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**The Foaming Behavior of a CO₂-soluble, Viscoelastic Diamine
Surfactant in Porous Media**

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**The Foaming Behavior of a CO₂-soluble, Viscoelastic Diamine Surfactant in
Porous Media**

By

Galang Bintang Ramadhan

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Dedication

To Papa, Mama, and Bunga.

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I would like to thank Dr. Quoc Nguyen for his guidance throughout my years of study. I would also like to thank Dr. Maša Prodanović for her careful review of this thesis. The work presented in this thesis was made possible by the financial support from the Abu Dhabi National Oil Company (ADNOC).

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Abstract

Aqueous foam has been demonstrated through laboratory and field experiments as an effective conformance control mechanism for gas enhanced oil recovery and carbon sequestration operations. The use of a polymer as an additive to an aqueous foam has been suggested to increase the viscosity of the foam liquid phase. This viscosification of the liquid phase improves the foam conformance performance by increasing the foam apparent viscosity and reducing the rate of foam bubble coalescence. This study explores the use of worm-like micelle (WLM) as an alternative viscosifying agent to polymer. We utilized a cationic, amine-based surfactant; whose micelle transforms from spherical conformation to WLM at an elevated salinity. Another distinguishing feature of this surfactant is its ability to dissolve in supercritical carbon dioxide (CO₂). The delivery of surfactant in the gaseous phase may alleviate injectivity issue around the injection well, typically associated with high viscosity polymer-surfactant solution. Additional potential advantages of WLM over polymer include reversible shear degradation, reduced filtration in low permeability formations and resistance to extreme temperature and salinity.

This study investigates how the presence of WLM structures affect the transient foam behavior in microfluidic porous media model, sand pack, and limestone core. In these porous media, we performed various foam floods with two liquid phase salinities: low salinity (15 wt. % NaCl or below) associated with spherical-shaped micelle and high salinity (20 wt. % NaCl or above) associated with WLM.

The microfluidic experiments were conducted at 55 psi back pressure and 22°C. In these experiments, the DTM surfactant was solubilized in the liquid phase. Foaming experiments of

two DTM salinities (5 wt. % NaCl vs. 20 wt. % NaCl) revealed that the DTM foam with the lower salinity liquid phase produced a finer foam texture. The DTM foam with the higher salinity liquid phase possesses a higher foam apparent viscosity, despite its coarser texture. The high salinity DTM foam also exhibited better stability.

The sand pack (~3.5 Darcies permeability) experiments were conducted at 1700 psi back pressure and 40°C. In these experiments, the DTM surfactant was solubilized in the gaseous phase (CO₂). We compared the foaming behavior of two DTM salinities (15 wt. % vs. 20 wt. % NaCl) in co-injection and water-alternating injection (WAG) strategies. In co-injection, we observed an earlier onset of strong foam generation and a more rapid rate of apparent viscosity buildup in the higher salinity DTM case. In WAG, we observed a strong foam generation delay in the higher salinity DTM case due to severe gas fingering. The rate of apparent viscosity buildup of the DTM high salinity case was higher in WAG experiments.

The limestone core (~80 mDarcies permeability) experiments were conducted at 1700 psi back pressure and 40°C. We compared the foaming behavior of two DTM salinities (15 wt. % vs. 20 wt. % NaCl) in co-injection and water-alternating injection (WAG) strategies. In the WAG experiments, we performed a comparison between DTM delivery in the gaseous phase vs. DTM delivery in the liquid phase. We were not able to generate strong foam in the co-injection and WAG foam floods when the DTM was delivered in the gaseous phase. A strong foam was generated in the WAG flood where the DTM was delivered in the liquid phase. We propose that the lack of strong foam development, when DTM was delivered in the gaseous phase, is due to insufficient DTM protonation.

Contents

List of Figures	x
List of Tables	xiii
Chapter 1 Introduction.....	1
1.1 Foam for Conformance Control in Miscible Gas Enhanced Oil Recovery.....	1
1.2 Research Objective.....	3
1.3 Description of Chapters.....	4
Chapter 2 Literature Review.....	6
2.1 Foam Generation Mechanisms.....	6
2.2 Foam Stability	9
2.3 Foam Conformance Control Mechanisms	11
2.4 Polymer-enhanced Foam.....	12
2.5 WLM as a Polymer Alternative in Foam	15
Chapter 3 Diamine Surfactant Bulk Solution Characterization.....	17
3.1 Overview	17
3.2 Diamine Surfactant Introduction.....	17
3.3 DTM Solubility in CO ₂	18
3.4 DTM CO ₂ /Brine Partition	20
3.5 DTM Aqueous Stability	21
3.6 DTM Salinity-induced Viscosification	22
Chapter 4 Foaming in Microfluidic Chip	24
4.1 Materials and Methods.....	25
4.1.1 Liquid Phase/CO ₂ Interfacial Tension	25
4.1.2 Bulk Aqueous Solution Rheology	26
4.1.3 Microfluidics Foam Experiment.....	29
4.2 Results and Discussion.....	31
4.2.1 Effect of Interfacial Tension	31
4.2.2 Effect of the Liquid Phase Shear-Thinning	39
4.2.3 Effect of Liquid Phase Viscosity	49
4.2.4 Effect of Interfacial Tension at a High Liquid Phase Viscosity	62
4.2.5 Effect of Pressure Gradient in Gas Injection	68
4.2.6 Effect of Pressure Gradient in Co-injection.....	71
4.3 Conclusion.....	74

Chapter 5	Foaming in Sand Pack	76
5.1	Materials and Methods	77
5.2	Sand pack flood results	80
5.2.1	Single Phase Injection with Salinity Gradient	80
5.2.2	Salinity effect on transient foam behavior in co-injection of CO ₂ and brine.....	82
5.2.3	Salinity Effect on the Transient Foam Behavior in Water-alternating-gas (WAG) Scheme	89
5.2.4	Salinity Effect on Displacement Efficiency.....	94
5.3	Conclusions	95
Chapter 6	Foaming Experiment in Limestone Core	98
6.1	Materials and Methods	99
6.2	Core flood result.....	103
6.3	Single Phase Injection with Salinity Gradient.....	103
6.4	Salinity Effect on Foam Transient Behavior in Limestone Core Co-injection at 40°C	104
6.5	Salinity Effect on Foam Transient Behavior in Limestone Core WAG at 40°C.....	107
6.6	Salinity Effect on Foam Transient Behavior in Limestone Core Co-Injection at 120°C	110
6.7	Conclusion.....	112
Chapter 7	Conclusions and Recommendations	114
7.1	Foaming in Microfluidics Model	114
7.2	Foaming in Sand Pack.....	115
7.3	Foaming in Limestone Core	116
References		118

List of Figures

Figure 2.1 Illustration of a neck snap-off showing (a) gas entry into pore throat, (b) gas finger and formation of a wetting collar, and (c) formation of the new lamella. Reproduced from reference [13].	7
Figure 2.2 Illustration of a lamella division showing (a) mobile gas bubble encounters a branch point and (b) division of the gas bubble. Reproduced from reference [13].	8
Figure 2.3 Illustration of leave behind showing (a) gas invasion and (b) formation of lamella perpendicular to flow direction. Reproduced from reference [13].	8
Figure 2.4 Pressure differences between the center of lamella and the plateau border. Reproduced from reference [8].	9
Figure 3.1 Chemical structure of DTM surfactant head in the non-ionic form (left) and the cationic form (right).	18
Figure 3.2 DTM solubility in supercritical CO ₂ as a function of CO ₂ pressure at 60°C and 40°C.	19
Figure 3.3 Partition coefficient result for DTM surfactant in CO ₂ and brine (1 wt.% NaCl) system.	20
Figure 3.4 Phase behavior of 1 wt.% DTM solution in 20 wt.% NaCl brine as a function of pH and temperature.	21
Figure 3.5 Viscosity of 0.5 wt.% DTM surfactant solution at 40°C as function of NaCl concentration at different shear rates.	22
Figure 3.6 Illustration of packing parameter of a surfactant monomer along with micelle shape evolution as packing parameter increases. Reproduced from reference [49].	23
Figure 4.1 Rheology measurements of seven liquid phase bulk solutions at ambient conditions.	28
Figure 4.2 Diagram of the microfluidic injection setup.	30
Figure 4.3 Foam apparent viscosity measurements for DTM Low and IOS solutions in gas injection (top) and co-injection (bottom) microfluidic foaming.	32
Figure 4.4 In-situ images of DTM Low and IOS gas-injection and co-injection foaming experiments	36
Figure 4.5 Foam apparent viscosity measurements for 125 and 3330 solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming.	40
Figure 4.6 In-situ images of 125 and 3330 gas-injection and co-injection foaming experiments	43
Figure 4.7 Foam apparent viscosity measurements for 125+IOS and 3330+IOS solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming	45
Figure 4.8 In-situ images of 125+IOS and 3330+IOS gas-injection and co-injection foaming experiments	48

Figure 4.9 Foam apparent viscosity measurements for DTM Low and DTM High solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming	50
Figure 4.10 In-situ images of DTM High and DTM Low gas-injection and co-injection foaming experiments	54
Figure 4.11 Foam apparent viscosity measurements for IOS, 125+IOS and 3330+IOS solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming	56
Figure 4.12 In-situ images of IOS, 125+IOS and 3330+IOS gas-injection and co-injection foaming experiments.....	61
Figure 4.13 Foam apparent viscosity measurements for DTM High, 125+IOS and 3330+IOS solutions in gas injection (top) and co-injection (bottom) microfluidic foaming.....	63
Figure 4.14 In-situ images of DTM High, 125+IOS and 3330+ IOS gas-injection and co-injection foaming experiments.....	67
Figure 4.15 Gas Injection foam apparent viscosity measurements at varying upstream gas pressures.....	69
Figure 4.16 In-situ images of gas-injection foaming experiments at varying upstream gas pressure after 10 TPV of injection.....	71
Figure 4.17 Co-injection foam apparent viscosity measurements at varying upstream gas pressures.....	72
Figure 4.18 In-situ images of co-injection foaming experiments at varying upstream gas pressure showing peak foam texture and gas saturation	73
Figure 5.1 Process diagram for sand pack foam flood experiment.....	78
Figure 5.2 (a) Apparent viscosity (top), (b) effluent conductivity (bottom) for Flood 1.....	81
Figure 5.3 Sectional pressure gradient of four foam floods (Floods 2-5). Start of strong foam propagation at each section is marked with dashed line after surpassing 1 psi/ft.....	83
Figure 5.4 Sectional and total apparent viscosity for four simultaneous injection foam floods...	88
Figure 5.5 Sectional pressure gradient for four WAG foam floods. Start of strong foam propagation at each section is marked with a dashed line after surpassing 2 psi/ft.....	90
Figure 5.6 Sectional and total apparent viscosity for four WAG foam floods.	93
Figure 5.7 Water desaturation for (top) simultaneous injection, and (bottom) WAG injection...	95
Figure 6.1: Process diagram of foam flood experiment.....	100
Figure 6.2 (a) Apparent viscosity, (b) effluent conductivity for flood 1.	103
Figure 6.3 Sectional and total apparent viscosity for co-injection floods in limestone core	105
Figure 6.4 Water desaturation for the co-injection floods 2 and 3 in limestone core.....	107
Figure 6.5 Sectional and total apparent viscosity for WAG floods in limestone core. The vertical lines demarcate gas and liquid injections.....	108
Figure 6.6 Water desaturation for the co-injection floods 4, 5 and 6 in limestone core.....	109

Figure 6.7 Sectional and total apparent viscosity for co-injection floods in limestone core at 120°C	110
Figure 6.8 Viscosity as a function of temperature extrapolation for 0.5 wt.% DTM solution at 15 wt.% NaCl (top) and 0.5 wt.% DTM solution at 20 wt.% NaCl	111
Figure 6.9 Water desaturation for the co-injection floods 7 and 8 in limestone core.....	112

List of Tables

Table 4.1 Composition of seven liquid phase solutions and their IFT values with CO ₂ at ambient conditions.....	26
Table 4.2 Microfluidic porous media chip initial parameters.....	29
Table 5.1 Initial sand pack properties	77
Table 5.2 Experimental design of nine sand pack foam flood experiments	79
Table 5.3 Critical TIPV for strong foam propagation.....	84
Table 5.4 Critical TIPV for strong foam propagation.....	91
Table 6.1 Limestone cores specifications	99
Table 6.2 Experimental design of eight limestone foam flood experiments	102

Chapter 1 Introduction

This chapter begins with a brief discussion about the use of foam as a gas conformance agent in miscible gas enhanced oil recovery (EOR) processes. This discussion involves the introduction of a novel foaming concept that is the subject of this study. Next, the research objectives are outlined. The chapter closes with an overview of the remaining chapters of this thesis.

1.1 Foam for Conformance Control in Miscible Gas Enhanced Oil Recovery

Miscible gas flooding is an EOR method whereby carbon dioxide (CO₂), nitrogen and/or hydrocarbon gases are injected into an oil-bearing reservoir above the minimum miscibility pressure (MMP) of the select gas and oil species. The objectives of this injection include: to maintain/increase reservoir pressure, to reduce oil/water interfacial tension, and to reduce the oil viscosity. Miscible gas flooding has been recognized as one of the most effective tertiary recovery methods for reservoirs containing light to medium-gravity oil [1].

One of the major challenges encountered in miscible gas flooding operations is poor mobility control of the injection gas. A combination of the following factors causes this adverse mobility: the low viscosity of the injection gas (causing viscous fingering), the low density of the injection gas (causing gravity override), and the reservoir heterogeneity (causing gas channeling). The reservoir heterogeneity issue is especially prevalent in carbonate reservoirs; which contain more than 60% of the world's remaining oil reserves [2]. Foam is one of the most extensively studied solutions for mobility control enhancement in porous media. Over the years, foam has been proven to alleviate gas conformance issues and ultimately improve the recovery of oil both in the laboratory setting [3], [4] and field trials [5], [6].

In its most basic form, foam is a dispersion of gas in a continuous liquid phase. A surface active material is generally required in the liquid phase to lower the interfacial tension between the foam gaseous and liquid phases [7]. The addition of polymer to the foam liquid phase has frequently been studied to enhance the foam's conformance control performance [8]. The addition of polymer to the foam liquid phase increases the foam liquid phase viscosity; which raises the foam's ability to divert the gas flow and reduces the rate of foam destruction.

Despite the benefits, the inclusion of polymers in a foaming solution does have several drawbacks. Some of these drawbacks include low injectivity of the viscous liquid phase, irreversible polymer shear degradation, low polymer temperature ceiling, polymer instability in high salinity environments, and polymer filtering in low permeability formations. Due to the limitations associated with polymers, there is a need for an alternative viscosifying agent that can be used in porous media foam operations.

One promising substitute for polymers is the worm-like micelle (WLM). WLM is a self-assembled structure comprised of surfactant monomers [9]. WLM possesses characteristics similar to polymers. WLM entanglement leads to an increase liquid viscosity [10]. Like polymers, WLM structures also form a mesh-like structure in thin foam film that contributes to the steric disjoining pressure; which reduces the rate of foam destruction [11]. Some WLM-forming surfactants can also be solubilized in supercritical CO₂. The delivery of surfactant in the foam gaseous phase may help the near-wellbore injectivity issues. Unlike polymer macromolecules, WLM comprised of ionic surfactants can withstand high temperature and high salinity environments [9]. In addition, shear-induced degradation of WLM is reversible. WLM filtering in low permeability formations is minimal due to the smaller molecular weights of WLMs relative to polymers [9].

1.2 Research Objective

The overall objective of this study is to explore the foaming behavior of a surfactant that forms WLM in high salinity conditions (> 17 wt.% NaCl). Below a critical salinity of 17 wt.% NaCl, the surfactant forms a spherical micelle. The primary objective of this study is to compare the transient foaming behavior of the surfactant under the critical salinity (associated with a spherical micelle, and a low liquid phase viscosity) vs. foaming behavior of the surfactant above the critical salinity (associated with WLM, and a high liquid phase viscosity).

This study comprises foaming experiments in three different types of porous media: microfluidic porous media chip, sand pack, and limestone core. The objectives for each of the three experimental categories are as follows.

Microfluidic chip. The microfluidic chip provides in-situ visual observation of foam gas saturation and foam texture. The objective of this segment is to use the microfluidic visualization to explain the mechanisms behind the different foaming behavior of the surfactant at low vs. high salinities. This segment also compares the WLM foam behavior with that of a typical surfactant and polymer foam. Lastly, this segment explores the effect of liquid phase shear-thinning rheology on foam behavior through foaming experiments using different polymer molecular weights.

Sand pack. The objective of this segment is twofold. The first objective is to examine the possibility of delivering the WLM-forming surfactant in the foam gaseous phase (supercritical CO₂). The second objective is to investigate the foaming behavior of the surfactant at low vs. high salinity in a granular porous medium at a moderate temperature (40°C). This segment compares the foaming behavior of these two surfactant salinities in co-injection (simultaneous

injection of the gas and liquid phases) and alternate-injection (individual gas and liquid phase slug injection) strategies. In each injection strategy, the effect of injection quality (volumetric injection ratio between the gaseous and liquid phases) was tested. The results presented in this chapter has been published as an SPE conference paper [12].

Limestone core. The objective of this segment is to investigate the foaming behavior of the surfactant at low vs. high salinity in a carbonate porous media at 40°C. Like in the sand pack, this segment compares the foaming behavior of two surfactant salinities in co-injection and alternate-injection strategies. Lastly, this segment inquires into the behavior of the two surfactant salinities at a high temperature (120°C) condition.

1.3 Description of Chapters

Chapter 2: This chapter reviews the fundamental concepts of foam in porous media, including: foam generation mechanisms, contributing factors to foam stability, and foam conformance control mechanisms. In addition, this chapter discusses the concept of polymer-enhanced foam along with its benefits and limitations. Finally, a novel foaming concept using a WLM-forming surfactant is introduced.

Chapter 3: This chapter presents the diamine surfactant utilized in this study. This chapter also recaps several surfactant characterization experiments; which include surfactant solubility in supercritical CO₂, surfactant partition in a CO₂/brine system, aqueous surfactant stability, and surfactant bulk solution rheology as a function of salinity. The characterization is necessary to design the porous media foaming experiments; as well as explaining the foaming results.

Chapter 4: This chapter details the materials required and the procedure for the microfluidic foaming experiments. The chapter compares the foaming behavior of DTM at low salinity vs. DTM at high salinity, DTM at low salinity vs. internal olefin sulphonates (IOS), and DTM at high salinity vs. IOS + polymer. Foaming behavior is discussed through an analysis of foam apparent viscosity and the foam in-situ visualization.

Chapter 5: This chapter details the materials required and the procedure for foaming experiments in a sand pack. The chapter compares the foaming behavior of DTM at low salinity vs. DTM at high salinity in co-injection experiments of gaseous and liquid phases at a wet and dry injection qualities. In the water-alternating-gas experiments, the two salinity foam behavior is again compared at equal water-gas slug sizes and 3-to-1 water-gas slug sizes. In all of the sand pack experiments, the DTM surfactant was delivered in the gaseous phase. Experiments were done at a moderate temperature (40°C).

Chapter 6: This chapter details the materials required and the procedure for foaming experiments in a limestone core. The chapter compares the foaming behavior of DTM at low salinity vs. DTM at high salinity in co-injection and water-alternating-gas injection schemes at a moderate temperature (40°C) and a high temperature (120°C).

Chapter 7: This chapter outlines the takeaways from the foaming experiments in the microfluidics chip, sand pack, and limestone core. Finally, the chapter proposes possible future research ideas and directions.

Chapter 2 Literature Review

This chapter reviews the fundamental information on foam in porous media; which include: foam generation mechanisms, contributing factors to foam stability, and foam conformance control mechanisms. In addition, this chapter discusses polymer-enhanced foam along with its benefits and limitations. Finally, a novel foaming concept using a WLM-forming surfactant is discussed.

2.1 Foam Generation Mechanisms

Foam generation in porous media can be defined as a generation of a new foam lamella. The creation of a new foam lamella has been attributed to three mechanisms: snap-off, lamella division, and leave-behind [8].

Snap-off. In an aqueous foam, a snap off is a dispersion of the gaseous phase into the liquid phase. Three types of snap-off events have been observed. The first, is the neck or Roof snap-off. The neck snap-off begins with a gaseous phase arriving at a throat constriction. Should the upstream pressure exceed the capillary pressure, the gaseous phase starts to invade the pore throat. As the leading edge of the bubble enters the downstream pore body, liquid phase rushes into the throat due to capillary pressure gradient, resulting from the reduction of the curvature of bubble leading edge as it expands. The rushing liquid phase forms a liquid collar until bubble snap-off ensues. An illustration of the neck-snap off mechanism is shown in Figure 2.1.

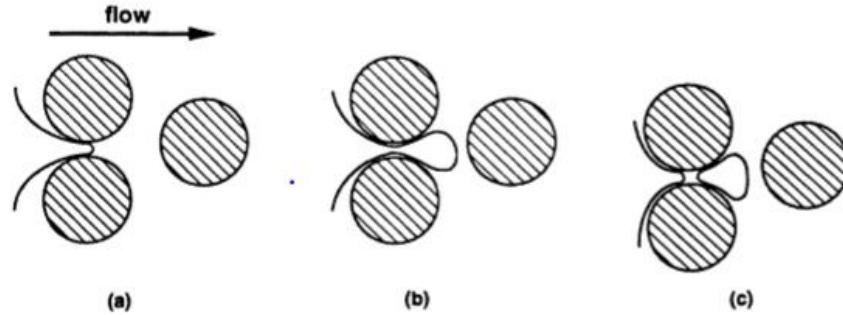


Figure 2.1 Illustration of a neck snap-off showing (a) gas entry into pore throat, (b) gas finger and formation of a wetting collar, and (c) formation of the new lamella. Reproduced from reference [13].

The second type of snap-off is the pre-neck snap-off; which occurs when a gas bubble blocks a pore throat. An ensuing liquid pressure gradient drives the accumulated liquid upstream of the pore throat to pinch of a smaller gas bubble. The third type of snap-off is the rectilinear snap-off; where a gas bubble is separated as it exits a long, straight and sharp-cornered channel. All three snap-off mechanisms may occur without the presence of a surfactant.

Lamella division. Lamella division is a subdividing of an existing foam bubble when the bubble flows around a branch point. Lamella division occurs when the mobile foam bubble is at least as large as the upstream pore body. In addition, lamella division may not occur if a trapped foam already occupies either of the branching flow paths. A lamella division illustration is presented in Figure 2.2.

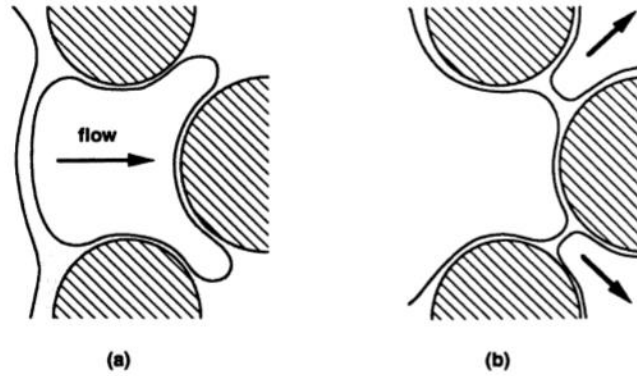


Figure 2.2 Illustration of a lamella division showing (a) mobile gas bubble encounters a branch point and (b) division of the gas bubble. Reproduced from reference [13].

Leave-behind. Leave-behind occurs when a portion of a mobile gas bubble is entrapped in a junction perpendicular to the flow path. The leave behind mechanism produces a lamella that is perpendicular to the flow direction. Leave-behind is the least significant foam creation mechanism in terms of gas diversion ability. A study [13] found that foam generation solely through leave-behind resulted in a five-fold reduction in steady-state gas permeability. Foam generated through snap-off, in comparison, can produce several hundred-fold decrease in steady-state gas permeability [14]. An illustration of leave-behind is presented in Figure 2.3.

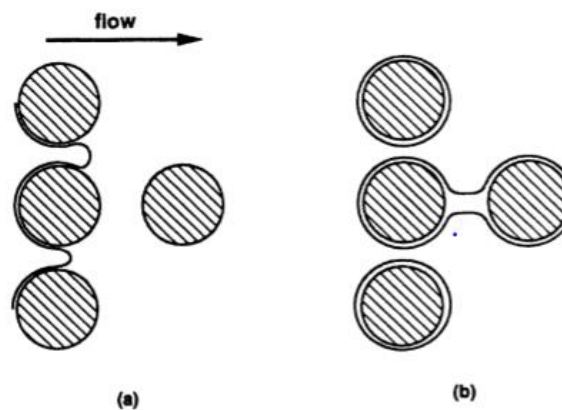


Figure 2.3 Illustration of leave behind showing (a) gas invasion and (b) formation of lamella perpendicular to flow direction. Reproduced from reference [13].

2.2 Foam Stability

Immediately after the formation of new foam bubbles, the lamellae are subjected to disturbance forces that reduce the thickness of the lamellae's liquid phase (film). The thinning process continues until the film reaches a critical thickness where the lamella is not stable and tend to coalesce. [15]. Thinning in relatively thick films ($> 100\text{nm}$) is driven primarily by the capillary and gravitational forces [7]. For horizontal (ignoring gravity-driven drainage) thick films, drainage is primarily driven by the pressure gradient between the center of lamella and the plateau border.

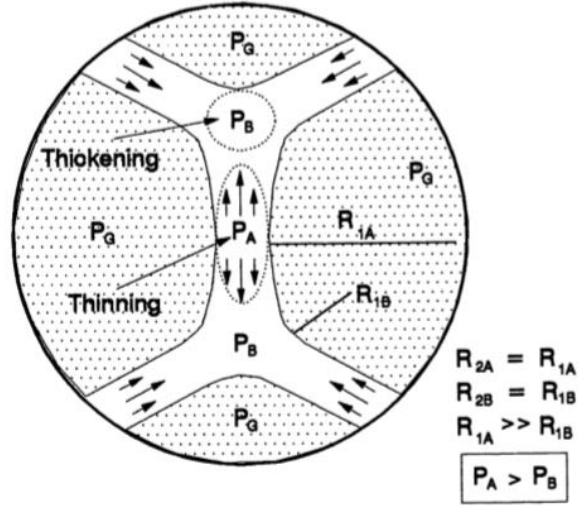


Figure 2.4 Pressure differences between the center of lamella and the plateau border. Reproduced from reference [8].

The following equation expresses the rate of thick film drainage [7].

$$-\frac{dh}{dt} = \frac{2h^3\Delta P}{3\eta R^2} \quad (1)$$

Where the variables are as follows:

$-dh/dt$: rate of film thinning (m/s)

h : instantaneous thickness of the film (m/s)

ΔP : pressure difference between the film and plateau border (Pa)

η : viscosity of the liquid (Pa.s)

R : the radius of the foam bubble (m)

The above equation implies that the rate of film drainage is inversely related to the viscosity of the film. Another influential factor that influences thick-film foam stability is foam surface elasticity and viscosity; which are commonly discussed together and evaluated as the Marangoni effect [8]. This effect reduces the rate of film drainage by opposing the liquid flow out of the high surface tension region of the film. A previous study shows that drainage time is proportional to an increased Marangoni effect [16].

For thin films (thinner than 100 nm), the rate of film drainage deviates from that predicted in Equation (1). The deviation is mainly due to the increasing influence of disjoining pressure. Disjoining pressure resists film thinning forces through an interplay of long-range repulsive electrostatic (Π_{elec}), short-range repulsive steric (Π_{steric}), and short-range attractive London dispersion-van der Waals (Π_{vdw}) pressures [17]. The Π_{elec} arises from an overlap in the electrical double layers (EDL) surrounding both lamella interfaces [8]. The Π_{steric} arises from an interaction between the lamella interfaces and a structure in the lamella film that resists film thinning. The structures providing resistance could be in the form of entangled polymers, stratified oil droplets, stratified spherical micelles [8], or entangled cylindrical micelles [11]. The Π_{vdw} typically contributes a conjoining pressure originating from the instantaneous induced-dipole interactions between particles residing on both lamella interfaces [17].

2.3 Foam Conformance Control Mechanisms

Foam acts as a gas conformance control agent through two means. First, foam increases the “apparent viscosity” of the gas by dispersing the gas phase into small bubbles divided by liquid lamellae. Second, foam may become entrapped in the porous media pore body; thus reducing the available channels for the gas to flow (a reduction in the porous media effective permeability to gas).

A study on foam apparent viscosity in a smooth capillary tube [18] identified three factors that contribute to the apparent viscosity of foam: viscosity of the liquid phase, resistance to deformation of the interface between the liquid and gas phase, and surface tension gradient along the interface that resists flow. A study on foam mobility in a periodically diverging-converging channel [19] describes a foam apparent viscosity through the following equation.

$$\mu_f \approx \mu_g + \frac{(n_l \bar{R})}{4} \left(\frac{2\mu_l}{a} \left(\frac{3\mu_l v_f}{\sigma_{gl}} \right)^{-\frac{2}{3}} + \frac{\lambda E_g \ln \bar{A}_s}{v_f} \right) \quad (2)$$

Where the variables are as follows:

- μ_f : apparent viscosity of foam (Pa.s)
- μ_g : viscosity of foam gaseous phase (Pa.s)
- μ_l : viscosity of foam liquid phase (Pa.s)
- σ_{gl} : gas liquid interfacial tension (N/m)
- n_l : lamella density per unit length
- $\bar{R}$: average pore diameter (m)
- v_f : mean velocity of lamellae train (m/s)
- λ : porous media geometric correction factor
- E_g : gibbs surface elasticity (Pa)
- $\bar{A}_s$: average foam bubble aspect ratio

Equation (2) suggests that the primary contributing factors to an apparent viscosity of a single foam lamella moving in a particular porous medium channel are the viscosity of the foam liquid phase, the Gibbs surface elasticity, and the gas-liquid interfacial tension. In a bulk foam system, these factors are multiplied as a function of the foam texture. Foam texture itself can be defined as the density of lamellae per unit volume of bulk foam [8]. The density of lamellae increases as the average bubble size in a bulk foam system decreases. As such, foam texture can be altered by controlling the rate of foam generation events; as well as the average bubble size generated. Another factor that controls foam texture is the rate of foam lamellae destruction.

In addition to increasing the gas apparent viscosity, foam can potentially reduce the porous medium effective permeability to gas. In porous media, the foam bubble ability to flow from one pore to another is heavily dependent upon overcoming the capillary forces imposed by the pore throat constrictions. Due to this pressure gradient requirement, a large portion of foam system in porous media may not be mobile. This fraction of trapped foam could occupy up to 65% of total pore volume; depending on foam injection quality, injection velocity, and porous media morphology [20]. Trapped foam severely reduces the effective permeability of gas by reducing the number of conduits through which the gas can flow [8].

2.4 Polymer-enhanced Foam

The addition of a polymer to the surfactant foaming solution has been suggested to improve foam's efficacy as a gas mobility control agent [21], [22]. Polymer/surfactant interaction can be broadly divided into two categories: a strongly-interacting polymer/surfactant system (due to opposite charges) and a weakly-interacting polymer/surfactant system (due to like or neutral charges). For oil field applications, one general requirement is to minimize the adsorption of the surfactant and polymer components to the rock matrix. To achieve this

objective, the polymer and surfactant used must be of the same charge. Based on this assumption, the following discussion only pertains to weakly-interacting polymer/surfactant system.

The addition of polymer to a surfactant foaming solution typically increases the foam liquid phase viscosity due to polymer chain entanglement [23]. From the perspective of foam generation, an addition of polymer to the surfactant solution seems to decrease the rate of foam generation events. A study [24] found the rate of snap-off frequency may be expressed as linearly proportional to liquid velocity and to gas velocity. Assuming a constant pressure gradient, a higher liquid phase viscosity could translate to lower liquid and gas phases velocity. The lower liquid and gas velocities could lead to fewer foam generation events and potentially limit foam generation to the near well-bore region.

From the perspective of foam stability, the addition of polymer seems to reduce the occurrence of lamellae destruction. Polymer improves the stability of thick foam film by increasing its viscosity and reducing the rate of film drainage. In thin films, polymers resist thinning forces by forming a mesh-like structure. This structure creates a steric repulsion between adjacent film surfaces [25].

The addition of polymer to surfactant solution typically increases the foam apparent viscosity. This phenomenon can be attributed to the increase in the viscosity of the foam's liquid phase due to polymer chain entanglement [23]. The effect of polymer addition to foam interface Gibbs elasticity is less clear. This component of foam viscosity is a function of interface viscoelasticity; which itself is controlled by the rate of surfactant exchange between the interface and the bulk solution. This exchange phenomenon is quantified by a term called dynamic surface tension. Studies were performed on the equilibrium surface tension of anionic polyelectrolyte-

anionic surfactant system [26] and dynamic surface tensions of nonionic polyelectrolyte-anionic surfactant system [27]. The results suggested no significant difference before and after the addition of polymer. Effect of polymer addition on trapped foam saturation has not been investigated. However, increased foam apparent viscosity and stability could very well lead to an increase in trapped foam saturation in porous media.

