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Oil effect on CO_2 foam stabilized by a switchable amine surfactant at high temperature and high salinity

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ABSTRACT

Despite the possible detrimental effect of oil on foam displacement processes in CO_2 EOR the effect of oil on dense CO_2 foams has received little attention relative to air foams or low density CO_2 foams. Herein, the effect of both a first contact miscible hydrocarbon (dodecane) and crude oil on CO_2/water (C/W) foams generated by a switchable surfactant, $C_{12–14}N(EO)_2$ was examined at dense CO_2 conditions at temperatures up to 120 °C (393 K) and 3400 psia (23 MPa). Upon increasing the fractional flow of dodecane, a gradual decrease in foam viscosity was observed as the foam becomes unstable. Since only two phases are present, traditional destabilization mechanisms for three phase oil/gas/water systems based on the entering and spreading are invalid. Therefore, an alternative mechanism is suggested whereby added dodecane strengthen the surfactant tail interactions with the nonaqueous phase (mixture of CO_2 and dodecane) to shift the hydrophilic-CO_2 philic balance (HCB) towards an unstable region. This mechanism is supported by a decrease of the CO_2–water interfacial tension from ∼5 mN/m to 0.5 mN/m for dodecane–water systems at 120 °C and 3400 psia. The effect of crude oil was more profound than for dodecane, whereby rapid destabilization of foam occurred at an oil fractional flow as low as 0.2. In this case, the immiscible portion of the crude oil can enter and spread at the lamellae to destabilize the foam as is evident in positive entering and spreading coefficients. Also, other foam destabilizing parameters such as temperature and capillary pressure were studied in the presence of oil and the results were consistent with those in the absence of oil.

1. Introduction

High displacement efficiency may be achieved with CO_2 flooding [1] whereby crude oil is displaced through multiple contact miscibility (MCM) [2]. Here, pure CO_2 is originally immiscible with the crude but gains miscibility as lighter components of the oil (C5-C30) are extracted [2]. In contrast, miscible displacement for pure n-alkanes is achieved by first contact miscibility whereby the alkane is miscible with CO_2 in all proportions [2]. However, miscible CO_2 EOR often leads to low recovery of 10–20% of original oil in place, (OOIP) as a consequence of the properties of CO_2 and the reservoir heterogeneity [3]. First, the low density of high pressure CO_2 relative to oil promotes gravity override causing a reduction in oil recovery in the lower parts of the reservoirs [1,3,4]. Also, the spatial heterogeneity in permeability may lead to

channeling of CO_2 through high permeability sections of the reservoirs and lower the sweep efficiency [5]. The addition of small amounts of surfactants to form CO_2-in-water (C/W) emulsions (commonly referred to as foams) has been shown to mitigate these problems by reducing CO_2 mobility [6,7]. Foams are comprised of CO_2 bubbles (discontinuous phase) separated by a continuous aqueous phase composed of lamellae [8,9]. The reduced mobility of C/W foams is due to an enhancement in the viscosity by 2–4 orders of magnitude compared to that of pure CO_2 [9,10]. The enhanced viscosity may be attributed to: 1) resistance to flow of the lamellae separating the bubbles 2) the penalty in interfacial energy during deformation of the bubbles caused by shear 3) interfacial tension gradients between the front and the rear ends of the bubbles, as the surfactant is swept from the front to the back of the bubble [11] and 4) resistance to flow due to pore restrictions in porous

media [12].

A key property for the design of surfactant for CO_2 foam is the hydrophilic/CO_2-philic balance (HCB) of the surfactant – analogous to HLB for oil water systems [13–20]

$$\frac{1}{HCB} = \frac{A_{TC} - A_{TT} - A_{CC}}{A_{HW} - A_{HH} - A_{WW}} \qquad (1)$$

where A_{ij} is the interaction potential for components including CO_2 (C), the hydrocarbon tail (T), water (W) and the surfactant head group (H) [20]. The HCB of the surfactant can be manipulated by changing surfactant structure and other formulation variables such as temperature, pressure and salinity [20]. When the HCB is above unity the surfactant prefers the aqueous phase and the preferred curvature is CO_2 in water macroemulsions (C/W foam) according to Bancroft rule. At HCB values very close to the balanced point, the interfacial tension becomes extremely small and emulsions become unstable [21]. Therefore, the optimum surfactant structure for stable foam is achieved when the HCB is shifted by a modest amount away from the balanced state in favor of a more hydrophilic surfactant.

