DI water was still water soluble in CO₂ foam

flooding, because the core plug phenomena, as demonstrated in Figure 4-11, was not observed.

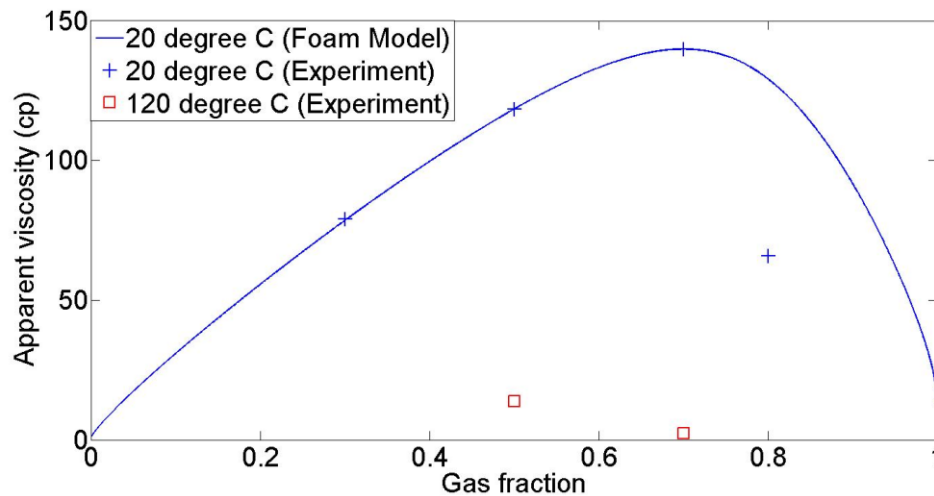


Figure 4-28 The comparison of foam apparent viscosity for C12/DI and CO₂ co-injection at 4 ft/day at 20 and 120 °C

The Blend of C12 and CPC in DI Water and CO₂ Foam at 120 °C

The blend of C12 and CPC with weight ratio 1:1 and total active concentration 1.0% in DI water was evaluated at both room temperature and 120 °C. The cloud point of the blend was higher than 120 °C from original pH=8.6 to pH=4. However, foam was generated at room temperature (Figure 4-29), but was not at 120 °C (Figure 4-30).

The comparison of the steady apparent viscosity of foam at 20 and 120 °C is shown in Figure 4-31. Clearly, the blend of C12 and CPC didn't generate strong foam at 120 °C.

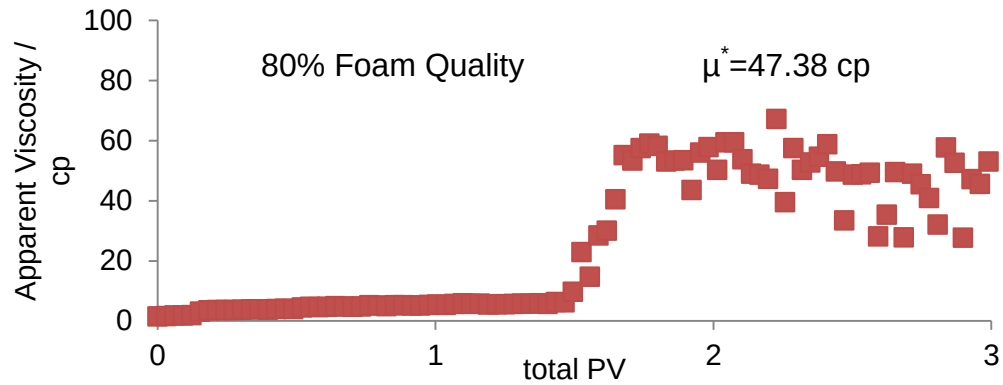


Figure 4-29 The apparent viscosity of CO₂ foam for blend of C12 and CPC with weight ratio 1:1 and total activity 1.0% in DI water at room temperature and 4 ft/day

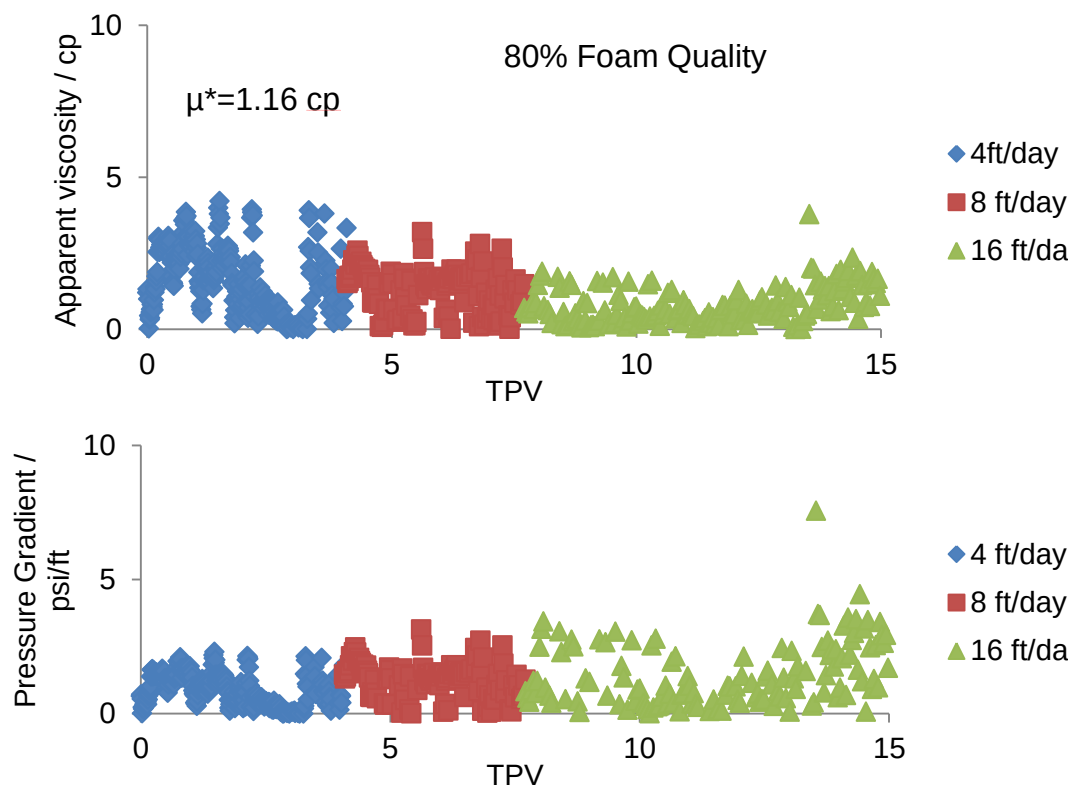


Figure 4-30 The foam apparent viscosity and pressure gradient history for the co-injection of blend of C12 and CPC in DI water and CO₂ at 80% foam quality and 120 °C. Start at 4 ft/day total superficial velocity, and then increase to 8 and 16 ft/day

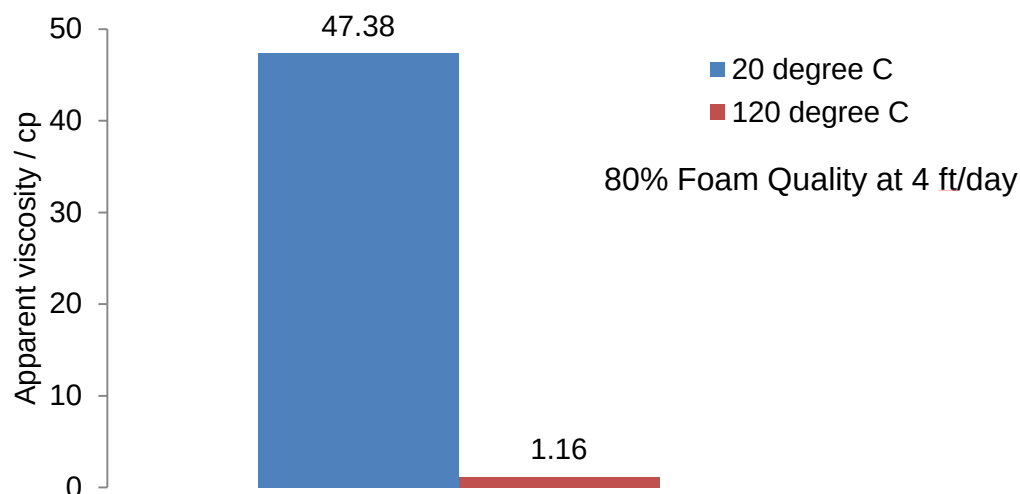


Figure 4-31 The comparison of foam apparent viscosity at 20 and 120 °C for the co-injection of blend of C12 and CPC in DI water and CO₂ with 80% foam quality at 4 ft/day

Dissolution of Carbonate Core

The carbonate mineral was dissolved in DI water and CO₂ at elevated temperature, as shown in Figure 4-32. The kinetics of carbonate mineral dissolution may have been too slow to affect the carbonate rock at the room temperature. However, the kinetics of carbonate mineral dissolution in DI water and CO₂ at 120 °C was fast enough to dissolve the carbonate rock and likely significantly changed the composition of the brine. Thus, brine containing sufficient divalent cations, *i.e.*, Ca²⁺ and Mg²⁺, is suggested to reduce carbonate mineral dissolution for foam evaluation in carbonate rocks.



Figure 4-32 The Silurian dolomite core after C12/DI and blend of C12 and CPC in DI water flooding at 120 °C. The solid core was greatly dissolved by surfactant solution in DI water

The Discussion for Elevated Temperature Influence on Foam Strength

The temperature affects the foam strength by changing the surfactant surface density. Two competitive factors, *i.e.*, the dehydration of EO and OH head groups and the enhancement of thermal motion for surfactant molecules, dominate the surfactant surface density at elevated temperature (Muruganathan, et al., 2003). Elevated temperature reduces the size of EO and OH groups, which causes the closer packing, higher surfactant surface density and more stable foam (Wongwailikhit, et al., 2001). The enhancement of thermal motion decreases the surfactant surface density, increases the gas permeability through the liquid film, consequently, destabilizes the foam (Muruganathan, et al., 2003 and 2006; Exerowa, et al., 1992; Krustev and Müller, 1999).

The destabilization mechanism of elevated temperature apparently dominated the C12 and C12/CPC blend CO₂ foams at reservoir temperature. Especially for C12 and C12/CPC blend in DI water, strong foam was not

generated at 120 °C. The increase of salinity can enhance the C12 and CO₂ foam strength at elevated temperature.

4.2.4 The pH in CO₂ Foam Flooding Process

The calculated pH by PHREEQC software for CO₂ flooding conditions was verified by experimental data.

Firstly, the pH at 2 atm CO₂ was measured for the verification. DI water or synthetic formation brine was in equilibrium with dolomite at 2 atm CO₂ in a pressure vessel. The pressure vessel was opened, and the supernatant in the vessel was gently withdrawn for pH measurement. The pH was measured by pH electrode (Ross pH electrode, from Thermo Scientific Co.) equipped in a pH meter (Corning 320). The comparison of calculated and measured pH is shown in Figure 4-33. The measured pH was slightly higher than the calculated pH as expected, because of the diffusion or effusion of dissolved CO₂ out of liquid. The consistency of calculated and measured pH indicates the satisfactory prediction of pH by Phreeqc software.

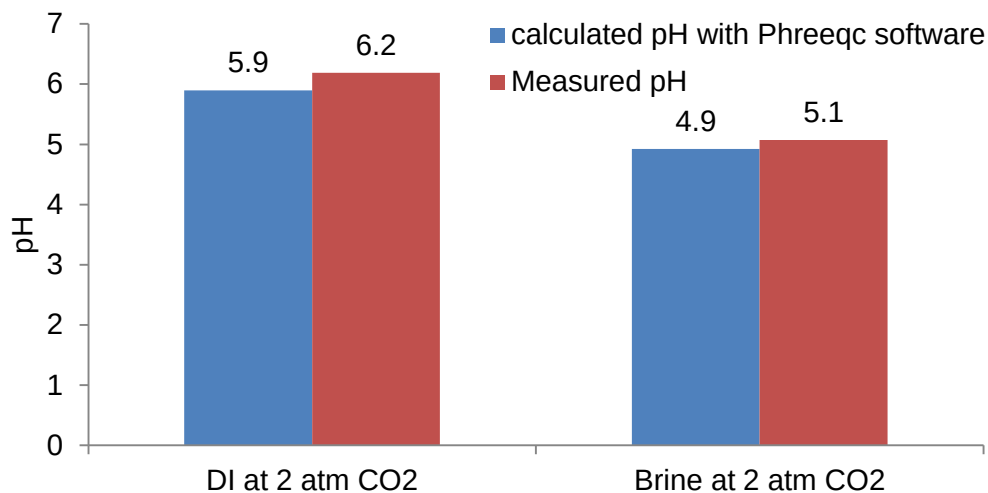


Figure 4-33 The comparison of simulated and measured pH for DI and synthetic formation brine equilibrium with dolomite at 2 atm CO₂

The pH at high pressure was determined by pH indicator in a visual cell. The color of Bromocresol Green (BCG) was yellow at pH<3.8, was green at pH=3.8-5.4 and was blue at pH>5.4 in the absence of surfactant (Sabnis, 2007), as shown in Figure 4-34. The pH of BCG solutions was adjusted by HCl solution and potassium dihydrogen phosphate/ disodium hydrogen phosphate buffer (pH=7, from Fluka[®] Sigma-Aldrich Co.) for the color code in Figure 4-34.

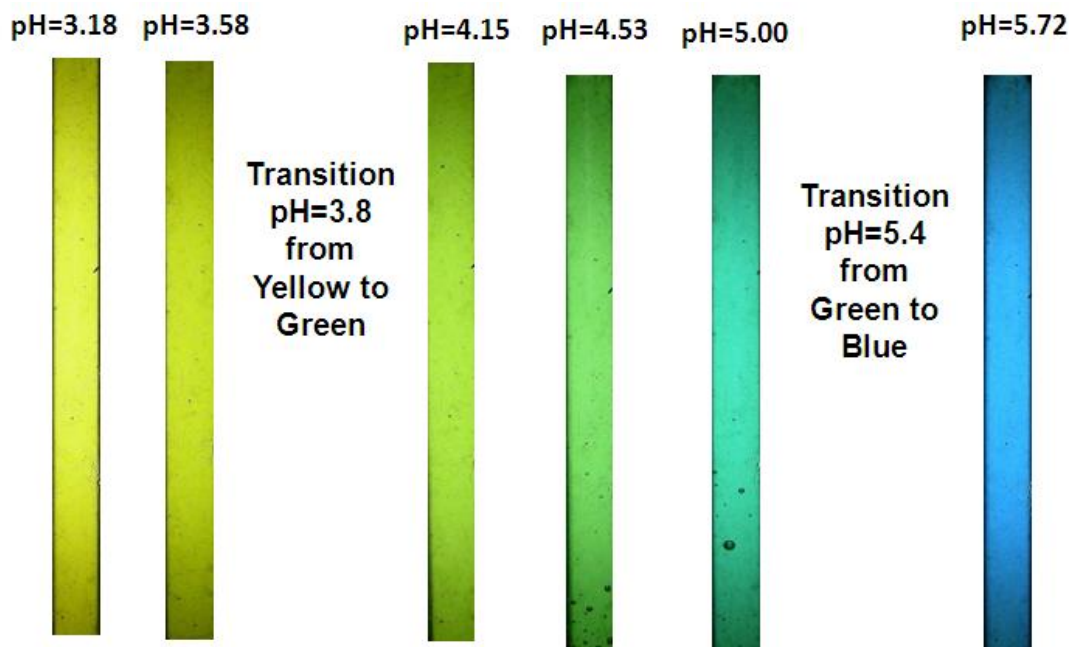


Figure 4-34 The color code of Bromocresol Green (BCG) in the absence of C12

The local pH on the surface of micelles may be different from that in the bulk (inter-micellar) electrolyte solution. In the presence of C12, the positively charged hydrogen ion can be expected to be repelled from the surface of positively charged C12 micelle. This resulted in pH on the surface of the micelle being higher than in the bulk electrolyte solution. This is analogous to the difference of divalent/monovalent cations associated with micelles and in the inter-micellar electrolyte (Hirasaki and Lawson, 1986). The BCG is expected to be attracted by C12 micelle, because of the opposite charge and similar hydrophobicity. Thus, the color of BCG is likely determined by the micelle surface pH, which results in the color change occurred at lower measured pH, as shown in Figure 4-35. The pH in bulk electrolyte solution which was a blend of 35 ml BCG solution and 5 ml 1% C12/synthetic formation brine solution, was adjusted

by HCl and buffer solution (pH=7). The color code in the presence of C12 is shown in Figure 4-35. The measured transition pH in bulk electrolyte solution was shifted to 3.1 from 3.8 for yellow to green, and to 4.1 from 5.4 for green to blue in the presence of C12, *i.e.*, the color is green at pH=3.1-4.1 in the presence of C12.