Despite the previously discussed benefits, incorporating polymer into the surfactant foaming solution does have several drawbacks and limitations. One of the drawbacks is a reduced injectivity due to the high viscosity of the liquid slug. Moreover, additional surface facility is required to mix the polymer into the surfactant foaming solution. The application of polymer-enhanced foam is also confined by several limitations. One of these limitations is that polymers typically have a low temperature ceiling, above which the polymer molecules are hydrolyzed [28]. Additionally, polymers have a tendency to be unstable in high salinity conditions. A study [29] has shown that polymer and surfactant co-exist only below a certain critical salinity, beyond which polymer-rich and surfactant-rich phases are formed. Moreover, high-molecular-weight polymers are known to be shear sensitive [30]. Polymer macromolecule breaks down beyond certain critical shear rate. This event is irreversible and leads to a severe loss of viscosifying power [31]. Polymer stabilizers are commonly used to extend the operating window of polymers into higher temperature and higher salinity conditions. However, these stabilizers, most notably formaldehyde, are highly toxic and heavily regulated [29]

2.5 WLM as a Polymer Alternative in Foam

Due to the limitations associated with polymers, there is a need to develop an alternative additive to foam. One promising substitute is the worm-like micelle (WLM) [9], [33], [34]. WLM is a self-assembled structure comprised of surfactant monomers. WLM's radius, length, and degree of flexibility could be fine-tuned by adjusting variables such as: salinity, temperature, and addition of co-surfactant [35].

WLM possesses characteristics that improve foam's apparent viscosity and stability. Similar to polymer macromolecules, WLM entanglement leads to liquid phase viscosification [10]. In comparison to spherical micelles, WLMs pose less barrier to surfactant monomer diffusion from bulk phase to the interface; which leads to a relatively low dynamic surface tension [36]. In addition, WLM structures also form a mesh-like structure in thin foam film that contributes to the steric disjoining pressure; which helps resist film thinning [11].

Another potential advantage of WLM over polymer is the ability of its surfactant monomers to be solubilized in supercritical CO₂ [37]. This feature is especially advantageous given the fact that CO₂ is the most common gas used in miscible gas flooding EOR due to its abundant availability and the lower pressure required for miscibility in comparison to nitrogen or hydrocarbon gases [38]. This particular characteristic of CO₂-soluble surfactant opens the possibility of surfactant delivery in CO₂ phase. When the surfactant comes into contact with the liquid phase in the reservoir, the surfactant can then partition to the liquid phase [39]. The delivery of surfactant in the gas phase could alleviate injectivity issues typically associated with high viscosity polymer-surfactant solutions. This injection strategy has also been proven to

reduce the surfactant adsorption to the rock matrix; thus reducing the amount of surfactant loss and shortening the delay in foam formation and propagation [40].

Unlike polymer macromolecules, WLM comprised of some ionic surfactants are able to withstand high temperature and high salinity environments [9]. In addition, shear-induced degradation of WLM is reversible. The time required for a WLM structure to recover from a shear-induced degradation and return to its original conformation is defined as micellar relaxation time. Micellar relaxation time typically spans over a short period of time (e.g. milliseconds to fractions of a second) [36].

The development of foam-assisted miscible gas flooding EOR using CO₂-soluble surfactant have been well-studied for non-ionic surfactants [37], [41]–[43]. However, non-ionic surfactants have several issues such as poor solubility in liquid phase at high temperature and high salinity conditions [8]. These limitations greatly reduce the potential of non-ionic surfactant for field applications. An alternative surface agent to cationic surfactants in high salinity environments include surface active nanoparticles. Nanoparticles coated with carbosilane ligands were shown to achieve a low hydrophilic/CO₂-phillic balance (HCB). A low HCB value indicates a preference towards the CO₂ phase [44]. Carbosilane ligands are covalently bound to the silica nanoparticle surface; thus are expected to be chemically stable in harsh reservoir environments. Surface active nanoparticles with favorable hydrophilic/CO₂-phillic balance (HCB) has been proven to produce long, lasting, stable, and high apparent viscosity foam [45], [46]. The delivery of these nanoparticles, however, is confined to the foam liquid phase.

Chapter 3 Diamine Surfactant Bulk Solution Characterization

3.1 Overview

This chapter introduces the diamine surfactant used in this study. In addition, this chapter presents several characterization of the surfactant bulk solution, which include:

1. Surfactant solubility in supercritical CO₂
2. Surfactant partition in the CO₂-brine system
3. Surfactant aqueous stability
4. Surfactant rheology as a function of salinity

These surfactant bulk solution characterization is essential in designing the porous media foaming experiments; as well as interpreting their result. The bulk solution characterization presented in this chapter is reproduced from the work of Madalyn Liebum, a former member of Dr. Quoc Nguyen's research group at the University of Texas at Austin [47].

3.2 Diamine Surfactant Introduction

The surfactant used in this study is the N.N.N'-trimethyl-N'-tallow-1,3-diaminopropane (DTM). DTM is an amine-based surfactant developed by Akzo Nobel (CAS# 68783-25-5). DTM is a member of a class of amine-based switchable surfactants. This group of surfactants exhibit an interconversion between nonionic and cationic forms. The molecular structures of the two forms of DTM surfactant are illustrated in Figure 3.1.

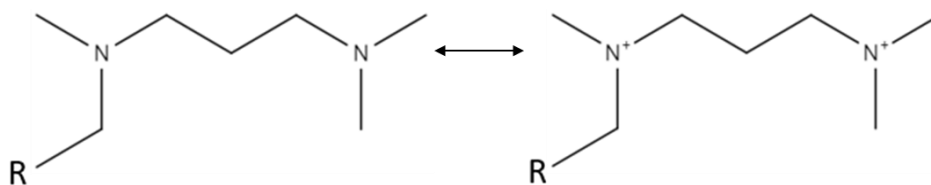


Figure 3.1 Chemical structure of DTM surfactant head in the non-ionic form (left) and the cationic form (right).

The interconversion between the two DTM forms is triggered by the concentration of surrounding hydrogen ions (H^+). At a low H^+ concentration (high pH environment), the two amine head groups of DTM are not protonated, and DTM assumes its non-ionic form. At a higher concentration of H^+ (low pH environment), one or both amine head groups of DTM are protonated, and DTM assumes its cationic form. Both the non-ionic form and the cationic forms of DTM offer unique characteristics as will be elaborated in the following sub-sections.

3.3 DTM Solubility in CO_2

The non-ionic form of DTM possesses a higher solubility in supercritical CO_2 in comparison to its cationic counterpart. The higher solubility of the non-ionic DTM is attributed to the weak molecular interaction between DTM monomer hydrocarbon tail and the dense CO_2 [37]. The DTM cationic form, on the other hand, is not soluble in CO_2 at tractable pressures due to the low polarizability of dense CO_2 [37]. One of the objectives of this study is to explore the foaming behavior of DTM with the surfactant delivery in the gaseous phase. Therefore, the solubility capacity of DTM in supercritical CO_2 needed to be determined. Figure 3.2 presents the result of the DTM solubility test. The materials required and the procedure for this solubility test can be found in reference [47].

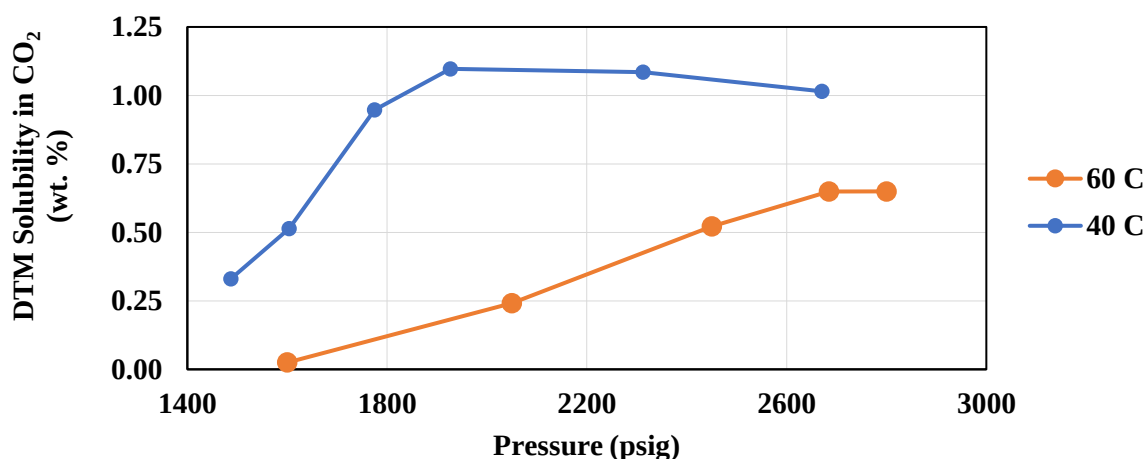


Figure 3.2 DTM solubility in supercritical CO₂ as a function of CO₂ pressure at 60°C and 40°C.

A typical surfactant concentration for sub-surface foam operations is 0.5 wt.% relative to the brine/liquid phase. Figure 3.2 shows that 0.5 wt.% of DTM can be solubilized at a relatively tractable pressure of 1604 psi (note: the density of CO₂ at 1604 psi and 40°C is 660.82 kg/m³). Figure 3.2 also suggests that the solubility of DTM increases with increasing pressure. As pressure increases at a constant temperature, the number of CO₂ molecules per unit volume (density) increases. The greater number of CO₂ molecules interacting with the surfactant tail leads to an increase in the solubility of DTM in CO₂ [43]. Additionally, an increase in temperature seemed to decrease the solubility of DTM in CO₂. Again, the lower DTM solubility can be directly related to the decreasing CO₂ density at a higher temperature and constant pressure.

Overall, the solubility test revealed that a sufficient amount of DTM can be solubilized in supercritical CO₂ at lab-accessible pressures (< 2000 psi). Thus, foaming experiments with DTM surfactant delivery in the gaseous phase is possible.

3.4 DTM CO₂/Brine Partition

In its application as a foaming agent in a foam-assisted miscible gas flooding, DTM could be delivered in the CO₂ phase. In the reservoir, upon contact with the liquid phase, DTM monomers would migrate to the interface where the head groups would be protonated by carbonic acid produced by the reaction of CO₂ and water. In a brine/CO₂ system, the protonated DTM molecule has a strong partition preference towards the brine phase. The partition coefficient is a measure of surfactant solubility preference in a gas/liquid system. A value close to one indicates that the surfactant tends to solubilize in the gaseous phase; while a value near zero means that the surfactant favors to solubilize in the liquid phase. The details of the partition coefficient measurement can be found in reference [47]. Partition coefficient data of DTM in brine/CO₂ system as a function of pressure at 60°C is presented in Figure 3.3.

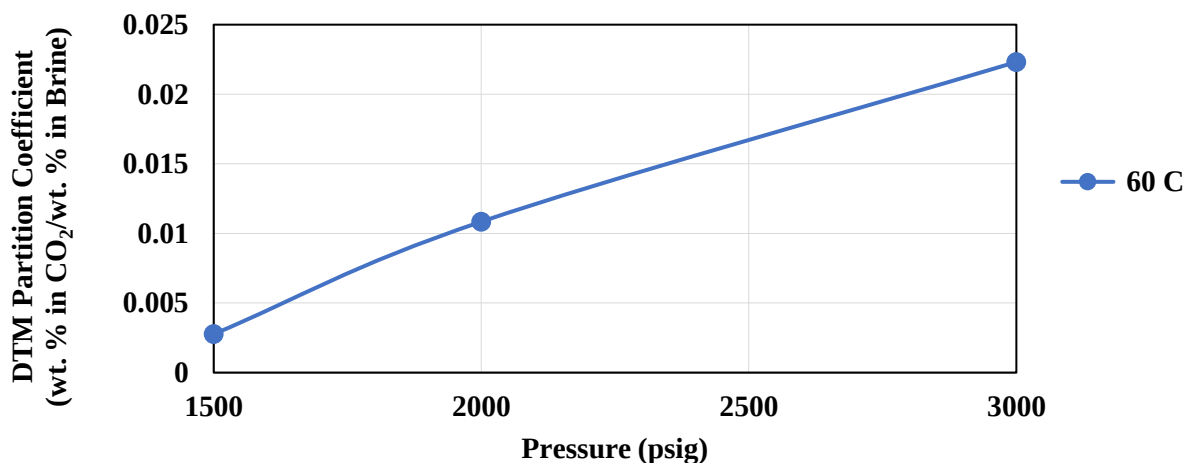


Figure 3.3 Partition coefficient result for DTM surfactant in CO₂ and brine (1 wt.% NaCl) system.

Figure 3.3 shows very low partition coefficient under 3000 psi at 60°C. The preference of DTM surfactant to partition into the liquid phase is due to the strong ion-dipole interaction between DTM ionic head groups and the water molecules overcoming the weak molecular

interaction between DTM hydrocarbon tail and dense CO₂ [37]. Because of its strong partition preference to the brine phase, DTM molecules would diffuse out of the CO₂ phase once the maximum excess surface concentration on the interface is reached.

3.5 DTM Aqueous Stability

In the liquid phase of a CO₂/brine system, the DTM surfactant begins to assume its cationic form owing to the protonation of its amine head groups by carbonic acid. The degree to which the DTM head groups are protonated can be measured through the pH of the surfactant liquid phase. Phase behavior experiments were done to assess DTM aqueous stability as a function of pH and temperature. The result is presented in Figure 3.4 below. The detail of the aqueous stability test can be found in reference [47].

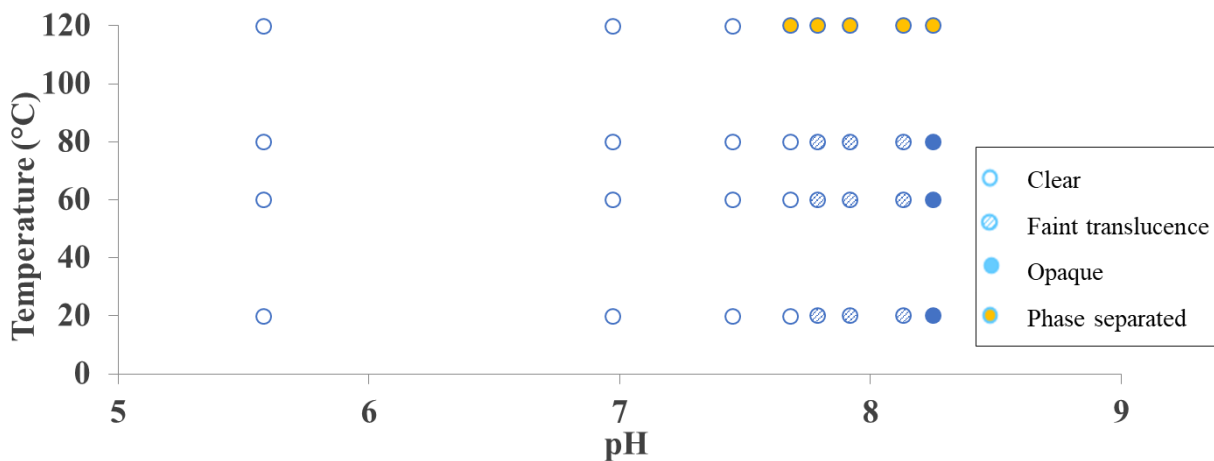


Figure 3.4 Phase behavior of 1 wt.% DTM solution in 20 wt.% NaCl brine as a function of pH and temperature.

The phase behavior tests suggest that the DTM solution with a higher degree of amine protonation (lower solution pH values) exhibits better stability at every temperature tested.

3.6 DTM Salinity-induced Viscosification

A feature of interest of the DTM cationic form is its salinity-induced viscosification of a liquid solution. Viscosity measurements were performed for 0.5 wt.% DTM at 40°C solution as a function of NaCl concentration. The result is presented in Figure 3.5. The detail of the DTM rheology measurements can be found in reference [47].

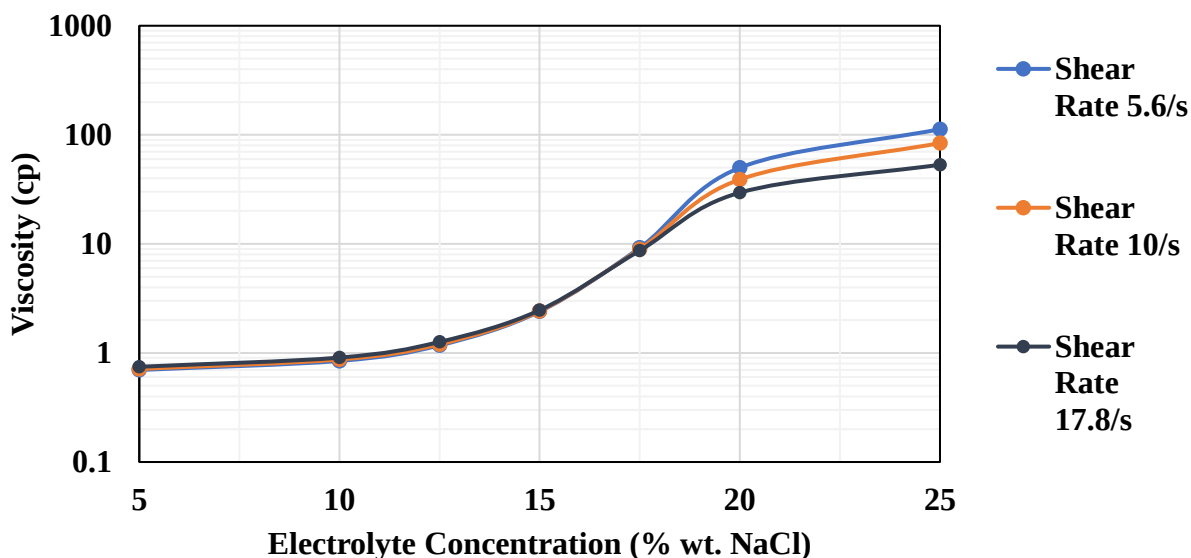


Figure 3.5 Viscosity of 0.5 wt.% DTM surfactant solution at 40°C as function of NaCl concentration at different shear rates.

At a concentration above the critical micelle concentration (CMC), DTM solution exhibits a sharp increase in salinity above 15 wt.% NaCl. This sharp increase in viscosity is attributed to the salinity-triggered transformation of spherical micelle to WLM. This phenomenon is well explained by the concept of packing parameter [48]. An increase in the electrolyte concentration effectively screens the ionic surfactant head groups charges. This screening effect reduces the effective geometrical volume of the surfactant head; thus allowing closer interaction between surfactant monomers. An illustration of the packing parameter concept and the micelle evolution from a spherical conformation to worm-like is presented in Figure 3.6.

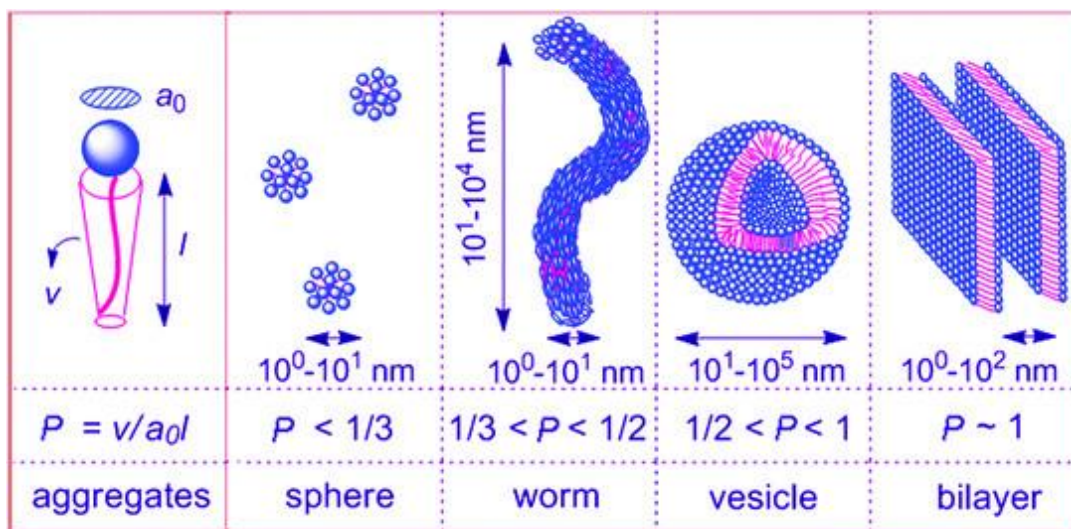


Figure 3.6 Illustration of packing parameter of a surfactant monomer along with micelle shape evolution as packing parameter increases. Reproduced from reference [49].

As the electrolyte concentration increases, the packing parameter value of an ionic surfactant monomer increases. The result is that surfactant monomers are able to agglomerate in a denser manner; and eventually evolve from spherical to worm-like shape. Additionally, an increase in salinity has been attributed to a shortening of micellar persistence length [50]. Persistence length is the extent of the rigid portion of a WLM [35]. A reduction in the micellar persistence length leads to a more flexible WLM structure. The increased flexibility could lead to a larger micellar entanglement network; thus resulting in a higher viscosity liquid solution.

Chapter 4 Foaming in Microfluidic Chip

DTM is an attractive surfactant for porous media foaming applications due to its dual ability to reduce the gas-liquid IFT and to viscosify the foam liquid phase. The objective of this study is to evaluate how the salinity of the DTM solution influences its foaming behavior in porous media. This study compares two DTM salinities: (i) a “low” salinity solution (5 wt.% NaCl, 0.5 wt.% DTM) associated with the low liquid phase viscosity and (ii) a “high” salinity solution (20 wt.% NaCl, 0.5 wt.% DTM) associated with the high liquid phase viscosity.

To help explain some of the viscosity effects between the DTM low salinity and DTM high salinity foams, analogous foaming experiments were designed using a commonly used surfactant and surfactant-polymer coupling. The surfactant chosen for the analogous system is the internal olefin sulphonates (IOS) along with two types of polyacrylamide at different molecular weights: AN 125 VLM at 2 million Dalton (MDa) and FLOPAAM 3330S at 8 MDa. The higher molecular weight polymer was expected to have a more non-Newtonian (a greater degree of shear thinning) rheological behavior. The intention in comparing these two polymers was to investigate the effect of liquid phase shear thinning characteristic on foam behavior in porous media.

One tool used to study foam behavior is the foam apparent viscosity (μ_f) analysis. The dynamic behavior of μ_f through the duration of foam injection may provide some insights into foam generation, foam stability, and individual lamella viscosity. In this study, the foam apparent viscosity was calculated through the following equation.

$$\mu_f = \frac{k\Delta PA}{QL} \quad (3)$$

Where the variables are as follows:

- μ_f : apparent viscosity of foam (cp)
- k : absolute permeability of the chip (Darcies)
- A : cross-sectional area of the chip (cm²)
- Q : volumetric injection rate (cm³)
- L : length of the chip (cm)

The second tool used in this study is *in-situ* foam observation in a microfluidic porous media model. Microfluidics porous media model to enables qualitative observation of foam texture, mobile gas saturation, and trapped foam saturation. The discussion in this study revolves around the theory of foam mobility expressed by Equation (2) supported by experimental data through the μ_f analysis, microfluidic images, and bulk solution measurements of foam liquid phase (μ_l), and gas-liquid interfacial tension (σ_{gw}).

4.1 Materials and Methods

4.1.1 Liquid Phase/CO₂ Interfacial Tension

The IFT between the gaseous and liquid phases is a component to foam apparent viscosity. As such, we performed IFT measurements with respect to CO₂ for the seven liquid phase solutions to be used in the microfluidic foam experiments. IFT measurements were performed using the pendant bubble-up method under ambient conditions. The result is tabulated in Table 4.1.

Table 4.1 Composition of seven liquid phase solutions and their IFT values with CO₂ at ambient conditions

Solution Name	Surfactant Type and Concentration (wt. %)	Polymer Type and Concentration (ppm)	Polymer Molecular Weight (MDa)	Salinity (wt. % NaCl)	IFT (dyne/cm)
DTM High	DTM, 0.5	0	-	20	35.15
DTM Low	DTM, 0.5	0	-	5	35.30
IOS	IOS, 0.5	0	-	5	27.61
125+IOS	IOS, 0.5	AN 125 VLM, 8000 ppm	2	5	27.30
3330+IOS	IOS, 0.5	FLOPAAM 3330s, 3000ppm	8	5	26.82
125	0	AN 125 VLM, 8000 ppm	2	5	66.20
3330	0	FLOPAAM 3330s, 3000ppm	8	5	65.14

4.1.2 Bulk Aqueous Solution Rheology

The liquid phase viscosity is another component of a foam apparent viscosity. The primary objective of this study is to explain the effect of the DTM solution liquid phase viscosity on foam behavior. To help explain some of the DTM viscosity effects, experiments on analogous systems of commonly used surfactant-polymer coupling (125+IOS and 3330+IOS per Table 1) were performed. For accurate comparisons, we tried to match the viscosities of these three solutions between the shear rate values of 38.8 and 45.7 s⁻¹. This target shear rate window was obtained through the apparent shear rate calculation of a liquid injection rate at 0.6 μL/min (liquid phase injection rate in foaming experiments) through a porous media with a length of 2 cm, a permeability of 2.75 Darcies, and a porosity of 0.57 (microfluidic chip specifications). The apparent shear rate calculation was based on the following equation [51].

$$\dot{\gamma}_{app} = \left(\frac{3n+1}{4n} \right)^{\frac{n}{n-1}} \frac{12u}{\sqrt{150k\phi}} \quad (4)$$

Where the variables are as follows:

- $\dot{\gamma}_{app}$: apparent shear rate in chip (s^{-1})
- n : bulk solution power law index
- u : darcy velocity (m/s)
- k : permeability (m^2)
- ϕ : porosity of porous media

The above method resulted in an apparent shear rate of $45.7s^{-1}$. It is important to note, however, that the microfluidic chip is a quasi-2D porous media. Equation (3) was developed for a fluid flow in 3-dimensional core. Therefore, we required an alternative apparent shear rate calculation method for validation. We performed an apparent shear rate calculation of a liquid flow rate at $0.6 \mu L/min$ through a slit with a length of 2 cm, an opening height of $22.4 \mu m$, an opening width of 9 mm, and porosity of 0.57 (microfluidic specifications). The equation used is as follows [52].

$$\dot{\gamma}_{app} \approx 3 \dot{\gamma}_{wall} \approx \frac{3(8u)}{d} \approx 12 \frac{Q}{\phi h^2 w} \quad (5)$$

Where the variables are as follows:

- $\dot{\gamma}_{wall}$: shear rate at the wall (s^{-1})
- u : fluid velocity (m/s)
- d : hydraulic diameter (m)
- Q : fluid volumetric flow rate (m^3)
- ϕ : porosity of microfluidic chip
- h : height of microfluidic chip opening (m)
- w : width of microfluidic chip opening (m)

The above method resulted in an apparent shear rate of $38.8 s^{-1}$. Apparent shear rate values given by the two methods did not differ significantly. We proceeded by scanning for appropriate polymer concentrations that would match the viscosity of DTM High solution

between 38.8 s^{-1} and 45.7 s^{-1} at ambient conditions. We found the appropriate concentrations to be 8000 and 3000 ppm for AN 125 VLM and FLOPAAM 3330s polymers, respectively. A complete result of rheology measurements for all seven liquid phase solutions is presented in Figure 4.1.

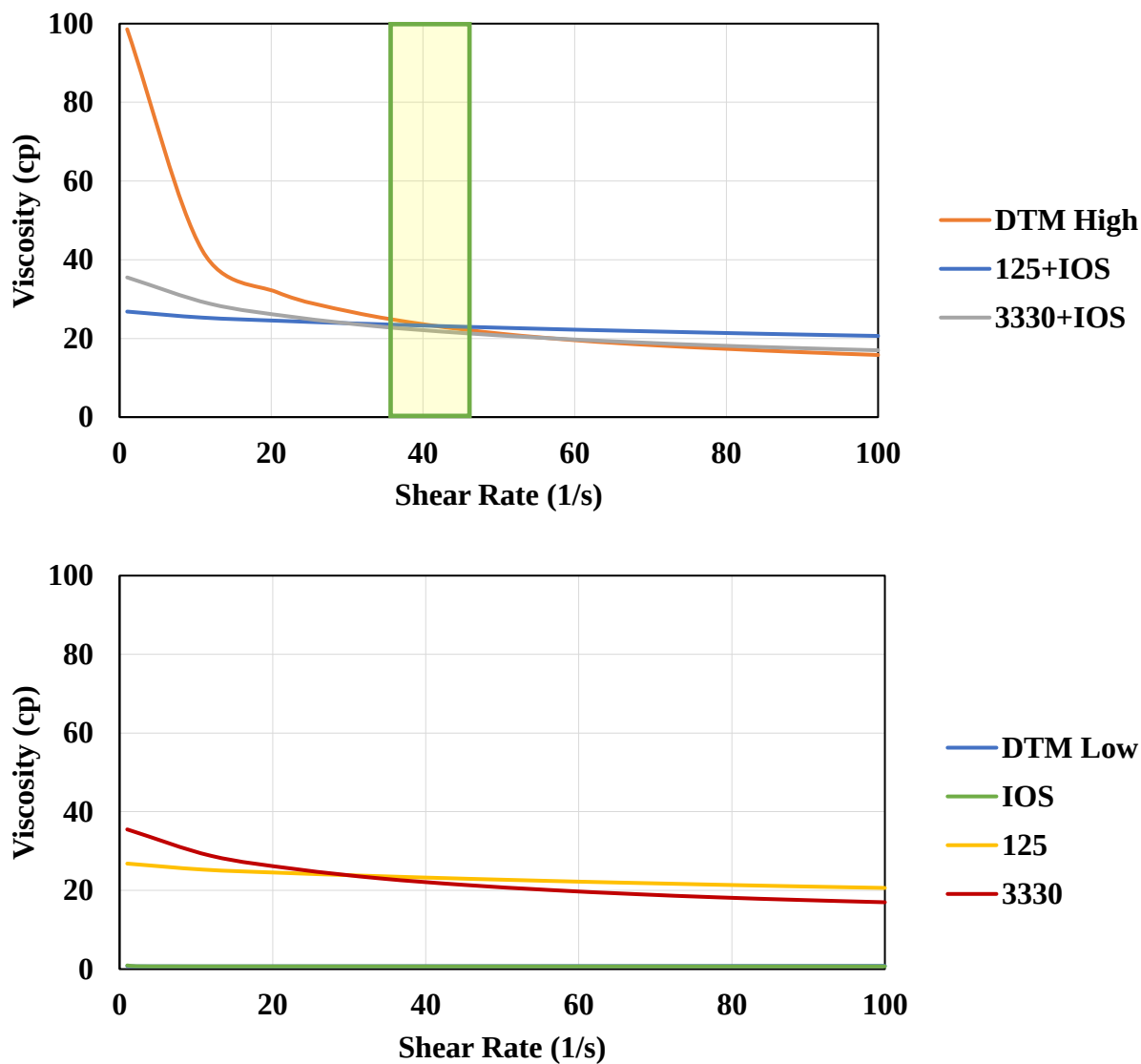


Figure 4.1 Rheology measurements of seven liquid phase bulk solutions at ambient conditions.

The rheology of the 125 solution did not differ from the rheology of the 125+IOS. The same is true for the rheology of the 3330 and 3330+IOS solutions. The viscosities of the DTM

Low and IOS solutions were low in the shear rate range tested (0.71 and 0.70 cp, respectively at 40 s^{-1}).

4.1.3 Microfluidics Foam Experiment

We used one type of microfluidic porous media chip produced by micronit for all foam injection experiments. The initial parameters of this chip are tabulated in Table 4.2.

Table 4.2 Microfluidic porous media chip initial parameters

Parameter	Value	Unit
Permeability	2.75	Darcies
Pore Volume	2.30	μL
Porosity	0.57	-
Chip Length	0.02	m
Channel Width	0.009	m
Channel Thickness	2.24×10^{-5}	m

The microfluidic chip is put under a microscope with an attached video camera. Two flow lines lead up to the entrance of the microfluidic chip: the gas injection line and the liquid injection line. In all experiments, the gas injection was done under a constant upstream pressure; which is regulated by a gas tank pressure regulator and a pressure relief valve. The liquid injection in all experiments was done at a constant volumetric flow rate by a positive displacement syringe pump. Two absolute pressure transducers are placed at the inlet of the chip and the back-pressure regulator (BPR). The BPR itself was set at a pressure of 55 psi to reduce the gas compressibility effect. We quantified the gas injection rate through volumetric water displacement method; where we kept track of the mass of the water collected throughout the injection period. The schematic diagram of the injection setup is provided in Figure 4.2.