Recently, Chen et al. studied the effect of different destabilization mechanisms on the apparent viscosity of foams generated with two novel surfactants, namely protonated ($C_{12-14}N(EO)_2$) [22,23] and a cationic alkylammonium surfactant ($C_{12-14}N(CH)_3Cl$) in a crushed limestone bed [24]. While $C_{12-14}N(CH)_3Cl$ is a permanently cationic surfactant, $C_{12-14}N(EO)_2$ is a switchable surfactant that is nonionic at high pH but is protonated at lower pH values to become cationic. As shown in a previous publication, at 22%TDS (255 kg/m^3), the surfactant completely protontates (cationic) at pH values lower than 5.5 at temperatures up to 90 °C. Hence, in the presence of high pressure CO_2, where the pH is ~(~3) [25] the surfactant is cationic. For $C_{12-14}N(EO)_2$ and $C_{12-14}N(CH)_3Cl$, capillary pressure was varied by increasing the CO_2 volume fraction (foam quality) from 70% to 95% [22]. The foam was found to resist coalescence up to a foam quality of 90%, but a higher qualities the foam became unstable. Here the capillary pressure reached a threshold (limiting capillary pressure) where it exceeded the disjoining pressure required between the two lamellae interfaces to prevent coalescence [26]. Secondly, increasing temperature from 25 °C to 120 °C was found to decrease the foam apparent viscosity from ~35 to 15 cP [22]. The decrease in foam apparent viscosity was attributed to the decrease of the viscosity of the aqueous phase that resulted in faster film drainage and bubble coalescence. Despite these destabilization effects, both of these surfactants were found to generate and stabilize foam with viscosities up to ~14 cP even at a high temperature of 120 °C and 90% foam quality [22]. The foam stability at high temperature was enabled by the high aqueous solubility of these surfactants given the enhanced solvation of the cationic amine head group [22]. In addition, the high adsorption of $C_{12-14}N(EO)_2$ at the CO_2-brine interface produced a large reduction of the interfacial tension even at 120 °C and stabilized the lamellae against drainage and rupture [22].

The effect of oil on destabilization of foam in porous media has been studied extensively and described by various mechanisms [27]. Lau et al. attributed the breaking of steam foam generated by alpha olefin sulfonate (AOS) surfactants in the presence of oil to the depletion of the surfactant from the gas–water interface to the oil phase [28]. However, this hypothesis cannot be generalized because foam was destabilized in the presence of oils that were pre-equilibrated with surfactants. Others argued that oil can destabilize foam by changing the wettability of the porous media from water – wet to oil – wet which hinders the formation of aqueous lamellae necessary for foam generations through mechanisms such as snap off [29–31]. Lau et al. suggested that the destabilization of nitrogen foam was due to entering and spreading of oil at the gas water – interface that causes lamellae to thin and eventually break due to capillary pressure [32]. These foam formed with gases with relatively low densities provide a basis for understanding CO_2 foams where the density of the gas phase is much larger.

The effect of oil on C/W foams has received little attention for dense

CO_2 and has been treated similarly to the case of foams with much lower density gases [33]. Kuhlman studied the effect of oil on C/W foam at low pressure (low density) and high pressure (highly dense) CO_2. For low density CO_2, foam stability generally correlated with the oil spreading coefficient where the half life of foam decreased as the spreading coefficient increased [31]. In all high pressure experiments – except for first contact miscible experiments – oil was observed to spread in the C/W foams because of the low interfacial tension between oil and CO_2 at high pressure. Unlike the case for the low pressure experiments, the stability of the C/W foams were attributed to the stability of the oil-in-water emulsions within the lamellae rather than the negative spreading coefficients [31]. Also, different researchers found that C/W foams generated at conditions of first contact miscibility with oil are usually more stable [31,34]. It was hypothesized that miscible flooding restored the porous media from oil –wet to water – wet. Furthermore, the spreading of the oil in the immiscible flooding destroyed the foam and increased the CO_2 mobility [31,34]. Recently, Chabert et al. studied the effect of dodecane on C/W foams at first contact miscible conditions and observed that C/W foams generated by surfactants that also were effective for O/W emulsification were unstable. This result was attributed to preferential adsorption of the surfactant at the O-W interface rather than the C-W interface [33].