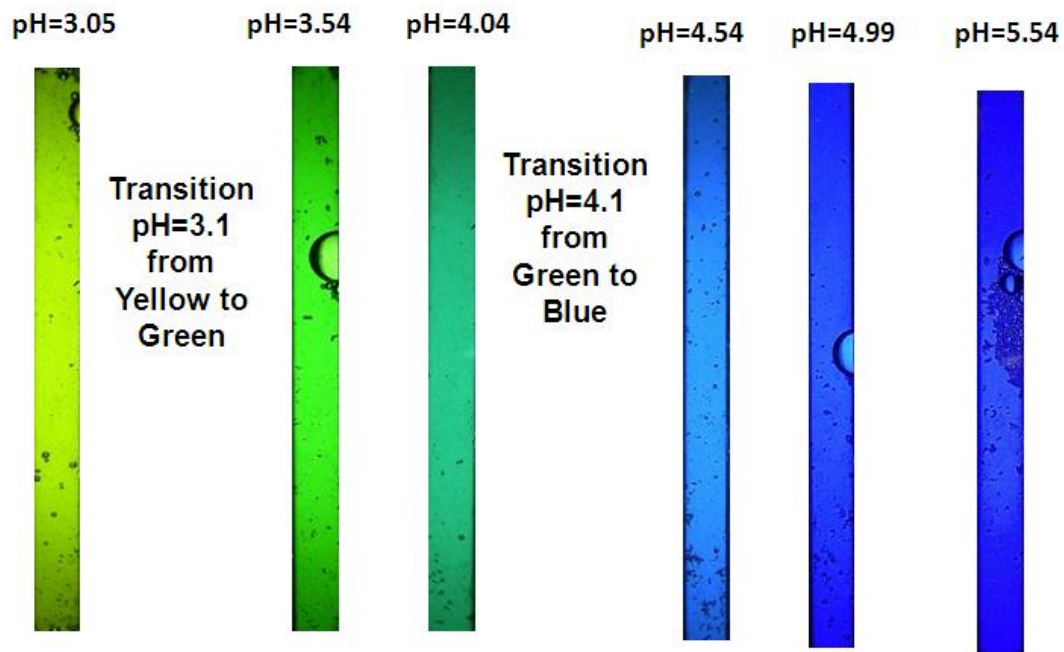


Figure 4-35 The color code of Bromocresol Green (BCG) in the presence of C12/brine. The pH is measured value in bulk aqueous phase

The pH of effluent out of core was determined by color code in Figure 4-34 in the absence of C12, and by color code in Figure 4-35 in the presence of C12. The color change in WAG (brine alternating CO₂) at 120 °C was shown in Figure 4-36. BCG solution at pH=4.42 was injected at 6.86 ml/min directly into the visual cell by auxiliary pump in the flooding process. The synthetic formation brine was injected at 0.98 ml/min (4 ft/day) through the core into the visual cell. This results

in the change of color from green to blue ($\text{pH} > 5.4$) because the equilibrium pH without CO_2 is 6.2 calculated by PHREEQC software. Brine alternating CO_2 (WAG) was injected at 50% foam quality and 0.98 ml/min of total flow rate, the color change to yellow after 4 PV ($\text{pH} < 3.8$), which was lower than the calculated result ($\text{pH} = 4.0$) in Figure 4-10. That's probably because that the equilibrium in dolomite core-brine- CO_2 system wasn't reached owing to the early break-through of injected fluids in WAG.

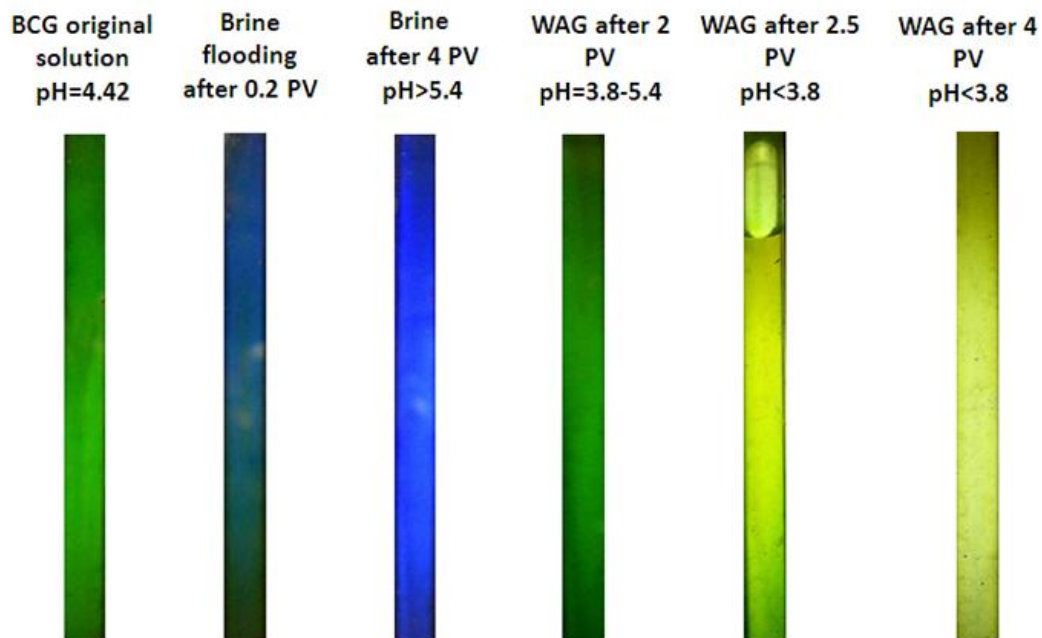


Figure 4-36 The color change of BCG during synthetic formation brine flooding and brine alternating CO_2 (WAG) flooding at 120 °C

C_{12} /brine and CO_2 were co-injected at 50% foam quality, room temperature and 0.98 ml/min of total flow rate, *i.e.*, 4 ft/day of superficial velocity. The pH of the effluent was interpreted from Figure 4-37. The color becomes green ($\text{pH} = 3.1-4.1$) after 1.5 PV. The fine bubbles were filled in the visual cell,

but the color of liquid was still green, as demonstrated at 3 and 4 PV in Figure 4-37, which implies the pH was 3.1-4.1 in the foam flooding process and was consistent with the calculated results (pH=4.0) in Figure 4-10.

Thus, the pH during CO₂ flooding is low enough to maintain C12 solubility at reservoir conditions and the equilibrium pH can be well predicted by PHREEQC software.

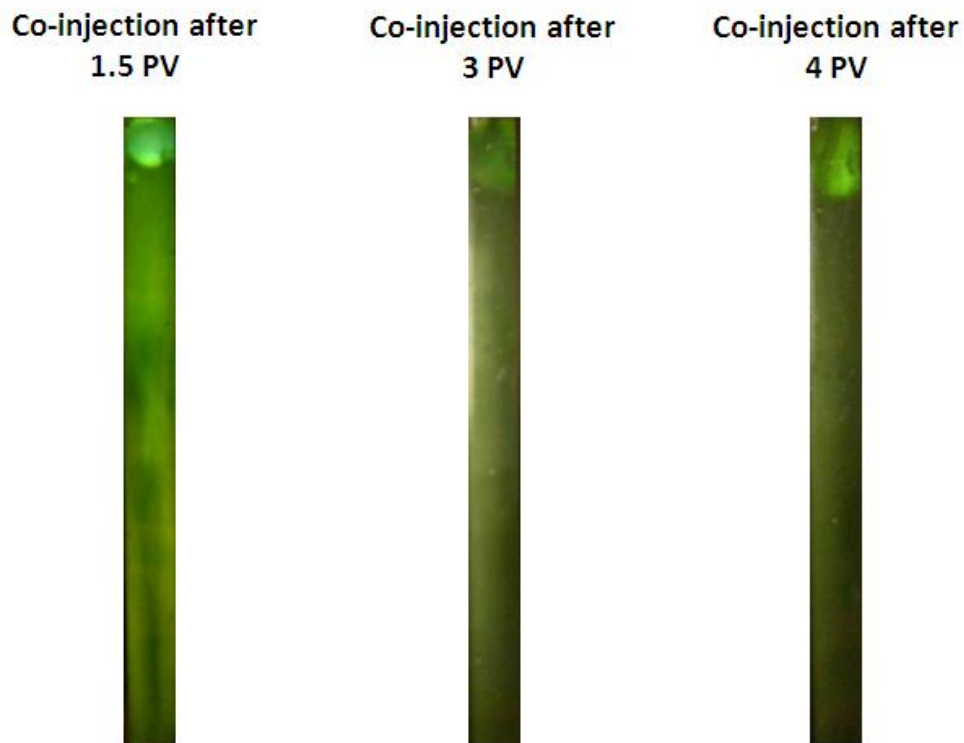


Figure 4-37 BCG is green color during C12/brine and CO₂ foam flooding. The pH=3.1-4.1

4.3 Conclusions

CO₂ foam can be generated by C12 at reservoir conditions. The high salinity in synthetic formation brine is favorable to foam strength, but the elevated reservoir temperature is detrimental.

The foam strength depends on the foam quality, salinity, temperature. The foam strength increased with foam quality in the “low quality” regime, reached the maximum value at transition foam quality, and decreased with increasing foam quality in the “high quality” regime because of the limiting capillary pressure.

The increase of salinity can enhance the packing density of surfactant on the water-gas interface, and decrease the electrostatic repulsion (Π_{elec}) of the double layers in the liquid film. These two competitive effects dominate the change of foam strength. The high salinity in reservoir brine was favorable to C12 and CO₂ foam, but was detrimental to glycidyl ether sulfonates, *i.e.*, N25-7EO and N67-9EO GS, and N₂ foam.

The temperature also affects the foam strength by two competitive effects, *i.e.*, the dehydration of EO and OH head groups and the enhancement of thermal motion for surfactant and gas molecules. The reservoir temperature (120 °C) detrimentally affected the C12 and CO₂ foam, *i.e.*, the strong foam at the reservoir temperature when it did form had lower apparent viscosity than that at room temperature. The minimum pressure gradient for C12/Brine and CO₂ foam at 120 °C was 10 psi/ft, above which the strong foam was generated.

The carbonate minerals can be significantly dissolved in DI water and CO₂. Thus, brine with sufficient Ca²⁺ and Mg²⁺ was suggested to be used for carbonate reservoirs.

The calculated pH in the carbonate-H₂O-CO₂ system at reservoir conditions was 4.0, which is low enough to maintain the solubility of C12 in CO₂ flooding process. And the calculated pH by PHREEQC software was verified by experimental observation.

4.4 References

- Alargova, R., Petkov, J., Petsev, D., Ivanov, I. B., Broze, G., & Mehreteab, A. (1995). Light scattering study of sodium dodecyl polyoxyethylene-2-sulfonate micelles in the presence of multivalent counterions. *Langmuir*, 11(5), 1530-1536.
- Angus, S., Armstrong, B., & de Reuck, K. M. (1976). *International Thermodynamic Tables of the Fluid State: Carbon Dioxide* (1st edition ed.). Oxford: A. Wheaton & Co., Exeter.
- Aronson, A. S., Bergeron, V., Fagan, M. E., & Radke, C. J. (1994). The influence of disjoining pressure on foam stability and flow in porous media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 83(2), 109-120.
- Bennion, B., & Bachu, S. (2008). Drainage and Imbibition Relative Permeability Relationships for Supercritical CO₂/Brine and H₂S/Brine Systems in Intergranular Sandstone, Carbonate, Shale, and Anhydrite Rocks. *SPE Reservoir Evaluation & Engineering*, 11(03), 487 - 496. SPE-99326-PA
- Bergeron, V., & Radke, C. J. (1992). Equilibrium Measurements of Oscillatory Disjoining Pressure in Aqueous Foam Films. *Langmuir*, 8(12), 3020-3026.
- Bhakta, A., & Ruckenstein, E. (1996). Modeling of the Generation and Collapse of Aqueous Foams. *Langmuir*, 12(12), 3089-3099.
- Chen, Y., Elhag, A. S., Poon, B. M., Cui, L., Ma, K., Liao, S. Y., Reddy, P. P., Worthen, A. J., Hirasaki G. J., Nguyen, Q. P., Biswal, S. L. and Johnston, K. P. (2014). Switchable Nonionic to Cationic Ethoxylated Amine Surfactants for CO₂ Enhanced Oil Recovery in High-Temperature, High-Salinity Carbonate Reservoirs. *SPE Journal*, 19 (02), 249 - 259. SPE-154222-PA

- Cheng, L., Reme, A. B., Shan, D., Coombe, D. A., & Rossen, W. R. (2000). Simulating Foam Processes at High and Low Foam Qualities. *SPE/DOE Improved Oil Recovery Symposium*. Tulsa, Oklahoma. SPE-59287-MS
- Energy Institute. (2010). *Good plant design and operation for onshore carbon capture installations and onshore pipelines* (1st edition ed.). London: the Energy Institute.
- Exerowa, D., Kashchiev, D., & Platikanov, D. (1992). Stability and permeability of amphiphile bilayers. *Advances in colloid and interface science*, 40, 201-256.
- Hirasaki, G., & Lawson, J. (1986). An Electrostatic Approach to the Association of Sodium and Calcium With Surfactant Micelles. *SPE Reservoir Engineering*, 1(2), 119-130. SPE-10921-PA
- Hurter, S., Berge, J. G., & Labregere, D. (2007). Simulations for CO₂ injection projects with Compositional Simulator. Aberdeen, Scotland, U.K.: Society of Petroleum Engineers. SPE-108540-MS
- Joye, J., Hirasaki, G. J., & Miller, C. A. (1994). Asymmetric Drainage in Foam Films. *Langmuir*, 10(9), 3174-3179.
- Kakaç, S., & Liu, H. (2002). *Heat Exchangers: Selection, Rating, and Thermal Design* (2nd edition ed.). CRC press.
- Krustev, R., & Müller, H. J. (1999). Effect of film free energy on the gas permeability of foam films. *Langmuir*, 15(6), 2134-2141.
- Langevin, D. (2000). Influence of interfacial rheology on foam and emulsion properties. *Advances in Colloid and Interface Science*, 88(1-2), 209–222.
- Ma, K., Lopez-Salinas, J. L., Puerto, M. C., Miller, C. A., Biswal, S. L., & Hirasaki, G. J. (2013(a)). Estimation of Parameters for the Simulation of Foam Flow through Porous Media. Part 1: The Dry-Out Effect. *Energy Fuels*, 27(5), 2363–2375.
- Muller, N., Qi, R., Mackie, E., Pruess, K., & Blunt, M. J. (2009). CO₂ injection impairment due to halite precipitation. *Energy Procedia*, 1(1), 3507-3514.
- Muruganathan, R. M., Krastev, R., Mueller, H. J., & Moehwald, H. (2006). Foam films stabilized with dodecyl maltoside. 2. Film stability and gas permeability. *Langmuir*, 22(19), 7981-7985.
- Muruganathan, R. M., Krustev, R., Ikeda, N., & Müller, H. J. (2003). Temperature dependence of the gas permeability of foam films stabilized by dodecyl maltoside. *Langmuir*, 19(7), 3062-3065.
- Pandey, S., Bagwe, R. P., & Shah, D. O. (2003). Effect of counterions on surface and foaming properties of dodecyl sulfate. *Journal of Colloid and Interface Science*, 267(1), 160-166.
- Ransohoff, T. C., & Radke, C. J. (1988). Mechanisms of Foam Generation in Glass-Bead Packs. *SPE Reservoir Engineering*, 3(02), 573 - 585. SPE-15441-PA

Rossen, W. R., & Wang, M. W. (1999). Modeling Foams for Acid Diversion. *SPE Journal*, 4(02), 92 - 100. SPE-56396-PA

Sabnis, R. W. (2007). *Handbook of acid-base indicators*. CRC Press. Boca Raton, FL.

Sammalkorpi, M., Karttunen, M., & Haataja, M. (2009). Ionic surfactant aggregates in saline solutions: sodium dodecyl sulfate (SDS) in the presence of excess sodium chloride (NaCl) or calcium chloride (CaCl₂). *The Journal of Physical Chemistry B*, 113(17), 5863-5870.

Vassenden, F., & Holt, T. (2000). Experimental Foundation for Relative Permeability Modeling of Foam. *SPE Reservoir Evaluation & Engineering*, 3(02), 179 - 185. SPE-62506-PA.

Wongwailikhit, K., Ohta, A., Seno, K., Nomura, A., Shinozuka, T., Takiue, T., et al. (2001). Temperature effect on the adsorption and micelle formation of pentaethylene glycol monoalkyl ethers. *The Journal of Physical Chemistry B*, 105(46), 11462-11467.

Yang, S. H., & Reed, R. L. (1989). Mobility Control Using CO₂ Forms. *SPE Annual Technical Conference and Exhibition*. San Antonio, Texas: Society of Petroleum Engineers. SPE-19689-MS

Chapter 5

Adsorption of Switchable Cationic Surfactants on Natural Carbonate Minerals

The adsorption of a switchable cationic surfactant, *i.e.*, Ethomeen C12, is discussed here. The surfactant concentration is determined by an improved methylene blue two-phase titration method, which is also introduced and demonstrated in this chapter.

5.1 Experimental

5.1.1 Materials

The chemicals used in this chapter were ACS or higher grade. All solutions were prepared in deionized (DI) water (18.2 M Ω).

0.03 g of methylene blue hydrate was dissolved in 1.0 L of Na₂SO₄-H₂SO₄ buffer which contained 50 g/L Na₂SO₄ and 6 ml/L fuming H₂SO₄, as the traditional MB color indicator for methylene blue (MB) two-phase titration. However SO₄²⁻ will precipitates with Ca²⁺ in brine, the MB solution has to be improved for the present work. 0.03 g methylene blue hydrate was dissolved in 1

L of a KCl-HCl acid solution which contained 5.52 g/L KCl and 126 ml/L HCl (1 M) as the new MB solution.

The immiscible organic phase was Chloroform (HPLC grade, catalog # 439142, Sigma-Aldrich Co.).