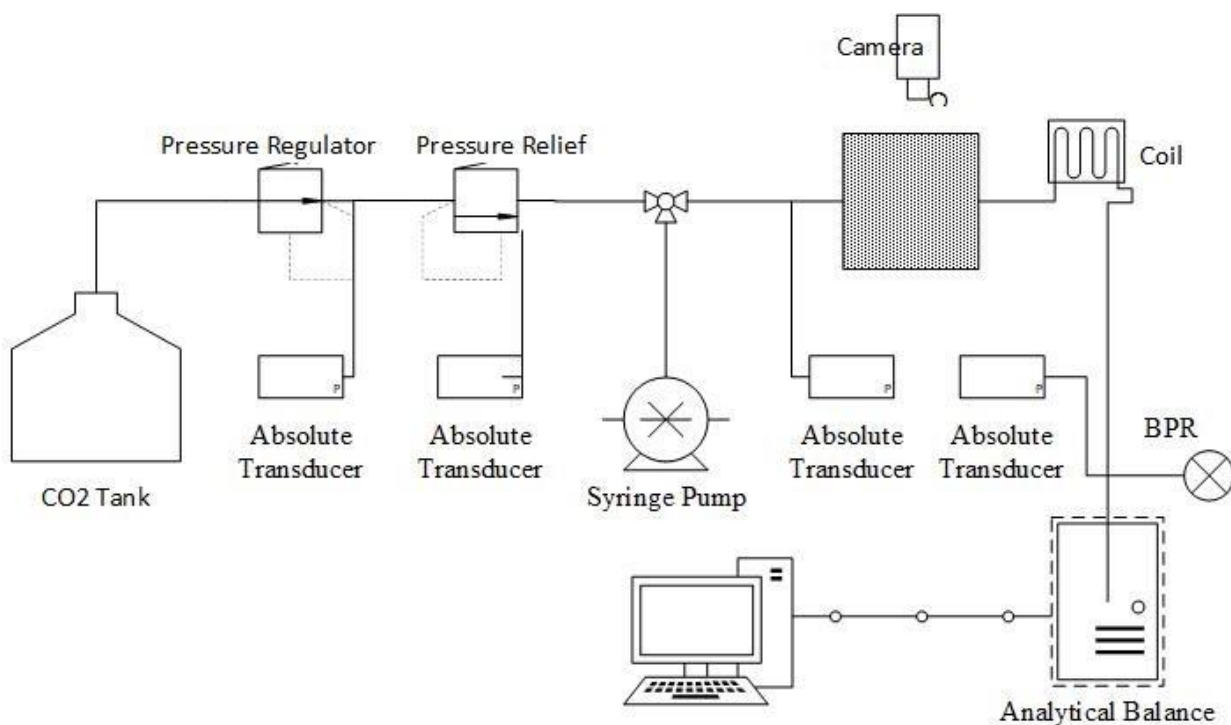


Figure 4.2 Diagram of the microfluidic injection setup

We conducted two types of foam injection strategies in this study.

1. Constant upstream CO₂ injection (gas injection)
2. Constant upstream CO₂ injection + constant liquid phase volumetric flow rate (co-injection)

In the gas injection strategy, we began by saturating the microfluidic chip with the desired liquid phase solution. Once the chip had been saturated, and the liquid phase flow had ceased, we opened the valve to the CO₂ injection line. We performed gas injection foam experiments with all seven solutions listed in Table 4.1. For each solution, we performed three gas injection experiments at three different upstream CO₂ pressures: +1, +2, and +3 psi relative to the set pressure of the BPR.

In the co-injection strategy, we also began by saturating the microfluidic chip with the desired liquid phase solution. Once the chip had been saturated, we opened the valve to the CO₂

injection line without closing the valve to the liquid phase injection line. We performed co-injection foam experiments with all seven solutions listed in Table 4.1. For each solution, we performed three co-injection experiments at three different upstream CO₂ pressures: +3, +4, and +5 psi relative to the set pressure of the BPR. The liquid phase injection was kept constant at 0.6 $\mu\text{L}/\text{min}$ for all experiments.

All experiments were done at room temperature. After each experiment, the microfluidic chip was rinsed with 10 ml of DI water over the duration of 30 minutes. We performed a permeability test before each experiment to ensure that deviation is less than 10% of the initial values listed in Table 4.2.

4.2 Results and Discussion

4.2.1 Effect of Interfacial Tension

We first examined the foaming behavior of the DTM and IOS surfactants without liquid phase viscosification (DTM Low and IOS solutions per Table 4.1). These two solutions had the same concentration of surfactants (0.5 wt.%), NaCl salinity (15 wt.%), and nearly identical viscosity (0.71 and 0.70 cp for DTM Low and IOS, respectively, at the shear rate of 40 s^{-1}). The notable difference between the two surfactant solutions is their gas-liquid IFT (σ_{gl}) value with CO₂ (35.30 and 27.61 dyne/cm for DTM Low and IOS, respectively). With these two solutions, we performed microfluidic foam gas injection at a constant upstream CO₂ pressure of +1 psi relative to the BPR set pressure; and a co-injection at a constant upstream CO₂ pressure of +3 psi relative to the BPR set pressure and constant liquid phase flow rate of 0.6 $\mu\text{L}/\text{min}$. The foam apparent viscosity (μ_f) measurements are presented in Figure 4.3.

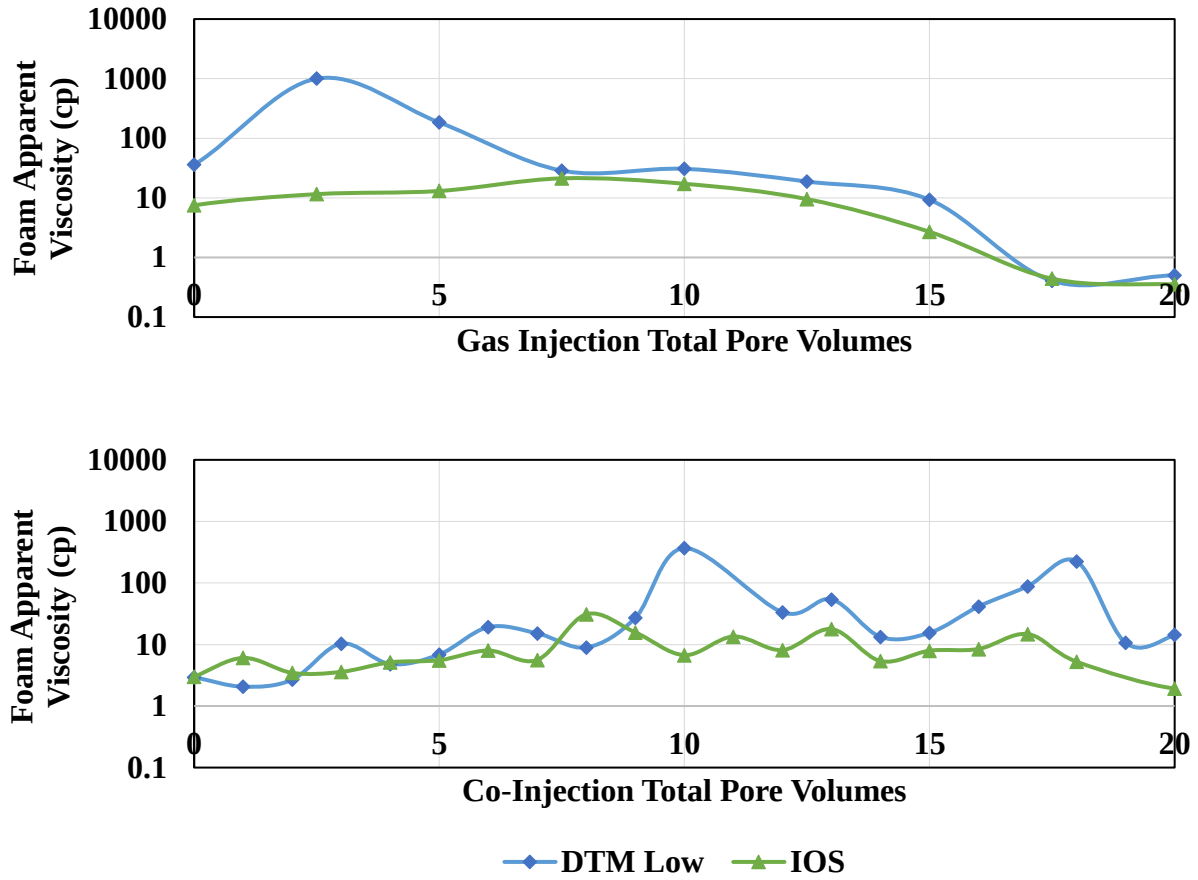


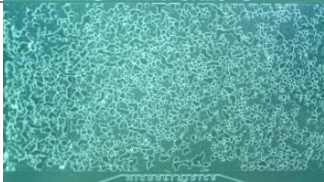
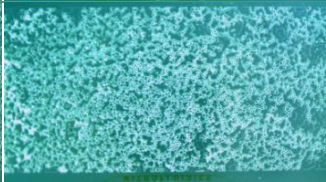
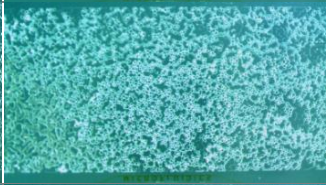
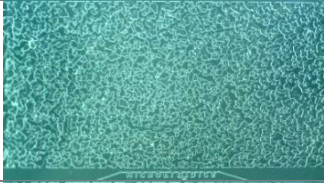
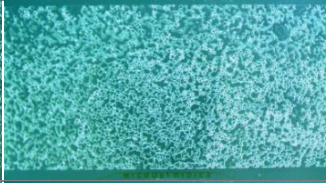
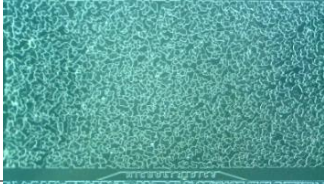
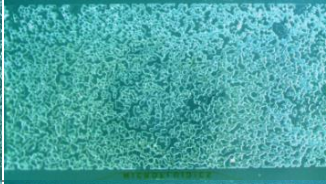
Figure 4.3 Foam apparent viscosity measurements for DTM Low and IOS solutions in gas injection (top) and co-injection (bottom) microfluidic foaming

Gas injection μ_f . DTM Low foam exhibited greater μ_f value than the IOS foam at the early injection period. DTM Low μ_f climbed to a maximum value at 3 injected total pore volumes (TPV). The DTM Low μ_f then declined over the rest of injection period and fell to a minimum value of less than 1 cp. The IOS μ_f increased during the first half of the injection and reached a maximum value at around 8 TPV. The IOS μ_f then declined through the second half of the injection period and fell to a minimum value of less than 1 cp.

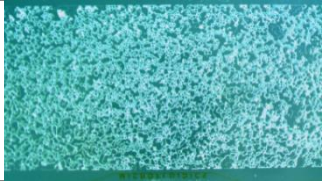
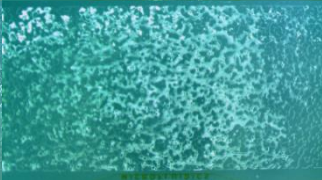
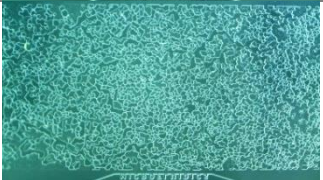
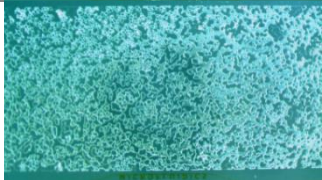
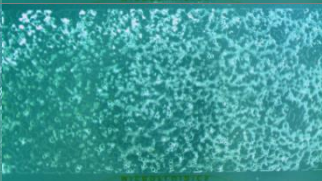
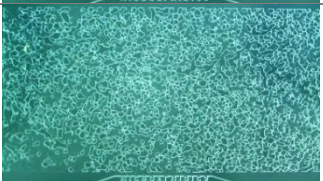
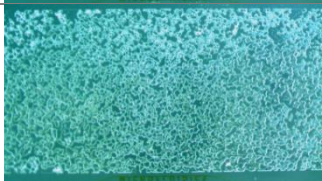
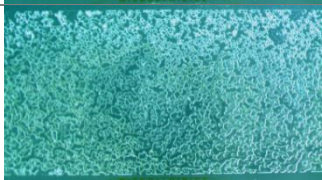
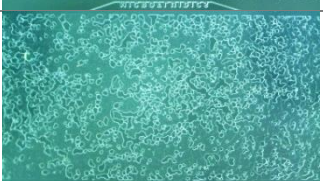
Co-injection μ_f . Both DTM Low and IOS foams exhibited similar μ_f behavior through the first half of the injection. The μ_f values during early injection period in the co-injection are

lower than those in the gas injection for both DTM Low and IOS foams. After 10 TPV, the DTM Low μ_f displayed a sinusoidal plateau behavior. The IOS μ_f displayed similar oscillatory behavior around a lower μ_f value. The decline in μ_f , observed in the later period of gas injection, did not occur in the co-injection cases.

We required in-situ visual evidence to examine the mechanisms behind the behavior of foam μ_f . We recorded the in-situ interaction between the gas and liquid phases inside the microfluidic chip via a microscope video camera. The video recording was processed and synchronized with the gas injection rate data. Still-images were cut at specific times throughout the experiment duration. The visualization of the gas-injection and co-injection foaming experiments of DTM Low and IOS foams is presented in Figure 4.4. The microfluidic images in Figure 4.4 and the rest of this chapter are enlarged by 1.2 times.

Effect of IFT in Gas Injection		
TPV	DTM Low	IOS
0		
2.5		
5		
7.5		
10		
12.5		
15		
17.5		
20		

Effect of IFT in Co-Injection

TPV	DTM Low	IOS	TPV	DTM Low	IOS
0			9		
1			10		
2			11		
3			12		
4			13		
5			14		
6			15		
7			16		
8			17		

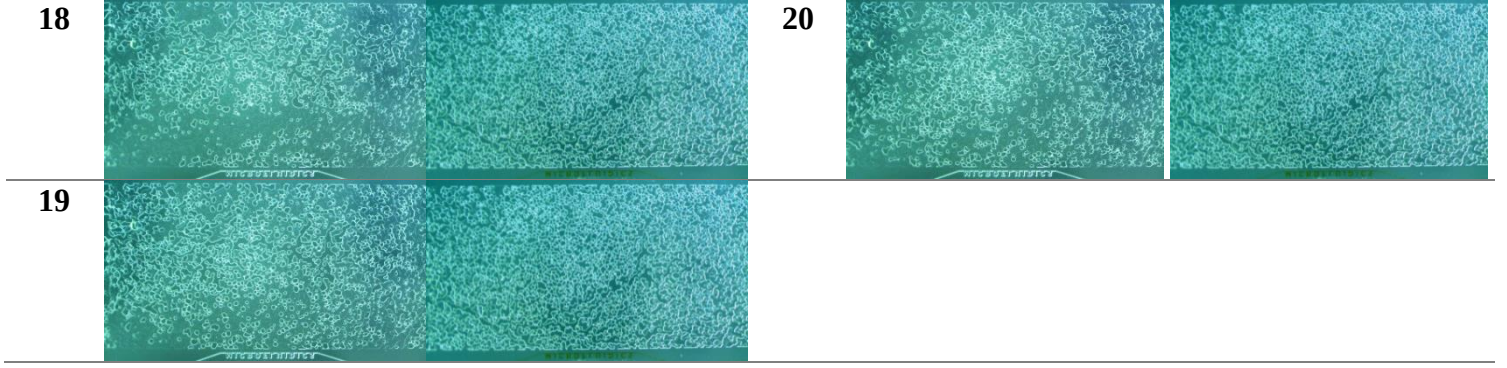


Figure 4.4 In-situ images of DTM Low and IOS gas-injection and co-injection foaming experiments

Gas injection discussion. By looking at the gas injection images at 2.5 TPV, it is apparent that strong foam developed early in the injection period for both DTM Low and IOS foams. Gas saturation is relatively high in both cases indicating a good conformance performance. There is, however, a marked difference in foam texture; where the DTM Low foam is appreciably rougher than the IOS foam. Foam generation in porous media occurs when the gaseous phase flows through a pore constriction (snap-off), stretches around a branch point in a flow path (lamellae-division), or being caught in a junction perpendicular to a flow path (leave-behind) [8]. In snap-off, a certain pressure gradient must be applied to overcome the capillary forces in pore constrictions. Equation (2) suggests that a lower σ_{gl} may reduce the minimum pressure gradient necessary for gas flow through a pore throat; thus promoting snap-off events. In lamellae division, a lower σ_{gl} may also aid in the expansion of the gas-liquid interface. DTM Low solution had a higher σ_{gl} than the IOS solution. It may be the case that foam generation events occurred at a higher rate in the IOS foam due to its lower σ_{gl} , resulting in a finer textured foam.

Despite the coarser texture, the DTM Low foam had higher μ_f in the early injection period. Equation (2) suggests that foam μ_f is obtained through multiplication of lamella density (analogous to foam texture) and the apparent viscosity of a single bubble lamella. The higher

overall μ_f in DTM Low indicates that DTM Low foam has a significantly higher per lamella apparent viscosity. This result is to be expected due to the larger σ_{gl} value in the DTM Low solution. The higher σ_{gl} in DTM Low led to a coarser foam texture due to less frequent snap-off and lamella division events. However, DTM Low's greater single lamella apparent viscosity compensated for the lack of lamella density. This resulted in the higher μ_f observed in DTM Low foam.

Later in the injection period (5 TPV onwards), foam generation ceased in both cases due to extremely low liquid saturation. After reaching peak texture and apparent viscosity, foam lamellae began to be subjected to disturbance forces that reduce the foam film's thickness. This process continues until film thins below a critical thickness; where the film is not stable and tend to coalesce [15]. As the bubbles start to coalesce, the number of lamellae decrease and the foam starts to lose its ability to divert gas from the highest permeability channels. A weakening foam maybe pushed/displaced from the porous media by the flow of gas.

The rate of film drainage is inversely related to the viscosity of the foam liquid phase [7]. Both DTM Low and IOS solutions had lower than 1 cp viscosity; thus their film drainage rate is expected to be relatively high. The μ_f reading of both foam cases after 15 TPV indicates that foam offered inadequate resistance to gas flow. Microfluidic visual evidence at 10 TPV and beyond display a marginal reduction in foam texture; but not a complete collapse. It is important to acknowledge that most of the gas in both cases is trapped in the later injection period. Trapped gas severely reduces the effective permeability of gas moving through a porous media by reducing the number of conduits through which the gas can flow [20]. However, a gas breakthrough inevitably occurred through the highest permeability channel after the collapse of foam in that channel only.

Co-injection discussion. In the early period of co-injection, the texture of foams generated in both the DTM Low and IOS cases were rougher compared to their respective equivalence in the gas injection scheme. In co-injection, there is a constant injection of liquid; which may have partially displaced the newly formed foam. This phenomenon prevents a rapid buildup of fine- textured foam. The μ_f data in Figure 4.3 confirms the visual observation. The μ_f values for both foam cases were lower through the first 5 TPV in the co-injection scheme compared to gas injection. The foam textures in DTM Low and IOS cases continued to build up until it reached a maximum at approximately 10 TPV. At this point, the texture of the DTM Low foam is coarser than that of the IOS foam. As previously discussed, this result could be explained by the higher DTM Low σ_{gl} ; thus resulting in a less frequent foam generation event.

We saw a higher peak μ_f in the DTM Low case; despite its coarser texture. Again, this could be attributed to the higher per lamella apparent viscosity in the DTM Low case due to its higher σ_{gl} . Unlike in gas injection, foam generation events in co-injection did not stop after reaching the peak texture. In our observation, the constant injection of liquid could displace a significant portion of the foam already generated. This phenomenon is evident in the images of 13 and 14 TPV in DTM Low co-injection. The cycle of foam generation by gas flow and foam displacement by liquid flow created the sinusoidal plateau observed in the co-injection μ_f data in figure 4.3. In the IOS co-injection, the sinusoidal behavior did not occur as in the DTM Low foam due to severe gas breakthrough. IOS foam is more prone to gas breakthroughs due to its lower maximum μ_f . Looking at the co-injection images of IOS after 10 TPV, the foam texture did not change significantly. Foam displacement by incoming liquid phase did not take place in the duration of the injection. Past 10 TPV, the flow of fluid through the microfluidic chip is dominated by the flow of gas breaking through the highest permeability channel. This

breakthrough is not permanent, however, since incoming liquid phase may fill the gas-breakthrough channel and allowing for another cycle of foam generation.

4.2.2 Effect of the Liquid Phase Shear-Thinning

Next, we examined the effect of polymer addition into the IOS surfactant solution. First, we elected to perform experiments on polymer solutions without the addition of surfactant as a basis of comparison (125 and 3330 solutions per Table 4.1). These two solutions had similar IFT values with CO₂ (66.20 and 65.14 dyne/cm for 125 and 3330, respectively). In the target shear rate between 38.8 and 45.7 s⁻¹, these two solutions exhibited similar rheological behavior. However, over a wider range of shear rate, the 125 solution is less shear thinning than the 3330 as presented in Figure 4.1. With these two solutions, we performed microfluidic foam gas injection at a constant upstream CO₂ pressure of +1 psi relative to the BPR set pressure; and a co-injection at a constant upstream CO₂ pressure of +3 psi relative to the BPR set pressure and a constant liquid phase flow rate of 0.6 µL/min. The foam μ_f measurements are presented in Figure 4.5.

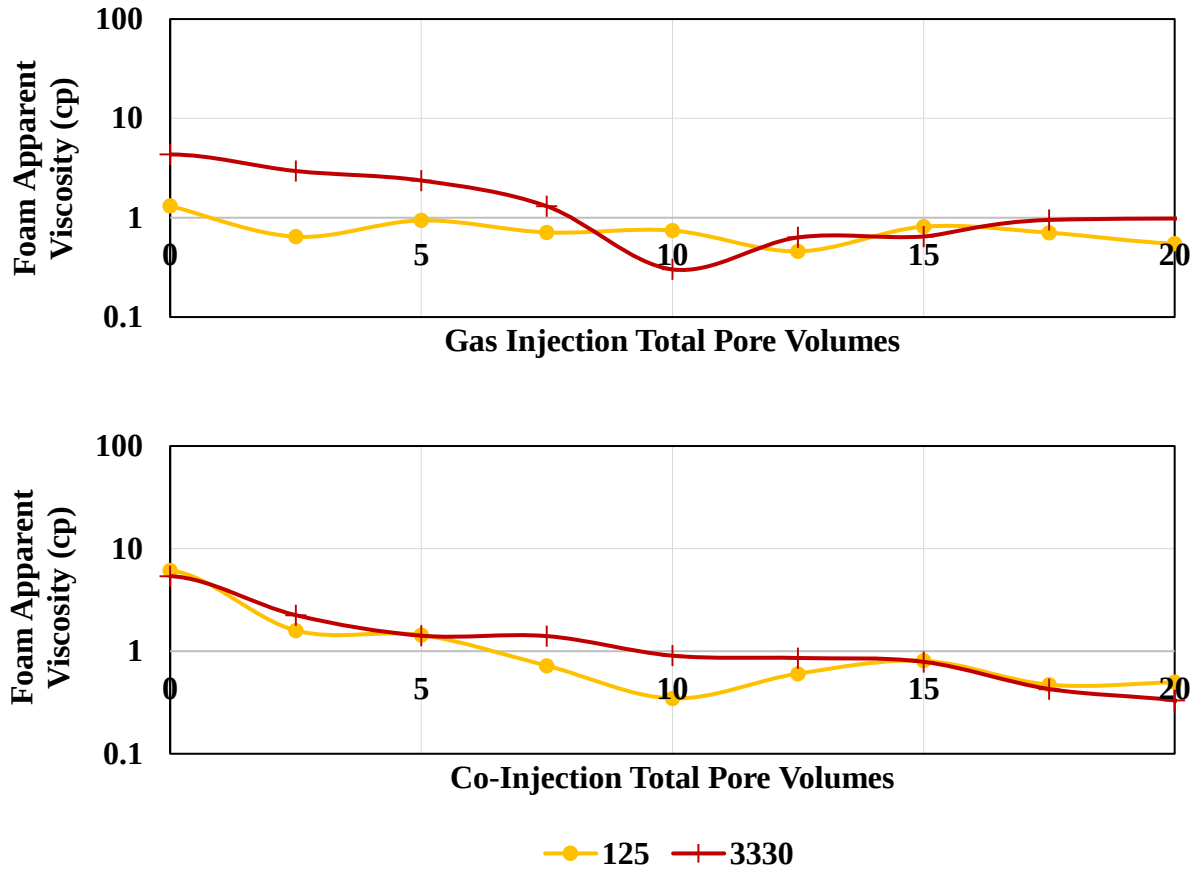
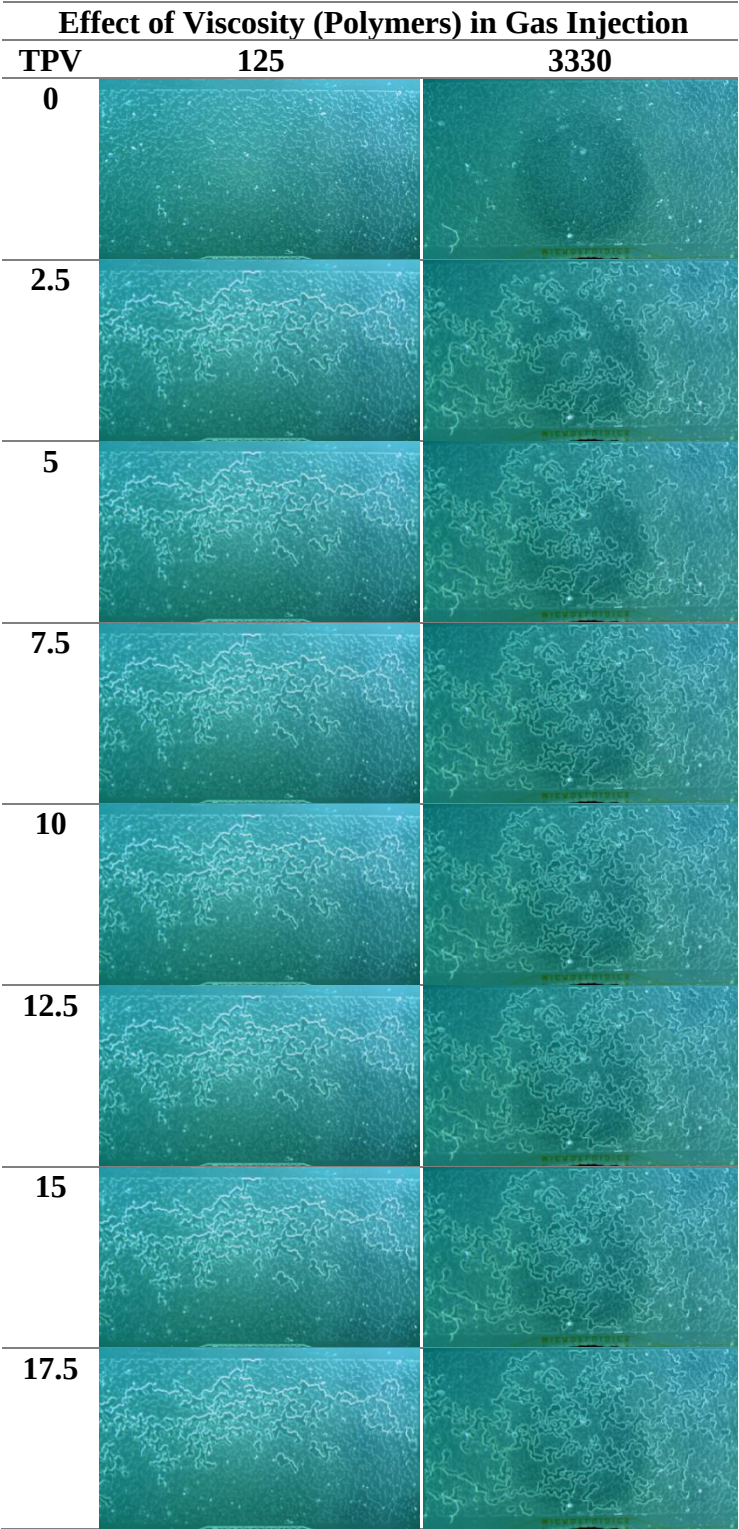


Figure 4.5 Foam apparent viscosity measurements for 125 and 3330 solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming

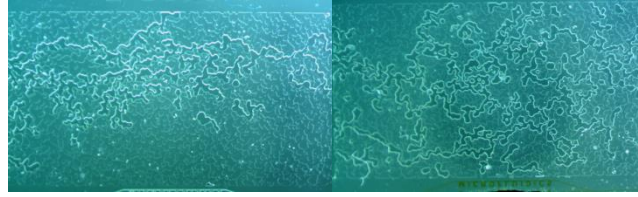
Gas injection μ_f . The μ_f in the 3330 case is slightly higher than that of 125 through the early injection period. However, the 3330 μ_f subsequently declined below 1 cp. The observed μ_f for 125 remained very low throughout the injection period.

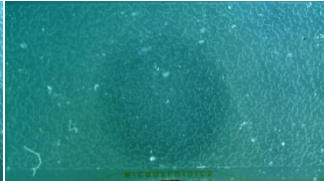
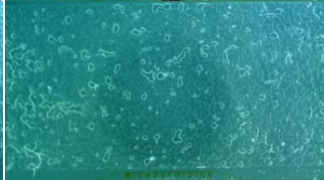
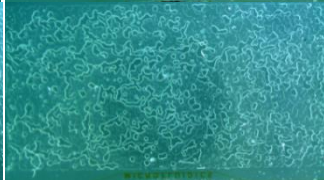
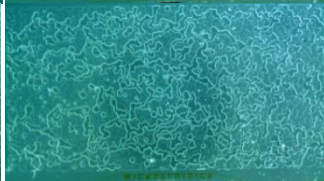
Co-injection μ_f . The observed μ_f of both 125 and 3330 cases behaved similarly; although the 3330 was marginally higher through 15 TPV. Both μ_f started at just under 10 cp and gradually declined to below 1 cp.

The visualization of the gas injection and co-injection foaming experiments of 125 and 3330 solutions is presented in Figure 4.6.



20



Effect of Viscosity (Polymers) in Co-Injection		
TPV	125	3330
0		
2.5		
5		
7.5		
10		
12.5		
15		

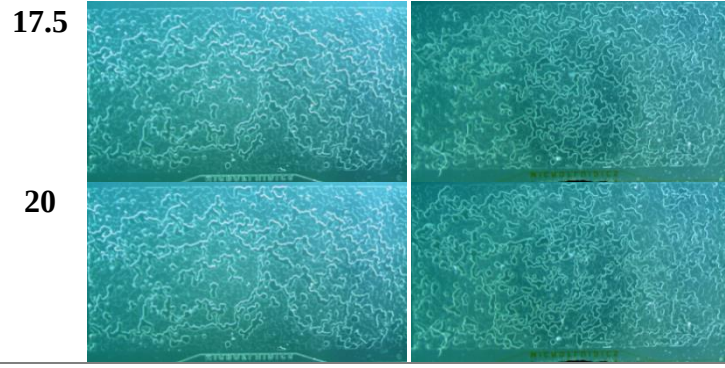


Figure 4.6 In-situ images of 125 and 3330 gas-injection and co-injection foaming experiments

Gas injection discussion. Looking at the gas injection images at 2.5 and 5 TPV, it is apparent that strong foam did not develop in either case. We observed that the gas saturation is higher in the 3330; which corresponds to the higher measured μ_f through the early injection period. As previously stated, the 125 solution is a less shear thinning solution than the 3330. The entry velocity of the gas into the microfluidic chip may have been very high due to the absence of strong foam generation. Therefore, the residence liquid phase may have been pushed and sheared at a higher shear rate than the target shear rate range. At this high shear rate, the 125 possessed a higher viscosity than the 3330. The displacement of the 125 at such shear rate by the incoming gas may have resulted in a more severe viscous instability; thus resulting in a more extreme gas fingering. In the late injection period, we observed that μ_f was similarly low at below 1 cp for both cases. At this point, the gas primarily flowed through the highest permeability channel.

Co-injection discussion. We did not observe strong foam generation in the co-injection cases. The gas saturation in both 125 and 3330 cases at 2.5 TPV was higher than in the gas injection counterparts. This result may be attributed to the constant flow of the liquid phase; which could momentarily fill the fingering channel and divert gas to other areas of the chip.

Overall, we still observed a higher gas saturation in the 3330 case; which explains the marginally higher μ_f observed.

Foaming experiments with 125 and 3330 solutions served as a reference point for the subsequent polymer + surfactant experiments. In the polymer and surfactant experiments, we used the IOS surfactant and two types of polyacrylamide with differing molecular weights: AN 125 VLM at 2 MDa (solution 125+IOS per Table 4.1) and FLOPAAM 3330s at 8 MDa (solution 3330+IOS per Table 4.1). The 125+IOS and 3330+IOS solutions had similar IFT values with CO₂ (27.30 and 26.82 dyne/cm, respectively). Within the shear rate range of 38.8 and 45.7 s⁻¹, the two solutions exhibited near-identical viscosity. The notable difference is the shear thinning characteristic; in which the 125+IOS solution is less shear thinning than 3330+IOS (figure 4.1). With these two solutions, we performed microfluidic foam gas injection at a constant upstream CO₂ pressure of +1 psi relative to the BPR set pressure; and a co-injection at a constant upstream CO₂ pressure of +3 psi relative to the BPR set pressure and constant liquid phase flow rate of 0.6 μ L/min. The foam μ_f measurements are presented in Figure 4.7. The results for 125 and 3330 are included as a reference.