The main objective of this paper is to determine the effect of crude oil on the stability of C/W foams generated by $C_{12-14}N(EO)_2$ in high salinity brine at 120 °C in a crushed limestone pack and to explain the mechanism. The effects of oils on foams have rarely if ever been reported at elevated temperatures above 100 °C. To gain further insight into the mechanism, we also examined the behavior of C/W foams in the presence of a model oil that is miscible with CO_2 in all proportions, dodecane, To our knowledge, very few studies have contrasted the behavior of miscible and immiscible hydrocarbons on the generation and stability of C/W foams [31,34]. These studies hypothesized that CO_2 mobility is reduced (higher C/W foam apparent viscosity) at miscible conditions because the decrease in oil saturation with oil production possibly restores the wettability of the porous media from oil-wet to water wet [31]. To test this hypothesis, in this study, dodecane was coinjected with CO_2 and surfactant solution to maintain constant oil saturation. In addition, for each oil, the effect of the fraction of the oil in the nonaqueous phase on the foam apparent viscosity was investigated. For the case of crude oil, traditional destabilization mechanisms based on the three phase surface balance are applicable, as characterized by the entering and spreading coefficients, which are described in detail in the subsequent theory section. For dodecane which is fully miscible with CO_2 an alternative mechanism is proposed based on an observed difference in the stabilities of C/W foams and O/W emulsions. Also, the effect of presence of oil (remaining oil) on the minimum surfactant concentration required for foam generation is studied and related to the change in oil saturation. Furthermore, the effect of temperature on defoaming, as characterized by the foam apparent viscosity, is examined in the presence of varying concentrations of dodecane from 50 to 120 °C. The effect of volume fraction of CO_2 from 60 to 98% on foam apparent viscosity has also been measured and is explained in terms of the change in water saturation and capillary pressure in the presence of dodecane.

2. Theory of foam stability in the presence of oil

The kinetic stability of foams requires that the lamellae prevent coalescence of the dispersed phase bubbles [35]. Several factors affect lamellae stability including capillary drainage [36–39], disjoining pressure [40,41], temperature [39,42,43] and the presence of oil [9,44].

The extent of the defoaming effect of oil depends on the stability of the pseudo emulsion film separating the oil phase from the foam liquid–gas interface (O/W/G film) [45]. For oil to break a foam, first it has to enter the gas–water interface which can be quantified by the
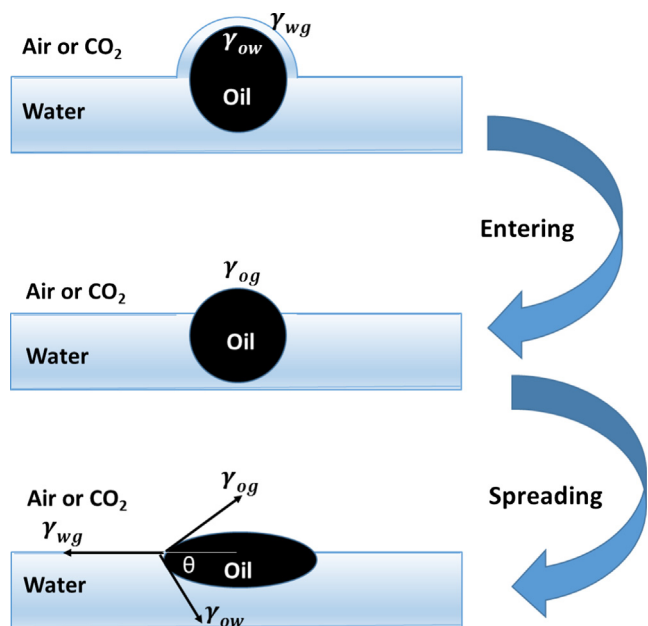
Fig. 1. Illustration of entering and spreading of an oil droplet at the gas (air or CO_2)–water interface. Adapted from Kralchevsky, 2001.