A synthetic formation brine contains high total dissolved solids (22% TDS) which was prepared with 182.31 g/L NaCl, 77.25 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 25.62 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in DI water.

Dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS) with chromatography analytical grade were accurately weighed and dissolved in DI water as stock solutions for calibrating the other surfactants. The concentration of SDS was $C_{\text{SDS}} = 4.009 \times 10^{-3} \text{ mol/L} = 4.009 \text{ mM}$, and the concentration of DTAB ranged from 2.001 to 20.08 mM.

A standard cationic titrant, *i.e.*, 1,3-Didecyl-2-methylimidazolium chloride (TEGO trant A 100), was used for determining anionic surfactant concentration (Gerlache, et al., 1997). The chemical was dissolved in DI water at a concentration of $C_{\text{TEGO}} = 3.823 \text{ mM}$ calibrated by SDS solution. A sodium lauryl ether sulfate with three ethylene oxide (EO) groups, *i.e.*, STEOL CS-330 (SDES, Stepan Co.), is more hydrophilic than SDS and can tolerate high salinity. SDES in DI water was used as an alternative anionic titrant in high salinity brine and was calibrated by TEGO. The concentration was $C_{\text{SDES}} = 5.313 \text{ mM}$.

A tertiary amine surfactant, *i.e.*, Ethomeen C12 (C12, AkzoNobel Co.), consists of one coco alkyl group (mixture from C6 to C18 alkyl chains) and two

EO group branches, as shown in Figure 5-1. C12 is a switchable cationic surfactant, *i.e.*, C12 is a nonionic surfactant at neutral and high pH, and is protonated to a cationic surfactant at low pH.

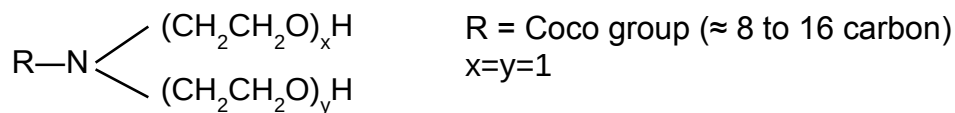


Figure 5-1 The molecular structure of Ethomeen C12

Table 5-1 The minerals used for adsorption measurement

Name	BET Surface Area (m ² /g)	Size (μm)	Resource	Preparation
Dolomite	0.97	≤74	Car Pool Co.	sieved through 200 mesh screen
Calcite	1.67	5	Alfa Aesar	N/A
Silica	1.16	≤10	US Silica Co.	washed with 1 mol/L HCl, 0.01 mol/L NaHCO ₃ and deionized water sequentially to remove the metal ions in original sands
Kaolin	26.61	0.1-4	Sigma-Aldrich	N/A

Four minerals as shown in Table 5-1 were used for the adsorption measurement. X-ray Photoelectron Spectroscopy (PHI Quantera XPS, Physical Electronics Inc.) analysis results for the surface chemistry of the minerals has been reported by Ma (2013, b) shown in Figure 5-2. The calcite, kaolin and silica sands are pure minerals and contain negligible impurities. However, the dolomite sands contain silica and aluminum impurities. Energy dispersive spectroscopy (EDAX, FEI Quanta 400) demonstrates that the silica and/or silicate impurity

distributed on the whole dolomite surface (1000X magnification, no coating on the surface), as shown in Figure 5-3.

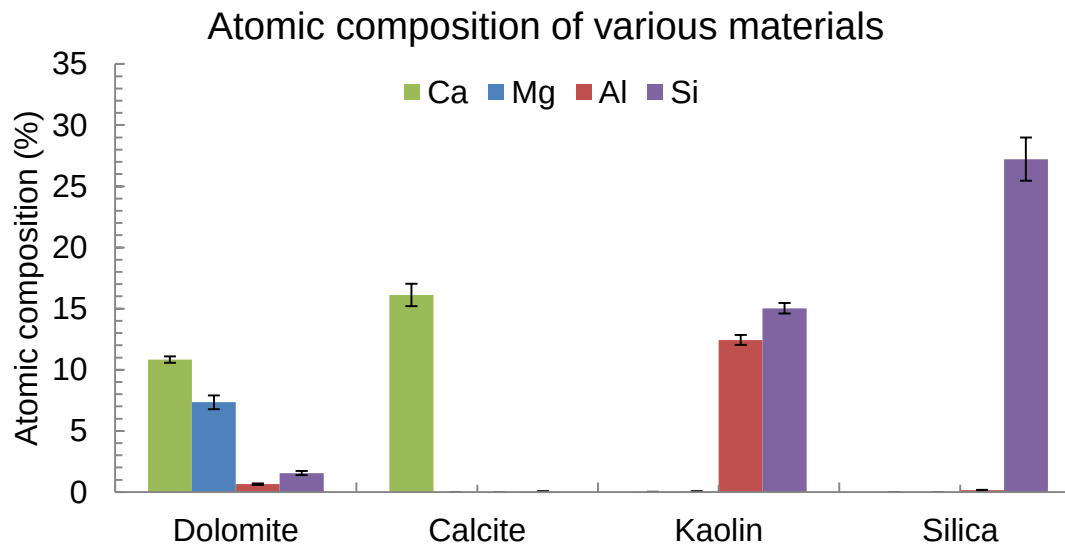


Figure 5-2 Analysis results of X-ray Photoelectron Spectroscopy (XPS) for mineral sands (Ma, 2013 b)

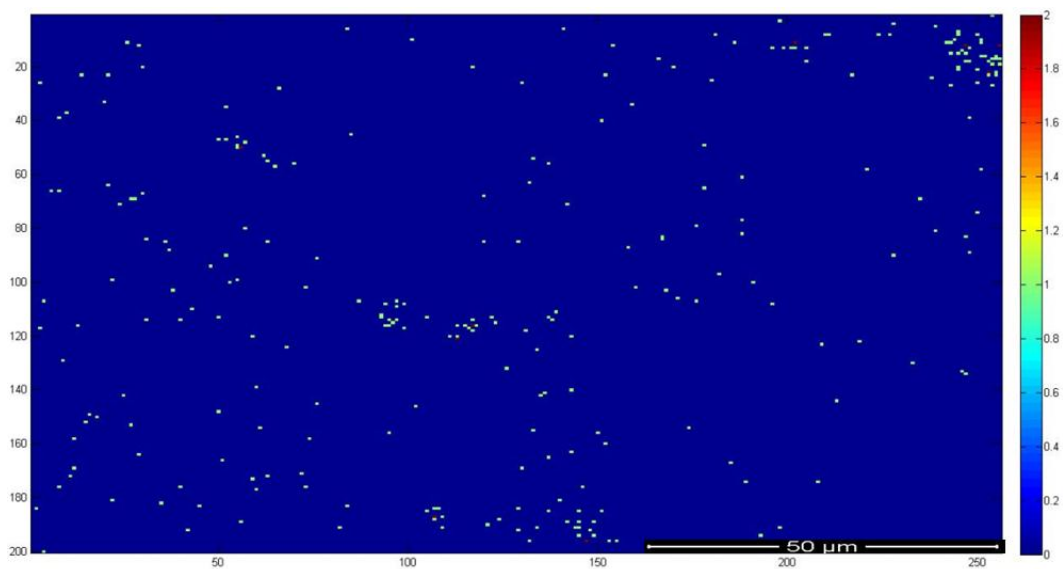


Figure 5-3 Energy dispersive spectroscopy scan of natural dolomite surface. The blue color is the carbonate surface background; other color spots are the silica and/or silicate impurity. The strength of silicon response increases from blue to red color

5.1.2 The Improved MB Two-Phase Titration

As discussed in section 2.4.1, the traditional MB two-phase titration can't accurately determine the surfactant concentration in high salinity brine. Thus, an improved MB two-phase titration was used to determine cationic surfactant concentration in various electrolytes, as described below.

The mixture of 5.0 ml chloroform, 2.0 ml MB solution and a specific amount of cationic surfactant sample (V_{sample}) was added in a glass vial (22.0 ml capacity). Initially, the anionic titrant was added by burette (10.0 ml capacity) for large amount, and was then added by pipette (2-20 μ l range) when approaching the end point. The vial was vigorously shaken to completely mix the two phases, after adding titrant. The two phases were clearly separated by centrifuging at 3,000 rpm for 1-3 minutes. The aqueous phase with volume of approximately 0.1 ml was transferred to a micro quartz cuvette for the light absorbance measurement at 655 nm (Hayashi, 1975) using a spectrophotometer (Genesys 10S UV-Vis). The light absorbance decreased with increasing titrant. The colorless end point defined as the point at which the absorbance fell below 0.04 was used as the stoichiometric end-point in high salinity brine. The volume of titrant added during the procedure was recorded as $V_{titrant}$.

A blank sample should be used to correct $V_{titrant}$, because of the consumption of titrant by MB. 5.0 ml chloroform, 2.0 ml MB solution, DI water at a volume of $V_{titrant}$, and the solvent used in the tested sample at a volume of V_{sample} were added to the vial to maintain the same ionic strength in the blank

test. For example, if 2.00 ml C12 in synthetic brine was titrated with 4.00 ml SDES titrant, 2.00 ml synthetic brine and 4.00 ml DI water should be combined with 5.0 ml chloroform and 2.0 ml MB solution for the blank test. The blank was titrated to reach the colorless end point. The volume of titrant used for the blank test was recorded as V_{blank} . Thus, the corrected volume of titrant consumed by blank test is calculated as $V_{cor.tit.} = V_{titrant} - V_{blank}$.

The sample concentration can be calculated by the following Equation 5-1:

$$C_{sample} \left(\frac{mol}{L} \right) = \frac{V_{cor.tit.}(ml) \times C_{titrant} \left(\frac{mol}{L} \right)}{V_{sample}(ml)}$$

Equation 5-1 Formula for sample concentration in MB two phase titration

5.1.3 Static Adsorption Measurement under 2 atm CO₂

The C12 was sparingly water-soluble at neutral and higher pH, but was completely or partially protonated to a water-soluble cationic surfactant at pH lower than 6 (the protonation degree is discussed in section 5.2.5), as shown in Figure 5-4. The cloud point of the C12 surfactant increases with decreasing pH, and can be enhanced above 120°C at pH=4, as discussed in Chapter 3.

Because acids will react with carbonate minerals, the pH of C12 solution was not suggested to be reduced by acid solutions for adsorption measurement or core flooding tests. The pH of aqueous solution can be stably reduced by CO₂, because of the buffer generated from carbonic acid and carbonate minerals. The pH of minerals-water-CO₂ system can be determined by PHREEQC software (de

Souza and Fjelde, 2013). The equilibrium pH at 2 atm. pressure of CO₂ is lower than 6 as demonstrated in Figure 5-5. This indicates that C12 was water soluble in the adsorption measurement at room temperature and 2 atmosphere pressure of CO₂.

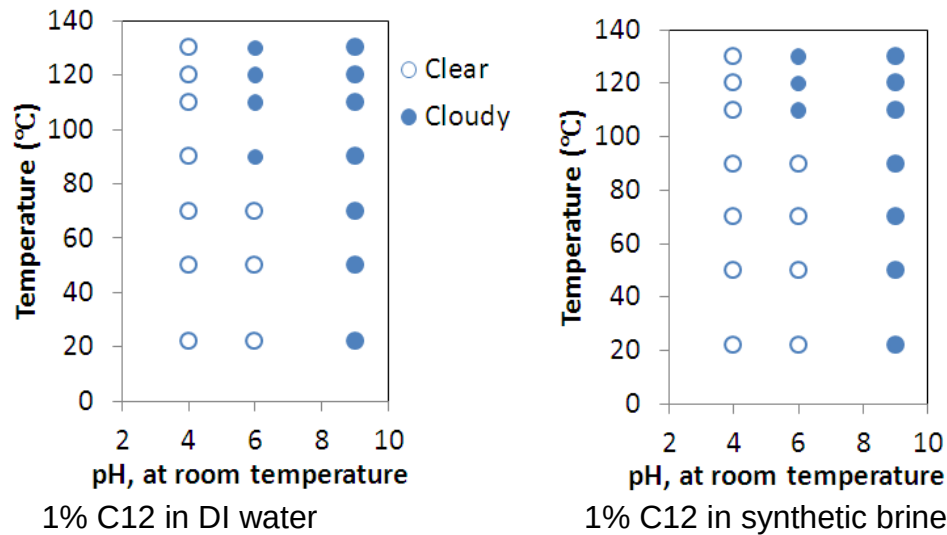


Figure 5-4 The cloud point of C12 at various pH. The pH is adjusted by HCl.

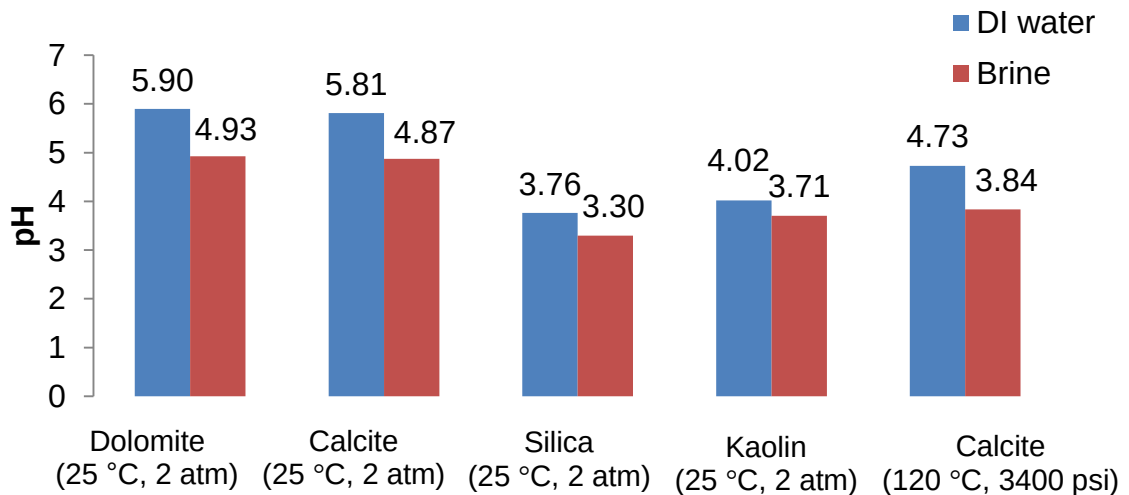


Figure 5-5 The equilibrium pH of minerals-water-CO₂ system, calculated with PHREEQC software. Equilibrium temperature and CO₂ pressure are in brackets.

Thus, static adsorption was measured at 2 atmosphere CO₂, as described below: (1) the clear C12 solution was obtained by purging CO₂ on the top of liquid surface. (2) The initial concentration of C12 solution was determined by MB two-phase titration. (3) Mineral sands and C12 solution were loaded in a 50 ml stainless steel cylinder. (4) 5 atmospheres (absolute pressure) of CO₂ was injected in the cylinder, and then was released to one atmosphere to purge the air out of the cylinder. (5) Previous step (4) was repeated for 5 times, so the residual air fraction was reduced to $(\frac{1}{5})^5 = \frac{1}{3125}$. (6) CO₂ at 2 atmospheres pressure (absolute pressure) was injected in the cylinder. (7) The equilibrium of adsorption was reached by shaking the cylinder for 24 hours. (8) The cylinder stood overnight to roughly separate the liquid and solid mineral. (9) The upper layer of the liquid was withdrawn and was centrifuged at 8,000 rpm for 30 minutes. (10) The supernatant of the centrifuged sample was titrated by MB two-phase titration for determining the residual C12 concentration. The adsorption can be calculated based on following Equation 5-2:

$$\text{adsorption} \left(\frac{mg}{m^2} \right) = \frac{\left(C_{initial} - C_{residual} \left(\frac{mol}{g} \right) \right) \times m_{C12} (g) \times MW \left(\frac{g}{mol} \right) \times 1000 \left(\frac{mg}{g} \right)}{m_{sand} (g) \times A_{sand} \left(\frac{m^2}{g} \right)}$$

Equation 5-2 Formula for adsorption calculation

where, $C_{initial}$ and $C_{residual}$ are the initial and residual concentration of C12 solutions; m_{C12} and m_{sand} are the mass of C12 solution and sands loaded in the

cylinder; MW is the molecular weight of C12, *i.e.*, 288 g/mol reported by Akzo Nobel Co. A_{sand} is the BET surface area of the sand.

5.2 Results and Discussions

5.2.1 Spectrophotometric Parameters in MB Two Phase Titration

The colorless end point was proposed by Cullum (1994) to replace the Epton's end point for minimizing the titration error. However, it is hard to determine the colorless end point by visual check, which results in the limited application in the two-phase titration methods. Here, we demonstrated that the colorless end point was accurately and efficiently determined by a spectrophotometer. The spectrophotometric parameters in the measurement, *i.e.*, the characteristic wavelength and threshold absorbance for the colorless end point, are discussed below.