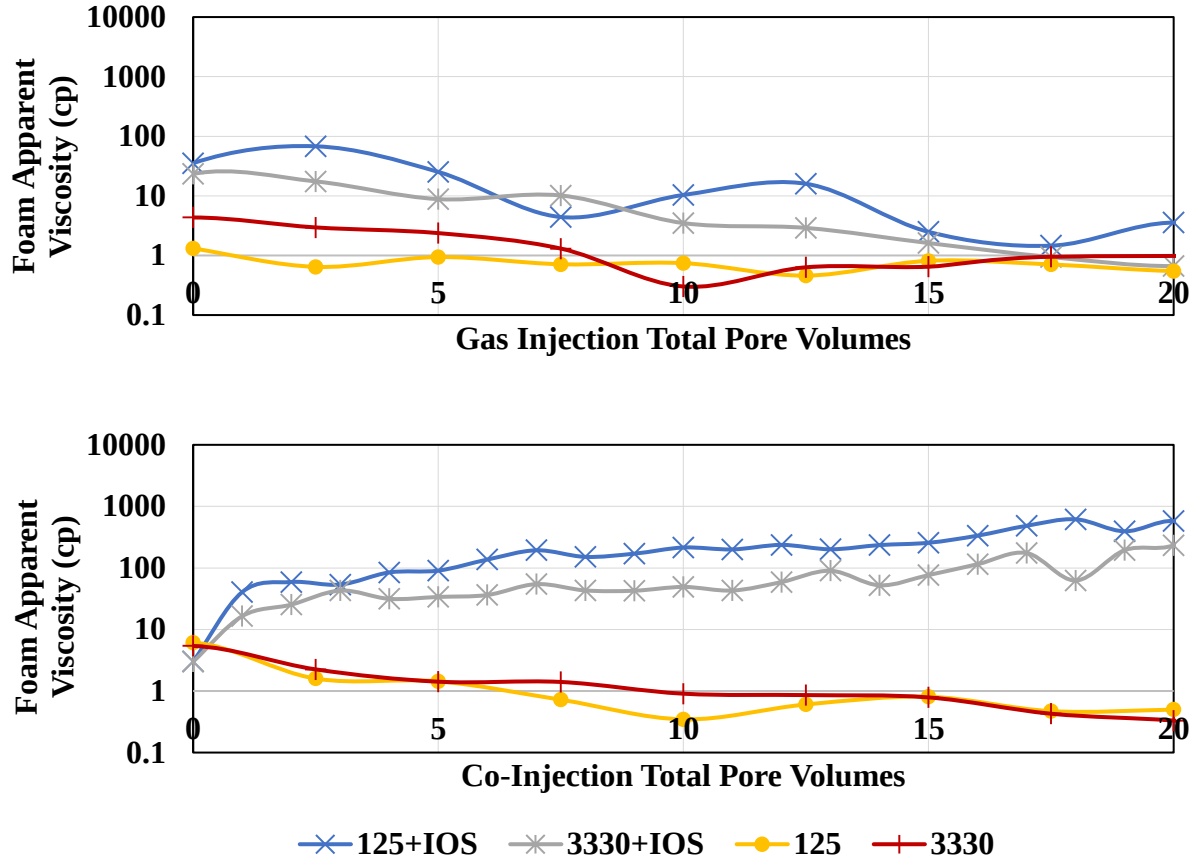


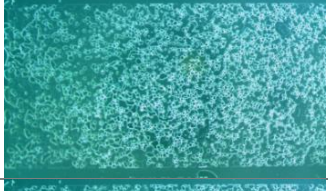
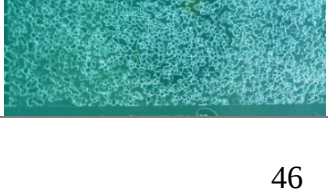
Figure 4.7 Foam apparent viscosity measurements for 125+IOS and 3330+IOS solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming

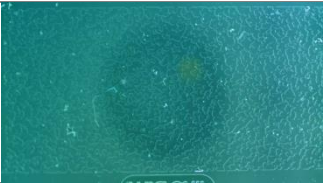
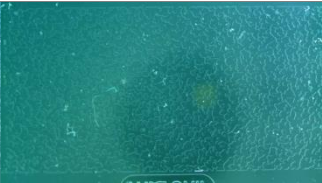
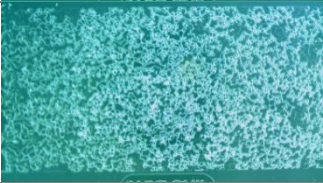
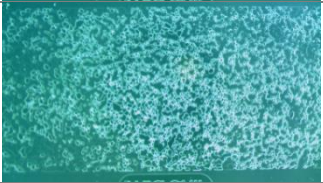
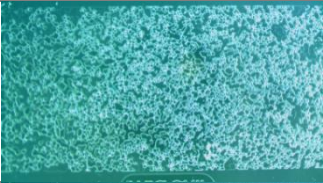
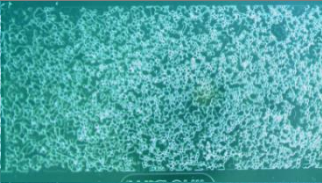
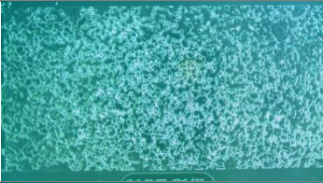
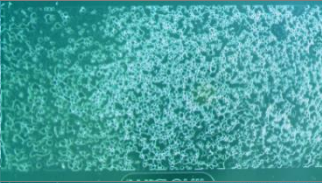
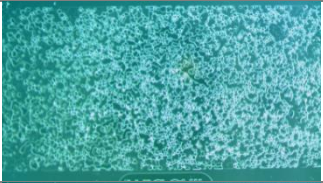
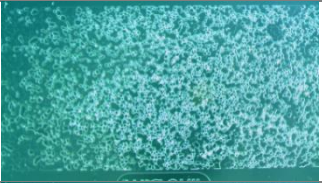
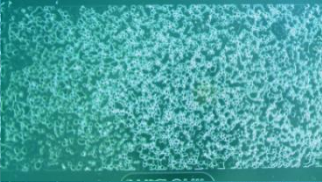
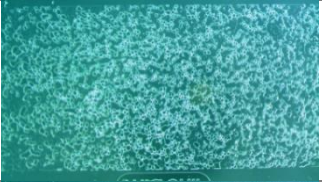
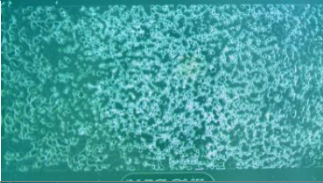
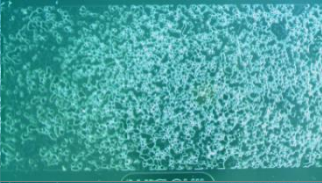
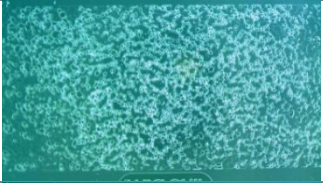
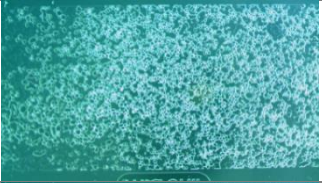
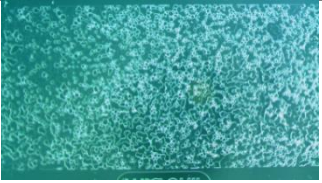
Gas injection μ_f . At the start of the injection, the 125+IOS foam exhibited greater μ_f .

Throughout the rest of the injection period, the μ_f of both cases gradually declined. The 125+IOS foam had a greater peak μ_f . Throughout the decline, the μ_f value of 125+IOS was in most parts higher, as well.

Co-injection μ_f . Both foam cases reached high μ_f values early. After the initial rise, both the 125+IOS and 3330+IOS foams displayed a similar rate of μ_f buildup. However, the μ_f of 125+IOS was higher at every point.

The visualization of the gas-injection and co-injection foaming experiments of 125+IOS and 3330+IOS solutions is presented in Figure 4.8.

Effect of Viscosity (Polymers + IOS) in Gas Injection		
TPV	125+IOS	3330+IOS
0		
2.5		
5		
7.5		
10		
12.5		
15		
17.5		
20		

Effect of Viscosity (Polymers + IOS) in Co-Injection					
TPV	125+IOS	3330+IOS	TPV	125+IOS	3330+IOS
0			9		
1			10		
2			11		
3			12		
4			13		
5			14		
6			15		
7			16		
8			17		

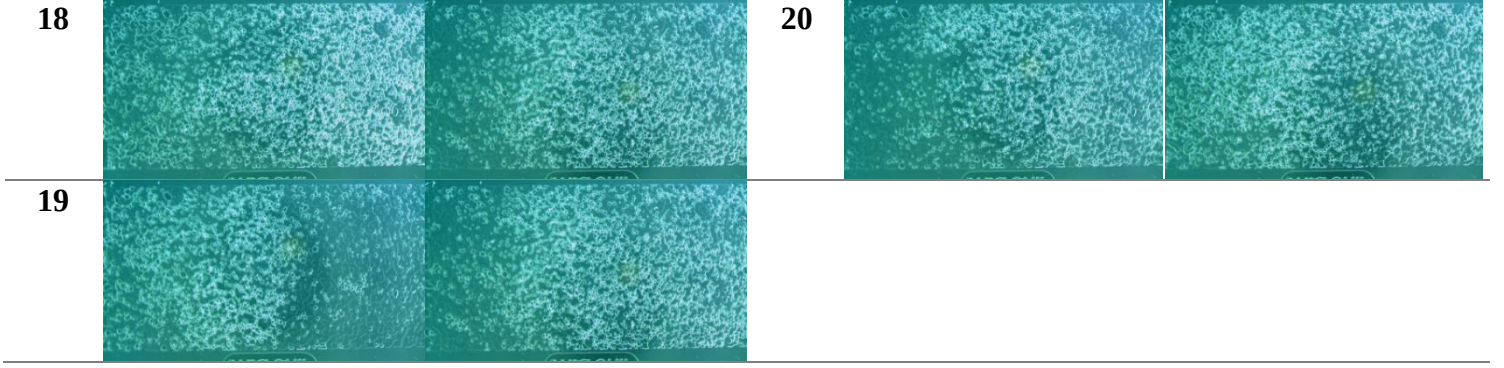


Figure 4.8 In-situ images of 125+IOS and 3330+IOS gas-injection and co-injection foaming experiments

Gas injection discussion. Looking at the gas injection images at 2.5 TPV, we saw fine-textured foam generated in 125+IOS and 3330+IOS cases. At 5 TPV, the gas saturation was very high in both cases; indicating a good conformance performance by both foams. At 7.5 TPV, both foams reached their finest foam texture. At this point in the injection, the 125+IOS foam had a slightly finer texture. This result may indicate that foam generation events occurred more frequently in the 125+IOS foam. Looking at the rheology behavior of 125+IOS and 3330+IOS solutions, the former had a lower viscosity at shear rates less than 30 s^{-1} . Due to an immediate strong foam formation, the entry velocity of the gas into the microfluidic chip may have been very low. Such that, the residence liquid phase was sheared at a lower shear rate than the target shear rate range. Therefore, the in-situ viscosity of 125+IOS liquid phase at this instance could be lower than that of 3330+IOS. Equation (2) suggests that a less viscous foam liquid phase (μ_l) may allow for easier passing of foam gas phase through pore constrictions. Such actions may lead to higher frequency of snap-off foam bubble generation; which may have led to the finer texture in the 125+IOS.

By the same reasoning, it would also be expected that 3330+IOS foam had a larger per lamella apparent viscosity due to a marginal difference in σ_{gl} but appreciably higher μ_l . However, we observed a consistently higher overall μ_f in 125+IOS foam. In this case, the finer

texture of 125+IOS may have compensated for its lesser per lamella apparent viscosity. After 7.5 TPV, foam generation was not observed due to extremely low liquid saturation. From this point on, the foam started to weaken due to film drainage.

Co-injection discussion. The first foam generation cycle in both foams occurred through the first 5 TPV. It is apparent in both cases that strong foams were generated early and reached their finest texture and highest gas saturation at 5 TPV for 125+IOS and 4 TPV for 3330+IOS. Comparing the textures of the 125+IOS and 3330+IOS foams, we saw a slightly finer foam in the 125+IOS case. This observation explains the higher μ_f of the 125+IOS foam showcased in Figure 4.7. It is to be noted, however, that the texture difference between the two foams is not as apparent as in the co-injection experiments. It may be the case that, in co-injection with a high liquid phase viscosity, foam generation is not sensitive to a slight variation in viscosity. We saw this result in the previous comparison between the weak foam behavior of 125 and 3330 solutions; where the stark texture difference they exhibited in the gas injection was not as apparent in the co-injection schemes. The constant injection of the viscous liquid phase may have aided in the diversion of foam gaseous phase into more pore constrictions by filling and blocking the gas fingering channels.

4.2.3 Effect of Liquid Phase Viscosity

In this section, we examined the effect of liquid phase viscosity on foam behavior. To do this, we performed foaming experiments on two DTM solutions at different salinities (DTM High and DTM Low per Table 4.1). These two solutions had marginal differences in σ_{gl} with CO₂ (35.15 and 35.30 dyne/cm for DTM High and DTM Low, respectively). The notable difference between the two is their viscosity. The salinity of DTM High is above the critical salinity for worm-like micelle (WLM) formation. Entanglement of WLM under shear conditions

results in the viscosification of the foam liquid phase [35]. The viscosity of the DTM High is 23.45 cp at 40 s^{-1} ; while the viscosity of DTM Low is only 0.71 cp at the same shear rate. Their rheology over a wider range of shear rates can be seen in Figure 4.1. With these two solutions, we performed a microfluidic foam gas injection at a constant upstream CO_2 pressure of +1 psi relative to the BPR set pressure; and a co-injection at a constant upstream CO_2 pressure of +3 psi relative to the BPR set pressure and constant liquid phase flow rate of $0.6 \mu\text{L}/\text{min}$. The foam μ_f measurements are presented in Figure 4.9.

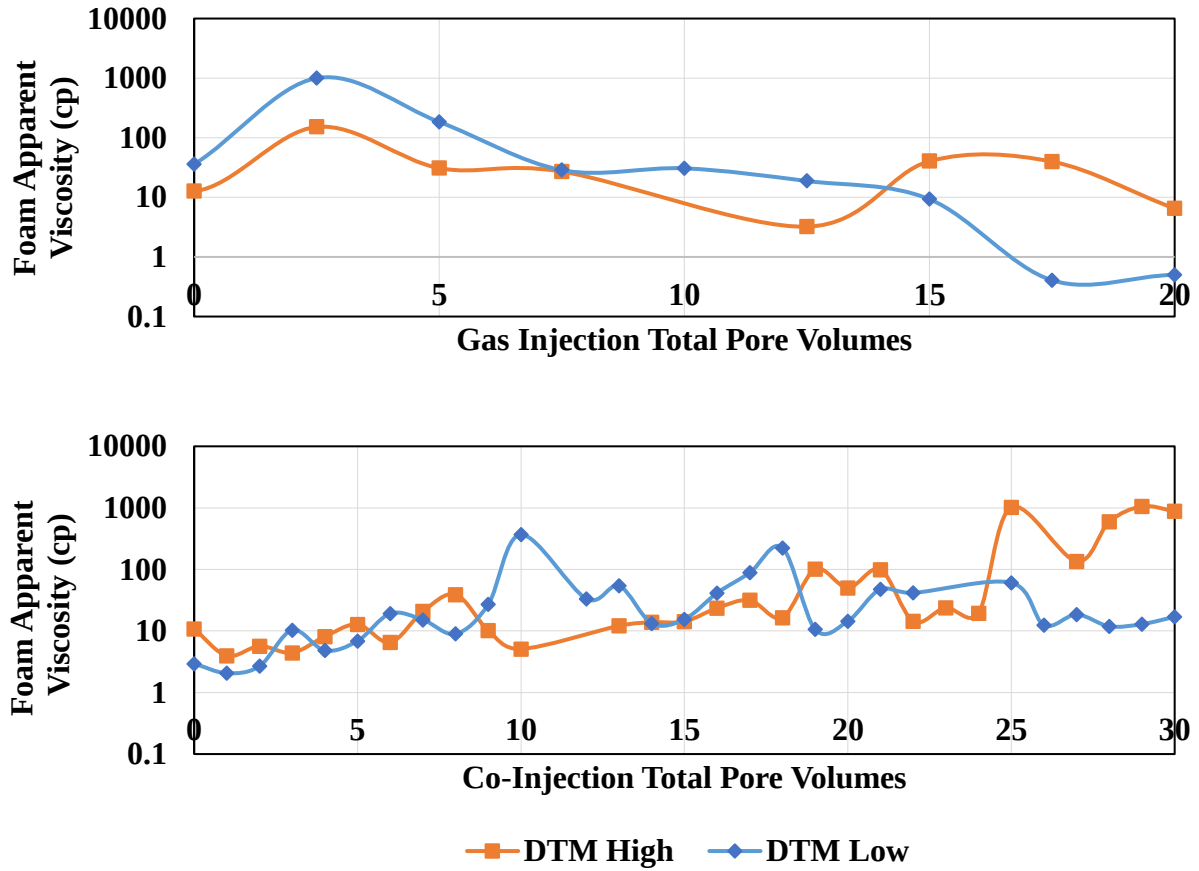


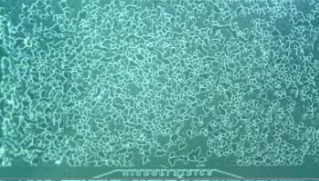
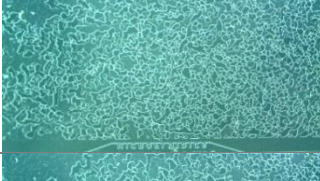
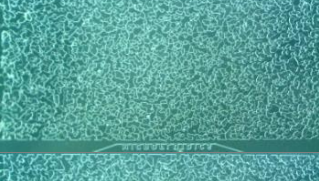
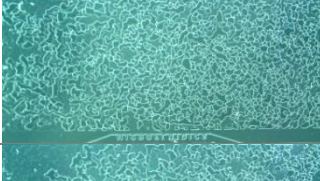
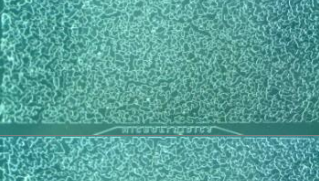
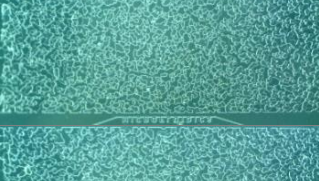
Figure 4.9 Foam apparent viscosity measurements for DTM Low and DTM High solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming

Gas injection μ_f . Through the first 5 TPV, DTM High foam exhibited lower μ_f value than DTM Low. Through the rest of the injection period, DTM High was able to maintain a

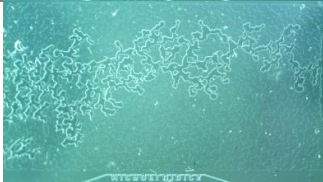
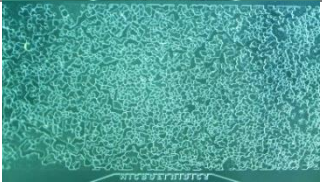
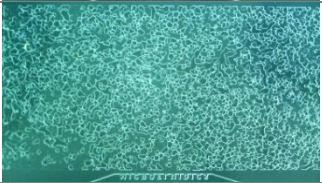
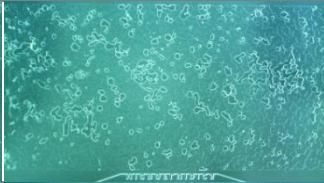
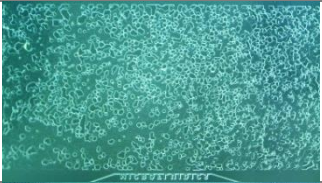
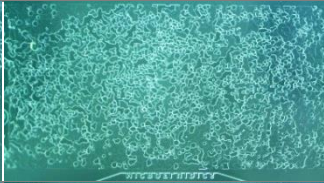
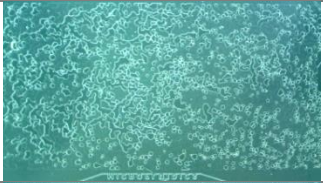
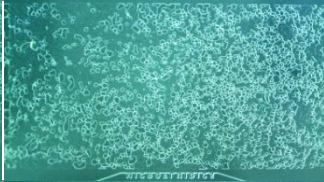
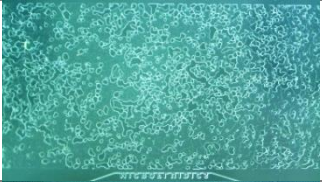
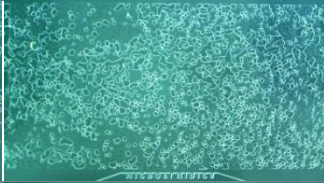
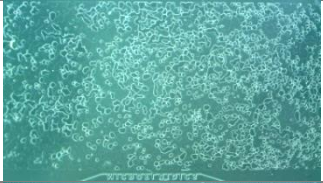
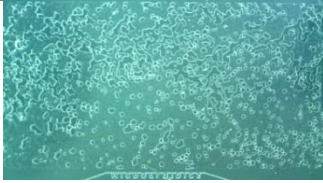
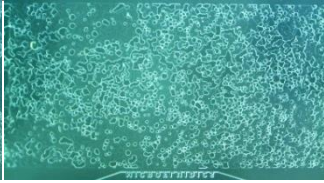
reasonably high μ_f . DTM Low μ_f , on the other hand, experienced a gradual decline and its μ_f dropped to below 1 cp at the end of the injection period.

Co-injection μ_f . Through the first 8 or so TPV, the μ_f build-up rate was similar between DTM High and DTM Low. Thereafter, DTM Low exhibited a sharp increase in μ_f and started its sinusoidal plateauing behavior. Past 8 TPV, DTM High continued its μ_f build-up. Over the extended duration of injection, DTM High foam eventually reached a higher μ_f value than that of DTM Low foam.

The visualization of the gas-injection and co-injection foaming experiments of DTM High and DTM Low solutions is presented in Figure 4.10.

Effect of Viscosity (DTM Salinity) in Gas Injection		
TPV	DTM High	DTM Low
0		
2.5		
5		
7.5		
10		
12.5		
15		
17.5		
20		

Effect of Viscosity (DTM Salinity) in Co-Injection

TPV	DTM High	DTM Low	TPV	DTM High	DTM Low
0			9		
1			10		
2			11		
3			12		
4			13		
5			14		
6			15		
7			16		
8			17		

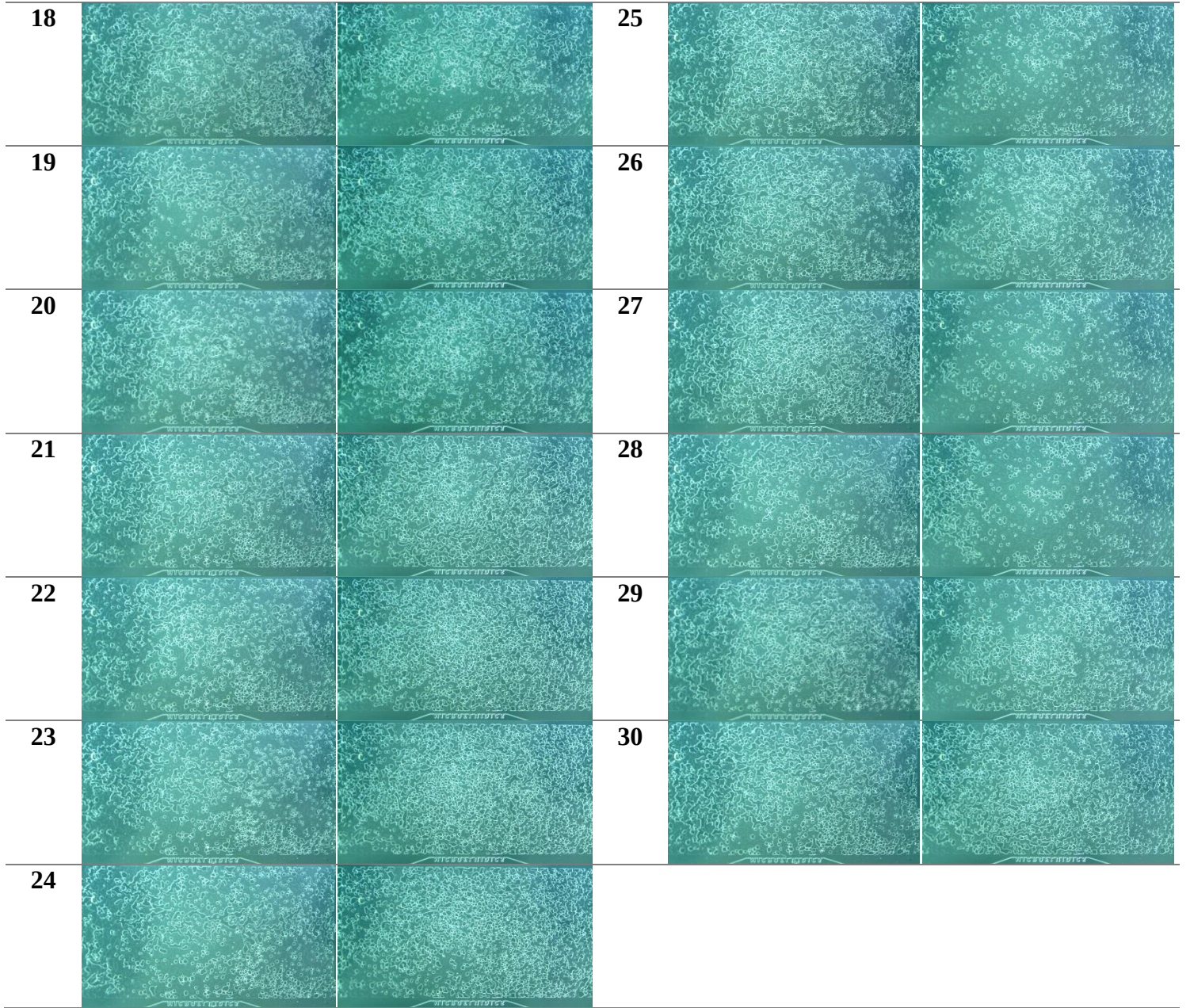


Figure 4.10 In-situ images of DTM High and DTM Low gas-injection and co-injection foaming experiments

Gas injection discussion. Looking at the images at 2.5 and 5 TPV, we noticed that the foam in DTM High did not develop as rapidly as that of DTM Low. DTM High foam had coarser texture, and its gas saturation was lower than DTM Low foam. Based on Equation (2), DTM High foam must have the higher per lamella apparent viscosity due to its more viscous liquid phase. However, because of its coarser texture, DTM High exhibited lower μ_f as

presented in Figure 4.9. Both foams reached their finest texture and highest gas saturation at 7.5 TPV. At this point, the foam generation ceased. Referring to Figure 4.9, we saw a gradual decline in the μ_f of DTM Low foam; while DTM High foam was able to maintain its μ_f . This difference in μ_f trend could be indicative of foam stability. The viscous liquid phase of DTM High may have reduced the rate of foam film thinning [7]. Moreover, the WLM structures in the DTM High liquid phase may contribute to the structural disjoining pressure [11]. This contribution may have further prolonged the foam thinning process and reduced the rate of bubble coalescence in the highest permeability channels; thus maintaining conformance performance over the duration of injection.

Co-injection discussion. Strong foam development in the DTM High foam was slower than in DTM Low foam. DTM Low foam reached its finest texture and highest gas saturation at 10 TPV. DTM High, on the other hand, went through more cycles of foam displacement and regeneration before eventually reaching its finest texture and highest gas saturation at 27 TPV. The viscous liquid phase of DTM High foam could have reduced the rate of snap-off foam generation. However, there is little discernible difference between the texture and gas saturation when comparing DTM High foam at 27 TPV and DTM Low foam at 10 TPV. With a negligible difference in texture, it is to be expected that DTM high would exhibit higher μ_f value due to its higher per lamella apparent viscosity.

Next, we investigate the effect of liquid phase viscosity in IOS foam. We compare foaming experiments on three IOS solutions (IOS, 125+IOS, and 3330+IOS). The σ_{gl} values of these three solutions are similar (27.61, 27.30, and 26.82 dyne/cm for IOS, 125+IOS, and 3330+IOS, respectively). The viscosity of the IOS solution is very low (0.70 cp at 40 s⁻¹) compared to the viscosities of the 125+IOS and 3330+IOS (23.4 cp and 22 cp, respectively at 40

s⁻¹). With these three solutions, we performed a microfluidic foam gas injection at a constant upstream CO₂ pressure of +1 psi relative to the BPR set pressure; and a co-injection at a constant upstream CO₂ pressure of +3 psi relative to the BPR set pressure and constant liquid phase flow rate of 0.6 $\mu\text{L}/\text{min}$. The foam μ_f measurements are presented in Figure 4.11.

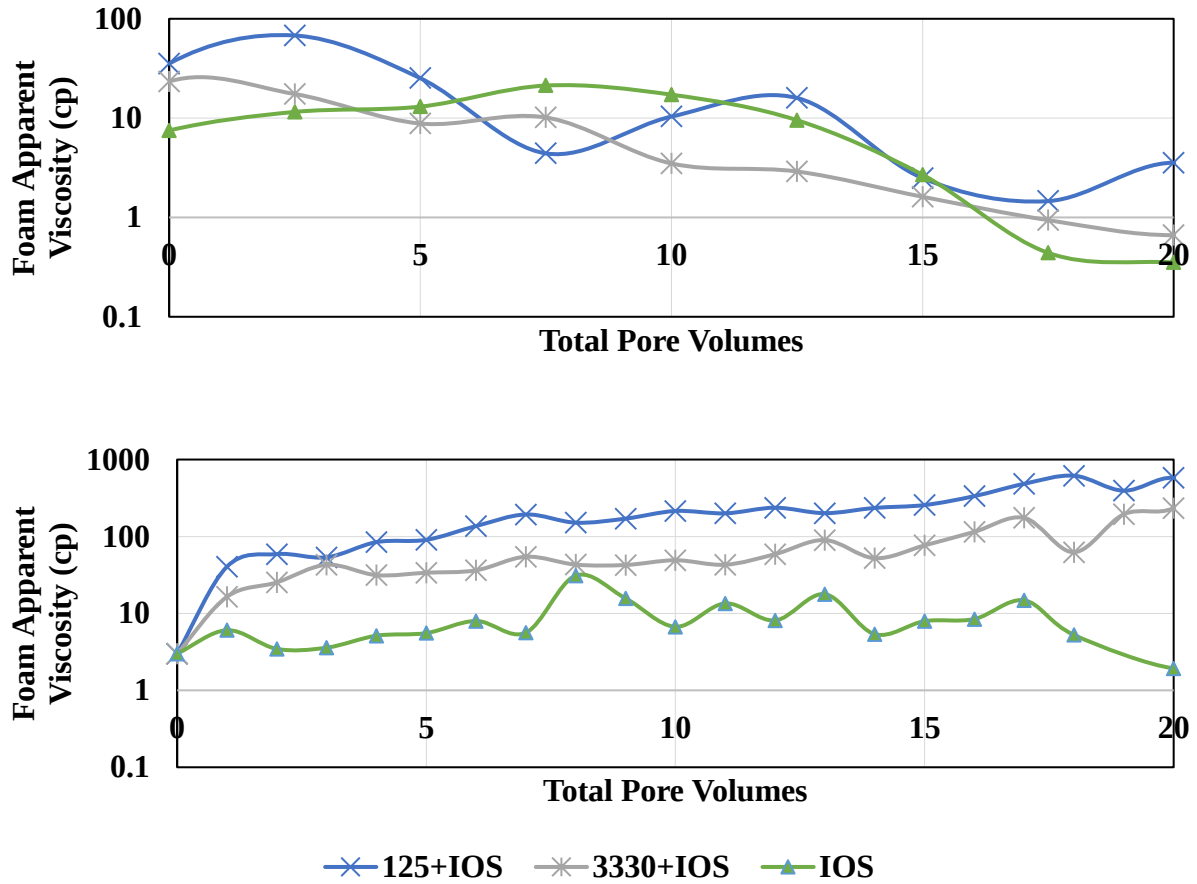
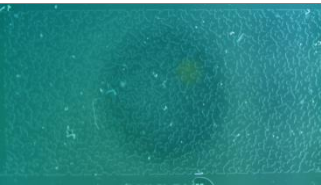
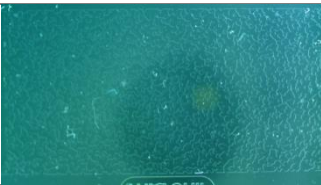
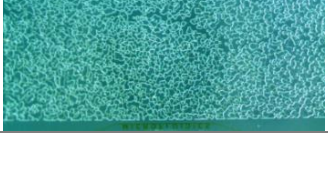
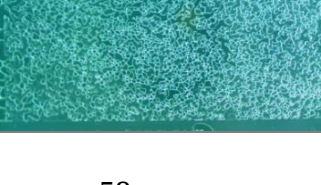


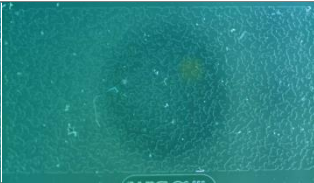
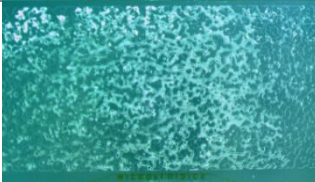
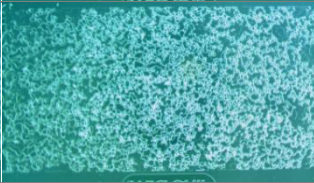
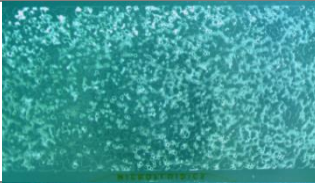
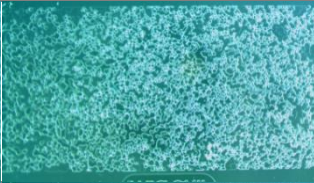
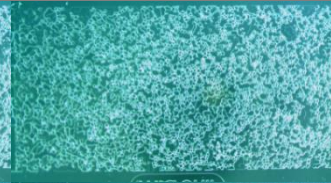
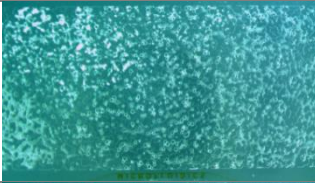
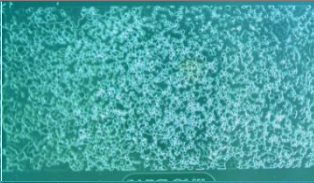
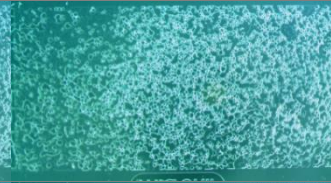
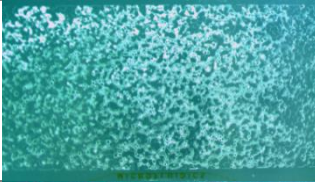
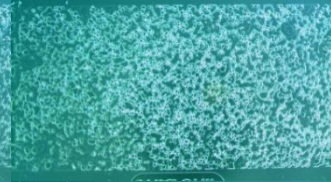
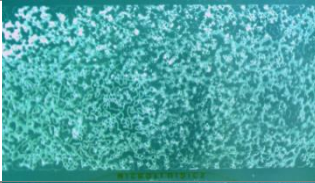
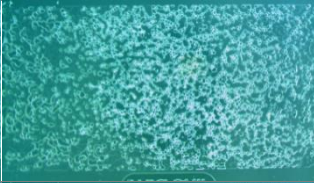
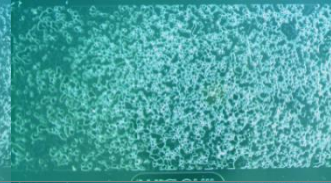
Figure 4.11 Foam apparent viscosity measurements for IOS, 125+IOS and 3330+IOS solutions in the gas injection (top) and co-injection (bottom) microfluidic foaming

Gas injection μ_f . Through the first 5 TPV, IOS foam exhibited lower μ_f value than the 125+IOS and the 3330+IOS foams. Through the rest of the injection period, the μ_f of all three foam cases experienced gradual decline.