Fig. 2. Illustration of lamellae numbers (oil droplets pinched into the plateau border by capillary pressure). Adapted from Shramm and Novosad, 1989.

3. Experimental

3.1. Materials

The surfactant Ethomeen C/12 (Bis (2-hydroxyethyl) cocoalkylamine, 97% active) was a gift from Akzo Nobel and was used as received. The structure of the surfactant is shown in Table 1. Sodium chloride (NaCl, certified ACS), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and hydrochloric acid (HCl, technical) were obtained from Fisher and used as received. Calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$, $99+\%$) and dodecane (99%) were purchased from Acros and used without further purification. The properties of dodecane at 3400 psia are shown in Table 2. Sodium chloride brines were prepared by adding NaCl to deionized (DI) water (Nanopure II, Barnstead, Dubuque, IA). The concentration of NaCl was 182 g/L. A synthetic brine with 22% TDS (255 g/l) was prepared by the addition of 182 g/L NaCl, 77 g/L $CaCl_2 \cdot 2H_2O$, 26 g/L $MgCl_2 \cdot 6H_2O$ to DI water. The 22%TDS was used as model reservoir brine. The initial pH of surfactant water/brine solution/mixture was adjusted to 6 by adding HCl and measuring the pH using a Mettler Toledo FG2 FiveGo pH meter. The crude oil was a gift from Abu Dhabi National Oil Company and has a minimum miscibility pressure of 3400 psia. Detailed composition of the crude oil was not provided.

3.2. Air/water foam generation

Air/water foam was generated by strong hand mixing (10 s) of 1 wt % $C_{12–14}N(EO)_2$ surfactant solution in 22% TDS brine at pH 6 at 24 °C and atmospheric pressure. For a constant surfactant solution volume, the effect of the addition of dodecane at different ratios ($V_{dodecane}/V_{aq}$) on A/W foam stability was investigated in terms of foam height and half-life by measuring foam heights every five minutes.

3.3. Interfacial tension measurements

At room temperature and atmospheric pressure, interfacial tension (IFT) measurements between air or dodecane and 1 wt% $C_{12–14}N(EO)_2$ surfactant solution in 22% TDS brine at pH6 was conducted using a pendant drop of the aqueous phase as reported previously [50]. At 120 °C and 3400 psia, the interfacial tensions between nonaqueous phases (CO_2, dodecane or crude oil) and 1 wt% $C_{12–14}N(EO)_2$ surfactant solution in 22% TDS were determined from axisymmetric drop shape analysis of a captive bubble of the nonaqueous phase [51], as described in detail previously [50]. The standard deviation of ten interfacial

entering coefficient ($E_{o/w}$) derived from a surface energy balance where W-G and O-W interfaces disappear and an O-W interface is created as illustrated in Fig. 1. $E_{o/w}$ is defined by Harkins et al. [46] as.

$$E_{o/w} = \gamma_{wg} + \gamma_{ow} - \gamma_{og} \tag{2}$$

where w, g and o are water, gas, and oil, respectively. Negative entry coefficients suggest that oil will remain in the aqueous phase, whereas it enters the gas–water interface for positive values [1,35]. For porous media [35]. a generalized entering coefficient, $E_{o/w}^g$ was defined by Bergeron et al. (Eq. (3)) [47]

$$E_{o/w}^g = \gamma_{wg} + \gamma_{ow} - \gamma_f \tag{3}$$

where γ_f is the interfacial tension of the pseudoemulsion films. This approach incorporates the disjoining pressure and the thickness of the film [35,47]. Upon entering the interface, defoaming can occur via either spreading of the oil droplet at the interface or bridging of the foam film [35]. Spreading is characterized by a spreading coefficient ($S_{o/w}$) defined by Eq. (4) and derived from the balance of an oil lens at the W-G interface as shown in Fig. 1 [48].

$$S_{o/w} = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \tag{4}$$

If $S_{o/w} < 0$, then the oil droplet is contained in the W-G interface as an equilibrated lens and spreading is unfavorable [1,35]. If $S_{o/w} > 0$, the lens shaped droplet will spontaneously spread at the air water interface [48].