The light absorbance curves of the MB active substance in DI water and chloroform are compared in Figure 5-6. The "MB in the DI water" sample is the same as the new MB solution. The "MB in chloroform" was prepared by adding excess SDS titrant in the mixture of 2.0 ml of the new MB solution and equaled volume of chloroform. Thus, the same volumetric concentration of MB active substance was archived in DI water and chloroform. In the range of light wavelength from 655 to 671 nm, the absorbance of the two phases overlapped and reached peaks, indicating that the measurement achieved optimal sensitivity in this range, as demonstrated in Figure 5-6. 655 nm was proposed to be used

as the characteristic wavelength in the present work, because of the sharp decrease beyond the right boundary (671 nm),

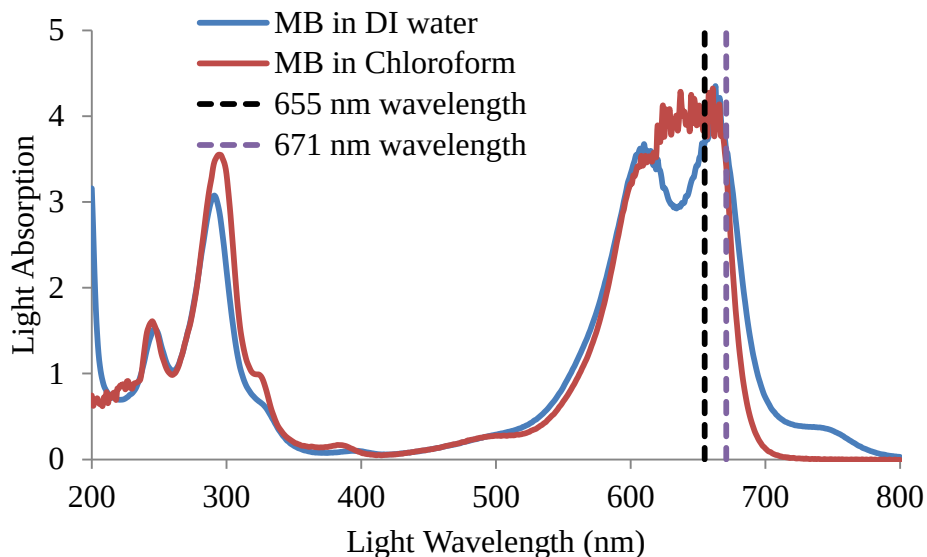


Figure 5-6 The curves of light absorbance for MB active substance in DI water and chloroform

The color change from slightly blue to completely colorless was difficult to ascertain by visual check. The light absorbance measurement at $\lambda=655$ nm can be used as a reference. The light absorbance decreased with dilution factor which represents the ratio of the original volume of the MB sample to the total volume of the diluted sample, as demonstrated in Figure 5-7. At absorbance equals to 0.04, the blue color was nearly visually undetectable. Thus, the threshold light absorbance was set at 0.04; that is, when the light absorbance at $\lambda=655$ nm fell below 0.04, the sample was said to have reached the colorless end point.

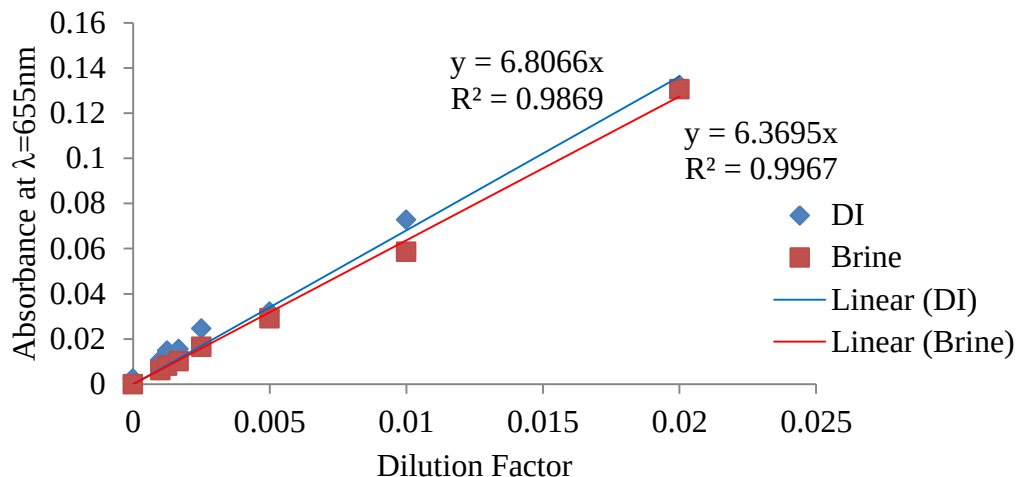


Figure 5-7 The light absorbance at $\lambda=655$ nm for various dilutions of MB solutions. DI indicates that the MB solution was diluted with DI water, and Brine indicates that the MB solution was diluted with synthetic brine

The dilution factor was 0.006 for MB in both water and chloroform at this point calculated from the equation in Figure 5-7, which indicates trace amount of MB was left at the absorbance threshold of 0.04. The ratio of unreacted MB to total MB at the threshold point is shown in Equation 5-3:

$$\frac{\text{unreacted MB}}{\text{total MB}} = \frac{C_{\text{residual}}}{C_{\text{initial}}} \times \frac{V_{\text{final}}}{V_{\text{initial}}} = \text{dilution factor} \times \frac{V_{\text{final}}}{V_{\text{initial}}} = 0.006 \times \frac{V_{\text{final}}}{V_{\text{initial}}}$$

Equation 5-3 The ratio of unreacted MB to total MB at the threshold point

where C_{residual} is the residual MB concentration in the aqueous phase, C_{initial} is the initial MB concentration in the MB solution, V_{final} is the final aqueous volume at the end point, and V_{initial} is the volume of the MB solution.

Usually, $\frac{V_{final}}{V_{initial}} < 5$, so $\frac{unreacted\ MB}{total\ MB} < 3.0\%$, which indicates that less than 3.0% of the MB was unreacted at the threshold point. This was deemed an acceptable error.

5.2.2 MB Two-Phase Titration with a Colorless End Point for Cationic Surfactants in DI Water

The cationic surfactant sample was DTAB in DI water. Two anionic titrants were SDS and SDES in DI water. MB two-phase titration with a colorless end point was the titration procedure, as described in section 5.1.2.

4.012 mM DTAB was titrated with 4.009 mM SDS, as demonstrated in Figure 5-8. Three DTAB samples with different sizes were titrated. The slope of the titration curve was equal to $\frac{V_{cor.tit.}(ml)}{V_{sample}(ml)}$. Thus, Equation 5-1 can be expressed as following Equation 5-4:

$$C_{sample} \left(\frac{mol}{L} \right) = Slope \times C_{titrant} \left(\frac{mol}{L} \right)$$

Equation 5-4 Formula for sample concentration with titration slope

The titrated concentration of the DTAB sample in Figure 5-8 was equal to:

$$C_{sample} = 0.9916 \times 4.009 = 3.975\ mM.$$

The error was determined as:

$$Error = \frac{|C_{mass} - C_{sample}|}{C_{mass}} = \frac{|4.012 - 3.975|}{4.012} = 0.92\%$$

where C_{mass} is the DTAB concentration calculated from the mass and was taken to be the true concentration.

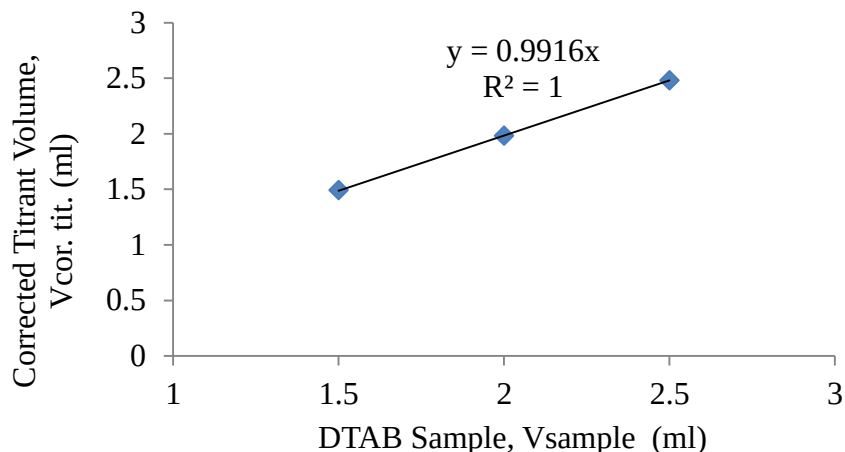
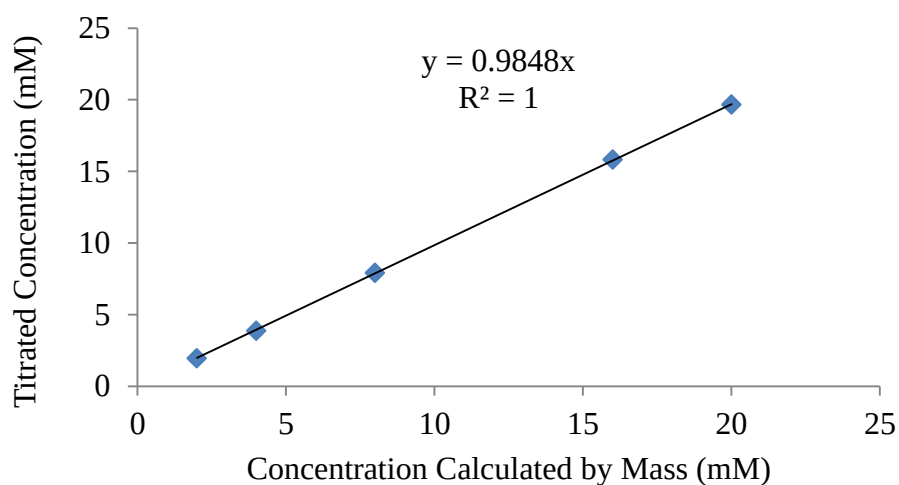


Figure 5-8 DTAB (4.012 mM) was titrated by SDS (4.009 mM). The corrected volume of the SDS titrant is determined by $V_{cor.tit.} = V_{titrant} - V_{blank}$

DTAB samples ranging from 2 mM to 20 mM in DI water were titrated by SDES in DI water using the same procedure. Figure 5-9 and Table 5-2 demonstrated the comparison of the titrated concentration and concentration calculated by mass. The largest error was 3.3%, and the overall error calculated from the slope in Figure 5-9 was 1.5%, both of which are acceptable error in our titration work.

Table 5-2 The results of DTAB in DI water titrated by SDES

Concentration Calculated by Mass (mM)	Titrated Concentration (mM)	Error (%)	Overall Error (%)
2.001	1.936	3.3	
4.002	3.872	3.3	$= 1 - \text{slope} \times 100$
8.004	7.911	1.2	$= 1 - 0.9848 \times 100$
16.01	15.82	1.2	$= 1.5$
20.01	19.67	1.7	

**Figure 5-9 A comparison of the titrated concentration and concentration calculated by mass of DTAB in DI water**

Thus, the MB two-phase titration with a colorless end point can be used to accurately determine cationic surfactant concentrations in DI water.

5.2.3 The Influence of Salinity on the MB Two-Phase Titration

MB can form ion pairs with inorganic anions, such as Cl^- , and be extracted into the chloroform phase, which results in the color transfer in the absence of surfactant. Additionally, SO_4^{2-} ions in the traditional MB solution precipitated with Ca^{2+} in brine.

5.0 ml chloroform, 2.0 ml standard MB solution and 1.0 ml aqueous solution (DI water, NaCl solutions or synthetic brine) were added in a vial, vigorously shaken and centrifuged at 3,000 rpm for 1 minute. The colors and light absorbance at $\lambda=655$ nm for both phases are illustrated in Figure 5-10. The blue color in the chloroform phase became darker with increasing salinity. The equally blue in two phases was reached at a certain salinity threshold, indicating that Epton's end point was reached at this salinity even without the addition of anionic titrant and was never reached in higher salinity brine. Thus, Epton's end point cannot be used as the stoichiometric end point for MB two-phase titration in brine.

The white precipitate, *i.e.*, CaSO_4 , accumulated between the two phases, interfered with the color judgment, as shown for the synthetic brine case in Figure 5-10. Therefore, the KCl-HCl acid solution was used to replace $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$ buffer in the traditional MB if Ca^{2+} is present in the brine.

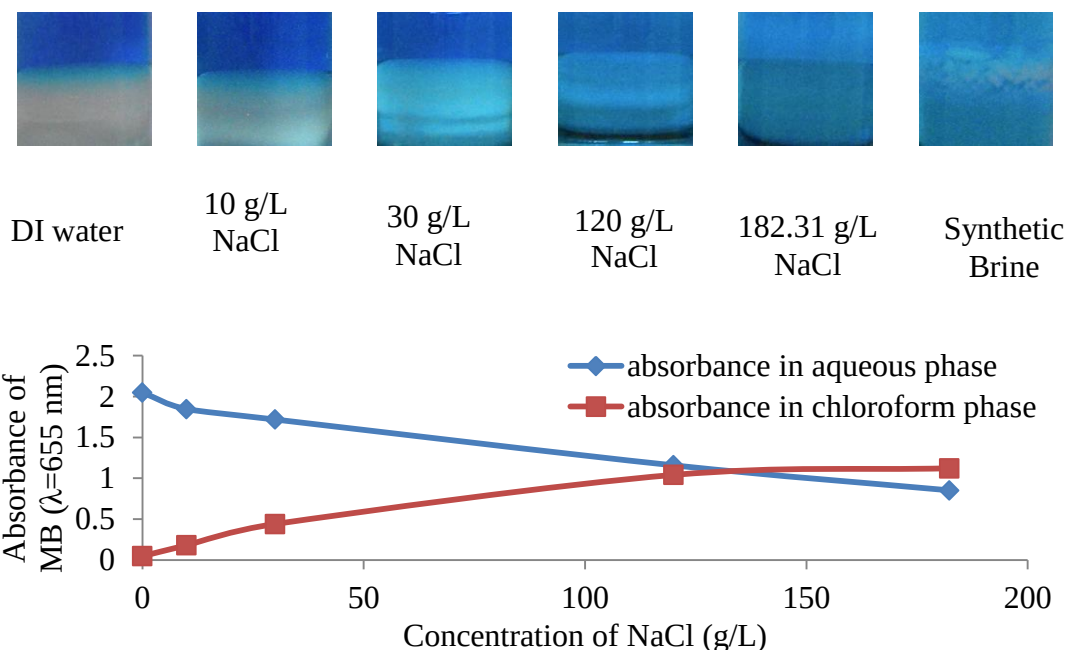


Figure 5-10 The influence of salinity on the MB two-phase titration. 5.0 ml chloroform, 2.0 ml traditional MB solution and 1.0 ml aqueous phase (various) were added in each vial

SDS which is a common anionic titrant for determining cationic surfactant concentrations (Jansson, et al., 1974; Ma, et al., 2013 b), precipitates in high salinity brine, especially in the presence of multivalent cations (Sammalkorpi, et al., 2009; Vasilescu, et al., 2004). Additionally, the inorganic cations in brine can screen the SDS negative electric potential (Sammalkorpi, et al., 2007 and 2009), which results in the insensitivity of end point to titrant, especially for potentiometric titration. As a result, the sample concentration is over-estimated with SDS titrant.

Three ethylene oxide (EO) groups are contained in SDES, *i.e.*, STEOL CS-330. Consequently, SDES is more hydrophilic and can tolerate higher salinity

in comparison with SDS. Precipitation was not observed for SDES dissolved in synthetic brine. Blank tests at various salinities were conducted. 5.0 ml chloroform, 2.0 ml new MB solution and 4.0 ml aqueous solution (synthetic brine and DI water) were added to the vial and titrated with SDS and SDES, respectively. The consumed SDS volume increased with salinity, but the SDES volume was nearly constant, as demonstrated in Figure 5-11. That's because the extra SDS was consumed by inorganic salts.

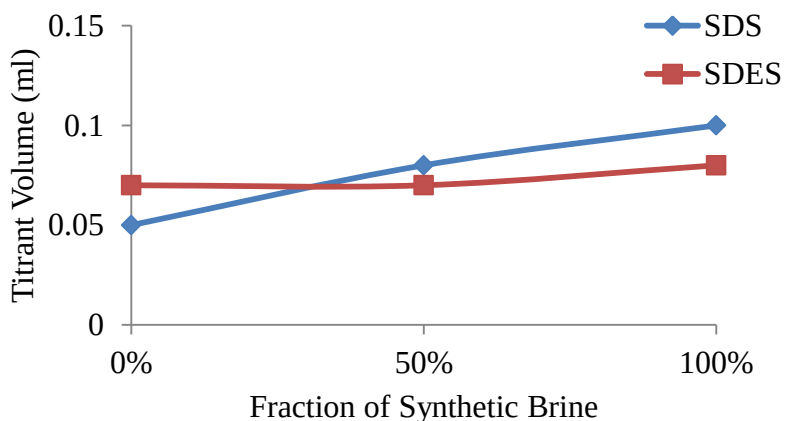
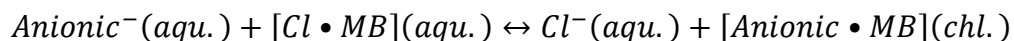


Figure 5-11 The consumed SDS and SDES volumes in the blank tests at various salinities

Therefore, for MB two-phase titration in high salinity brine, the colorless end point was chosen as the stoichiometric end point, because the influence of salinity on MB can be eliminated as shown in Reaction 5-1. The KCl-HCl acid solution was used to replace $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$ buffer in MB solution. Additionally, SDES was used instead of SDS as the anionic titrant.



Reaction 5 – 1

5.2.4 MB Two-Phase Titration for Cationic Surfactants in High Salinity Brine

DTAB in synthetic brine at concentrations ranging from 2 mM to 20 mM was titrated by SDES using MB two-phase titration at the colorless end point. Figure 5-12 demonstrates an example for DTAB in brine at 4.022 mM titrated by 5.313 mM SDES. The titrated concentration was 4.053 mM with an error of 0.77%.