Co-injection μ_f . Throughout the duration of injection, the μ_f of the IOS foam was consistently lower than the 125+IOS and the 3330+IOS foam. Additionally, the μ_f of the IOS reached its peak value after 10 TPV. While, the μ_f of the 125+IOS and 3330+IOS foams continued to rise.

The visualization of the gas-injection and co-injection foaming experiments of DTM High and DTM Low solutions is presented Figure 4.12.

Effect of Viscosity (IOS solutions) in Gas Injection			
TPV	IOS	125+IOS	3330+IOS
0			
2.5			
5			
7.5			
10			
12.5			
15			
17.5			
20			

Effect of IFT at High Viscosity in Co-Injection			
TPV	IOS	125+IOS	3330+IOS
0			
1			
2			
3			
4			
5			
6			
7			
8			

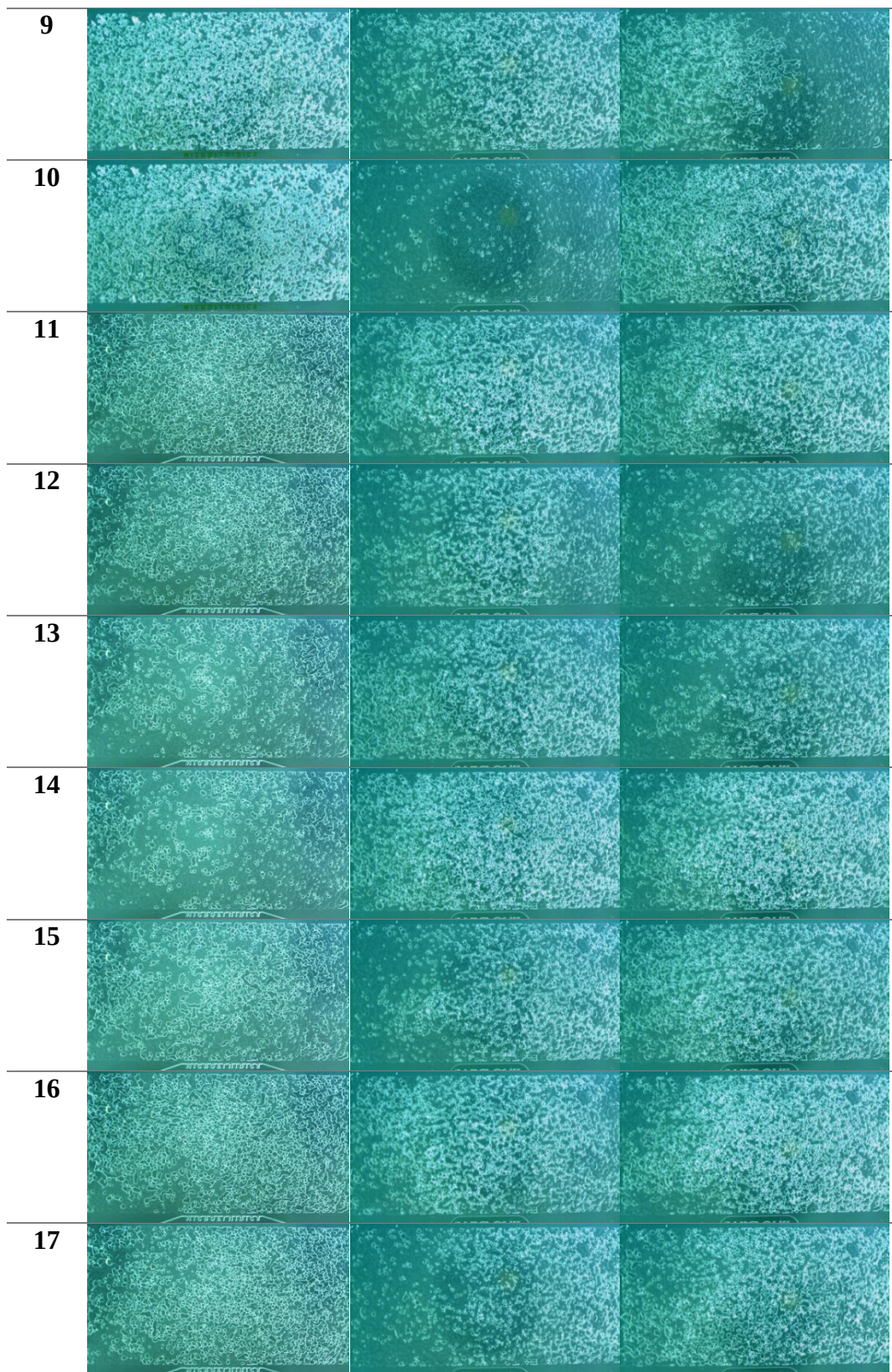




Figure 4.12 In-situ images of IOS, 125+IOS and 3330+IOS gas-injection and co-injection foaming experiments

Gas injection discussion. Looking at the images at 2.5 and 5 TPV, it is noticeable that the foam texture in the IOS foam is finer than the 125+IOS foam; which, in turn, is finer than 3330+IOS foam. The finer texture observed in the IOS foam is made possible by its considerably lower liquid phase viscosity. Despite the finer texture, the IOS foam posed the lowest overall μ_f due to its lowest per lamella viscosity. Towards the end of the injection, the μ_f of the IOS foam declined the farthest. The IOS foam is easier to displace (lowest μ_f) and is theoretically least stable due to the lower liquid phase viscosity. The decline in μ_f was also observed in the 125+IOS and 3330+IOS foams. In spite of their higher liquid phase viscosity, these two foams still experienced foam texture coarsening. Looking at the images from 5 TPV onwards, we observed a reduction in foam texture in 3330+IOS foam. The texture coarsening is less apparent in the 125+IOS foam.

Co-injection discussion. Strong foam development in the IOS foam was slower than in the 125+IOS and 3330+IOS foams. This result could be due to the lower per lamella μ_f of the IOS foam; which means that the IOS foam generated is more easily displaced by the constant

liquid phase flow. This result opposes the observation found in DTM foams; where we saw a higher rate of foam generation in the lower viscosity DTM Low foam. However, the σ_{gl} of DTM Low is higher than that of σ_{gl} . Thus, DTM low's per lamella viscosity is higher; and the foam generated is better able to resist displacement.

The IOS foam reached its peak texture at 9 TPV. At this point the texture of the IOS foam is finer than at any point in either of the 125+IOS or the 3330+IOS foams. However, the overall μ_f is still lower due to the lower liquid phase viscosity. Past 10 TPV, the IOS foam enters its sinusoidal plateauing phase. The 125+IOS and the 3330+IOS foams continued their buildup of μ_f . The continuous buildup of μ_f may indicate that the average foam texture in both cases get finer over the injection duration.

4.2.4 Effect of Interfacial Tension at a High Liquid Phase Viscosity

Earlier in the analysis, we looked at the foaming behavior comparison between DTM and IOS surfactants at viscosity lower than 1 cp. In this section, we examined the foaming of DTM and IOS surfactants at high viscosity. We present the foam μ_f data for DTM High, 125+IOS, and 3330+IOS in Figure 4.13.

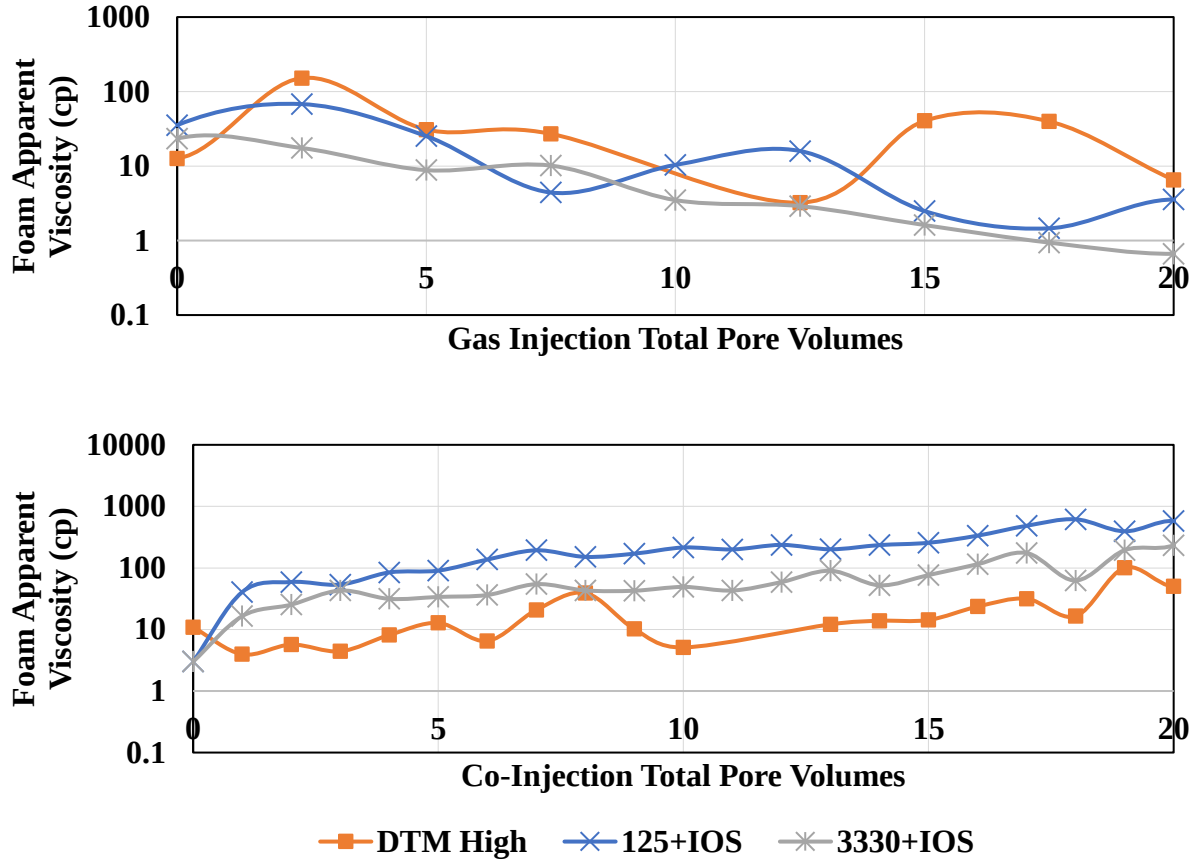
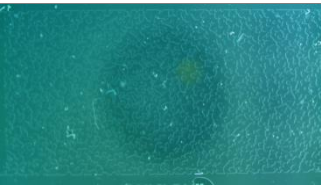
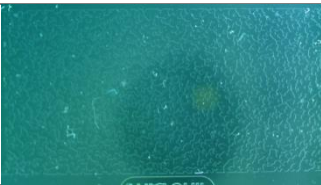
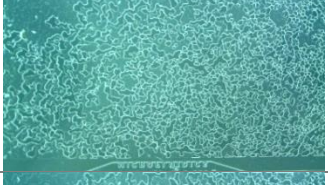
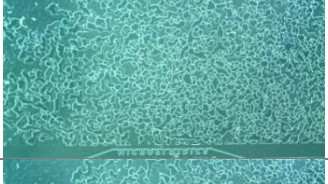
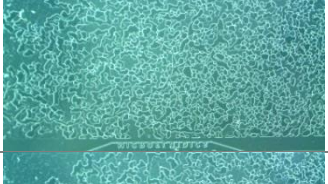
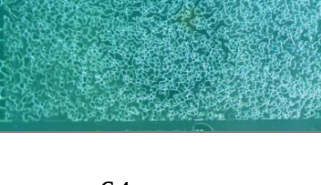


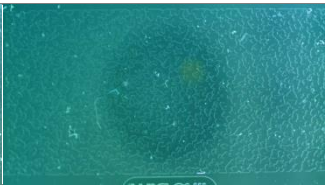
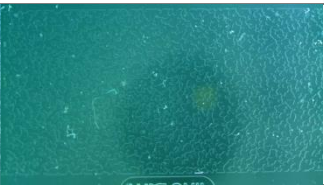
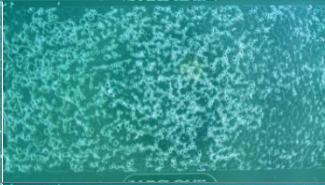
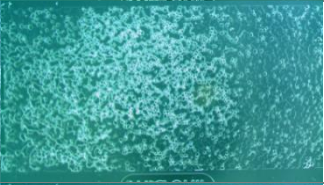
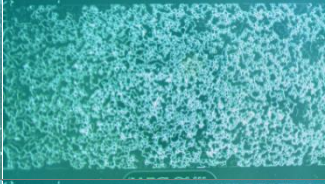
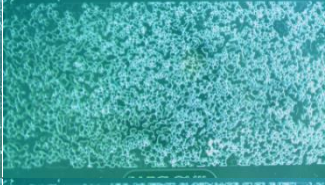
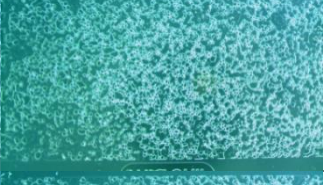
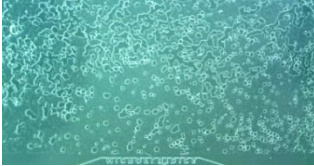
Figure 4.13 Foam apparent viscosity measurements for DTM High, 125+IOS and 3330+IOS solutions in gas injection (top) and co-injection (bottom) microfluidic foaming

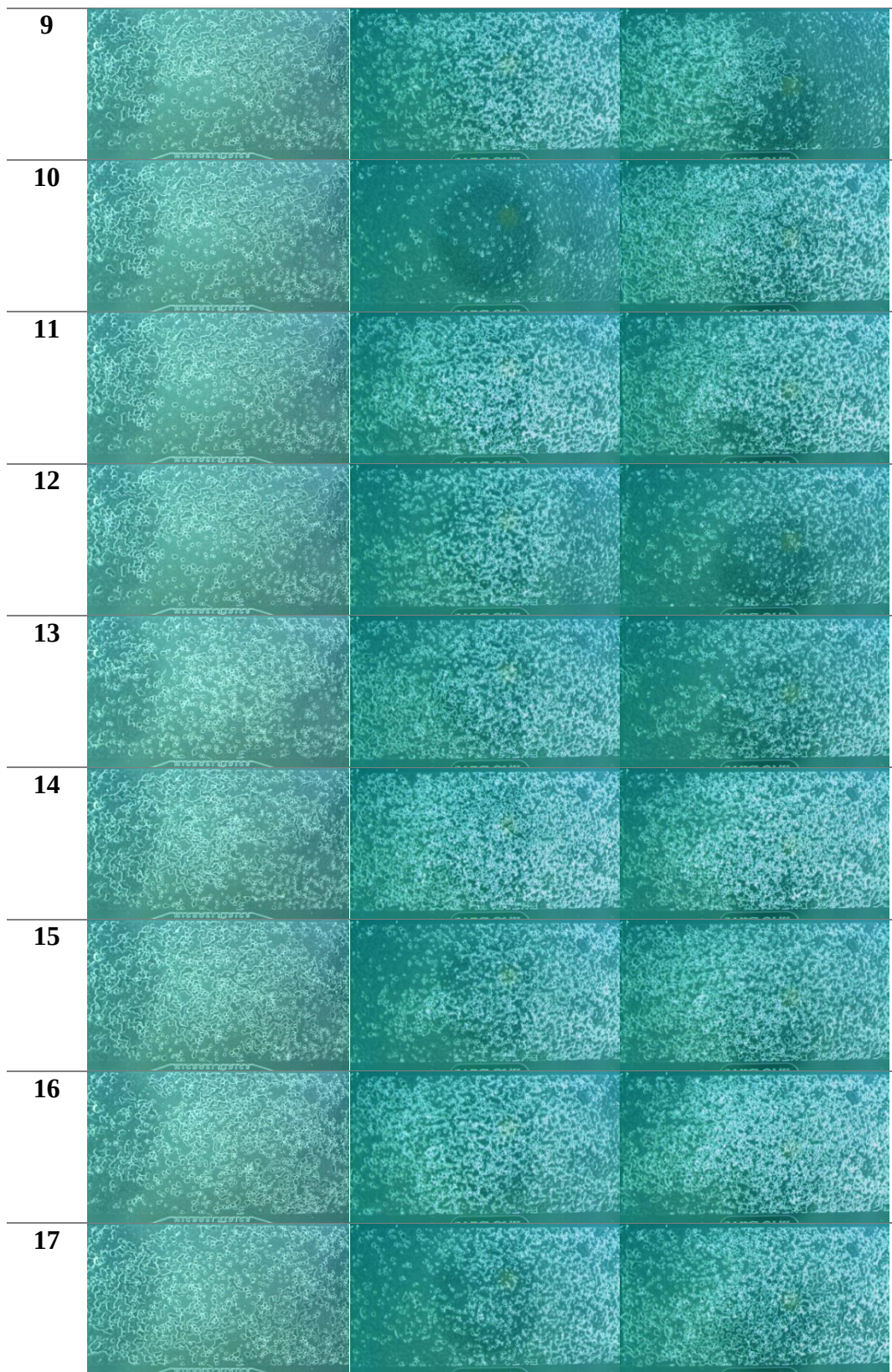
Gas injection μ_f . The μ_f of DTM High is marginally higher through 5 TPV. Another notable difference between DTM High and the two polymer + surfactant foams is that the DTM High μ_f did not experience a continuous gradual decline in the later injection period.

Co-injection μ_f . Throughout the injection duration, the μ_f value of DTM High is lower than 3330+IOS; which in turn, is lower than 125+IOS. The rate of μ_f build-up is approximately the same among the three cases.

The visualization of the gas-injection and co-injection foaming experiments of DTM High, 125+IOS, and 3330+IOS solutions is presented in Figure 4.14.

Effect of IFT at High Viscosity in Gas Injection			
TPV	DTM High	125+IOS	3330+IOS
0			
2.5			
5			
7.5			
10			
12.5			
15			
17.5			
20			

Effect of IFT at High Viscosity in Co-Injection			
TPV	DTM High	125+IOS	3330+IOS
0			
1			
2			
3			
4			
5			
6			
7			
8			



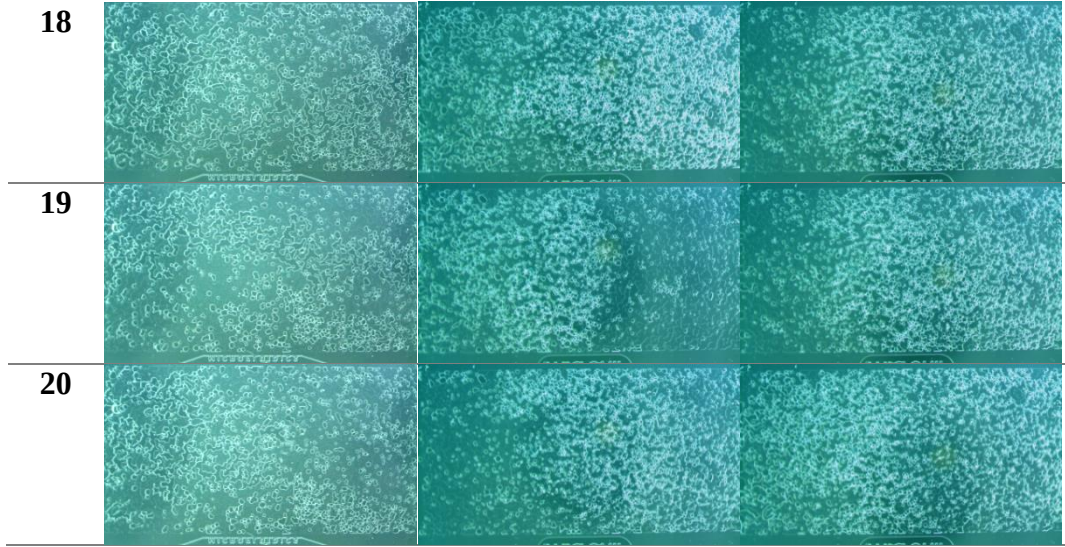


Figure 4.14 In-situ images of DTM High, 125+IOS and 3330+ IOS gas-injection and co-injection foaming experiments

Gas injection discussion. Overall, we observed a coarser foam texture in DTM High than either of the 125+IOS or 3330+IOS foams. We attributed this outcome to the higher σ_{gl} of the DTM surfactant, which reduces the frequency of snap-off and lamella division events. Despite the coarser texture, DTM High exhibited the highest peak apparent viscosity among the three. The DTM High per lamella viscosity is expected to be the largest among the three cases due to two reasons. First, is the contribution of higher σ_{gl} . Second, DTM High solution is the most shear thinning out of the three solutions. While all three solutions possessed very similar viscosity in the target range between 38.8 and 45.7 s⁻¹, DTM High's viscosity in the low shear rates region is significantly higher than either 125+IOS or 3330+IOS. We saw strong foam generation in all three cases; thus resulting in very low gas injection rate. In this circumstance, the liquid phase shear rate may have been lower than the target shear rate velocity. Thus, the actual in-situ liquid phase viscosity of DTM High may have been higher than those of 125+IOS or 3330+IOS. The higher in-situ liquid phase viscosity of DTM may have also led to better foam resistance against coalescence as indicated by the absence of gradual decline in its μ_f throughout the injection period.

Co-injection discussion. Throughout the injection period, foam DTM High was noticeably coarser than in 125+IOS and 3330+IOS. Unlike in the co-injection case, DTM High per lamella viscosity was not able to compensate for the lack of texture, indicated by the low value of DTM High μ_f . In co-injection, there was a constant injection of liquid; which increased the in-situ shear rate of the foam liquid phase. Therefore, the in-situ viscosity of DTM High solution may have been closer to the target shear rate and did not differ significantly from those of 125+IOS or 3330+IOS.

4.2.5 Effect of Pressure Gradient in Gas Injection

In previous discussions, we examined the foaming behavior of different surfactant solutions. In previously discussed gas-injections experiments, we set the upstream gas pressure at +1 psi relative to the BPR. In this section, we examined the effect of pressure gradient on gas-injection foam behavior. For each of the DTM and IOS solutions, we performed three foaming experiments at low (+1 psi), medium (+2 psi), and high (+3 psi) upstream pressures relative to BPR. The μ_f results are in Figure 4.15.

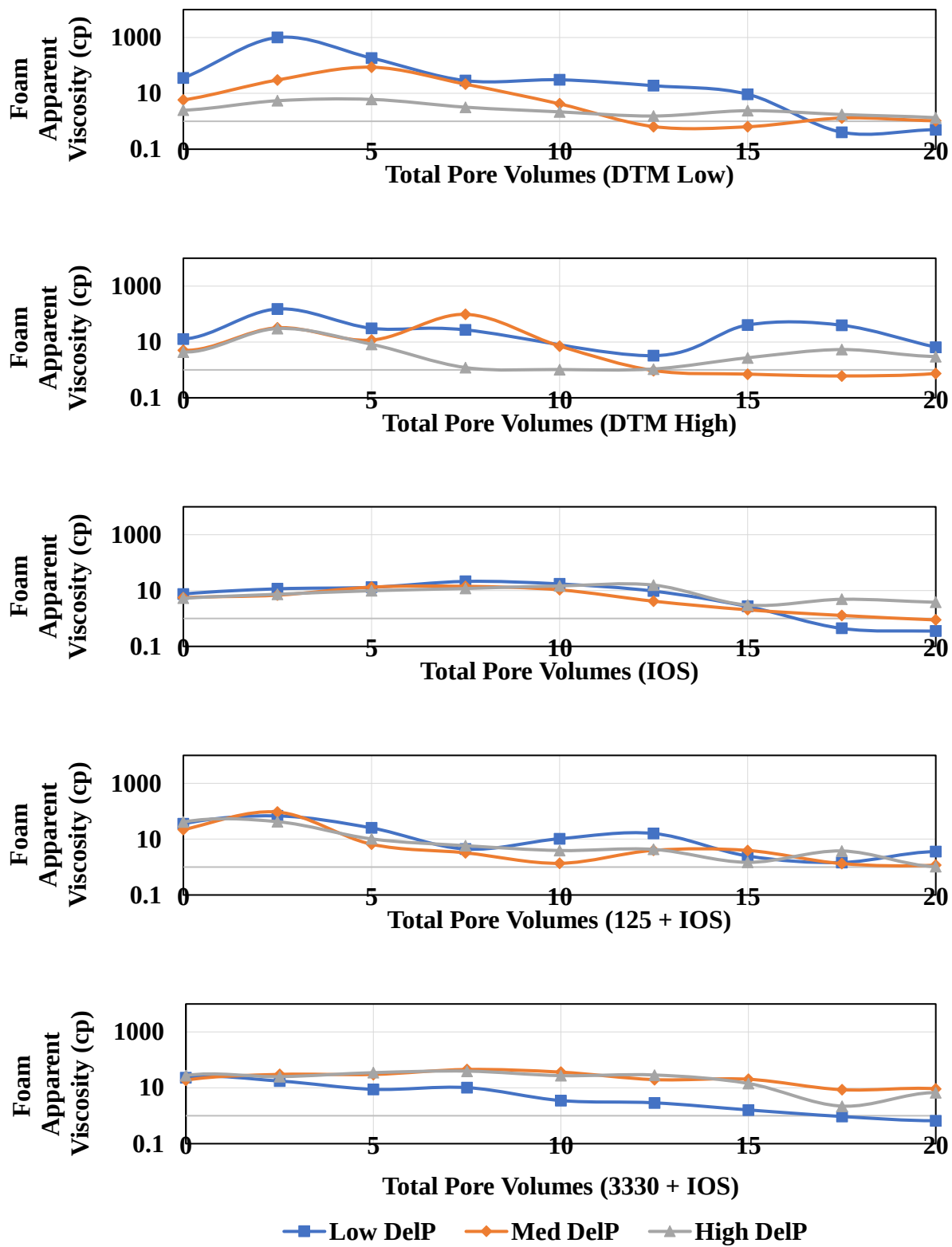
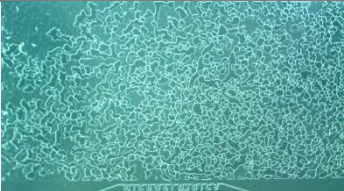
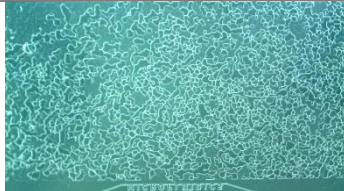
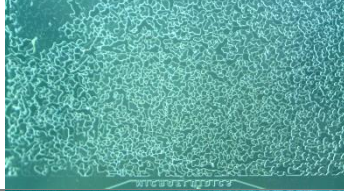
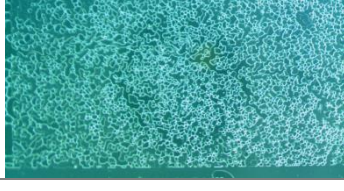
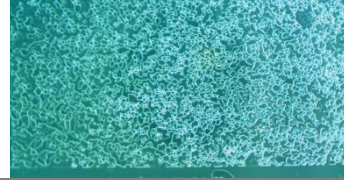


Figure 4.15 Gas Injection foam apparent viscosity measurements at varying upstream gas pressures

In the DTM High and DTM Low solutions, we observed that increasing upstream gas pressure delayed the foam peak μ_f and reduced its magnitude. At the highest upstream gas pressure, we did not observe high μ_f in either DTM cases. In the IOS and 125+IOS cases, increasing upstream gas pressure did not seem to significantly affect foam behavior. In the 3330+IOS case, increasing gas upstream pressure seemed to have increased μ_f . Moreover, the gradual decline of μ_f seen in the low-pressure gradient 3330+IOS was alleviated in the medium and high pressure gradient cases.

The visualization of these gas-injection foaming experiments is presented in Figure 4.16; where, we present the images at 10 TPV of gas injection.

Liquid Phase	Effect of Pressure Gradient in Gas Injection		
	Low DelP	Med DelP	High DelP
DTM High			
DTM Low			
IOS			
125+IOS			

3330+IOS

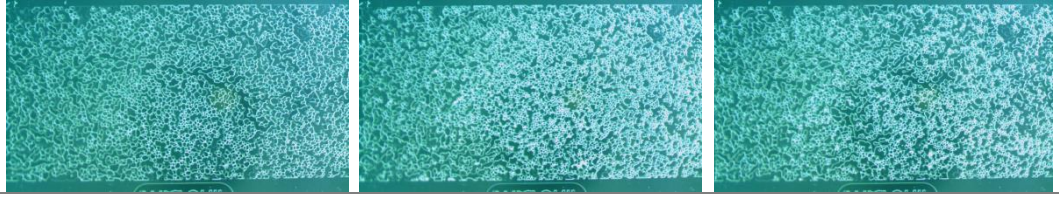


Figure 4.16 In-situ images of gas-injection foaming experiments at varying upstream gas pressure after 10 TPV of injection

In the two DTM cases, we saw a reduction in foam texture and gas saturation as upstream gas pressure increased. The most distinguishable of which occurred in the highest pressure gradient cases; where we observed severe gas fingering. DTM surfactant's relatively high σ_{gl} may prevent pore invasion by gas flowing at a high velocity as may have occurred in the High DelP cases. In the IOS and 125+IOS cases, we did not observe a notable variation in foam texture or gas saturation at different upstream gas pressures. In the 3330+IOS case, however, the higher upstream gas pressure seemed to have improved the texture of foam generated.

From the previous discussions, we established that IOS surfactant is a better foam generator than DTM due to IOS's lower σ_{gl} . Through our experiments, we found that foam generation may reduce or eliminate viscous instability created when an immiscible gas displaces a high viscosity liquid. In the case of 3330+IOS, the higher upstream gas pressure may have increased foam generation events; thus leading to finer foam textures.

4.2.6 Effect of Pressure Gradient in Co-injection

In previous co-injection experiments, we set the upstream gas pressure at +3 psi relative to the BPR with a constant liquid phase injection at 0.6 $\mu\text{L}/\text{min}$. In this section, we examined the effect of pressure gradient on co-injection foam behavior. For all the DTM and IOS solutions, we performed three foaming experiments at low (+3 psi), medium (+4 psi), and high (+5 psi) upstream pressures relative to BPR. The liquid phase injection rate was kept constant at 0.6 $\mu\text{L}/\text{min}$. The μ_f results are presented in Figure 4.17.