An alternative mechanism is to describe the degree of oil emulsification in the foam lamellae as suggested by Schramm and Novosad [49]. Here, a lamellae number (L) describes the ratio of the capillary suction ($ħp_c$) in the plateau border to the opposing pressure drop across the interfacial area ($ħp_R$) and is illustrated in Fig. 2 and defined by Eq. (5)

$$L = \frac{ħp_c}{ħp_R} = \frac{r_o \gamma_{wg}}{r_p \gamma_{ow}} \tag{5}$$

where r_o and r_p are the radii of the oil droplet and the plateau border, respectively. If L < 1, the equation predicts that oil cannot be emulsified and foam is stable. Foam was observed to be moderately stable for $1 < L < 5.5$ and unstable at values > 5.5 [49].
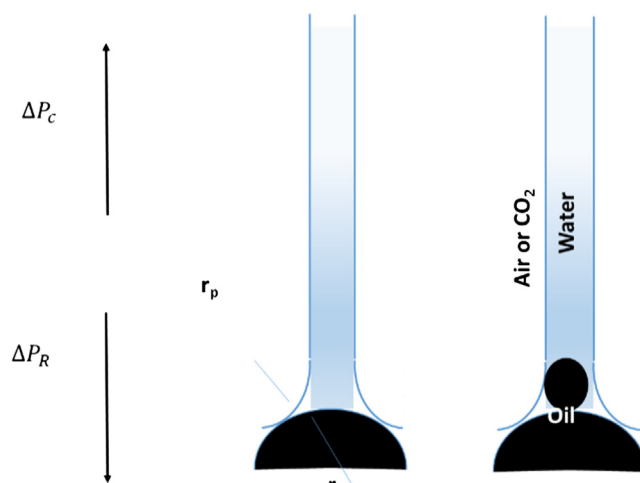
Table 1
Composition of the selected surfactant.

Surfactant	Composition and comments	HLB	Activity
$C_{12-14}N(EO)_2$		12.2	> 97%

(chemical structure: a long alkyl chain bonded to N with two CH_2CH_2OH groups, labeled OH and OH)

Table 2
Physical properties of dodecane at 3400 psia.

Purity	Density (g/ml)			Surface tension mN/m		
	24 °C	90 °C	120 °C	24 °C	90 °C	120 °C
99%	0.746	0.719	0.700	25.35	19	17

tension measurements was typically < 2% of the mean

3.4. C/W foam or O/W emulsion formation and apparent viscosity in porous media

A schematic for measurement of the foam apparent viscosity up to 120 °C ± 1 °C and 3400 psia ± 100 psia (23 MPa ± 0.69 MPa) psia is shown in Fig. 3. The experimental procedure for foam generation and apparent viscosity measurements were similar to our previous publication [23] except for the addition of a second HPLC pump (Scientific Systems, Inc. series III) to introduce oil into the porous medium. In this work, the porous medium was a crushed calcium carbonate packed bed (22.9 cm long, 0.62 cm inner diameter tube) with a permeability to deionized water of 76 Darcy (75 µm^2) (calculated from Darcy's law for 1-D horizontal flow) and 38% porosity (2.6 mL pore volume) determined by the mass of loaded material. The crushed calcium carbonate (Franklin Industrial Minerals) was 420–840 µm in diameter (20–40 mesh) after washing with copious amounts of water and ethanol. The non-spherical calcium carbonate particles were held in place by a 100 mesh wire screen at each end of the pack. The capillary tube for measuring bulk foam apparent viscosity was 660 µm ID, 1.5 m in length, and made of hastelloy tubing. The errors in apparent viscosity readings are ± 15%.