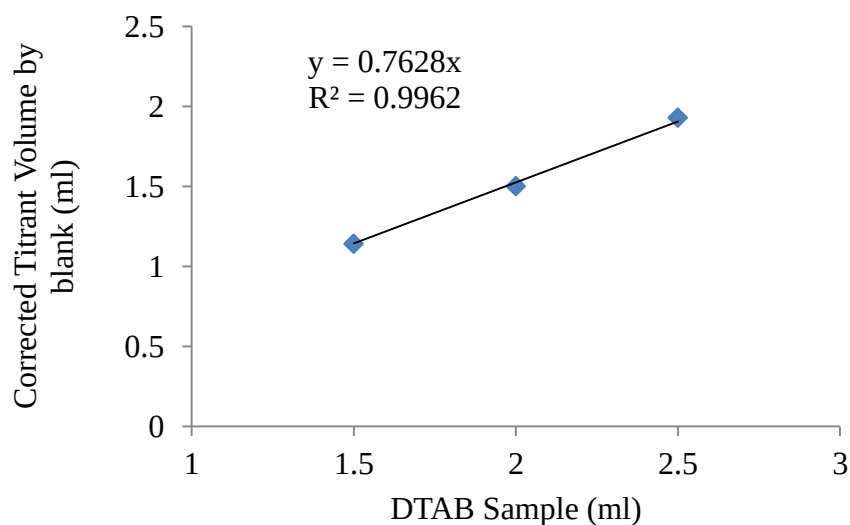


Figure 5-12 Titration curve for DTAB in synthetic brine (4.022 mM) titrated with SDES in DI water (5.313 mM)

The comparison of the titrated concentration and concentration calculated by mass for DTAB in synthetic brine is demonstrated in Figure 5-13 and Table 5-3. The largest error observed was 1.7%, and the overall error was 0.98%. The

errors were acceptable, indicating that the concentrations of cationic surfactants can be determined by MB two-phase titration at the colorless end point using SDES as the anionic titrant.

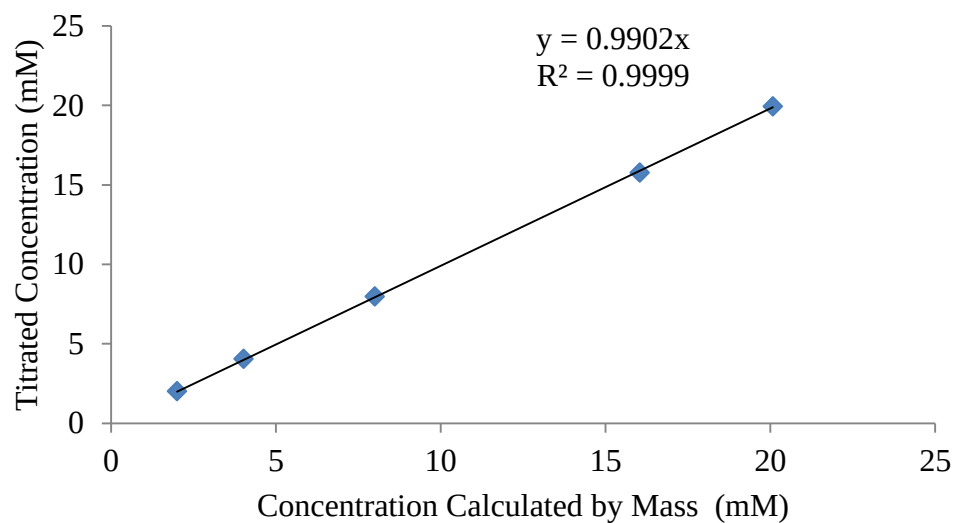


Figure 5-13 The comparison of the titrated concentration and concentration calculated by mass for DTAB in synthetic brine samples

Table 5-3 The results for DTAB in synthetic brine titrated by SDES

Concentration Calculated by Mass (mM)	Titrated Concentration (mM)	Error (%)	Overall Error (%)
2.001	2.013	0.58	
4.022	4.053	0.77	$= 1 - \text{slope} \times 100$
8.004	7.967	0.47	$= 1 - 0.9902 \times 100$
16.04	15.77	1.7	$= 0.98$
20.08	19.94	0.68	

5.2.5 MB Two-Phase Titration for Switchable Cationic Surfactants

Acid-base titration method can determine the concentrations of amine surfactants, *e.g.*, Ethomeen C12, using hydrochloric acid (HCl) solution (Underwood, 1977; Kakehashia, et al., 2001). The changes of pH in bulk solution during acid-base titration was demonstrated in Figure 5-14, in which 1.007 g C12 was added to 50 ml DI water and titrated with 1.000 mol/L HCl solution. C12 solution was initially cloudy but gradually became clear with the addition of HCl solution, which is consistent with the cloud point tests in Figure 5-4. The potentiometric end point was reached at 3.30 ml HCl solution. The activity of C12 can be calculated by the following Equation 5-5:

$$Activity = \frac{\text{titrated mass}}{\text{weighted mass}} = \frac{\text{titrated mole} \times \text{molecular weight}}{\text{weighted mass}}$$

Equation 5-5 Formula for activity of surfactant

Thus, the activity of C12 commercial sample determined by the acid-base titration is $\frac{3.30 \times 10^{-3} \text{ (mol)} \times 288 \text{ (g/mol)}}{1.007 \text{ (g)}} = 94.4\%$.

The pH of the bulk solution at the end point was 4.2. The bulk pH is expected to be lower than the pH near the cationic micelle surface, because hydronium ions are partially excluded from the double layer of the micelle due to electric repulsion (Hirasaki and Lawson, 1986). This electric repulsion is reduced by increasing the ionic strength. Thus, the equilibrium pH at the acid-base titration end point in high salinity brine is expected to be higher than 4.2.

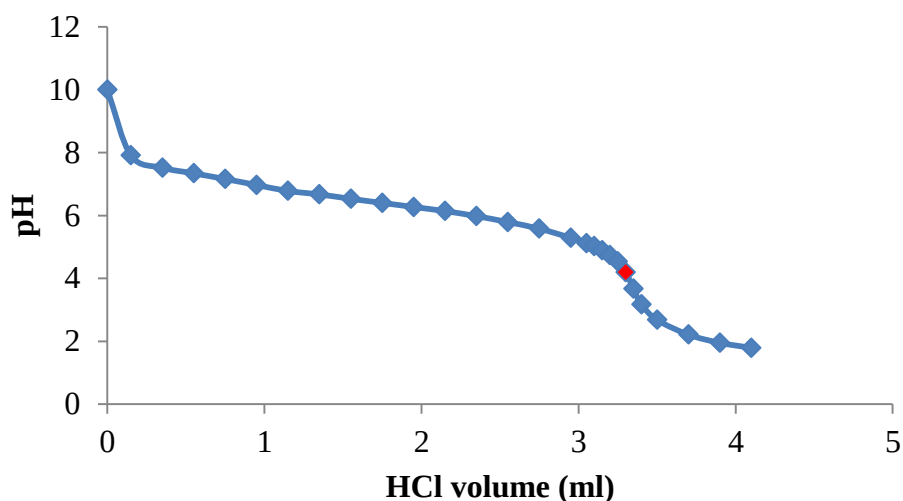
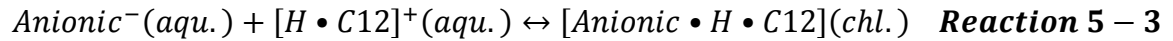
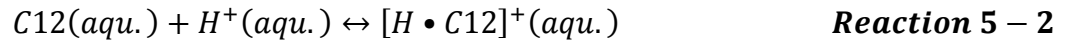


Figure 5-14 The pH changed with added HCl volume

In CO₂ flooding process, the pH in the carbonate reservoir is approximately pH 4-5 (Friedmann, et al., 1999; Oddo and Tomson, 1982), at which point either all or a portion of the C12 is protonated. Thus, the acid-base titration method cannot be used for determining C12 concentration. The MB two-phase titration provides a better alternative.

The pH of the new MB solution was approximately 1. The dilution factor of the MB solution was typically higher than 0.2 in the titration process, which indicates that the pH of the aqueous phase remained far below 4. The C12 was completely protonated in the titration process. The reactions in titration process are described below:



The activity of C12 commercial sample was also determined by MB two-phase titration at colorless end point, as described below: (1) a specified amount of C12 surfactant was dissolved in DI water or synthetic brine. (2) CO₂ is purged from the top of the solution to obtain a clear solution. (3) C12 molar concentration is determined with SDES and MB two-phase titration at colorless end point. (4) Finally, the molar concentration was converted to a weight percentage using the molecular weight of C12 (288 g/mol, as reported by AkzoNobel Co.). A comparison of the titrated and weighted C12 concentration is shown in Figure 5-15. The slope (0.9102=91.02%) is equal to the activity of C12 commercial sample, which is lower than the activity (94.4%) determined by acid-base

titration. The error is 3.6% if the activity determined by the acid-base titration is assumed to be the true value.

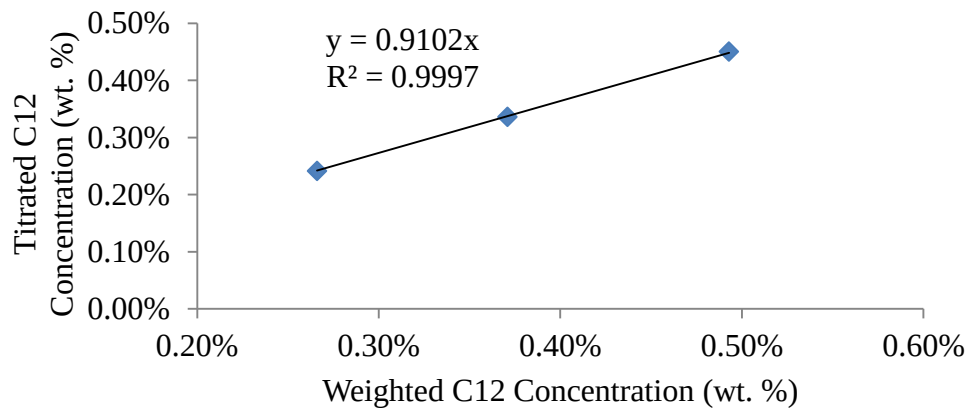


Figure 5-15 A comparison of the weighted and titrated concentration for C12 in DI water.

Both C12 activities measured above are lower than the activity (97%-100%) reported in the MSDS from the AkzoNobel Company. This is most likely due to an underestimation of the average molecular weight of C12. The average molecular weight of the coco alkyl group in C12 was accounted from C6 to C18 carbon chains (AkzoNobel, 2008). However, our HPLC analysis revealed that the C12 surfactant contained negligible amount of C6 to C10 components, as demonstrated in Figure 5-16, which results in the lower reported molecular weight than real value and the underestimation of C12 activity. The calibration of the molecular weights of fatty amines (Lang, et al., 1999) is beyond the scope of this study, so we still used the molecular weight (288 g/mol) provided by the manufacturer in the present work.

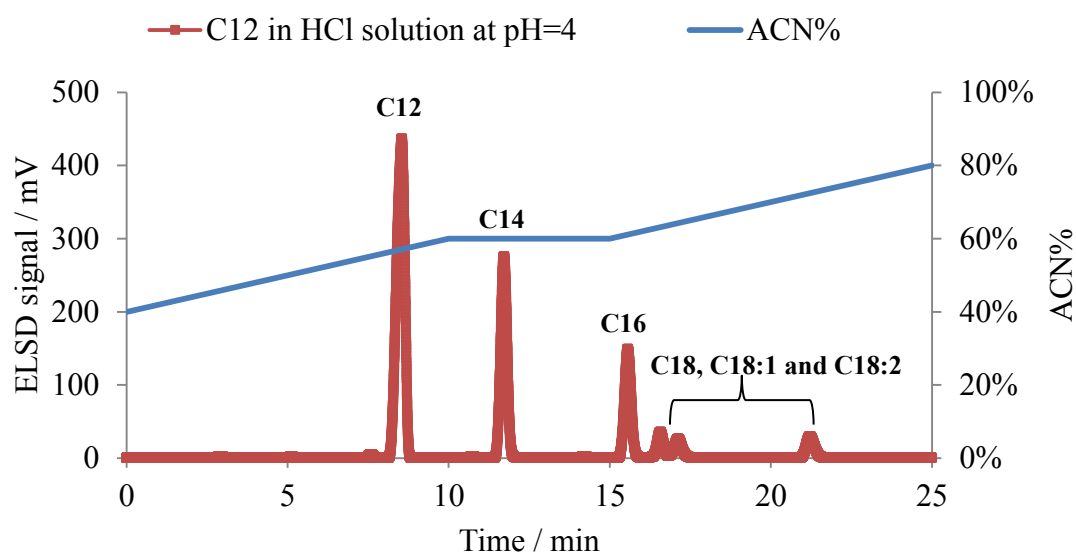


Figure 5-16 The results of HPLC analysis for 1% C12 in DI water. A surfactant column (Dionex Acclaim Surfactant, 4.6×250 mm, at 25°C) and an evaporative light scattering detector (ELSD, at 60°C) were used. C18:1 and C18:2 indicate the degrees of unsaturation are 1 and 2, respectively

Thus, MB two-phase titration at the colorless end point can be used for determining the concentration of the switchable cationic surfactant. Additionally, the activity of C12 commercial sample determined by MB two-phase titration (91.0%) was lower than the value determined by acid-base titration method (94.4%) with 3.6% error.

5.2.6 The Surface Charge and Zeta Potential of Carbonate Minerals

The adsorption of cationic surfactant on carbonate minerals is generally expected to be low, because of the positive surface charge of carbonate minerals at $\text{pH} < 9$ (Somasundaran and Agar, 1967; Pokrovsky, et al., 1999). However, the potential determining ions, e.g., Ca^{2+} and CO_3^{2-} , can affect the surface charge and cause negative zeta potential at neutral or lower pH (Hirasaki and Zhang,

2004; Heberling, et al., 2011). Thus, potential determining ions should be analyzed for determining the surface charge.

Calcite-H₂O-CO₂

Calcite-H₂O-CO₂ system was analyzed as an example. Ca²⁺ and CO₃²⁻ are assumed to be the potential determining ions (Somasundaran and Agar, 1967; Heberling, et al., 2011). Higher calcium ions concentration leads to more positive surface charge, and higher carbonate ions concentration leads to more negative surface charge.

There are 9 species constrained by 5 reactions in 3 phases, as listed in Table 5-4. Thus, the total freedom degree of the system is 3. Here, the surface charge is considered as a variable which is constrained by concentrations of potential determining ions and does not affect the total degrees of freedom. At 25 °C, the concentrations of potential determining ions are functions of two arbitrary variables, e.g., pH and partial pressure of CO₂, expressed in Equation 5-6 and Equation 5-7.

$$[Ca^{2+}] = \frac{K_{sp}[H^+]^2}{K_1K_2K_HP_{CO_2}}$$

Equation 5-6 Calcium concentration in Calcite-H₂O-CO₂ system

$$[CO_3^{2-}] = \frac{K_1K_2K_HP_{CO_2}}{[H^+]^2}$$

Equation 5-7 Carbonate concentration in Calcite-H₂O-CO₂ system

Table 5-4 The reactions and equilibrium constants of calcite-CO₂-H₂O system at 25 °C and low ionic strength (activity coefficient=1), (Ma, et al., 2013)

Reaction	Equilibrium Constant	-log ₁₀ (K) at 25 °C
$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	$K_{sp} = [Ca^{2+}][CO_3^{2-}]$	8.42
$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3$	$K_H = \frac{[H_2CO_3]}{P_{CO_2}}$	1.47
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$	6.35
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$	10.33
$H_2O(l) \leftrightarrow H^+ + OH^-$	$K_W = [H^+][OH^-]$	14.0

Zero surface charge (zeta potential=0) was added as another constrain, so the system depends on only one variable, *i.e.*, the pH is determined by the partial pressure of CO₂ as well. Heberling, et al. (2011) reported a linear relationship between pH and log(*P*_{CO₂}) at 25 °C and zero zeta potential in low ionic strength solutions with empirical regression: log(*P*_{CO₂})= -1.71 pH+11.2, as shown in Figure 5-17. Thus, the potential determining ions concentrations can be calculated as expressed in Equation 5-8 and Equation 5-9 at zero zeta potential and 25 °C. Note that the potential determining ion concentration at the condition of zero zeta potential is denoted with the superscript (*).