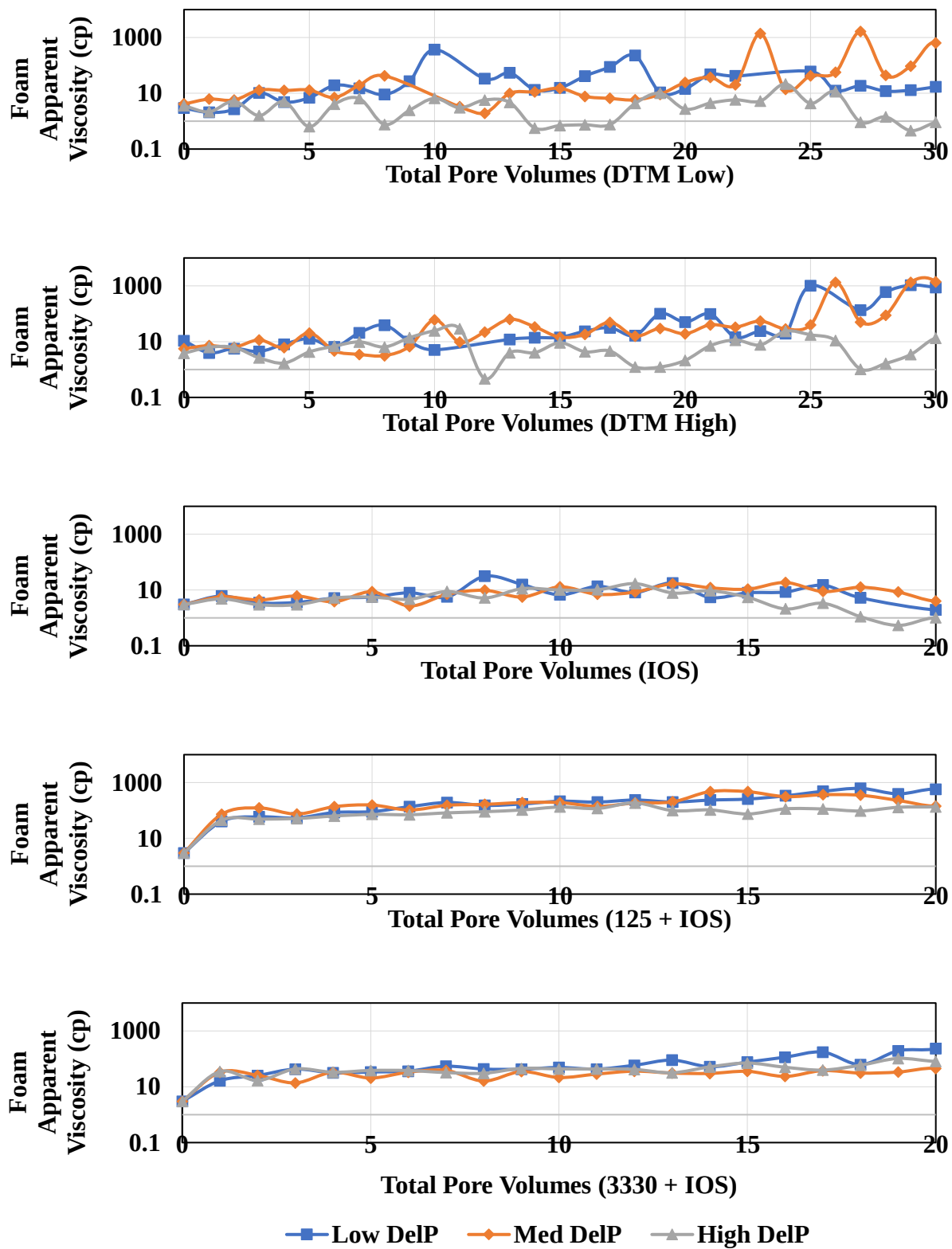


Figure 4.17 Co-injection foam apparent viscosity measurements at varying upstream gas pressures

We observed a similar trend in co-injection as in gas-injection experiments as we varied the upstream gas pressure. In the DTM cases, increasing upstream gas pressure seemed to suppress their μ_f . While, in the IOS cases, increasing upstream gas pressure did not seem to affect the μ_f behavior.

The visualization of these co-injection foaming experiments is presented in Figure 4.18. We present the images of each experiments at their respective peak gas saturation and finest foam saturation.

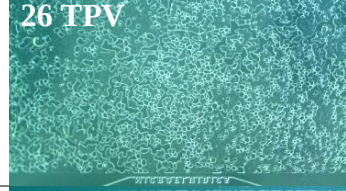
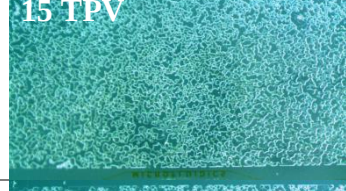
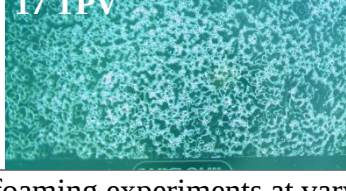
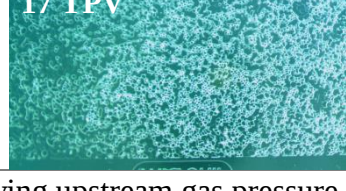
Effect of Pressure Gradient in Co Injection (Showing Peak Foam Texture and Gas Saturation)			
Liquid Phase	Low DelP	Med DelP	High DelP
DTM High	27 TPV 	28 TPV 	13 TPV 
DTM Low	10 TPV 	26 TPV 	26 TPV 
IOS	15 TPV 	15 TPV 	15 TPV 
125+IOS	14 TPV 	15 TPV 	15 TPV 
3330+IOS	16 TPV 	17 TPV 	17 TPV 

Figure 4.18 In-situ images of co-injection foaming experiments at varying upstream gas pressure showing peak foam texture and gas saturation

In the two DTM cases, we saw a decrease in foam texture and gas saturation as upstream gas pressure increased. However, the reduction in texture and gas saturation is not as extreme as in the gas-injection experiments. In the IOS cases variations in peak gas saturation and foam texture were not observed.

4.3 Conclusion

Our foaming experiments in the microfluidic chip yielded the following conclusions:

- Comparing the foaming behavior of DTM and IOS at a low viscosity, we found that foam with the lower gas-liquid interfacial tension (σ_{gl}) produced an appreciable finer foam. However, the finer foam may not possess the greater apparent viscosity (μ_f) due to lower per lamella apparent viscosity.
- Comparing the foaming behavior of surfactant + polymer solutions with different shear thinning characteristic, we found that local variation in shear rate plays a large role in determining gas fingering tendencies, foam generation, and foam apparent viscosity.
- Comparing the DTM solutions at a low and high salinities, we found that the foam with the higher liquid phase viscosity (μ_l) produced a coarser foam due to higher gas fingering occurrences and lower rate of snap-off foam generation events. However, the higher liquid viscosity foam may offer similar, if not greater, overall μ_f because of the higher per lamella viscosity. In addition, higher liquid viscosity foam is better able to resist foam film thinning and foam bubble coalescence.
- In comparing the gas injection and co-injection strategies in microfluidic chip, we found that co-injection foaming reduces the gas fingering tendency as the constant flow of liquid phase may fill the fingering channels and allow for subsequent foam generation.

- The foaming behavior of the DTM surfactant is sensitive to pressure gradient because of its relatively high σ_{gl} . At higher gas injection pressure gradient, foam generation is severely limited by gas fingering. The foaming behavior of the IOS surfactant is fairly consistent over a larger range of delta pressure because of its lower σ_{gl} .

Chapter 5 Foaming in Sand Pack

The objective of this work is twofold: (i) to investigate the possibility of DTM delivery in supercritical CO₂ and (ii) to assess how the salinity-sensitive DTM bulk solution would affect the transient behavior of DTM foam in an ideal porous medium.

We conducted a total of 9 sand pack flood experiments to achieve these objectives. The first experiment was designed to ascertain the propagation of WLM structures through the sandpack. This is a single-phase injection with a salinity gradient between the resident (25 wt.% NaCl, no surfactant) and injectant (15 wt.% NaCl, 0.5 wt.% DTM) liquids. The formation of WLM structures is expected to take place in the salinity mixing zone. The fluctuation of the viscosity of the mixing zone through the period of injection would indicate the propagation characteristics of the WLM structures.

We also devised 8 foam flooding experiments which were performed with different salinities and gas/liquid injection strategies. The results between foam floods were compared based on the analysis of the dynamics of foam and its apparent viscosity. The conversion from measured pressure drop to apparent viscosity of foam flowing through the sand pack was performed with the aid of Darcy's law.

$$\mu_f = \frac{k\Delta P A}{QL} \quad (6)$$

Where the variables are as follows:

- μ_f : apparent viscosity of foam in *cp*
- k : absolute permeability of the sand pack in *darcies*
- A : cross-sectional area of the sand pack in *cm²*
- Q : volumetric injection rate in *cm³/s*

L : length of the sand pack column in *cm*

5.1 Materials and Methods

All foam flooding experiments in this study were performed using one sand pack. The sand pack is 1 ft. in length and has a 1 in. inner diameter. The sand pack is vertically mounted, placed in a convection oven and divided into three sections of equal length by two pressure taps. The sand pack holder was packed with 170-200 mesh-sized silica sand. The properties of the sand pack are shown in Table 5.1. The sand pack injection assembly is illustrated in Figure 5.1.

Table 5.1 Initial sand pack properties

Parameter	Value	Unit
Total Volume	169.38	mL
Pore Volume	65.99	mL
Porosity	0.39	-
Permeability	3.60	Darcy

Equipment used in the foam flooding system include Quizix QX 6000 pumps, 2L piston accumulators, Swagelok high pressure tubing, Autoclave engineer valves, Mity Mite back pressure regulator, Rosemount absolute and differential pressure transducers, and Teledyne Isco Retriever 500. The differential pressure transducers were calibrated only up to 50 psi. This decision was made to accurately read low pressure fluctuations during the early stages of foam generation and propagation. The assembly of previously listed equipment can be seen in Figure 5.1.

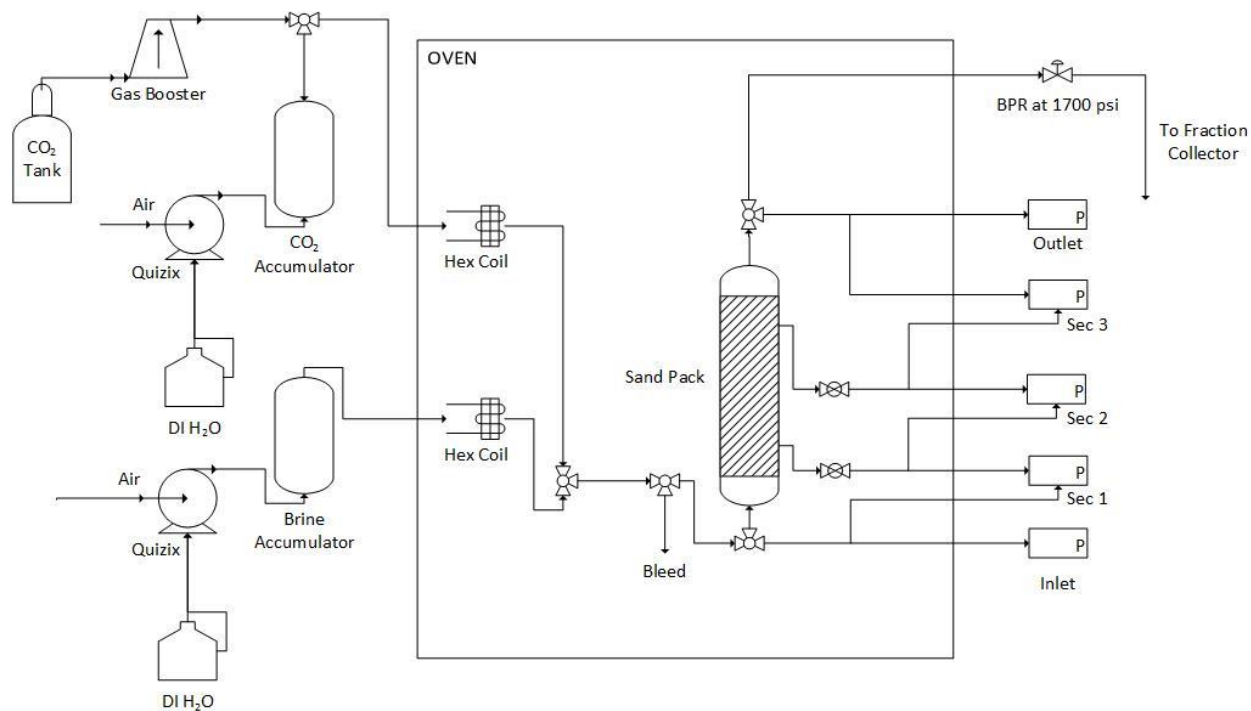


Figure 5.1 Process diagram for sand pack foam flood experiment.

In the single-phase injection experiment, we created a salinity gradient by filling the core with 25 wt.% NaCl brine and injecting a 15 wt.% NaCl brine with a 0.5 wt.% DTM concentration. We prepared the DTM surfactant preparation by adding the desired amount of the surfactant into a brine solution. We then adjusted the pH of this solution to 6.

In the foam flooding experiments, the DTM surfactant was always delivered in the gaseous phase. The procedure began by loading DTM surfactant into the piston accumulator. In all experiments, DTM surfactant was delivered in the CO₂ phase at a fixed concentration. The amount of DTM used was 0.5 wt. % of the mass of CO₂ occupying a 500 mL volume at 1700 psi and 22°C. Afterwards, CO₂ was pumped in using a gas booster.

Temperature of the sand pack was maintained across all experiments at 40°C. A single sand pack was used in all the experiments to ensure a sound basis of comparison. Electrical and pH of effluent fluid were measured. Liquid phase saturation in the sand pack column was calculated using a mass balance on water phase. After each run, 5000 mL of DI water was pumped through the sand pack column over a period of 48 hours in order to restore sand pack properties. In all nine foam floods performed, the listed parameters stayed within 10% of their original values listed in Table 5.1.

Nine flood experiments were performed to achieve the objectives of the study. The design of these experiments is tabulated in Table 5.2.

Table 5.2 Experimental design of nine sand pack foam flood experiments

Flood #	Injection Scheme	Liquid Phase Salinity	Foam Quality
1	Single phase at 10 PV/day	Gradient of 25 wt.% NaCl resident and 15 wt.% NaCl injection	N/A
2	Co-injection of water and gas at 10 PV/day	15 wt.% NaCl	50%
3	Co-injection of water and gas at 10 PV/day	20 wt.% NaCl	50%
4	Co-injection of water and gas at 10 PV/day	15 wt.% NaCl	90%
5	Co-injection of water and gas at 10 PV/day	20 wt.% NaCl	90%
6	Water-alternating- gas at 10 PV/day	15 wt.% NaCl	Brine and CO ₂ slug sizes of 0.2 pore volumes

7	Water -alternating- gas at 10 PV/day	20 wt.% NaCl	Brine and CO ₂ slug sizes of 0.2 pore volumes
8	Water-alternating- gas at 10 PV/day	15 wt.% NaCl	Brine and CO ₂ slug sizes of 0.1 and 0.3 pore volumes
9	Water -alternating- gas at 10 PV/day	20 wt.% NaCl	Brine and CO ₂ slug sizes of 0.1 and 0.3 pore volumes

5.2 Sand pack flood results

5.2.1 Single Phase Injection with Salinity Gradient

The objective of this flood experiment was to demonstrate the salinity-induced viscosification of bulk DTM solution in porous media and to analyze how the WLM structures propagate through the sand pack. Evidence of salinity-induced viscosification was sought by injecting a solution of 0.5 wt.% DTM and 15 wt.% NaCl into a sand pack column with a resident brine of 25 wt.% NaCl. The critical salinity for WLM formation should be attained in the mixing zone between the chasing and resident brines. Thus, the mixing zone should exhibit greater viscosity than either of the resident or the chasing fluids.

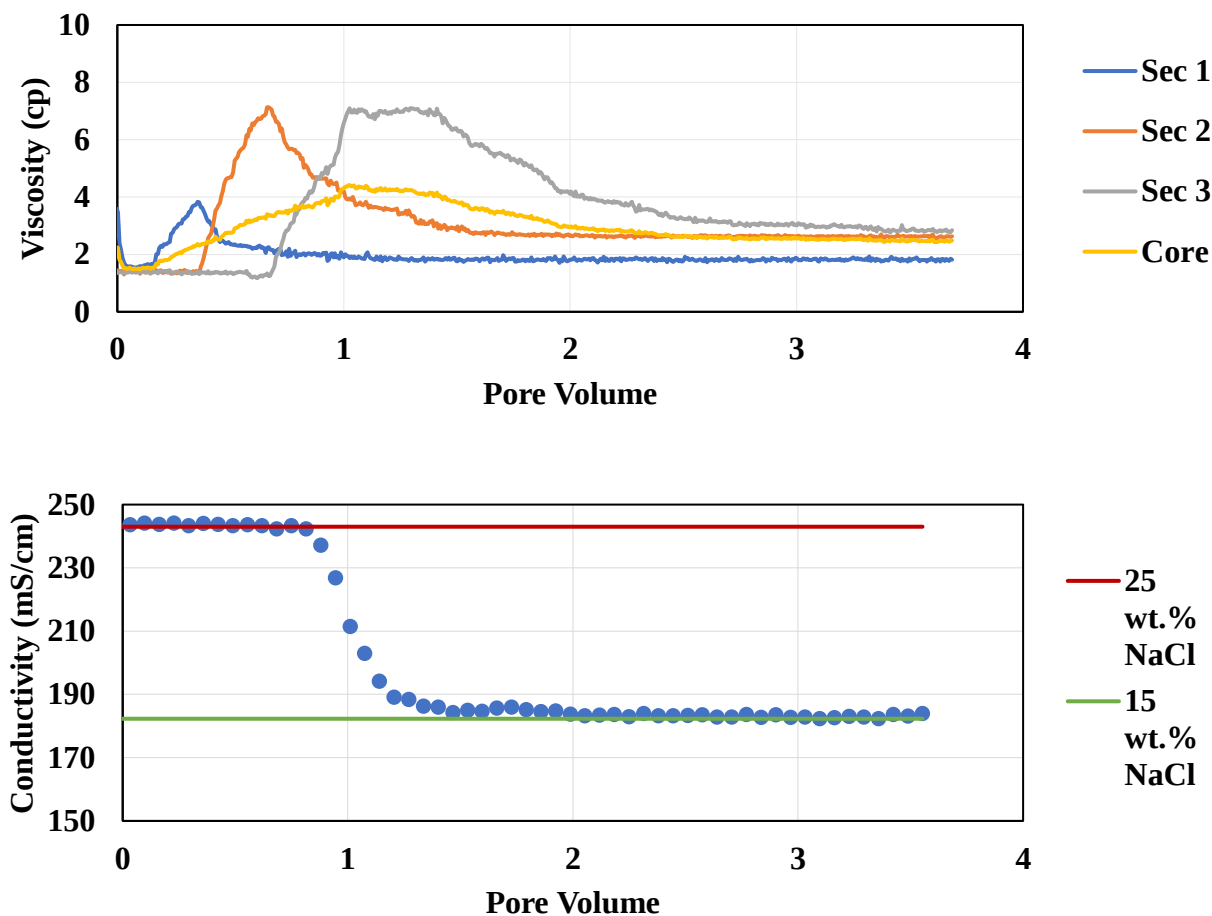


Figure 5.2 (a) Apparent viscosity (top), (b) effluent conductivity (bottom) for Flood 1

The data shows viscosification took place in the mixing zone (i.e. the zone in which the injection surfactant solution is mixed with the resident brine by mechanical dispersion and molecular diffusion). This phenomenon is indicated by the increase and subsequent decline in the apparent viscosity as the mixing zone propagates along the sand pack. The viscosification of DTM solution observed in this flood was likely caused by the transformation of micelle structure from spherical conformation to WLM at elevated salinity (i.e. critical salinity between 15 wt.% NaCl and 25 wt.% NaCl).

An increase in salinity of a surfactant solution above CMC has been known to trigger a viscosification effect. We observed that the worm-like structures appear to have lower mobility

than the spherical micelle as indicated by the consistent increase in the magnitude of the maximum apparent viscosity from sections one to three. Lower WLM mobility is also evident in the delay of viscosity decline relative to the mixing zone which exits the core after one injected pore volume, as indicated by Figure 5.2b. However, it is important to note that WLM structures are not trapped in the porous media as the apparent viscosity eventually declines to the viscosity value of injection fluid bulk solution (2.4 cp).

5.2.2 Salinity effect on transient foam behavior in co-injection of CO₂ and brine

The foam flood experiments presented in this section are focused on how the mechanisms that led to DTM solution viscosification influence the transient behavior of foam during simultaneous injection of brine and CO₂ with dissolved DTM. Figure 5.3 provides a magnified view of the sectional pressure gradients, which in turn provides insight into the behavior of foam through the onset of strong foam formation and propagation.

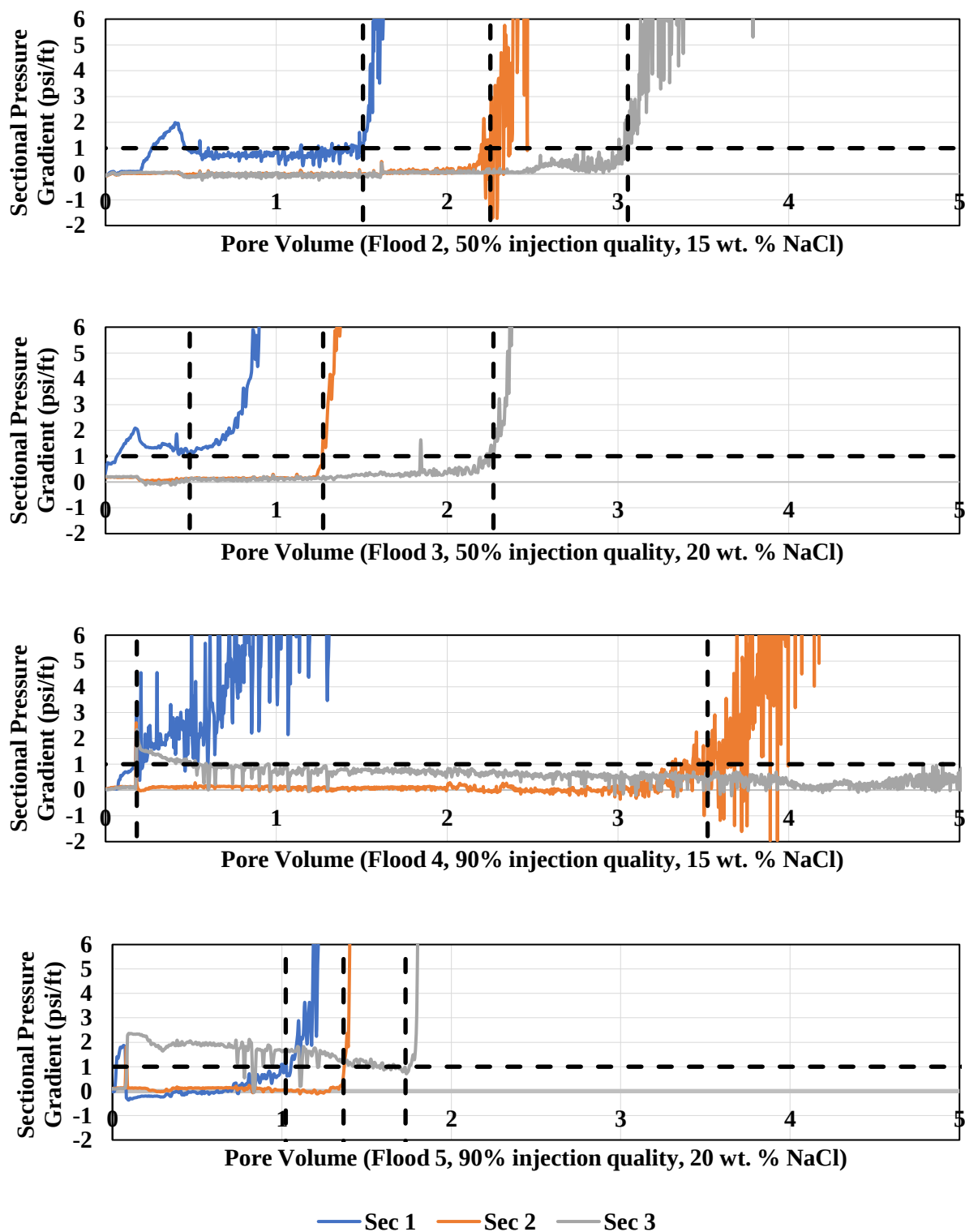


Figure 5.3 Sectional pressure gradient of four foam floods (Floods 2-5). Start of strong foam propagation at each section is marked with dashed line after surpassing 1 psi/ft.

Onset of strong foam generation. Foams are known to have a distinct minimum pressure gradient required for strong foam generation and propagation [53], [54]. The value of the minimum pressure gradient for strong foam mobilization has not been agreed upon. Values ranging from 1 psi/ft to 5 psi/ft have been proposed [55]–[58]. In Figure 5.3, the onset of strong foam mobilization was marked at 1 psi/ft. Critical total injection pore volumes (TIPV) required to surpass 1 psi/ft. at each section are tabulated in Table 5.3.

Table 5.3 Critical TIPV for strong foam propagation

Flood #	TIPV Sec 1	TIPV Sec 2	TIPV Sec 3
2	1.51	2.25	3.06
3	0.49	1.27	2.27
4	0.18	3.53	-
5	1.02	1.36	1.73

At 50% foam quality, the lower salinity (15 wt. % NaCl) Flood 2 began strong foam generation after 1.51 TIPV. The higher salinity (20 w.t % NaCl) Flood 3 began strong foam generation considerably sooner, at 0.49 TIPV. The results at 90% foam quality were quite consistent except for the inlet section (section1). In this section, the lower salinity Flood 4 started strong foam generation after 0.18 TIPV; while the higher salinity Flood 5 started strong foam generation at 1.02 TIPV. We attribute this phenomenon to viscous fingering of surfactant-carrying CO₂ past the foam generation region at the entrance of the sand pack column.

The Flood 5 pressure profiles in Figure 5.3 show that an immediate increase in pressure gradient is observed in section 3; while the pressures in sections 1 and 2 are still near zero. The most probable mechanism that could explain this observation is viscous fingering of the surfactant-carrying CO₂ past the sand pack column entrance and the formation of weak foam mostly in section 3 soon after injection commenced. This viscous fingering was caused by the

viscosification of the aqueous phase at and behind the displacement front: as DTM molecules partitioned into the aqueous phase, the viscosity of the phase increased considerably. The mobility ratio between the displacing CO₂ and the displaced brine became unfavorably high, promoting the onset of viscous fingering in the inlet section (section 1). Such sequential viscosification of aqueous phase with high foam injection quality would promote better weak foam generation in section 3 than in the upstream sections. It is important to note that the continuous generation of foam in this core section eventually triggered sequential strong foam propagation in sections 1 and 2. This phenomenon is known as secondary liquid desaturation [59].

Signs of CO₂ viscous fingering near the core inlet are not apparent in either Flood 2 or Flood 3 pressure profiles. This absence of viscous fingering could be due to lower foam injection quality and the lower surfactant mass per unit total injection volume.

From the foaming experiments in microfluidic chip, we learned that the DTM at a higher salinity produces a coarser foam (lower lamellae density) with a higher per lamella and overall apparent foam viscosity. The higher foam apparent viscosity of DTM high foam may accelerate the increase in pressure gradient beyond the critical pressure necessary for strong foam generation.

In addition, the rate of pressure gradient build-up is also determined by the foam resistance to coalescence (foam stability). Newly created bubbles must be able to resist film-thinning and coalescence as they move through constricted pores. Otherwise, fine-texture foam cannot accumulate and the critical pressure gradient for the onset of strong foam generation may not be overcome. For maximum foam stability, the rate of film thinning must be minimized in order to prevent film thickness from approaching the critical thickness for foam rupture. This

objective can be achieved by increasing the viscosity of the foam film. A study on surfactant behavior above CMC in a free standing foam films (thinner than 120 nm) showed that WLM get entangled and form a kind of network in the films comparable to that in the bulk solution [11]. For horizontal (ignoring gravitational drainage forces) thick films (> 100 nm thickness), the rate of foam drainage is expressed in Equation (1). From a foam film drainage perspective, an increase in the aqueous phase salinity increases the stability of the foam structure.

Another factor that influences foam stability is foam surface elasticity and viscosity which are commonly discussed together and evaluated as the Marangoni effect. This effect reduces the rate of film drainage by opposing the liquid flow out of the high surface tension region of the film. Marangoni's effect is weakened at higher salinity conditions due to a higher rate of surfactant exchange from interface to liquid as previously discussed. A study shows that drainage time is proportional to increased Marangoni effect [16]. Therefore, an increase in film salinity may reduce foam bubble resistance to coalescence.

For thin films (thinner than 100 nm), the rate of drainage deviates from that predicted in Equation (1). This deviation is mainly due to the increasing influence of disjoining pressure. Disjoining pressure resists film thinning forces through an interplay between long-range repulsive electrostatic (Π_{elec}), short-range repulsive steric (Π_{steric}), and short-range attractive dispersion-van der Waals (Π_{vdW}) pressures [17]. Π_{elec} arises from the overlap of adjacent electrical double layers (EDL) of counter-ions associated with the ionic surfactant head groups. An increase in electrolyte concentration reduces the thickness of the EDL, therefore, a lesser degree of overlap between adjacent EDLs. In our experiment, we compared two relatively high salinities (15 wt. % and 20 wt. %). It may be the case that Π_{elec} is negligible in both cases. Increased salinity may cause an increase in the Π_{steric} . As previously discussed, an increase in

salinity may transform micelle structure from spherical to WLM. Previous study [11] found that WLM structures get entangled in the foam film as they do in the bulk solution. This network of entangled WLM structures within the foam film may provide contribution to Π_{steric} due to the combination of protrusion and hydration forces. Π_{vdw} is theoretically not affected by electrolyte concentration [60]. Therefore, an increase in liquid phase salinity may improve foam stability, and thus the robustness of strong foam generation as observed from the onset of strong foam propagation shown in Figure 5.3.

Apparent viscosity buildup. In Figure 5.4, the apparent viscosity buildup rate ($\dot{\mu}_f$) was calculated as the slope of the linear fit to the apparent viscosity from the onset of strong foam generation to the plateau of foam propagation throughout the core. At 50% foam quality, the lower salinity Flood 2 had a lower $\dot{\mu}_f$ at 177.98 cp/TIPV in comparison to that of the higher salinity Flood 3 at 230.39 cp/TIPV. A similar trend was observed at 90% foam quality. The lower salinity Flood 4 had a significantly lower buildup rate at 73.79 cp/TIPV in comparison to that of the higher salinity Flood 5 at 978.03 cp/TIPV.

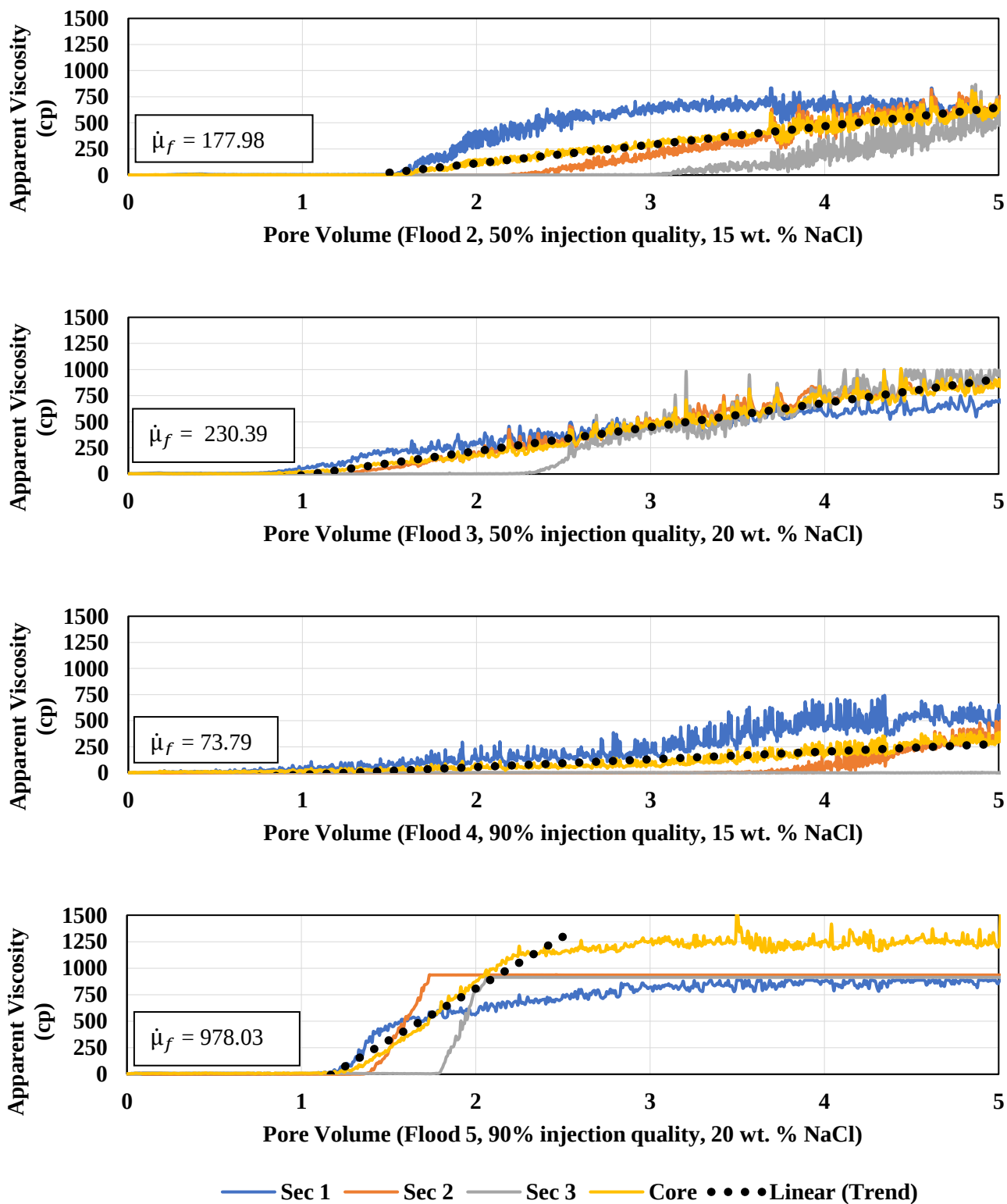


Figure 5.4 Sectional and total apparent viscosity for four simultaneous injection foam floods.