Experiments with remaining oil present were conducted by initially injecting the limestone pack with copious amount of DI water at atmospheric pressure and room temperature. The pack was then injected with dodecane at ambient conditions until no effluent water was detected. Finally, the pack was flushed with the aforementioned 22% TDS

synthetic brine until no effluent dodecane was detected. The amount of remaining dodecane was difficult to determine due to the small pore volume of the porous medium (2.6 mL) but is expected to be low as a result of the high permeability (76 Darcy).

4. Results and discussion

4.1. Effect of dodecane on the stability of A/W foams

The half-life and normalized volume of A/W foams generated by strong hand mixing of 1 wt% $C_{12-14}N(EO)_2$ surfactant solution in 22% TDS brine at pH6 and dodecane are shown in Fig. 4 and Table 3. The destabilization effect of dodecane on A/W foam was observed in a more rapid decrease of the normalized volume, as described by the decrease in the half-life. As the dodecane: surfactant solution ratio reached 0.15, the half-life decreased from > 90 min to 10 min. Similar defoaming behavior was observed by Lee et al. for A/W foams generated by SDS (sodium dodecyl sulfate) measured in the presence of dodecane [52]. The results were explained by the accumulation of oil droplets at the plateau border (PB) resulting in an increase in the PB radius and rupture of the pseudoemulsion film in the borders [52]. The dodecane–film interactions can be described in terms of the entering and spreading coefficients. According to the IFT results, the entering and spreading coefficients are all positive, as shown in Table 4. As a result, dodecane is expected to enter and spread in the lamellae of the foam resulting in destabilization. Schramm et al. argued that a precursor step for entering and spreading is pinching off of oil into very small droplets due to the capillary suction at the plateau border and can be quantified with lamellae numbers [49]. Table 4 showed the calculated Lamellae numbers to be greater than unity indicating that oil will be emulsified to droplets that are small enough to be sucked into the lamellae to further destabilize the foam.
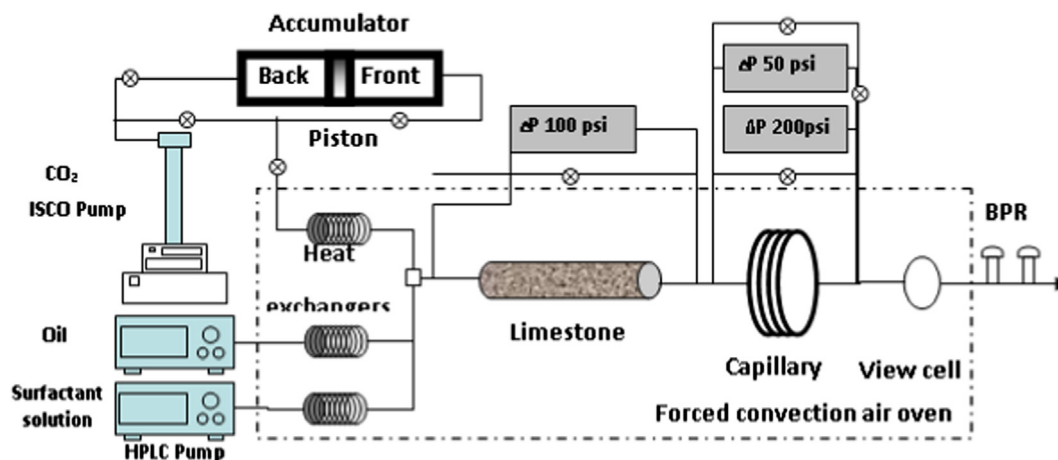