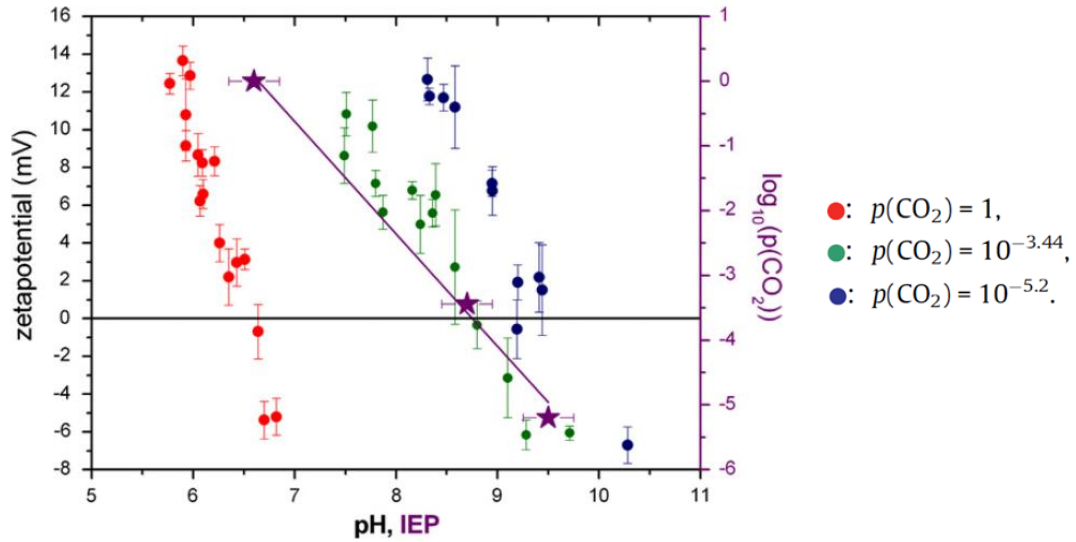


Figure 5-17 Zetapotential measurements in equilibrium solutions at various CO₂ partial pressures. Purple asterisks and line display the linear relation between IEP and log₁₀(pCO₂)), cited from Heberling, et al. (2011)

$$[Ca^{2+}]^* = \frac{K_{sp} (P_{CO_2})^{0.17}}{1.3 \times 10^{13} K_1 K_2 K_H}$$

Equation 5-8 Isoelectric calcium concentration in Calcite-H₂O-CO₂ system

$$[CO_3^{2-}]^* = \frac{1.3 \times 10^{13} K_1 K_2 K_H}{(P_{CO_2})^{0.17}}$$

Equation 5-9 Isoelectric carbonate concentration in Calcite-H₂O-CO₂ system

The carbonate ion concentration is constrained by calcium concentration and solubility product. Thus, only calcium concentration is needed to specify the condition of zero zeta potential at a given temperature. $[Ca^{2+}]^*$ can be assumed nearly a constant for P_{CO_2} higher than 1 atm, as demonstrated in Figure 5-18. This observation states that the concentrations of the potential determining ions

are approximately constant for the condition of zero zeta potential for a given temperature even though the CO_2 pressure may vary widely. This quantity may be called the isoelectric calcium concentration, $[\text{Ca}^{2+}]^*$. The sign of zeta potential and surface charge can be easily judged by comparison of $[\text{Ca}^{2+}]^*$ to calcium concentration in brine. If the calcium concentration of the brine is greater than $[\text{Ca}^{2+}]^*$, then the zeta potential should be positive; and if the calcium concentration of the brine is less than $[\text{Ca}^{2+}]^*$, then the zeta potential should be negative. Generally the sign of the surface charge is the same as that of the zeta potential.

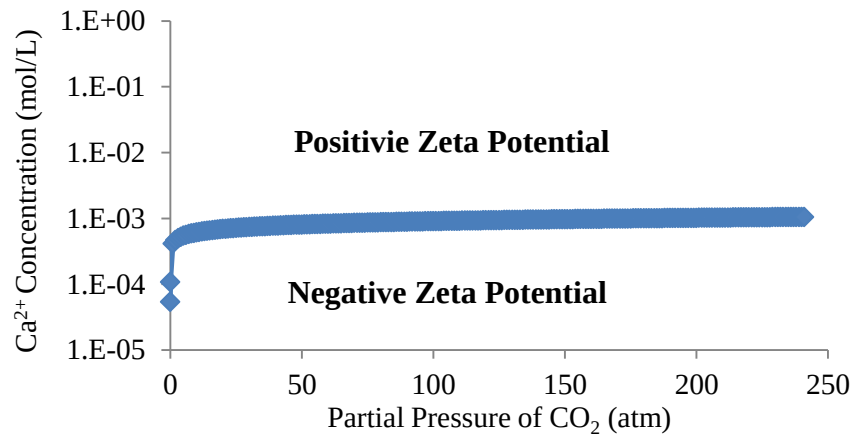


Figure 5-18 The Ca^{2+} concentrations at zero zeta potential and 25 °C at various partial pressure of CO_2

Dolomite- H_2O - CO_2

Dolomite- H_2O - CO_2 system contains one more potential determining ion, *i.e.*, Mg^{2+} , but the number of reactions is still 5, as listed in Table 5-5, which results the total degrees of freedom are 4. At a given temperature and zero zeta potential, the degrees of freedom are 2, which indicate that the pH and partial

pressure of CO₂ can be independent variables. The similar relationship between pH and P_{CO2} in Calcite- H₂O-CO₂ system does not exist in Dolomite-H₂O-CO₂ system. The isoelectric concentration of calcium and magnesium depends on both pH and P_{CO2}. The similar relationship in Figure 5-18 can't be archived for dolomite. However, Pokrovsky, et al. (1999) has measured the zeta potential data at various calcium and magnesium activities, from which similar interpretation for dolomite zeta potential may be possible. The measured isoelectric calcium and magnesium activities at zero zeta potential, respectively, *i.e.*, $a_{Ca^{2+}}^* = 3.16 \times 10^{-4}$ mol/L and $a_{Mg^{2+}}^* = 6.31 \times 10^{-4}$ mol/L.

Table 5-5 The reactions and equilibrium constants of dolomite-CO₂-H₂O system at 25 °C and low ionic strength (activity coefficient=1) (Ma, et al. 2013; Hyeonga and Capuano, 2001)

Reaction	Equilibrium Constant	-log ₁₀ (K) at 25 °C
$CaMg(CO_3)_2 \leftrightarrow Ca^{2+} + Mg^{2+} + CO_3^{2-}$	$K_{sp} = [Ca^{2+}][Mg^{2+}][CO_3^{2-}]^2$	16.9
$CO_2 (g) + H_2O (l) \leftrightarrow H_2CO_3$	$K_H = \frac{[H_2CO_3]}{P_{CO_2}}$	1.47
$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$	6.35
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$	10.33
$H_2O (l) \leftrightarrow H^+ + OH^-$	$K_W = [H^+][OH^-]$	14.0

High salinity brine

In high salinity brine, activities of Ca^{2+} and Mg^{2+} are used to determine the surface charge. The activities of Ca^{2+} and Mg^{2+} ions in adsorption tests calculated with PHREEQC (version 3.0.2) software are compared with the concentrations and activities at zero zeta potential, as listed in Table 5-6.

Table 5-6 Me^{2+} activities and isoelectric concentrations during adsorption tests on carbonate minerals

CO ₂ pressure (atm)	Sand	Solvent	Activity in Electrolyte of Adsorption Measurement		Concentrations or activities at zero zeta potential	
			$a_{\text{Ca}^{2+}}$ (mol/L)	$a_{\text{Mg}^{2+}}$ (mol/L)	$[\text{Ca}^{2+}]^* / a_{\text{Ca}^{2+}}^*$ (mol/L)	$[\text{Mg}^{2+}]^* / a_{\text{Mg}^{2+}}^*$ (mol/L)
2	Calcite	Water	5.6×10^{-3}	0	4.7×10^{-4}	0
2	Calcite	Brine	5.0×10^{-1}	2.2×10^{-1}	4.7×10^{-4}	0
2	Dolomite	Water	3.2×10^{-3}	3.3×10^{-3}	3.16×10^{-4}	6.31×10^{-4}
2	Dolomite	Brine	5.0×10^{-1}	2.2×10^{-1}	3.16×10^{-4}	6.31×10^{-4}

If the divalent ion activities in tests are higher than the concentrations or activities at zero surface charge, the surface charges of carbonate minerals are positive in the adsorption measurement. As demonstrated in Table 5-6, the divalent ion activities of the electrolyte solutions from DI water or brine are one or

three order of magnitude higher than the isoelectric (zero zeta potential) divalent ion concentration. Thus, the zeta potential of carbonate minerals in adsorption tests is positive.

The Ca^{2+} and Mg^{2+} activities at reservoir conditions (120 °C, 3400 psi and synthetic formation brine) are respectively 0.32 and 0.15 mol/L in dolomite formation, and 0.33 and 0.13 mol/L in calcite formation. The isoelectric divalent cation concentrations can be assumed to be a constant at $P_{\text{CO}_2} > 1$ as demonstrate in Figure 5-18. Thus, the divalent cation activities are three orders of magnitude higher than isoelectric divalent cation concentrations at reservoir conditions. This indicates that the surface charge of carbonate formations should be positive in CO_2 flooding processes.

5.2.7 Adsorption of C12 on Pure and Natural Carbonates

The concentrations of C12 in adsorption tests were determined by MB two-phase titration at colorless end point.

The Langmuir type isotherm curves of C12 adsorption on pure and natural carbonate minerals are shown in Figure 5-19. The adsorption curves reach their plateaus at about 0.1% (wt) residual concentration. The surfactant concentration in CO_2 foam flooding is higher than 0.1% (wt) (Chen, et al., 2014). Therefore, the average of the adsorption on the isotherm curve plateaus was taken as the equilibrium adsorption in flooding, as demonstrated in Figure 5-20.

The results in Figure 5-20 reveal that the adsorption on the pure calcite was as low as expected. But the adsorption on natural dolomite was significant, owing to the high adsorption of C12 on negatively charged impurities on natural dolomite surface (Figure 5-3). Thus, the adsorption of cationic surfactants is still needed to be investigated for natural carbonate reservoirs which contain the negative charged impurities. Tabatabal, et al. (1993) and Ma, et al. (2013b) reported similar results for dodecylpyridinium chloride (DPC) and hexadecylpyridinium chloride (CPC), respectively. However, the adsorption reported for permanent cationic surfactants, *i.e.*, DPC and CPC, on pure calcite is much lower than that of switchable cationic surfactant, *i.e.*, C12. That's because only a portion of C12 was protonated at the tested pH (pH=5.8), as listed in Figure 5-5. The other portion was nonionic surfactants which caused the relatively high adsorption compared to permanent cationic surfactants. In CO₂ flooding, the equilibrium pH under reservoir conditions is lower to around 4 (Figure 5-5) which implies that the C12 is completely protonated, as demonstrated in Figure 5-14, and the adsorption is less on pure calcite in CO₂ flooding.

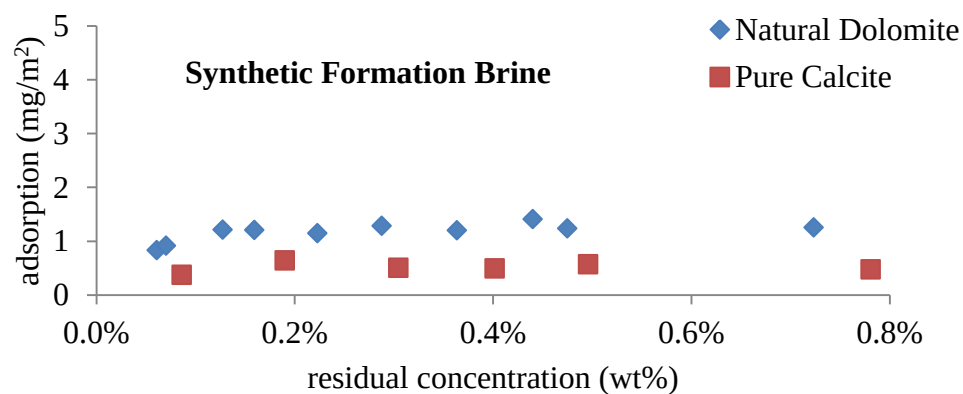
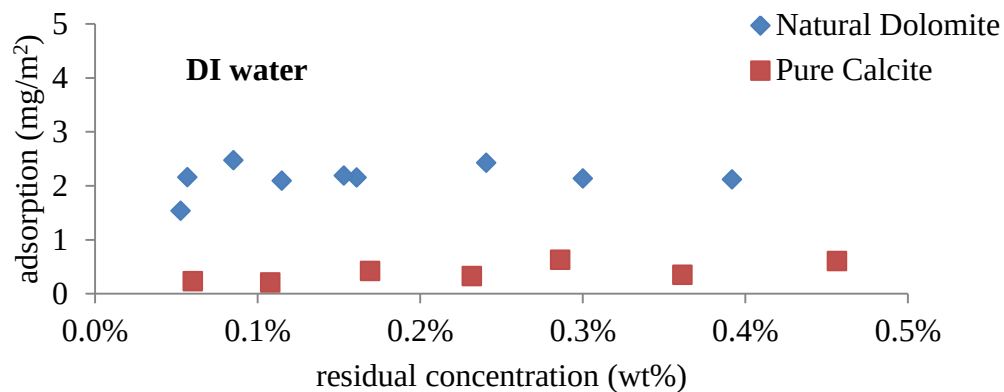


Figure 5-19 The adsorption curves of C12 in water and brine on both natural dolomite and pure calcite

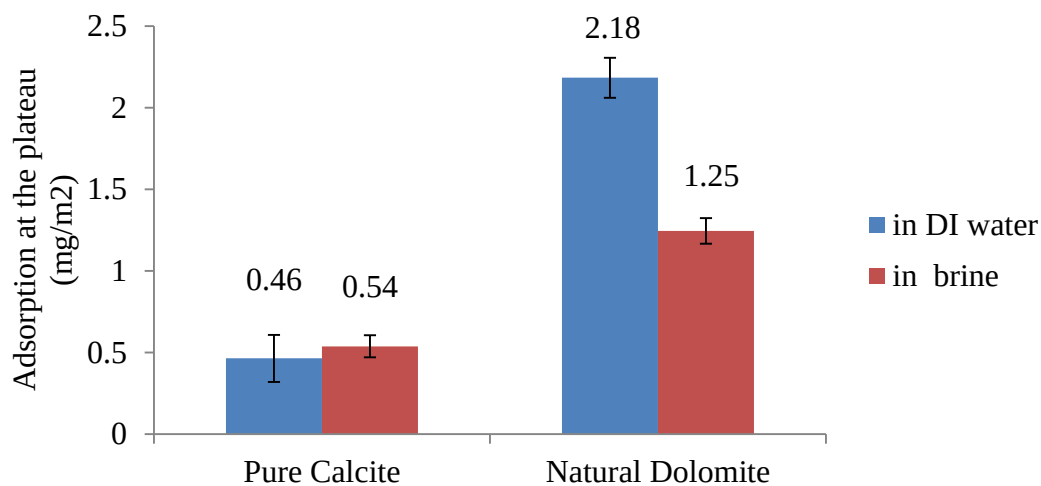


Figure 5-20 The equilibrium adsorption of C12 in different solutions on carbonate minerals

5.2.8 The Influence of Cations on Adsorption

The adsorption of C12 on natural carbonate minerals, *i.e.*, dolomite, can be reduced by adding multivalent cations, as demonstrated in Figure 5-20 because of the competition of the cations and C12 surfactant for the negative binding sites.

The adsorption of C12 in NaCl and MgCl₂ solutions with the same ionic strength as the synthetic brine (Table 5-7) was tested to investigate the influence of various cations. CaCl₂ solution wasn't prepared, because Ca²⁺ will precipitate under 2 atm CO₂ at such high ionic strength.

Table 5-7 Cations concentration of various solutions

	Brine	NaCl	MgCl ₂
Al ³⁺ (mol/L)	0	0	0
Ca ²⁺ (mol/L)	5.25×10 ⁻¹	0	0
Mg ²⁺ (mol/L)	1.26×10 ⁻¹	0	1.69
Na ⁺ (mol/L)	3.12	5.08	0
Ionic Strength (mol/L)	5.08	5.08	5.08

The reduction of adsorption by multivalent cations was attributed by Tabatabal, et al. (1993) to the increase of surface charge by lattice ions (Ca²⁺ and Mg²⁺), rather than the competition of cations and cationic surfactants. Thus, the adsorption on pure silica and kaolin was tested. The divalent cations are not lattice or potential determining ions for silica and kaolin, but can reduce the

adsorption of C12 on these minerals as well as for natural dolomite, shown in Figure 5-21.

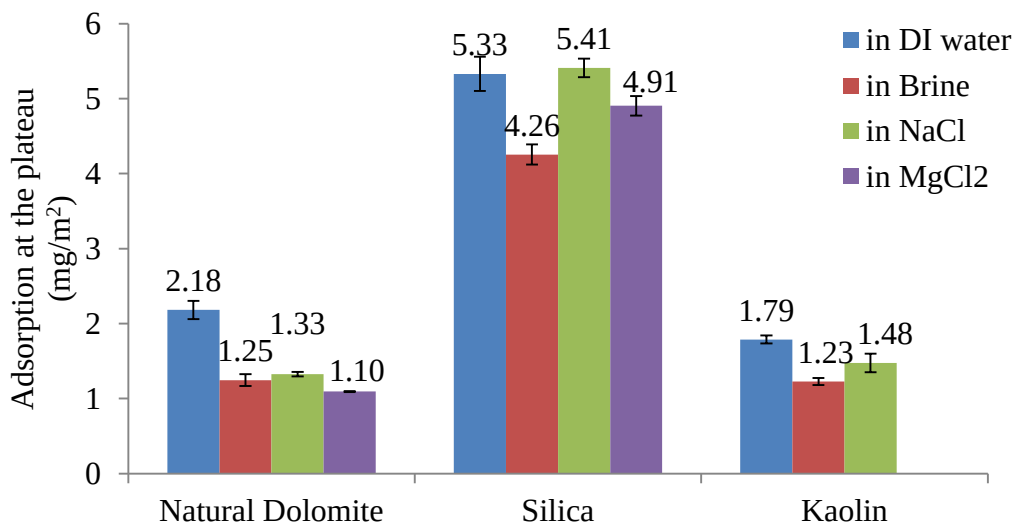


Figure 5-21 The adsorption of C12 on natural dolomite, pure silica and kaolin in various solutions

The adsorption on dolomite, silica and kaolin in brine is lower than that in DI water, which indicates that the cations in brine can reduce the adsorption on the negative binding sites. The adsorption on silica in NaCl solution is close to that in DI water, which discloses that the monovalent cation, *i.e.*, Na^+ , does not affect the adsorption of C12 on silica. The adsorption on silica in MgCl_2 solution is lower than that in DI water, and is higher than that in brine, which reveals that Mg^{2+} can reduce the adsorption, but is not as effective as Ca^{2+} . The different influence of Mg^{2+} and Ca^{2+} on the adsorption is caused by the diameters of their hydrated cations. The hydrated Mg^{2+} of 0.8 nm diameter is larger than the hydrated Ca^{2+} of 0.6 nm diameter in aqueous solutions, which results in the weaker electric potential of Mg^{2+} (Kielland, 1937).