The increase of foam film stability and higher apparent viscosity associated with an increase in salinity enhances the robustness of strong foam propagation as observed from the onset of foam generation and the apparent viscosity buildup shown in Figures 5.3 and 5.4. In particular, drier foam (higher injection quality) can be more unstable in porous media. This is confirmed by comparing μ_f between Flood 2 (177.98 cp/TIPV at 50% foam quality) and Flood 4 (73.79 cp/TIPV at 90% quality) for the lower salinity (15 wt% NaCl). However, the viscosification of DTM solution allows for a significant improvement in foam stability. As indicated by the increase μ_f between flood 4 and 5 (from 73.79 to 978.03 cp/TIPV at 90% foam quality).

5.2.3 Salinity Effect on the Transient Foam Behavior in Water-alternating-gas (WAG)

Scheme

The series of four flood experiments presented in this section was conducted to investigate the effect of viscosified DTM solution on the dynamics of foam propagation during alternating injection of brine and CO₂ with dissolved DTM. This is the most common injection strategy for gas mobility control in the field. Two different water-to-CO₂ volume ratios (WAG ratio = 1:1 and 1:3) were used to capture the effect of brine desaturation on transient foam behavior. Figure 5.5 provides a magnified view of the sectional pressure gradient for these floods. The higher WAG ratio represents high-quality foam flow regime that is often associated with less stable foam.

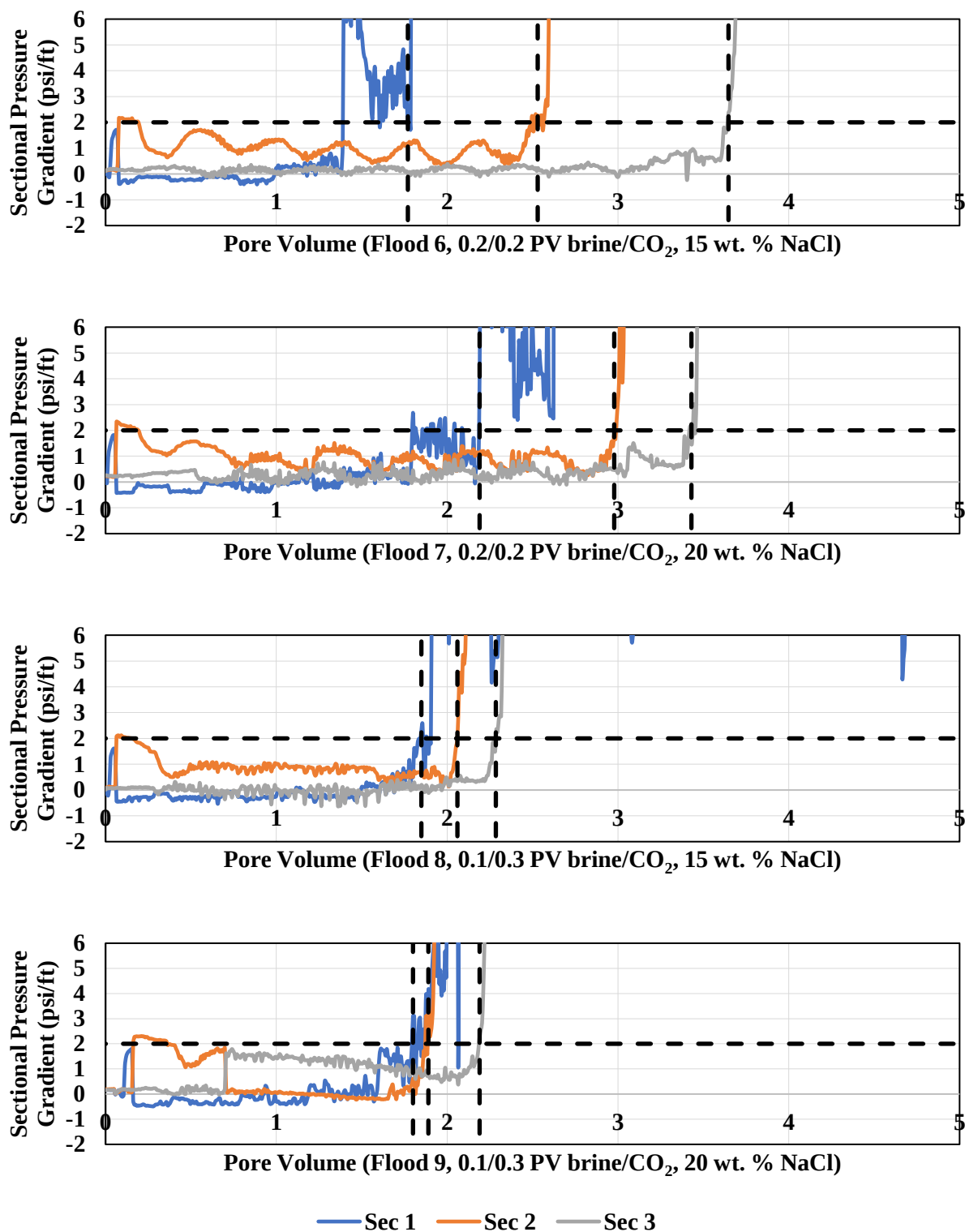


Figure 5.5 Sectional pressure gradient for four WAG foam floods. Start of strong foam propagation at each section is marked with a dashed line after surpassing 2 psi/ft.

Onset of strong foam generation. Figure 5.5 shows that the minimum pressure gradient for strong foam propagation during WAG injection is slightly higher than that for simultaneous injection (~ 1 psi/ft). Therefore, the value of 2 psi/ft was used to determine the critical total injection pore volumes (TIPV) at each core section as shown below.

Table 5.4 Critical TIPV for strong foam propagation

Flood #	TIPV Sec 1	TIPV Sec 2	TIPV Sec 3
6	1.77	2.53	3.65
7	2.19	2.98	3.43
8	1.89	2.06	2.29
9	1.85	1.89	2.19

For a WAG ratio of 1:1, the lower salinity Flood 6 exhibits strong foam propagation after about 1.7 TIPV. The higher salinity Flood 7 began strong foam propagation considerably later, at 2.2 TIPV. For WAG ratio of 1:3, the lower salinity Flood 8 and the higher salinity Flood 9 began strong foam propagation after approximately the same TIPV (~ 1.9). Similar to the observation made in Flood 5 (simultaneous injection with high foam quality and high salinity), we believe that viscous fingering of surfactant-carrying CO₂ caused delay in foam generation and propagation. This effect is expected to be more pronounced for the WAG process because of a strong tendency of unstable dry foam development and the continuous water viscosification during CO₂ cycle. However, the amount of surfactant injected in CO₂ per WAG cycle increases with decreasing WAG ratio. This could help reduce the number of WAG cycle (or critical TIPV) for strong foam propagation at elevated salinity as observed from Floods 7 and 8.

Apparent viscosity buildup. Figure 5.6 shows the apparent viscosity as a function time for Floods 6-9. For WAG ratio of 1:1, the lower salinity Flood 6 exhibits a lower apparent viscosity buildup rate ($\dot{\mu}_f$) at 81.73 cp/TIPV in comparison to that for the higher salinity Flood 7 ($\dot{\mu}_f = 170.98$ cp/TIPV). A similar result is observed for the reduced WAG ratio of 1:3. The lower salinity Flood 8 resulted in a lower $\dot{\mu}_f$ of 335.35 cp/TIPV compared to 650.28 cp/TIPV for the higher salinity Flood 9. The significant increase of $\dot{\mu}_f$ with decreasing WAG ratio confirms the important effect of increased surfactant mass per WAG cycle on strong foam propagation.

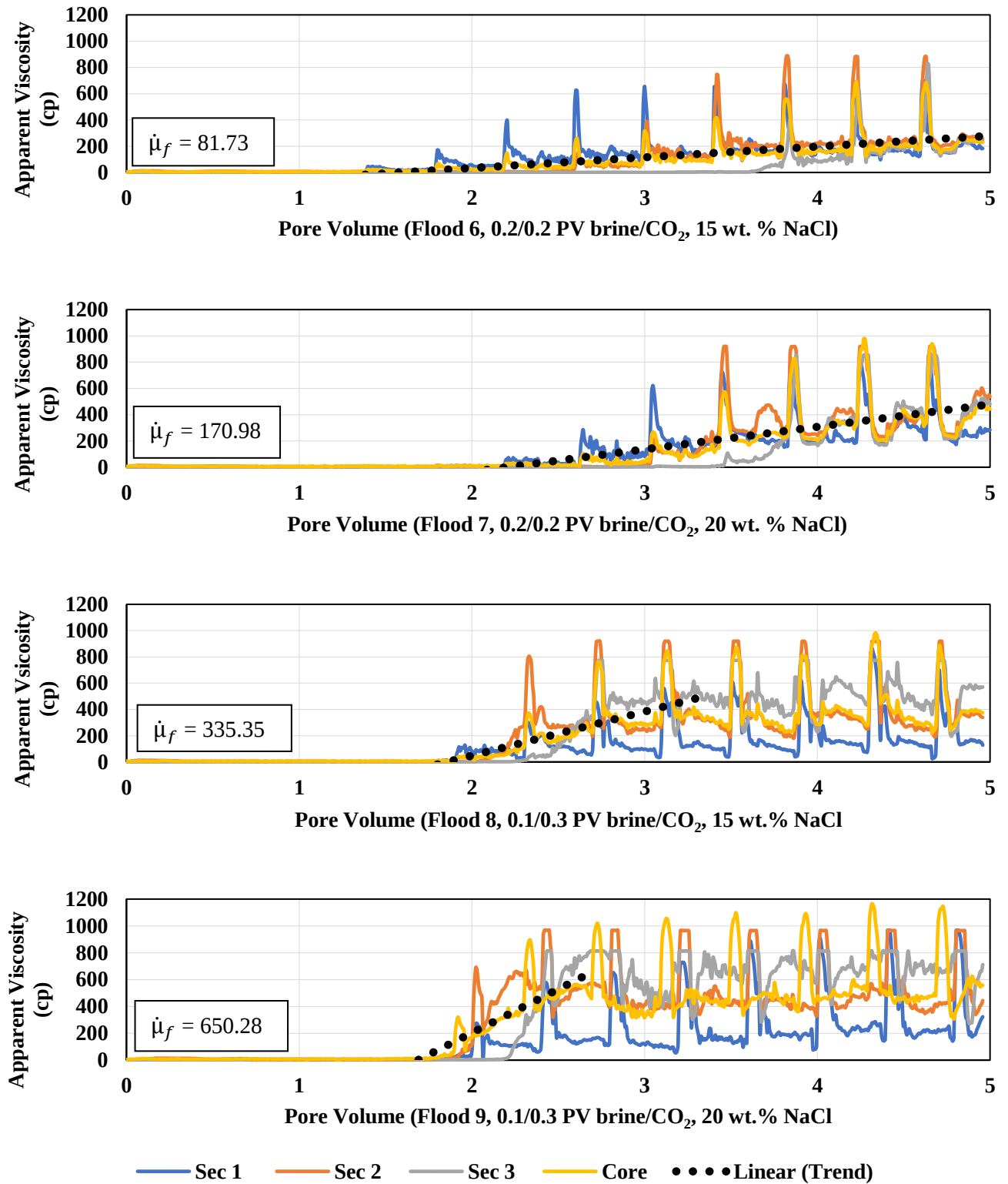
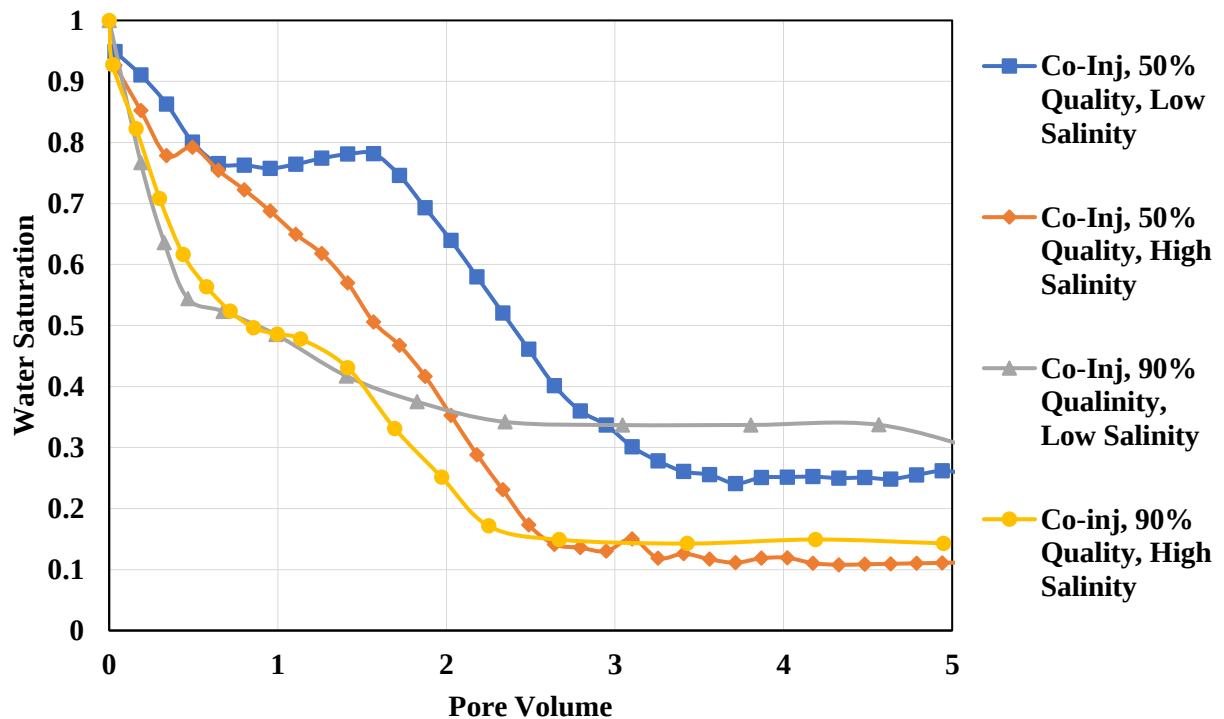


Figure 5.6 Sectional and total apparent viscosity for four WAG foam floods.

5.2.4 Salinity Effect on Displacement Efficiency

Comparing the impact of salinity on μ_f for all Floods 2-9 clearly indicates that strong foam propagation is greatly enhanced by the salinity induced viscosification of DTM solution. Through this mechanism, foam stability and its resistance to flow can be significantly improved. Such improvement becomes much more dramatic at elevated injection foam quality or reduced WAG ratio. This is a very significant advantage of DTM stabilized foam because it enables injection of much larger volume of CO₂ than water without reducing the mobility control capacity of foam. For miscible CO₂ flooding in macroscopically homogeneous reservoirs, reduced water injection promotes miscible displacement as well as accelerates oil production, particularly for water-wet reservoirs. This can be simply demonstrated by comparing water displacement efficiency for all the foam floods as shown in Figure 5.7.



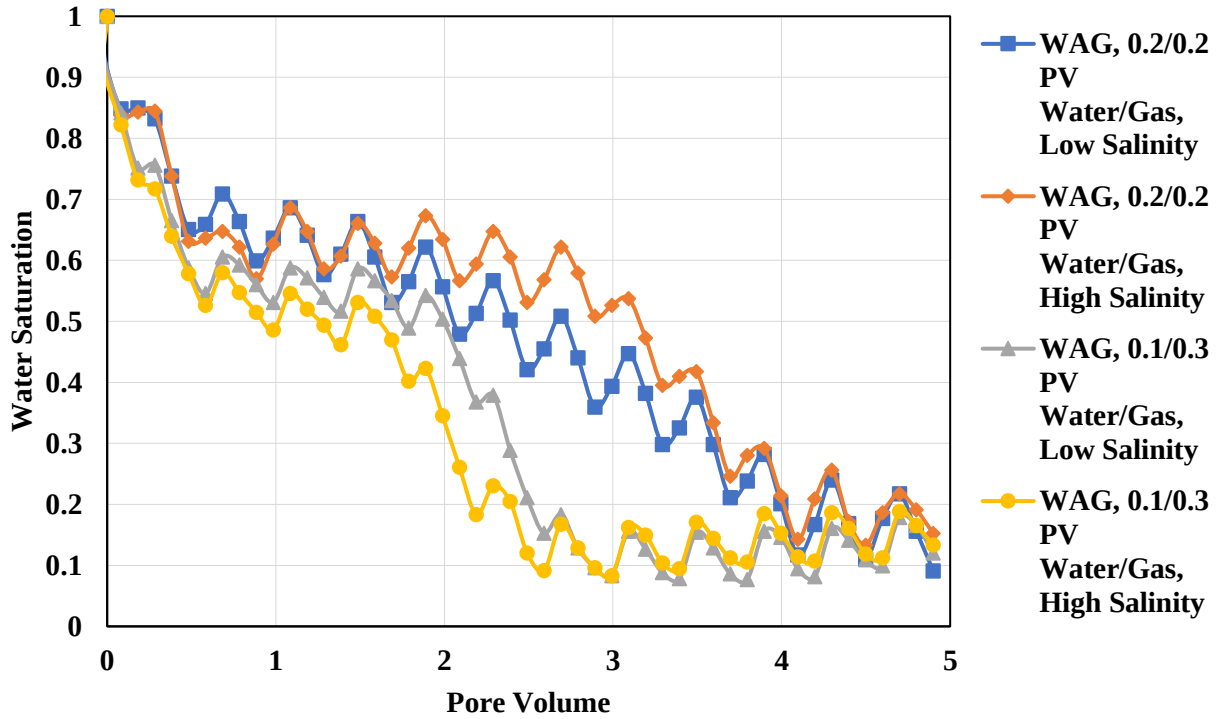


Figure 5.7 Water desaturation for (top) simultaneous injection, and (bottom) WAG injection

For simultaneous injection, the rate of water desaturation consistently increases with foam quality (or CO₂ volume injected) at fixed salinity, and the highest displacement efficiency (indicated by lowest water saturation) could be achieved with high foam quality and further viscosification of DTM solution at elevated salinity. These effects of salinity and injected CO₂ volume on transient foam behavior remains very consistent to both simultaneous and WAG injection.

5.3 Conclusions

In this study, we have successfully performed nine sand pack floods in an effort to understand the effect of aqueous phase viscosification with DTM surfactant and NaCl on the dynamics of foam flow in a sand pack for different injection water-to-CO₂ volume ratios. The following conclusions can be made from the analyses of the experimental results.

- Through the single aqueous phase injection with a salinity gradient between the resident and the injection fluids, we observed the transformation of DTM surfactant micelles from spherical to worm-like structures (WLM) in the salinity mixing zone as indicated by the increase in viscosity of the mixing zone as it propagated along the sand pack. It was also found that WLM had lower mobility than the spherical micelles; but were not significantly retained in the sand pack.
- In the simultaneous injection foam floods, the foam with higher salinity exhibited an earlier onset of strong generation. Viscous fingering occurred at high salinity and high foam quality could delay foam propagation near the injection point. However, it did not affect the rate of apparent viscosity buildup ($\dot{\mu}_f$). This phenomenon can be attributed to the increase in foam film resistance to flow and foam stability due to the presence of WLM structures in the foamed aqueous phase. The effect of salinity on foam stability is most dramatic for high foam quality as indicated by the biggest change of $\dot{\mu}_f$ with salinity.
- In the WAG floods, the viscous fingering of CO₂ was more obvious due to decreasing foam stability and continuous water viscosification during CO₂ cycles. For WAG ratio of 1:1, the onset of strong foam generation was delayed in the high salinity/high viscosity case. The delay of strong foam generation was alleviated for lower WAG ratio of 1:3 because the total mass of surfactant injected per WAG cycle was increased. The rate of foam propagation ($\dot{\mu}_f$) consistently increased with salinity for all WAG ratios.
- For both simultaneous and WAG injections, the improvement in foam stability and its resistance becomes much more dramatic at elevated injection foam quality or reduced WAG ratio is an important advantage of DTM stabilized foam because it enables

injection of much larger volume of CO₂ than water without reducing the mobility control capacity of foam. This is supported by the observed highest efficiency of water displacement by CO₂ with high foam quality and further viscosification of DTM solution at elevated salinity.

Chapter 6 Foaming Experiment in Limestone Core

The objective of this work is to translate the previous findings on DTM foaming behavior in sand-pack porous media to carbonate core. Additionally, we sought to investigate the foaming potential of DTM under reservoir temperature (120°C).

We designed a total of 8 core flood experiments to achieve these objectives. The first experiment was designed to ascertain the propagation of WLM structures through the porous media. We performed a similar experiment in the sand pack and found that the WLM structures were not retained in the porous medium. The carbonate cores that are used in the present study are significantly less permeable than the sand pack used in the previous study (~80 mD for carbonate core vs. ~3500 mD for the sand pack). Therefore, we wanted to ensure that WLM structures could flow through carbonate core pore constrictions.

We also performed 5 foam flooding experiments at 40°C with co-injection and WAG strategies. Finally, 2 foam floods were conducted at 120°C with co-injection strategy. In our analysis we utilized the foam apparent viscosity to elucidate the foam behavior. The conversion from measured pressure drop to apparent viscosity of foam flowing through the sand pack was performed with the aid of Darcy's law.

$$\mu_f = \frac{k\Delta PA}{QL} \quad (7)$$

Where the variables are as follows:

- μ_f : apparent viscosity of foam in *cp*
 k : absolute permeability of the limestone core in *darcies*
 A : cross-sectional area of the limestone core in *cm²*
 Q : volumetric injection rate in *cm³/s*
 L : length of the limestone core in *cm*

6.1 Materials and Methods

Each core flood was performed in separate 1-inch diameter Indiana limestone core. All eight cores originated from the same Indiana limestone outcrop block and were cut in the same batch by the same operator. The specification of each cores is presented in Table 6.1.

Table 6.1 Limestone cores specifications

Core #	Total Volume (mL)	Pore Volume (mL)	Porosity	Permeability (mD)
Core 1	146.5	41.50	0.28	84.4
Core 2	146.0	48.10	0.33	88.2
Core 3	146.2	42.39	0.29	87.1
Core 4	147.5	46.10	0.31	88.2
Core 5	149.6	46.67	0.31	94.7
Core 6	148.4	45.79	0.31	73.1

Core 7	150.1	47.28	0.31	59.7
Core 8	147.0	44.70	0.30	87.7

Equipment used in the foam flooding system include Quizix QX 6000 pumps, 2L piston accumulators, Swagelok high pressure tubing, Autoclave engineer valves, Mity Mite back pressure regulator, Rosemount absolute and differential pressure transducers, and Teledyne Isco Retriever 500. The differential pressure transducers were calibrated only up to 50 psi. This decision was made to accurately read low pressure fluctuations during the early stages of foam generation and propagation. The assembly of previously listed equipment can be seen in Figure 6.1.

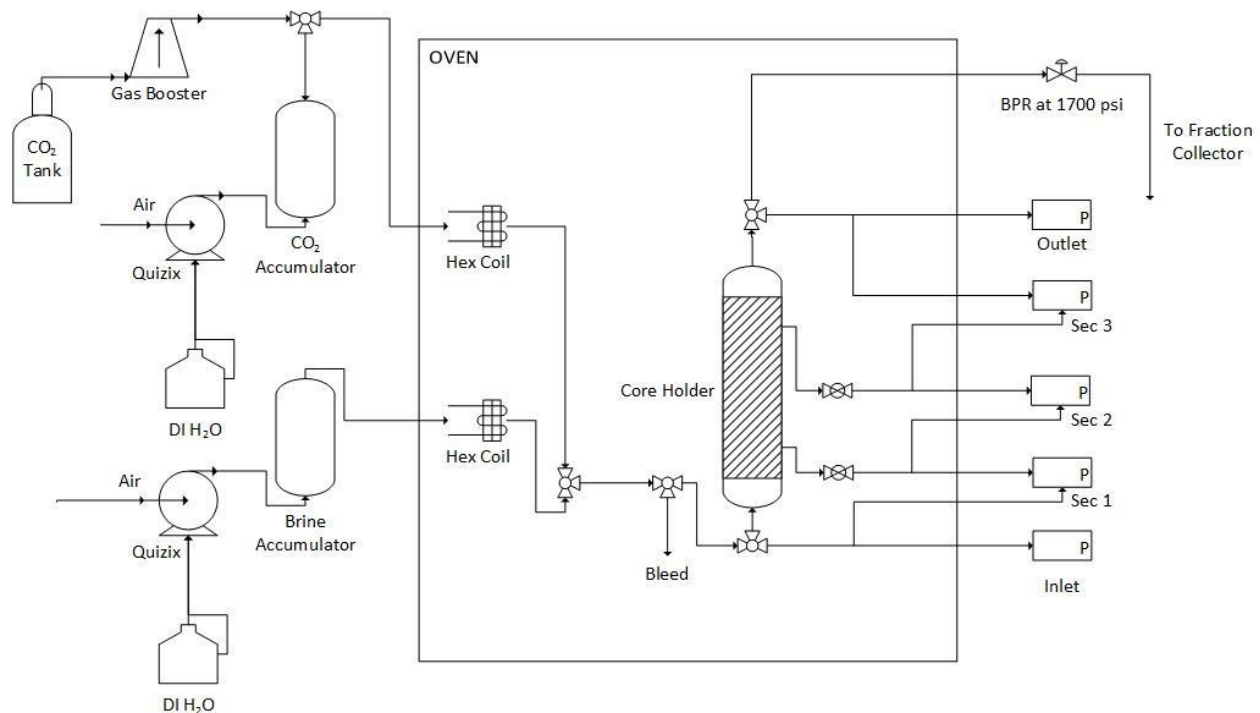


Figure 6.1: Process diagram of foam flood experiment.

In the single-phase injection experiment, we created a salinity gradient by filling the core with 25 wt.% NaCl brine and injecting a 15 wt.% NaCl brine with a 0.5 wt.% DTM concentration. We prepared the DTM surfactant preparation by adding the desired amount of the surfactant into a brine solution. We then adjusted the pH of this solution to 6.

In the foam flooding at 40°C, the DTM surfactant was always delivered in the gaseous phase. The procedure began by loading the DTM surfactant into the piston accumulator. In all experiments, DTM surfactant was delivered in the CO₂ phase at a fixed concentration. The amount of DTM used was 0.5 wt. % of the mass of CO₂ occupying a 500 mL volume at 1700 psi and 22°C. Afterwards, CO₂ was pumped in using a gas booster.

In the foam flooding at 120°C, the DTM surfactant was delivered in the liquid phase. Referring to Figure 3.2, the solubility of DTM decreases with increasing temperature. The delivery of DTM in the gaseous phase at 120°C is not possible at accessible laboratory pressures.

The electrical conductivity and pH of effluent fluid were measured. Liquid phase saturation in the sand pack column was calculated using a mass balance on water phase. The eight flood experiments were performed to achieve the objectives of the study. The design of these experiments is given in Table 6.2.

Table 6.2 Experimental design of eight limestone foam flood experiments

Flood #	Injection Strategy	Liquid Phase Salinity	Surfactant Concentration	Temp. (C)
1	Single phase at 1 PV/day	Gradient of 25 wt.% NaCl resident and 15 wt.% NaCl injection	0.5 wt.% in 25 wt.% NaCl brine 0 wt.% in 15 wt.% NaCl brine	40
2	50% Co-injection at 1 PV/day	15 wt.% NaCl	0.5 wt.% in CO ₂ at 1700 psi	40
3	50% Co-injection at 1 PV/day	20 wt.% NaCl	0.5 wt.% in CO ₂ at 1700 psi	40
4	0.2/0.2 PV Water-alternating-gas at 1 PV/day	15 wt.% NaCl	0.5 wt.% in CO ₂ at 1700 psi	40
5	0.2/0.2 PV Water-alternating-gas at 1 PV/day	15 wt.% NaCl	0.5 wt.% in CO ₂ at 1700 psi	40
6	0.2/0.2 PV Water-alternating-gas at 1 PV/day	20 wt.% NaCl	0.5 wt.% in CO ₂ in brine phase	40
7	50% Co-injection at 1 PV/day	15 wt.% NaCl	0.5 wt.% in brine phase	120
8	50% Co-injection at 1 PV/day	20 wt.% NaCl	0.5 wt.% in brine phase	120

6.2 Core flood result

6.3 Single Phase Injection with Salinity Gradient

The objective of this flood experiment is to ensure that WLM structures could flow unimpededly through the limestone core. WLM mobility in the limestone core is observed through the movement of the salinity mixing zone between the resident fluid (25 wt.% NaCl) and the injection fluid (15 wt.% NaCl, 0.5 wt.% DTM). The result of the single-phase salinity gradient injection is shown in Figure 6.2.

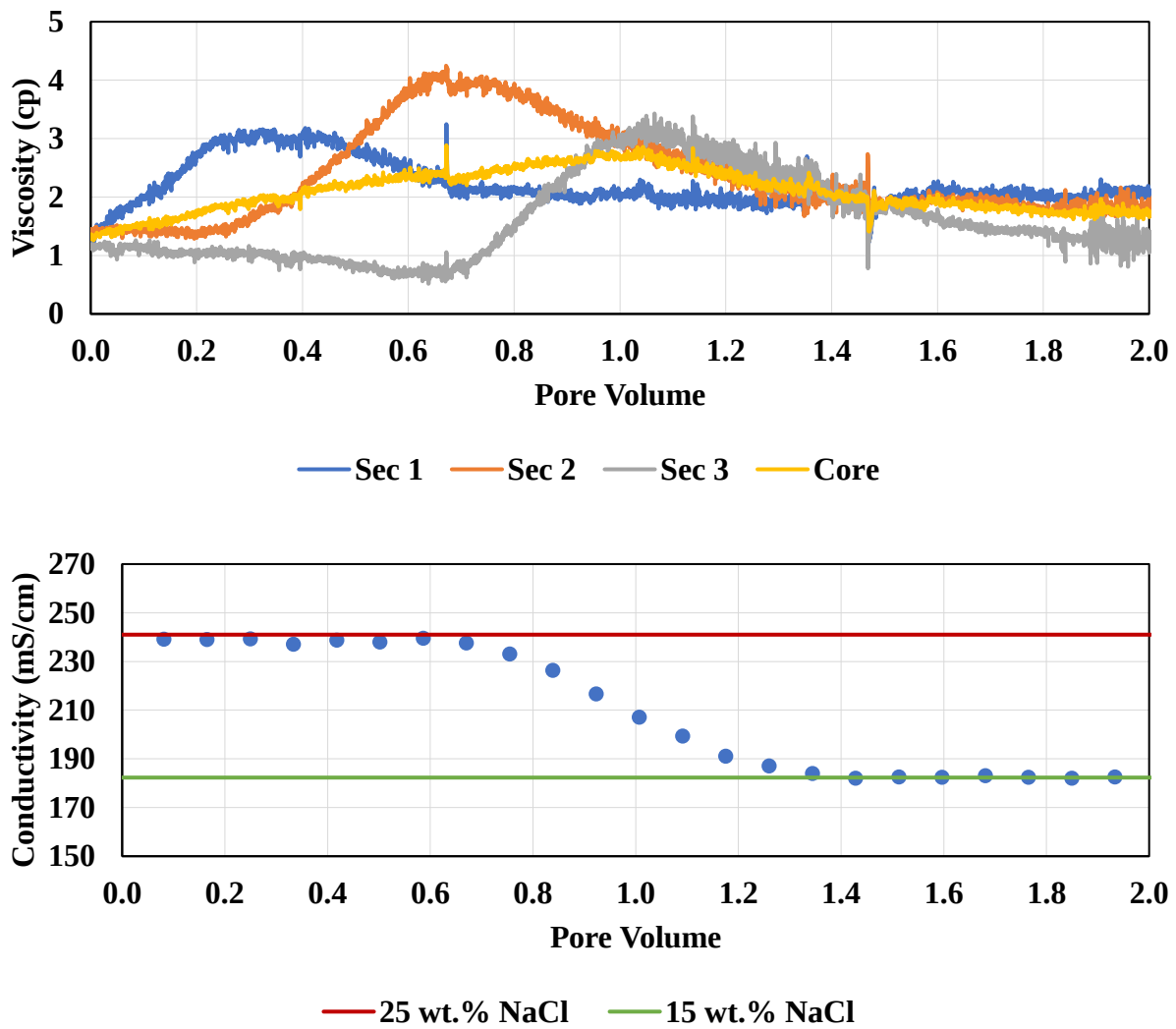
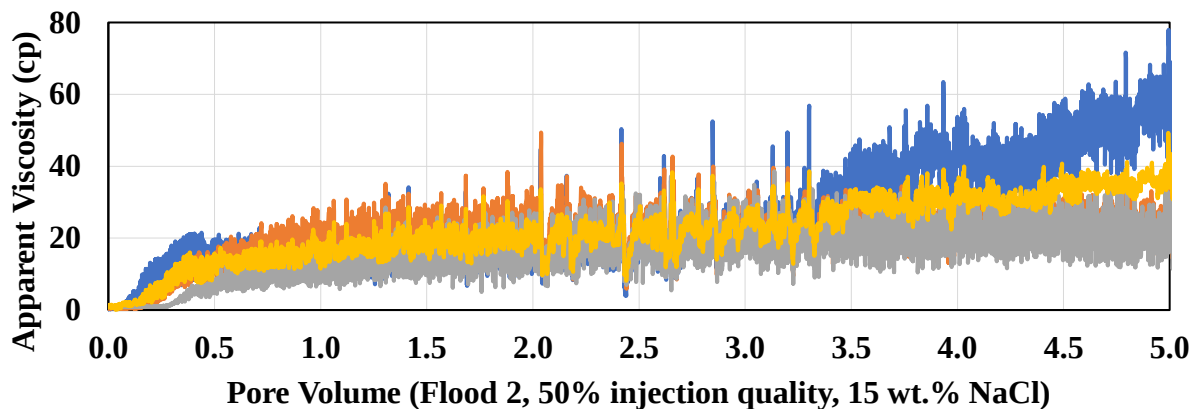


Figure 6.2 (a) Apparent viscosity, (b) effluent conductivity for flood 1.