Fig. 3. Apparatus for CO$_2$-water foam viscosity measurement. BPR:back pressure regulator. The crushed limestone pack is used as the foam generator.
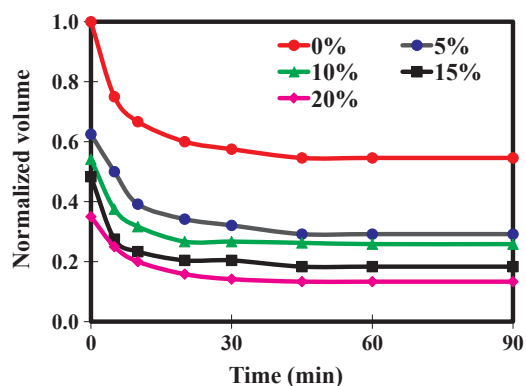
Fig. 4. Normalized volume of A/W foam generated by strong hand mixing (10 s) under different dodecane: surfactant solution ratios at 24 °C and atmospheric pressure. Surfactant solution is 1 wt% $C_{12-14}N(EO)_2$ in 22% TDS and pH6 (adjusted by HCl).

Table 3
Half life of the A/W foam upon strong hand mixing (10 s) under different dodecane: surfactant solution ratios at 24 °C and atmospheric pressure. Surfactant solution is 1 wt% $C_{12-14}N(EO)_2$ in 22% TDS and pH6 (adjusted by HCl).

Dodecane:surfactant solution ratio	0	0.05	0.1	0.15	0.2
Half life (min)	> 90	~30	~20	~10	~10

Table 4
Lamellae number, entering coefficient and spreading coefficient of A/W foam generated by 1 wt% $C_{12-14}N(EO)_2$ in 22% TDS and pH6 (adjusted by HCl) in the presence of dodecane at 1 atm and 24 °C.

O-W IFT (mN/m)	A-W IFT (mN/m)	A-O IFT (mN/m)	Lamella number (L)	Entering Coefficient (E) (mN/m)	Spreading Coefficient (S) (mN/m)
0.69	26.35	25.35	5.73	1.69	0.31

4.2. Effect of surfactant concentration on C/W foam in the presence of dodecane

The effect of surfactant concentration on the apparent viscosity of C/W foams stabilized by $C_{12-14}N(EO)_2$ at pH 6, 120 °C, 90% foam quality and 22%TDS brine was investigated in the absence and presence of remaining dodecane as shown in Fig. 5. In all cases, the apparent viscosity of the foam increased initially with the increase in surfactant concentration and then levelled off at concentration of 0.3 wt%. This concentration is 300 times the CMC of the surfactant in a CO_2–water system at 120 °C reported previously [53]. A similar plateau well above the CMC was observed by Lee et al. [54,55] Here, micelles act as a source for surfactant during creation of new lamellae propagating through porous media [9,54,55]. In the capillary tube, the foam apparent viscosity vs concentration profile was very similar in both cases as the remaining oil in the capillary tube is expected to be negligible due to the extremely high permeability. Notably, in the limestone pack, at surfactant concentrations lower than 0.2 wt%, weak foam with an apparent viscosity up to 7.3 cP was formed in the absence of dodecane, while foam was not generated in the presence of remaining dodecane. At higher surfactant concentration > 0.3 wt%, the results in the absence and presence of oil were similar. The difference between the results at low and high concentration can be explained by two interrelated factors, namely, lamellae stability and oil saturation. Below 0.2 wt%, the lamellae are less stable (low foam apparent viscosity in the absence of oil) and are more susceptible to defoaming by oil droplets. As a result of the low foam apparent viscosity, oil was not produced and the oil saturation remained high to further destabilize the foam. At
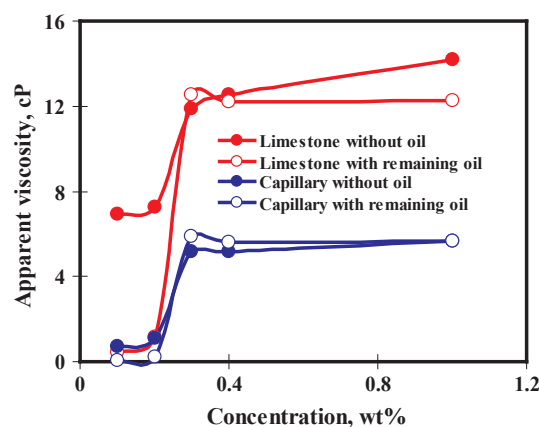