However, the adsorption on dolomite and kaolin in NaCl and MgCl₂ solutions are lower than those in DI water and are close to those in brine. That's because the concentrations of multivalent cations in NaCl and MgCl₂ solution are one order of magnitude higher than those in DI water, calculated by PHREEQC software listed in Table 5-8 and Table 5-9. Additionally, the natural dolomite also contains clays which can bring more Al³⁺ in NaCl and MgCl₂ solutions than in DI water to effectively reduce the adsorption.

Table 5-8 Cations concentration in various solutions equilibrium with dolomite

	DI	Brine	NaCl	MgCl ₂
Al ³⁺ (mol/L)	0	0	0	0
Ca ²⁺ (mol/L)	6.50×10 ⁻³	5.25×10 ⁻¹	1.36×10 ⁻²	3.24×10 ⁻²
Mg ²⁺ (mol/L)	6.55×10 ⁻³	1.26×10 ⁻¹	1.16×10 ⁻²	1.60
Na ⁺ (mol/L)	0	3.12	5.04	0

Table 5-9 Cations concentration in various solutions equilibrium with kaolin

	DI	Brine	NaCl	MgCl ₂
Al ³⁺ (mol/L)	7.21×10 ⁻⁵	5.95×10 ⁻⁴	2.92×10 ⁻⁴	1.21×10 ⁻³
Ca ²⁺ (mol/L)	0	5.25×10 ⁻¹	0	0
Mg ²⁺ (mol/L)	0	1.26×10 ⁻¹	0	1.69
Na ⁺ (mol/L)	0	3.12	5.08	0

The trivalent cations, *e.g.*, Al^{3+} , are expected to reduce the adsorption per unit cation concentration more effectively than divalent cations. The C12 solutions with various initial concentrations of Al^{3+} ions were prepared by mixing C12 solutions and high concentrations of AlCl_3 solutions. The adsorption of C12 on silica minerals in DI water and brine with various initial concentrations of Al^{3+} are shown in Figure 5-22. The adsorption was reduced from 5.33 to 4.48 mg/m^2 in DI water with 1.07×10^{-4} mol/L Al^{3+} , and was reduced from 4.26 to 3.31 mg/m^2 in the brine with 1.51×10^{-3} mol/L Al^{3+} , which exposes that Al^{3+} ions are more effective for reducing the adsorption compared to the high concentrations of divalent cations in brine. However, the adsorption did not decrease with increasing initial concentrations of Al^{3+} , but reached constant values after the initial concentrations of Al^{3+} were higher than 1.07×10^{-4} mol/L in DI water and 1.51×10^{-3} mol/L in brine. That's because the concentrations of Al^{3+} were limited by the pH and low solubility product of $\text{Al}(\text{OH})_3$, *e.g.*, the solubility product of $\text{Al}(\text{OH})_3$ at 25 °C and zero ionic strength is only 3.16×10^{-34} (Butler and Cogley, 1998), which implies the highest concentration of Al^{3+} is 3.16×10^{-4} mol/L in DI water at the equilibrium pH of 4. Thus, the concentration of Al^{3+} in solutions has reached a limit even with higher initial concentrations, and further addition results in precipitation of aluminum hydroxide ($\text{Al}(\text{OH})_3$).

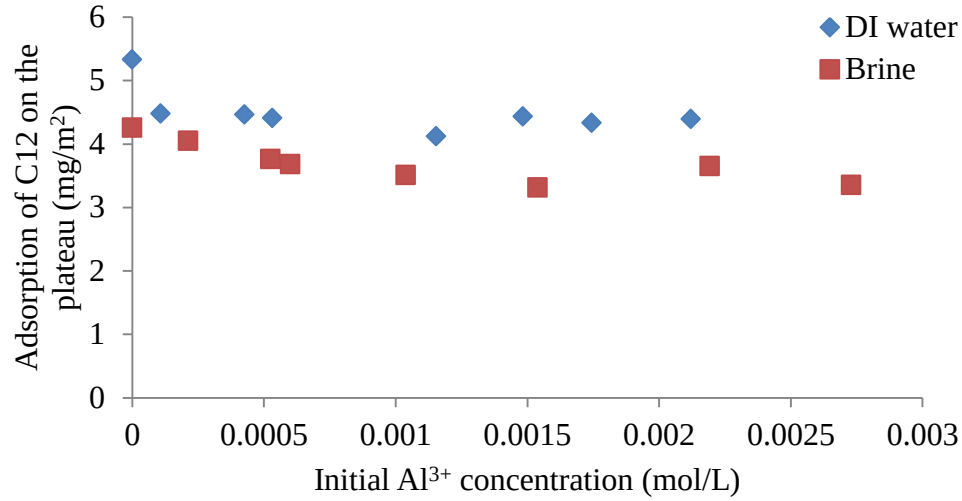


Figure 5-22 The adsorption of C12 on the silica minerals with various Al³⁺ concentrations

The adsorption reduction per unit cations concentration (AR) was defined in Equation 5-10 to distinguish the effect of each cations.

$$AR = \frac{\text{adsorption reduction by cation } M}{\text{concentration of cation } M}$$

Equation 5-10 Definition of adsorption reduction per unit cations concentration (AR)

The adsorption results on silica sands are analyzed. Na^+ doesn't affect the adsorption on silica, thus $AR(\text{Na}^+) = 0$. The adsorption in NaCl solution rather than in water was used as a reference for zero AR to exclude the ionic strength influence. The $AR(\text{Mg}^{2+})$, $AR(\text{Ca}^{2+})$ and $AR(\text{Al}^{3+})$ can be calculated based on Equation 5-11 to Equation 5-13.

$$AR(Mg^{2+}) = \frac{A_{NaCl} - A_{MgCl_2}}{[Mg^{2+}]_{MgCl_2}}$$

Equation 5-11 Formula for adsorption reduction per unit magnesium concentration

$$AR(Ca^{2+}) = \frac{A_{NaCl} - A_{brine} - [Mg^{2+}]_{brine} \times AR(Mg^{2+})}{[Ca^{2+}]_{brine}}$$

Equation 5-12 Formula for adsorption reduction per unit calcium concentration

$$AR(Al^{3+}) = \frac{A_{brine} - A_{brine+AlCl_3}}{[Al^{3+}]_{brine+AlCl_3}}$$

Equation 5-13 Formula for adsorption reduction per unit aluminum concentration

where A indicates the adsorption; the subscript $NaCl$, $MgCl_2$, and $brine$ indicate the corresponding aqueous solution as listed in Table 5-7; the subscript $brine + AlCl_3$ indicates the brine solution with 1.51×10^{-3} mol/L Al^{3+} .

The effect of each cation for reducing adsorption on silica is quantitatively described by AR , as compared in Figure 5-23. Al^{3+} is most effective for adsorption reduction per unit cation concentration.

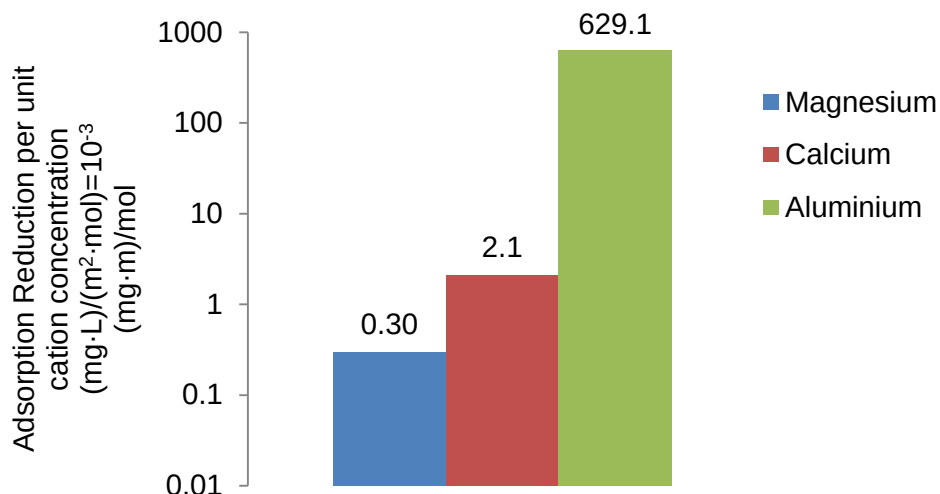


Figure 5-23 The adsorption reduction per unit cation concentration

5.2.9 Adsorption of C12 on Formation Mineral

C12 adsorption was measured on potential formation minerals. The core sample was washed sequentially with tetrahydrofuran, chloroform and methanol, and baked in an explosion-proof oven. The XPS results (Figure 5-24) shows that the core mainly contains calcium, and small amount of silicon and magnesium. Aluminum was not detected in the core, which indicates the carbonate core contains negligible negatively charged impurities.

The BET surface area was $4 \text{ m}^2/\text{g}$ reported by the Petroleum Institute (Cui, et al., 2014).

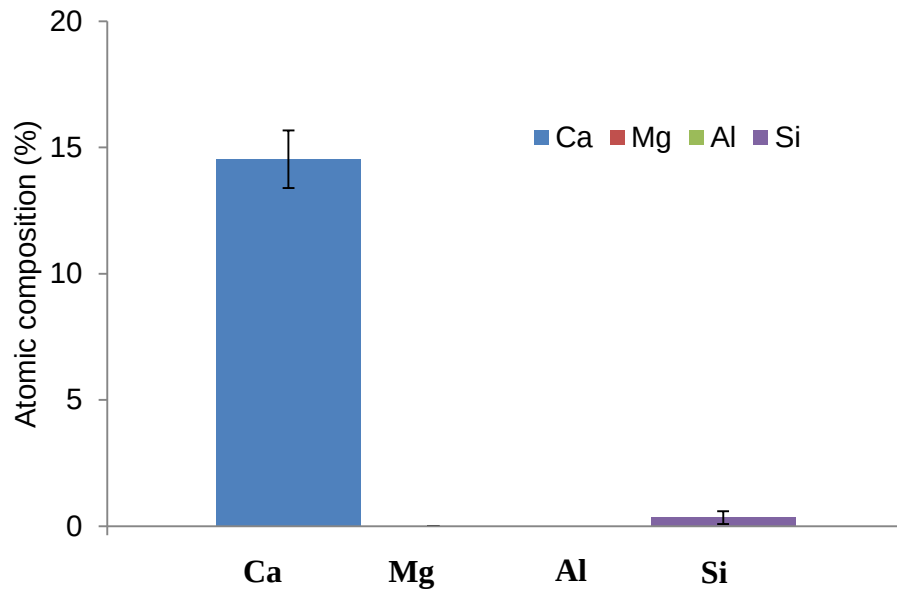


Figure 5-24 XPS results for potential minerals

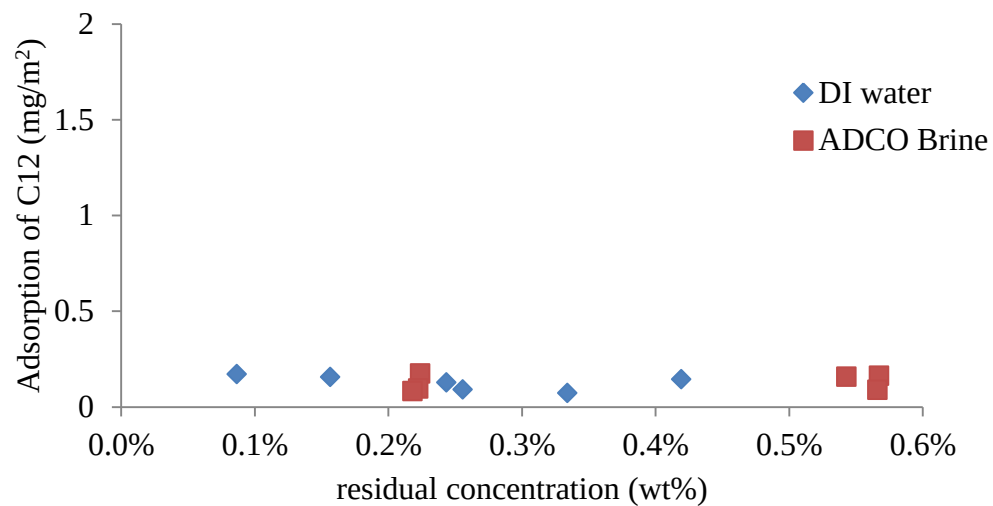


Figure 5-25 C12 adsorption on the potential formation minerals

The C12 adsorption on the formation core is comparative to that on the pure calcite, as demonstrated in Figure 5-25. Thus, the adsorption of C12 is low on the potential formation minerals which contains low amount of silica and

silicate impurities. This is consistent with the observation made in the Petroleum Institute (Cui, et al., 2014).

5.3 Conclusions

The MB two-phase titration was extended to determine the concentrations of cationic surfactants in DI water and high salinity brine. The MB dye was dissolved in KCl-HCl acid solution instead of $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$ buffer. SDES was used as an anionic titrant. The colorless end point was the stoichiometric end point for titration, which is recognized by the light absorbance at $\lambda=655$ nm. The sample is deemed colorless when the light absorbance at 655 nm is below the threshold value of 0.04. A switchable cationic surfactant, *i.e.*, the tertiary amine surfactant Ethomeen C12, was titrated with this improved method. The error is 3.6% compared to the traditional acid-base titration.

The adsorption of cationic surfactants on carbonate minerals is expected to be low, because of the expected positive zeta potentials of carbonate minerals. However, significant amount of cationic surfactant was adsorbed on the natural dolomite which contains negatively charged silica and/or clay impurities.

The sign of surface charge and zeta potential of carbonate minerals can be determined by concentration of potential determining ions. The isoelectric concentrations of Me^{2+} , *i.e.*, Ca^{2+} and Mg^{2+} , were utilized to judge the condition of surface charge and zeta potential: if the concentration of Me^{2+} in brine was

higher than isoelectric concentration, the surface charge and zeta potential is positive, vice versa.

The adsorption of switchable cationic surfactants, e.g., Ethomeen C12, can be reduced by adding multivalent cations. The adsorption of C12 on silica was reduced from 5.33 mg/m² in DI water to 3.31 mg/m² in synthetic brine with 1.51×10⁻³ mol/L Al³⁺. The effectiveness of cations per unit concentration for reducing adsorption ranges in the order of: Al³⁺>Ca²⁺>Mg²⁺. However, the low concentrations of Al³⁺ in solutions caused by low solubility product limits the benefit for reducing the adsorption.

The adsorption of C12 is low on the potential minerals which contains insignificant amount of negative charged impurities.

5.4 References

- AkzoNobel Surface Chemistry LLC. (2008). *Armeen Products: Description of Product Families and Application Areas*. Chicago IL: Akzo Nobel Surface Chemistry LLC.
- Butler, J., & Cogley, D. (1998). *Ionic Equilibrium: Solubility and pH Calculations*. Canada: John Wiley & Sons, Inc.
- Chen, Y., Elhag, A. S., Poon, B. M., Cui, L., Ma, K., Liao, S. Y., Reddy, P. P., Worthen, A. J., Hirasaki G. J., Nguyen, Q. P., Biswal, S. L. and Johnston, K. P. (2014). Switchable Nonionic to Cationic Ethoxylated Amine Surfactants for CO₂ Enhanced Oil Recovery in High-Temperature, High-Salinity Carbonate Reservoirs. *SPE Journal*,19 (02), 249 - 259. SPE-154222-PA
- Cui, L., Ma, K., Abdala, A. A., Lu, L. J., Tanakov, I., Biswal, S. L., et al. (2014). Adsorption of a Switchable Cationic Surfactant on Natural Carbonate Minerals. *SPE Improved Oil Recovery Symposium*. Tulsa, OK. SPE-169040-MS
- Cullum, D. C. (1994). *Introduction to Surfactant Analysis* (First edition ed.). Chapman & Hall.