The data shows evidence of salinity mixing zone viscosification. This viscosification is likely due to the formation of the WLM. We observed that the WLM has lower mobility as indicated by the increasing overall core pressure through the duration of the injection. Additionally, the salinity mixing zone exited the core at 1 injected pore volume. The core-fluid viscosity measurement, however, exhibited a delayed decline beyond 1 injected pore volume. However, we noted that the core-fluid viscosity did eventually decline to a value close to the viscosity value of injection fluid bulk solution (2.4 cp). This result indicates minimal WLM retention in the limestone core.

6.4 Salinity Effect on Foam Transient Behavior in Limestone Core Co-injection at 40°C

In the sand pack flooding experiments, we saw that the foaming behavior of DTM is significantly affected by the liquid phase salinity. We sought to translate the foaming behavior of DTM in the sand pack to limestone core. First, we examined the foaming behavior of co-injection at 50% injection quality. In the sand pack, we saw an earlier onset of strong foam and a higher rate of foam apparent viscosity buildup in the higher salinity DTM foam. The result for co-injection at 50% injection quality in limestone core is shown in Figure 6.3.



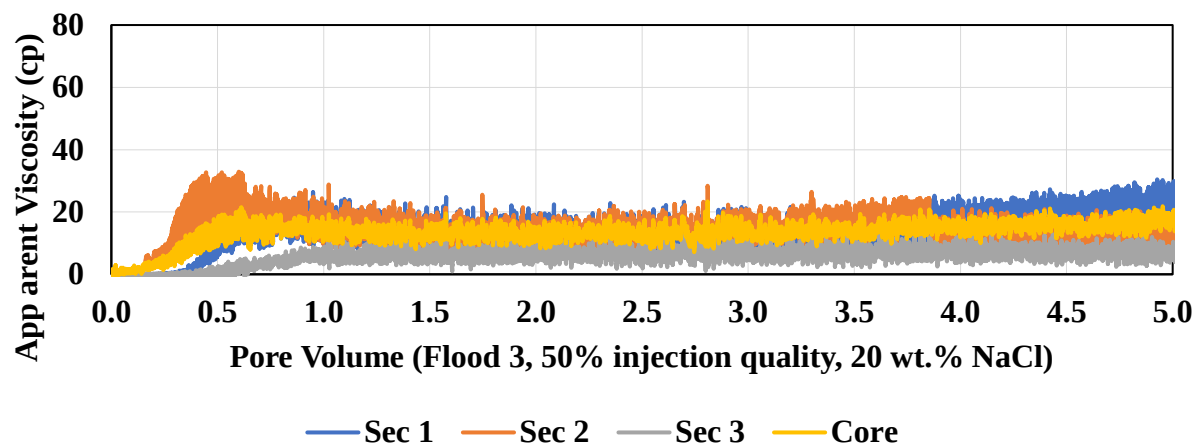


Figure 6.3 Sectional and total apparent viscosity for co-injection floods in limestone core

We observed a significant delay in the onset of strong foam generation in the lower salinity case (flood 2). A steady rise in apparent viscosity in section 1 was not observed until 3 total injected pore volumes (TIPV). In the higher salinity case (flood 3), we did not observe an apparent sign of strong foam generation. The apparent viscosity stayed approximately constant after the first TIPV.

The co-injection results in limestone core are patently different from those in the sand pack. In Figure 5.4, we observed strong foam generation in both the lower salinity and higher salinity cases in sand pack co-injection. We suspect that the delay in/lack of strong foam generation in limestone core is due to porous media heterogeneity. We chose to use the Indiana limestone core for its relative homogeneity and higher permeability among the available carbonate porous media. It was, however, expected that the degree of homogeneity in the Indiana limestone is less than that of sand pack.

In these limestone foam floods, we hypothesize that the injected gas flows primarily through the highest permeability channels. These higher permeability channels are associated with larger pore constrictions diameter and larger pore body volume. Foam generation in porous

media is a function of the porous media morphology. Large pore throats and pore bodies generate a larger foam bubble diameter (coarser foam texture). In order for a strong foam to be generated, the gas must be diverted to the lower permeability channels. Smaller pore bodies, associated with lower porous media permeability, may create a finer foam texture and provide larger resistance to gas flow.

We observed a marginal sign of strong foam generation in flood 2. The lower viscosity of the liquid phase in this flood may have allowed for easier/faster gas invasion to the lower permeability channels in the limestone core, as suggested by equation 2. Therefore, foam generation events may have occurred more frequently in flood 2 than flood 3. Once generated, the finer texture foam may migrate from the lower permeability channels to the higher permeability channels. This phenomenon may have strengthened the foam's ability to reduce gas flow in the higher permeability channels and divert a larger portion of the gas into the lower permeability channels.

Another possible reason for the lack of strong foam development in the limestone core is insufficient surfactant protonation. In floods 2 and 3, the surfactant was delivered in the gaseous phase. The DTM was in its nonionic form when dissolved in the supercritical CO₂. In order for the DTM molecules to be stable and function as a surfactant in a high salinity environment, they have to be transformed to the cationic form via an acid-base reaction with carbonic acid (H₂CO₃). The calcium carbonate (CaCO₃) compound which makes up limestone may also undergo an acid-base reaction with the carbonic acid. By comparing the pK_a values of their conjugate acid, calcium carbonate is a weaker base (less ready to take the H⁺ ion) than the amine heads of the DTM [61]. In spite of this, the presence of calcium carbonate may present an

alternate reaction pathway for the carbonic acid and thus reduce the rate of the protonation of the DTM amine heads.

The lack of strong foam development suggested by the apparent viscosity data is corroborated by the liquid phase saturation measurement presented in Figure 6.4.

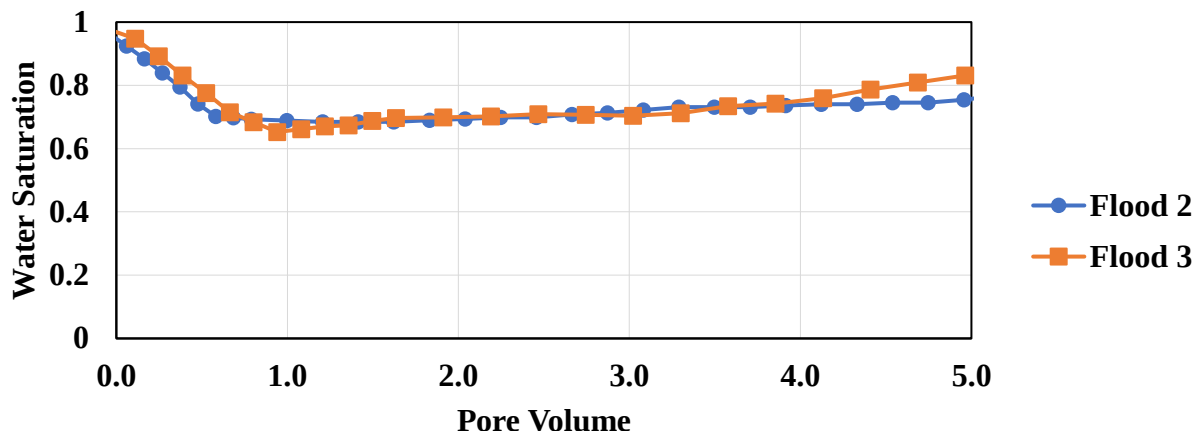


Figure 6.4 Water desaturation for the co-injection floods 2 and 3 in limestone core.

The water saturation values for both the low salinity and high salinity co-injection floods decreased through the first TIPV. Thereafter, the water saturation increased for both cases, indicating poor conformance performance by the in-situ foam. It could be noted, however, that the water saturation value in the low salinity case is marginally lower than the higher salinity case; which can be associated with the slightly stronger foam in flood 2 vs. flood 3 as observed through the apparent viscosity measurement.

6.5 Salinity Effect on Foam Transient Behavior in Limestone Core WAG at 40°C

Next, we examined the salinity effect on DTM foaming behavior of WAG at 0.2/0.2 PV slug ratio. For the high salinity liquid phase, we performed experiments with DTM surfactant delivered in the gaseous phase and DTM surfactant delivered in the liquid phase. The result for the WAG core floods in limestone core is show in Figure 6.5.

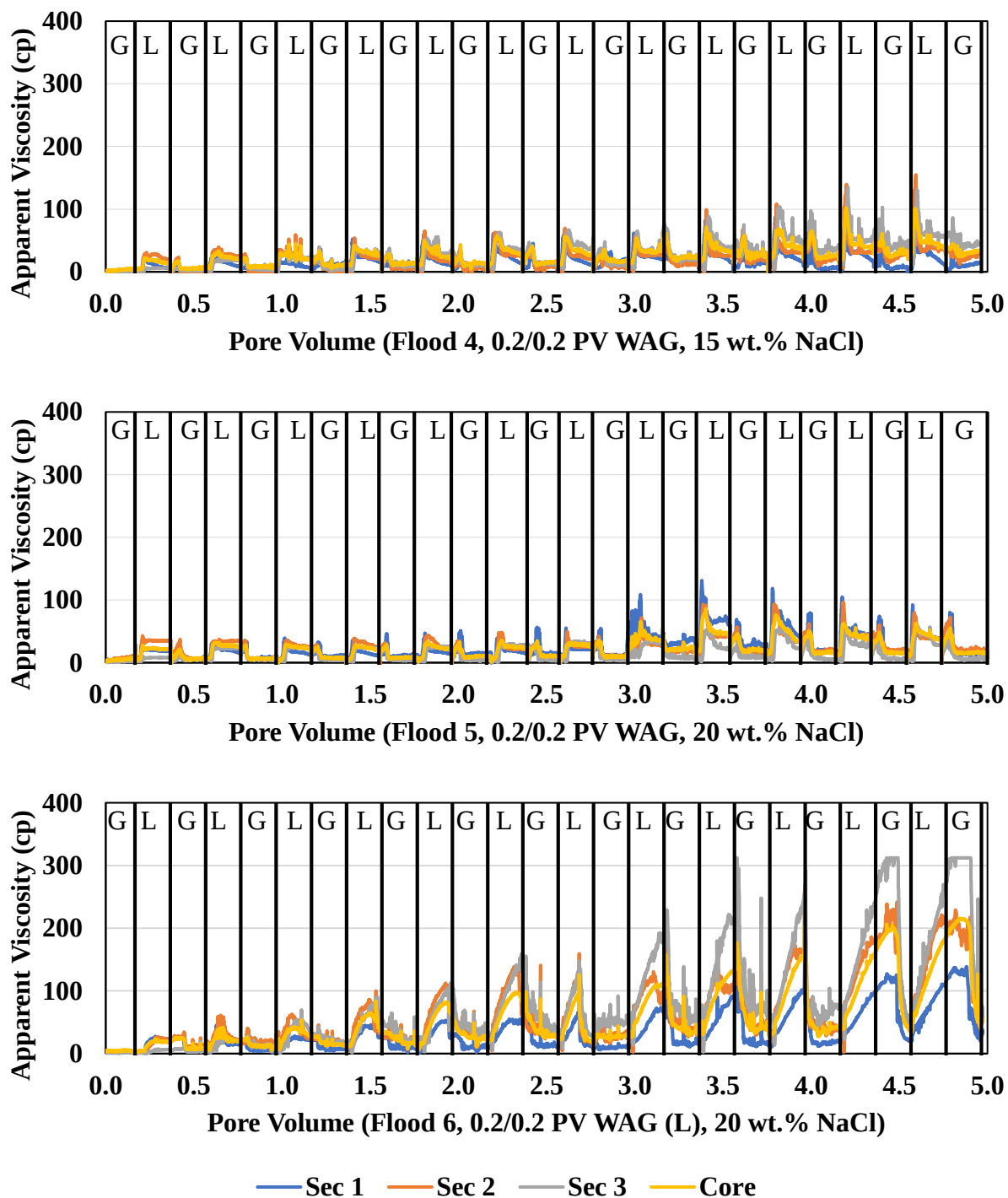


Figure 6.5 Sectional and total apparent viscosity for WAG floods in limestone core. The vertical lines demarcate gas and liquid injections.

The result of floods 4 and 5 did not show a substantial increase in foam apparent viscosity. Flood 6, however, exhibited a considerable increase in apparent viscosity, signifying

the development of a strong foam. The DTM surfactant in flood 6 was delivered in the liquid phase; where the pH of the solution was adjusted to 6 prior to the injection through the addition of HCl. Therefore, the DTM delivered to the core in flood 6 was already in the cationic form. The stark contrast in the result between floods 5 and 6 may indicate that the incomplete/delay in DTM protonation could cause a significant delay in strong foam development in a carbonate reservoir. Additionally, WAG injection strategy in a heterogenous porous media has been known to reduce gaseous phase mobility and improve overall sweep efficiency [62]. The WAG injection strategy may have alleviated the persistent gas fingering issue speculated in our analysis of co-injection floods 2 and 3. The apparent viscosity results in Figure 6.5 correlate well with the liquid phase saturation result presented in Figure 6.6.

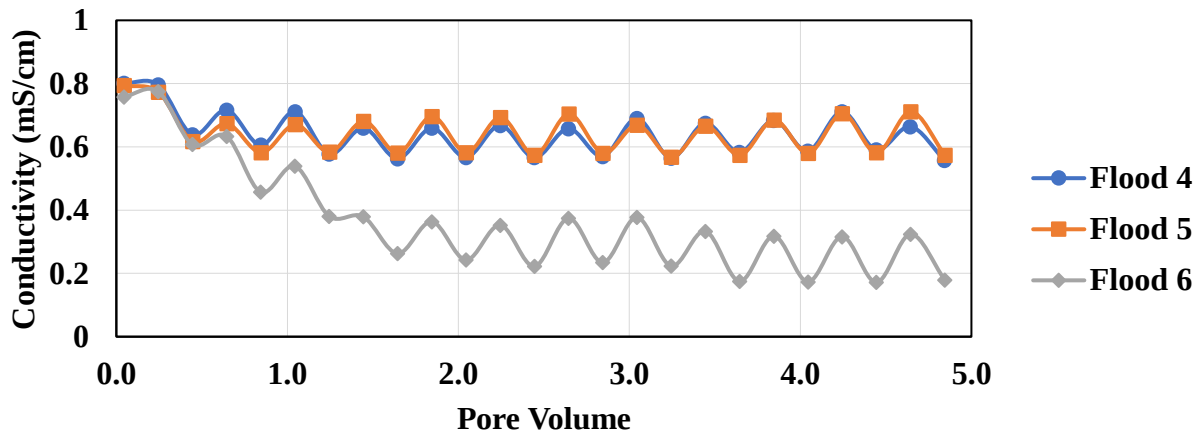


Figure 6.6 Water desaturation for the co-injection floods 4, 5 and 6 in limestone core.

Water saturation in floods 4 and 5 oscillated in the relatively high values between 0.6 and 0.7 throughout the injection period. While, the water saturation in flood 6 reached an oscillation value between 0.2 and 0.3, indicating a better gas conformance performance.

6.6 Salinity Effect on Foam Transient Behavior in Limestone Core Co-Injection at 120°C

The last set of experiments in the limestone core flood series is the investigation on the salinity effect on DTM co-injection at 120°C. In these series of core floods, we delivered the DTM surfactant in the liquid phase, after learning about the surfactant protonation issue associated with the surfactant delivery in the gaseous phase. The result of the co-injection floods at 120°C is shown in Figure 6.7.

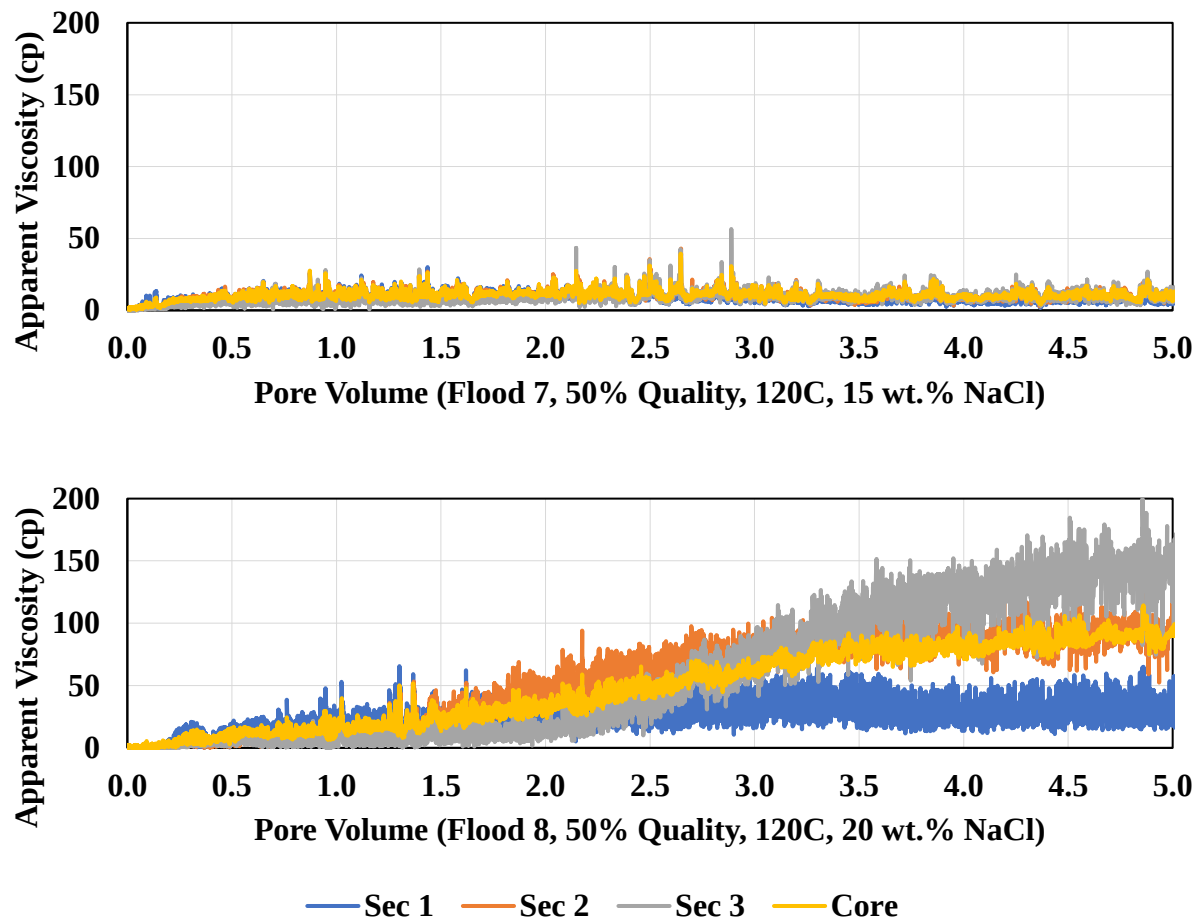


Figure 6.7 Sectional and total apparent viscosity for co-injection floods in limestone core at 120°C

Figure 6.7 suggests an absence of strong foam development in the lower salinity flood 7. In the higher salinity flood 8, the core apparent viscosity of foam reached an approximate value of 85 cp. We could not determine the viscosity of the two DTM bulk solution salinities at 120°C due to the temperature limitation of the rheometer used. However, we performed viscosity measurements of the two DTM bulk solution salinities from 40°C to 80°C and used the exponential fit to extrapolate viscosities at 120°C. The measured viscosity values and the extrapolation curve are presented in Figure 6.8.

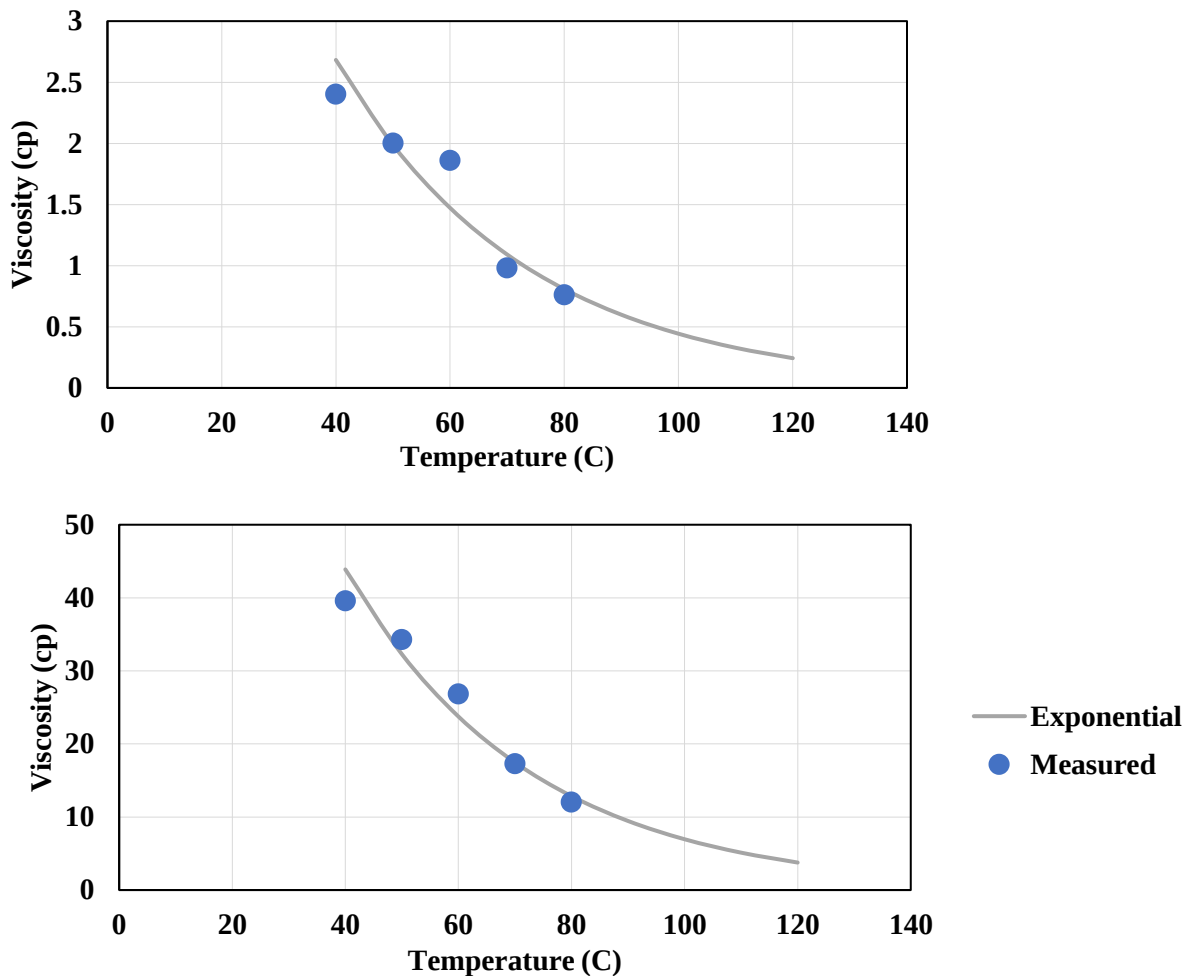


Figure 6.8 Viscosity as a function of temperature extrapolation for 0.5 wt.% DTM solution at 15 wt.% NaCl (top) and 0.5 wt.% DTM solution at 20 wt.% NaCl

Based on the extrapolation, the viscosity of the lower salinity DTM solution at 120°C is 0.24 cp; while the higher salinity DTM solution at 120°C is 3.76 cp. The higher viscosity of the liquid phase in flood 8, along with the additional steric disjoining pressure by the WLM structures, may have allowed for a buildup of a more stable foam. The liquid phase saturation results for floods 7 and 8 are as presented in Figure 6.9.

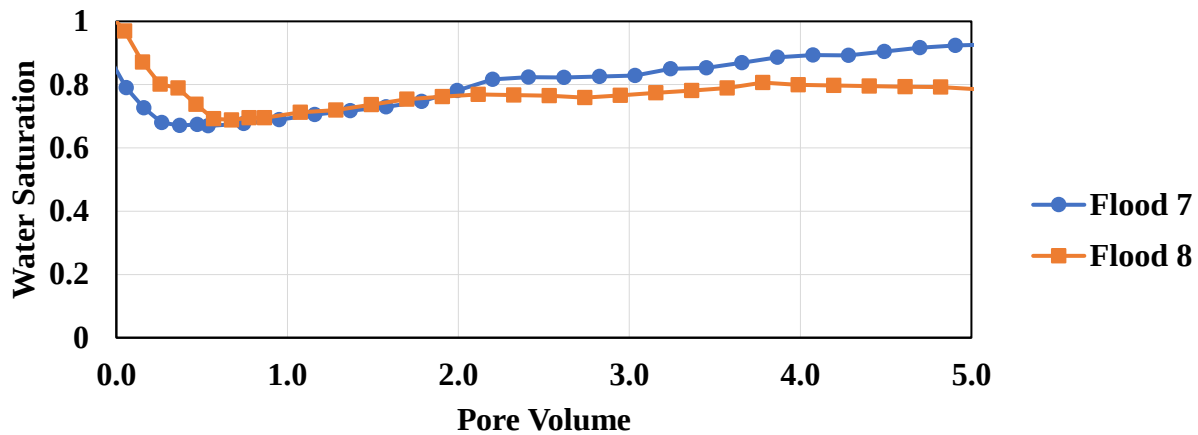


Figure 6.9 Water desaturation for the co-injection floods 7 and 8 in limestone core.

The weak foam is suggested by the low apparent viscosity in flood 7 is confirmed by the increasing water saturation beyond the initial liquid phase displacement by the injection fluids. Despite of the buildup of foam apparent viscosity, the water saturation in flood 8 still increased beyond the initial liquid phase displacement by the injection fluids. This result indicates that the foam developed in flood 8 did not provide sufficient conformance to divert the gas flow away from the highest permeability channels.

6.7 Conclusion

From the 8 limestone core floods we were able to gather the following conclusions:

- WLM structures are able to flow through the limestone core at a permeability of 80 mD.

- DTM foaming in co-injection at 40°C with surfactant delivery in the gaseous phase did not result in strong foam development in either salinity cases. Possible issues include persistent gas channeling through highest permeability channels and/or insufficient surfactant protonation due to the presence of calcium carbonate compound.
- DTM foaming in WAG at 40°C with surfactant delivery in the gaseous phase did not result in strong foam development in either salinity cases. The WAG flood with surfactant delivery in the liquid phase, however, yielded in successful strong foam development. This result may support our conjecture regarding insufficient surfactant protonation associated with surfactant delivery in the gaseous phase into a carbonate porous media.
- At 120°C, the higher salinity DTM foam exhibited greater pressure buildup than the lower salinity DTM foam. However, the higher salinity DTM foam still did not provide enough conformance performance for liquid phase desaturation.

Chapter 7 Conclusions and Recommendations

This thesis explores the foaming behavior of DTM surfactant in porous media. The primary focus was placed on how the surfactant solution salinity affects the transient foaming behavior. Three sets of experiments were performed in three different porous media: microfluidic model, sand pack, and limestone core. The summary, conclusion, as well as, recommendations for future work for each of the three experimental sets is as follows.

7.1 Foaming in Microfluidics Model

Through foaming experiments in the microfluidic model, we learned that the salinity of the DTM solution influences foam generation, foam apparent viscosity and foam stability. DTM foam with the lower salinity liquid phase (associated with spherical micelle and lower viscosity) could produce a finer foam texture. The DTM foam with the higher salinity liquid phase (associated with WLM and higher viscosity) possesses higher per lamella apparent viscosity and better foam stability.

The comparison between the DTM and IOS foams emphasized the importance of gas-liquid interfacial tension (σ_{gl}). The σ_{gl} determines the frequency of foam generation events; thus controlling the texture of foam produced. However, σ_{gl} is also a component of the foam apparent viscosity. A low σ_{gl} value could result in a finer foam with a lower per lamella apparent viscosity.

Experiments with the different molecular size polymers revealed the importance of local shear rate in porous media on foam generation. An extremely shear thinning (high viscosity at low shear rates and low viscosity at high shear rates) liquid phase may produce a coarse foam with a large per lamella apparent viscosity and better foam stability.

Foaming experiments at different upstream gas pressures suggested that foam generation at a high σ_{gl} may be sensitive to the velocity of the gas phase. A high σ_{gl} does not allow for the invasion of porous media pore at a high gas velocity and promote gas fingering. In contrast foam generation with a low σ_{gl} may be enhanced a high gas phase velocity due to greater frequency of foam generation events.

One recommendation for future research is to use an image analysis tool to quantify the foam texture/lamella density as well as gas saturation throughout the injection period. Currently, the foam texture and gas saturation are qualitatively assessed at different time intervals. A continuous and quantitative result may allow for more insight to foam behavior.

Another recommendation is to use a higher resolution camera for future microfluidic endeavor. Higher resolution videos and images could allow for pore scale observation of foam behavior. Pore scale observation may allow for quantification of snap-off and lamella division frequency.

7.2 Foaming in Sand Pack

The single-phase injection experiment showed that the WLM structure has a lower mobility in porous media. However, the flow of WLM structure is unimpeded in the 3.5 D sand pack column.

In the co-injection floods, DTM high salinity foam exhibited an earlier onset of strong foam generation and a greater rate of apparent viscosity build-up. The higher viscosity liquid phase of DTM high salinity foam led to a greater foam stability and higher per lamella apparent viscosity. The influence of liquid phase viscosity on foam stability is especially apparent in the higher quality (dry) injection.

The high viscosity DTM high salinity may delay the onset of strong propagation in water-alternating-gas (WAG) injection due to severe gas fingering. Once the strong foam generation commences, the DTM high salinity foam in WAG injection also exhibited a greater rate of apparent viscosity build-up.

Overall, strong foam generation was observed in all sand pack foam floods. This result indicates successful DTM delivery in the supercritical CO₂ and the subsequent DTM surfactant protonation by the carbonic acid.

One recommendation for future study is to perform a series of sand pack experiment with the DTM solubilized in the liquid phase. This set of experiments may serve as a baseline comparison for which to compare the current results with.

Another recommendation is to quantify the effluent surfactant concentration. This measurement could allow for determination of surfactant retention in the porous media. The sand pack may also be flushed with DI water at the end of each experiment to quantify the total amount of surfactant delivered to determine the efficiency of DTM delivery in supercritical CO₂. One possible method for surfactant concentration determination is through liquid chromatography light spectroscopy (LCMS).

7.3 Foaming in Limestone Core

We were not able to generate strong foam in the co-injection and WAG foam floods in limestone core where the DTM was delivered in the gaseous phase. A strong foam was generated in the WAG flood where the DTM was delivered in the gaseous phase. We proposed that the lack of strong foam development where DTM was delivered in the gaseous phase is due to insufficient DTM protonation.

In the co-injection floods at 120°C, the higher salinity DTM foam exhibited greater pressure buildup than the lower salinity DTM foam. However, the higher salinity DTM foam still did not provide enough conformance performance for liquid phase desaturation.

One recommendation for future study is to perform a series of foam floods where DTM is delivered in the gaseous phase using a heterogenous sandstone core with similar permeability to the Indiana limestone (~ 80 mD). In sandstone, the protonation rate of DTM should be similar to that in the sand pack. This series of experiment could determine whether insufficient protonation of DTM is the root of lack of strong foam development in carbonate core.

Another suggestion for future research is to perform co-injection foam flooding at 120°C at different injection qualities and/or injection rate to assess whether strong foam generation is at all possible at that temperature.

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