- de Souza, A. V., & Fjelde, I. (2013). Modeling of Interaction Between CO₂ and Rock in Core Flooding Experiments. *SPE Heavy Oil Conference-Canada*, Calgary, Alberta, Canada: Society of Petroleum Engineers. SPE-165500-MS
- Friedmann, F., Hughes, T., Hild, G., Wilson, A., & Davies, S. (1999). Development and Testing of a Foam-Gel Technology to Improve Conformance of the Rangely CO₂ Flood. *SPE Reservoir Evaluation & Engineering*, 2(1), 4-13. SPE-54429-PA
- Gerlache, M., Sentürk, Z., Viré, J., & Kauffmann, J. (1997). Potentiometric analysis of ionic surfactants by a new type of ion-selective electrode. *Analytica Chimica Acta*, 349(1-3), 59-65.
- Hanssen, J., & Surguchev, L. (1994). Foam Processes: An Assessment of Their Potential in North Sea Reservoirs Based on a Critical Evaluation of Current Field Experience. *SPE/DOE Improved Oil Recovery Symposium*. Tulsa, Oklahoma: Society of Petroleum Engineers. SPE-27768-MS.
- Hayashi, K. (1975). A rapid determination of sodium dodecyl sulfate with methylene blue. *Analytical Biochemistry*, 67(2), 503-506.
- Heberling, F., Trainor, T., Lützenkirchen, J., Eng, P., Denecke, M., & Bosbach, D. (2011). Structure and reactivity of the calcite–water interface. *Journal of Colloid and Interface Science*, 342(2), 843-857.
- Hirasaki, G. J., & Zhang, D. L. (2004). Surface chemistry of oil recovery from fractured, oil-wet, carbonate formations. *SPE Journal*, 9(2), 151-162. SPE-88365-PA.
- Hirasaki, G., & Lawson, J. (1986). An Electrostatic Approach to the Association of Sodium and Calcium With Surfactant Micelles. *SPE Reservoir Engineering*, 1(2), 119-130. SPE-10921-PA.
- Hyeonga, K., & Capuano, R. M. (2001). Ca/Mg of brines in Miocene/Oligocene clastic sediments of the Texas Gulf Coast: buffering by calcite/disordered dolomite equilibria. *Geochimica et Cosmochimica Acta*, 65(18), 3065–3080.
- Jansson, S., Modin, R., & Schill, G. (1974). Two-phase titration of organic ammonium ions with lauryl sulphate and methyl yellow as indicator. *Talanta*, 21(9), 905-918.
- Kakehashia, R., Yamamuraa, S., Tokaia, N., Takedaa, T., Kanedab, K., Yoshinagac, K., et al. (2001). Hydrogen Ion Titration of Long Alkyl Chain Amine Oxide Micelles. *Journal of Colloid and Interface Science*, 243(1), 233-240.
- Kielland, J. (1937). Individual activity coefficients of ions in aqueous solutions. *Journal of the American Chemical Society*, 59, 1675-1678.
- Lang, R., Parra-Diaz, D., & Jacobs, D. (1999). Analysis of ethoxylated fatty amines. Comparison of methods for the determination of molecular weight. *Journal of Surfactants and Detergents*, 2(4), 503-513.

- Ma, K., Cui, L., Dong, Y., Wang, T., Da, C., Hirasaki, G., et al. (2013(b)). Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. *J Colloid Interface Sci*, 408, 164–172.
- Oddo, J., & Tomson, B. (1982). Simplified Calculation of CaCO_3 Saturation at High Temperatures and Pressures in Brine Solutions. *Journal of Petroleum Technology*, 34(7), 1583-1590.
- Pokrovsky, O., Schott, J., & Thomas, F. (1999). Dolomite surface speciation and reactivity in aquatic systems. *Geochimica et Cosmochimica Acta*, 63(19-20), 3133–3143.
- Sammalkorpi, M., Karttunen, M., & Haataja, M. (2007). Structural properties of ionic detergent aggregates: A large-scale molecular dynamics study of sodium dodecyl sulfate. *The Journal of Physical Chemistry B*, 111(40), 11722-11733.
- Sammalkorpi, M., Karttunen, M., & Haataja, M. (2009). Ionic surfactant aggregates in saline solutions: sodium dodecyl sulfate (SDS) in the presence of excess sodium chloride (NaCl) or calcium chloride (CaCl_2). *The Journal of Physical Chemistry B*, 113(17), 5863-5870.
- Somasundaran, P., & Agar, G. (1967). The zero point of charge of calcite. *Journal of Colloid and Interface Science*, 24(4), 433–440.
- Tabataba, A., Gonzalez, M. V., Harwell, J. H., & Scaimehorn, J. F. (1993). Reducing Surfactant Adsorption in Carbonate Reservoirs. *SPE Reservoir Engineering*, 8(2), 117 - 122. SPE-24105-PA.
- Underwood, A. (1977). Acid—base titrations in aqueous micellar systems. *Analytica Chimica Acta*, 93(1), 267–273.
- Vasilescu, M., Angelescu, D., Caldararu, H., Almgren, M., & Khan, A. (2004). Fluorescence study on the size and shape of sodium dodecyl sulphate-aluminium salt micelles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 235(1-3), 57-64.

Chapter 6

Conclusions and Future Work

This thesis discusses the screening procedure for surfactant formulations in foam EOR process, and illustrates the influence of various factors on foam mobility control ability. The adsorption of switchable cationic surfactants on natural carbonate minerals was investigated, and a method for surfactant reduction was proposed. The methylene blue (MB) two-phase titration was extended for determining cationic surfactant concentration in high salinity brine. The main conclusions are summarized below:

6.1 The Systematic Procedure to Screen the Surfactant Formulations for Foam EOR Process

6.1.1 The Investigation of Surfactant Formulations

The solubility, thermal and chemical stability, and adsorption of surfactants were evaluated in this thesis.

For a qualified surfactant formulation, the surfactants must be soluble, thermally and chemical stable from injection to reservoir conditions. The Krafft point of ionic surfactant and cloud point of nonionic surfactant depends on the surfactant property, brine composition and pH. Krafft temperature of CTAB was depressed from 27°C in DI water to lower than 22 °C in synthetic formation brine.

But Krafft temperature of CPC was increased to approximately 40 °C in synthetic formation brine, which indicates CPC may not be injected in synthetic formation brine during winter time. The cloud point temperature of ethoxylated amine was enhanced at low pH. The cloud point temperature of Ethomeen C12 in synthetic formation brine was higher than 130 °C at pH=4, comparing to the insolubility of C12 at its originally high pH. This finding indicates that C12 is water-soluble in reservoirs during CO₂ flooding process, but can't be dissolved in brine without any additives in the injection process.

Some surfactants tend to hydrolyze in aqueous solution especially at extreme pH and temperature. CTAB was stable at neutral pH and 125 °C, but precipitated in 1% (wt) Na₂CO₃ solution at the same temperature. Cocamidopropyl-betaine (CAB) degraded at both low and high pH solution at 125 °C. Lauryl-betaine (LB) was stable in a wide range of pH at 125 °C for 24 days, which indicates that LB should be used as foam booster in hot reservoirs at extreme pH. C12 slowly degraded at pH=4 and 125 °C, which indicates that extra C12 may be required to maintain foam mobility control in long production period. However, oxygen was not eliminated from the above tests. The degradation of surfactant may have been resulted from the oxidization of surfactant.

The adsorption of surfactant should be low on reservoir minerals. The adsorption of cationic surfactants on carbonate minerals is expected to be low because of the electric repulsion between the positively charged surfactant molecules and the positive surface charge on the carbonate mineral surface. However, the negatively charged impurities on the carbonate surface can cause

significant adsorption. The adsorption on the negative binding sites can be reduced by adding multivalent cations. The adsorption of C12 on silica was reduced from 5.33 mg/m² in DI water to 3.31 mg/m² in synthetic brine with 1.51×10⁻³ mol/L Al³⁺. The effectiveness of cations per unit concentration for reducing adsorption ranges in the order of: Al³⁺>Ca²⁺>Mg²⁺.

The partitioning coefficient and interfacial tension (IFT) of surfactant formulations are important factors for miscible and immiscible foam flooding, respectively. Although we didn't attempt to discuss these two factors in this thesis, they are required to be evaluated for foam process.

6.1.2 The Pre-Screening for Foam Mobility Control

Foam mobility control ability was proposed to be first evaluated in sandpack for screening purpose. The properties of sandpack, *i.e.*, pore volume, permeability and heterogeneity, are reproducible, which indicates that the foam mobility control ability of surfactant formulations can be compared in controlled experiments.

The bulk foam test, *i.e.*, equilibrium foam volume method, couldn't predict the foam behavior in porous media.

AOS 16-18 in 2% NaCl and 1% NaCO₃ solution generated strong foam in the absence of crude oil, but didn't achieve adequate mobility control in the presence of oil. Cocamidopropyl-betaine (CAB) was not a good foaming agent by itself, but was a good foam booster. The blend of AOS and CAB generated

stronger foam than AOS only did in the absence of oil, and showed good mobility control in the presence of oil as well.

6.2 The Investigation of Foam Mobility Control at the Reservoir Conditions

Foam mobility control was evaluated in Silurian dolomite cores and at the reservoir conditions to provide the information and parameters for the injection strategy and simulation for foam flooding processes. C12 and CO₂ foam can be generated at 120 °C and 3400 psi in synthetic formation brine and wide range of foam qualities, as the pressure gradient was higher than the minimum pressure gradient (10 psi/ft). The foam apparent viscosity is a function of foam quality, which can be described by local equilibrium foam model, *i.e.*, “dry-out” foam model in CMG STARS. The strongest foam was archived at the transition foam quality. Foam strength decreased with increasing foam quality in “high quality” regime, owing to the limiting capillary pressure. Thus, some water should be injected to maintain foam strength, even though the CO₂-soluble surfactant is used. The evaporation of water in brine to dry CO₂ may cause the precipitation of salt and plug the porous media. The pre-saturation of CO₂ with water is proposed to be used for CO₂ flooding. The carbonate formation can be dissolved in DI water and CO₂ flooding. Thus, the brine should contain sufficient divalent cations, *i.e.*, Ca²⁺ and/or Mg²⁺, to prevent the damage of formation caused by the dissolution.

The influence of salinity and temperature on foam strength is governed by two pairs of competitive factors. With increasing the salinity, the packing density of surfactant on water-gas interface increases, but the electric repulsion (Π_{elec}) between double layers in the film decreases. The former factor enhances the disjoining pressure and stabilizes the foam, and the latter one reduces the disjoining pressure and destabilizes the foam. With increasing the temperature, the dehydration of EO and OH head groups results in the increase of the surfactant surface density and more stable foam, simultaneously the enhancement of the thermal motion of surfactant results in the decrease of the surfactant surface density and less stable foam. For C12 and CO₂ foam, the high salinity in synthetic formation brine was favorable for foam strength, but the elevated temperature was detrimental.

6.3 The Zeta Potential of Carbonate Minerals and Improved MB Two-Phase Titration

The analysis of zeta potential of carbonate minerals in CO₂ flooding and the extension of MB two-phase titration was conducted in the C12 adsorption measurement.

The surface charge of carbonate minerals is expected to be positive in CO₂ flooding process. Thus, cationic surfactants used in carbonate reservoirs are expected to have low adsorption. The surface charge can't be directly measured, but carries the same sign as zeta potential. The zeta potential of carbonate

minerals is determined by the potential determining ions, *i.e.*, CO_3^{2-} , Ca^{2+} and/or Mg^{2+} . For calcite, the carbonate concentration depends on calcium concentration and solubility product. An isoelectric calcium concentration was proposed to determine the sign of the zeta potential of carbonate minerals. If the calcium concentration in brine is higher than this isoelectric calcium concentration, the zeta potential is positive, and vice versa. Notice that the isoelectric calcium concentration is near a constant at CO_2 partial pressure higher than 1 atm. For dolomite, the isoelectric calcium and magnesium can't be directly calculated. So, the measured values in literature were used as isoelectric concentrations. The divalent cation concentrations in synthetic formation brine were three orders of magnitude higher than isoelectric concentrations. This indicates a positive surface charge of pure carbonate mineral surfaces in CO_2 flooding with synthetic formation brine. However, silica and silicate impurities on carbonate mineral surfaces can result in the high adsorption of cationic surfactants and thus should be examined.

MB two-phase titration was improved for cationic surfactant in high salinity brine. The traditional end point, *i.e.*, equally blue in two phases, is interfered by high concentrations of anions. A colorless end point was used as the stoichiometric end point in high salinity. The influence of salinity was eliminated at colorless end point. The color change was judged by the light absorbance at characteristic wavelength ($\lambda=655\text{ nm}$) of MB. The aqueous phase was said to be colorless when the light absorbance fell below 0.04. The MB color indicator and anionic titrant were improved for hard brine. Ca^{2+} precipitates with SO_4^{2-} in

traditional MB solution and SDS in anionic titrator. Therefore, KCl-HCl solution was used to replace the $\text{Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$ buffer in improved MB solution, and SDES was used to replace SDS in anionic titrator. The improved MB two-phase titration can determine the permanent and switchable cationic surfactants concentrations in high salinity brine.

6.4 Future Work

The influence of oil on foam mobility control should be investigated at reservoir conditions. CO_2 foam is expected to be unstable in the presence of light oil, and be stable in the presence of heavy oil (Talebian, et al., 2013; Li, et al., 2012). In CO_2 flooding, the light components of oil are extracted in CO_2 phase, and the heavy components are left as residual oil (Cao and Gu, 2013). Thus, the foam in CO_2 swept zone is expected to be stable and divert CO_2 into the unswept low permeability zone (Li, et al., 2010). The foam in unswept zone is expected to be unstable and not result in the high pressure drop in the low permeability zone. This idea can be tested with controlled experiments.

The influence of wettability on foam mobility control should be investigated at reservoir conditions, as well. A core saturated with crude oil is proposed to be aged at reservoir temperature for wettability alteration (Zhang, et al., 2006). The foam should be evaluated in the oil-wet core samples at typical flow rate in the reservoir to investigate: (1) can the wettability be altered by surfactant? (2) Can foam be generated in the oil-wet porous media, *i.e.*, can foam reach the similar

strength? The observation and conclusion from above experiment can guide design of the foam flooding process.

Effects of the inlet and outlet pieces are proposed to be investigated. The foam can't be immediately generated in situ at the inlet. A mixing zone is required for foam generation, which results in weak foam, high water saturation and fast gas break-through near the inlet (Chou 1991; Du, et al., 2007). At the outlet, the liquid saturation is relatively high because of the capillary end effect (Apaydin and Kovscek, 2001; Du, et al., 2007), discontinuous gas channels are easy to be created near outlet, which results in the stronger foam near outlet. The strong foam front was observed to propagate back from outlet to inlet in both experimental and simulation results (Apaydin and Kovscek, 2001; Ashoori, et al., 2012; Simjoo, et al., 2013), which results in delay of foam reaching the steady state. The core samples used in this thesis were only 3 inches long. The effects of inlet and outlet pieces may dominate the foam generation and strength. A longer core is suggested to be used to diminish the inlet and outlet effects. The pressure drop across the middle part of the core is suggested to be measured and used for calculating the apparent viscosity. X-ray computed tomography (CT) scan technique can visually determine the inlet and outlet effects (Du, et al., 2007; Farajzadeh, et al., 2010; Simjoo, et al., 2013). The foam apparent viscosity should be corrected to eliminate these effects in laboratory scale tests.

Other multivalent cations should be tested for reducing cationic surfactant on negatively charged binding sites. The concentration of water soluble Al^{3+} is

limited by low solubility product of $\text{Al}(\text{OH})_3$ at reservoir pH. Other trivalent or tetravalent cations with higher solubility are proposed to be evaluated.

6.5 References

- Apaydin, O. G. & Kovscek, A. R. (2001). Surfactant Concentration and End Effects on Foam Flow in Porous Media. *Transport in Porous Media*, 43(3), pp. 511-536.
- Ashoori, E., Marchesin, D. & Rossen, W. R. (2012). Multiple Foam States and Long-Distance Foam Propagation in Porous Media. *SPE Journal*, 17(04), pp. 1,231 - 1,245.
- Cao, M. & Gu, Y. (2013). Oil recovery mechanisms and asphaltene precipitation phenomenon in immiscible and miscible CO_2 flooding processes. *Fuel*, Volume 109, p. 157–166.
- Chou, S. I. (1991). Conditions for generating foam in porous media. *SPE Annual Technical Conference and Exhibition*, Dallas, TX. SPE-22628-MS.
- Du, D., Zitha, P. L. & Uijttenhout, M. G. (2007). Carbon Dioxide Foam Rheology in Porous Media: A CT Scan Study. *SPE Journal*, 12(02), pp. 245 - 252. SPE-97552-PA.
- Farajzadeh, R., Andrianov, A. & Zitha, P. (2010). Investigation of Immiscible and Miscible Foam for Enhancing Oil Recovery. *Ind. Eng. Chem. Res.*, pp. 1910-1919.
- Li, R. F., Hirasaki, G. J., Miller, C. A., & Masalmeh, S. (2012). Wettability Alteration and Foam Mobility Control in a Layered 2-D Heterogeneous System. *SPE Journal*. 17 (04), 1207-1220. SPE-141462-PA.
- Li, R. F., Yan, W., Liu, S., Hirasaki, G. J., & Miller, C. A. (2010). Foam Mobility Control for Surfactant EOR. *SPE Journal*. 15 (04), 928-942. SPE-113910-PA.
- Simjoo, M., Dong, Y., Andrianov, A., Talanana, M., & Zitha, P. L. (2013). Novel Insight Into Foam Mobility Control. *SPE Journal*, 18(03), 416 - 427. SPE-163092-PA
- Talebian, S., Masoudi, R., Tan, I. & Zitha, P. (2013). Foam assisted CO_2 -EOR; Concepts, Challenges and Applications. *SPE Enhanced Oil Recovery Conference*, Kuala Lumpur, Malaysia, Society of Petroleum Engineers. SPE-165280-MS
- Zhang, D. L., Liu, S., Puerto, M. C., Miller, C. A., & Hirasaki, G. J. (2006). Wettability alteration and spontaneous imbibition in oil-wet carbonate formations. *Journal of Petroleum Science and Engineering*, 52(1-4), 213–226.