Fig. 5. Effect of concentration of $C_{12-14}N(EO)$ with 22%TDS, pH 6 (adjusted by HCl)) on apparent viscosity of C/W foams with remaining oil at total superficial velocity of 939 ft/day (0.331 cm/s), 120 °C (393 K) and 3400 psia (23 MPa) and 90% foam quality in a 63 Darcy crushed limestone pack. The uncertainty in temperature is ± 1 °C. The errors in apparent viscosity readings are ± 15%.

concentrations > 0.3 wt%, strong foam is generated that can successfully produce higher pressure drops, enhance oil displacement and lower oil saturation to nearly zero. Furthermore, at high surfactant concentrations, the foam film stability against oil increases by increasing the number of micellar layers in a single foam film to add a structural component to the disjoining pressure, which may slow drainage [56,57]. Nikolov et al. claimed that the increase of SDS surfactant concentration increased the foam film stability against oil by this mechanism [56,57]. Further studies in this paper will involve co-injection of oil with CO_2 and surfactant solution to exclude the effect of varying oil saturation during experiments.

4.3. Effect of oil fraction in the nonaqueous phase

The effect of oil (crude or dodecane) fraction in the nonaqueous phase on foam apparent viscosity of C/W foams stabilized with 1 wt% $C_{12-14}N(EO)_2$, at constant aqueous surfactant solution fractional flow of 0.1 by volume is shown in Fig. 6, where the conditions are the same as in Fig. 5. As the oil fraction increased from 0 to 0.8, the apparent viscosity of the emulsions decreased gradually from 14 cP to 5 cP, respectively. Ultimately, when the nonaqueous phase was composed of
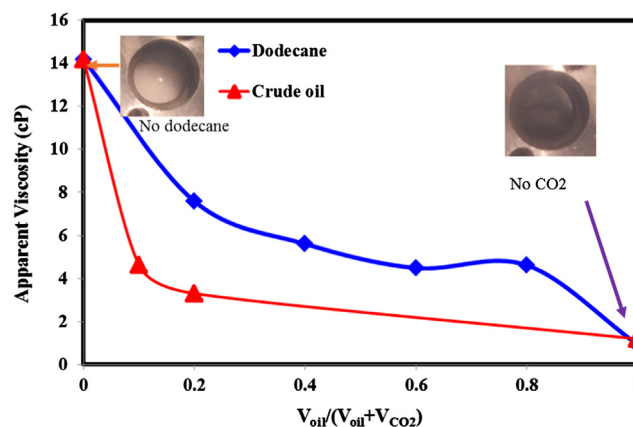

Fig. 6. Effect of $V_{oil}/(V_{oil} + V_{CO2})$ on apparent viscosity of C/W foams stabilized with 1 wt% $C_{12-14}N(EO)_2$, 22%TDS brine pH 6 (adjusted by HCl) solution with constant surfactant solution fractional flow of 0.1. Total superficial velocity is 939 ft/day in a 63 Darcy crushed limestone pack, 120 °C and 3400 psia. The inset is pictures from the view cell in the cases of absences of dodecane and absence of CO_2. The uncertainty in temperature is ± 1 °C. The errors in apparent viscosity readings are ± 15%.

pure dodecane (absence of CO_2), the apparent viscosity of the oil-water mixture was only ~0.5 cP similar to that of pure dodecane and pure water at the same conditions. The results were consistent with visual observation in a view cell where white C/W foams were generated in the absence of dodecane and unstable O/W emulsions were present in the absence of CO_2 (two separate phases) as shown in the insets in Fig. 6. For pure CO_2 in the nonaqueous phase, the interaction potential between the surfactant tail and CO_2 is weak (A_{TC}) given the low polarizability/volume of CO_2 [58]. As a result, the HCB is far enough from the balanced point that stable C/W foams are generated. In contrast, the foam may be expected to be unstable at the balanced point given the small bending energy of the interface and high tendency for coalescence [59–61].

At the experimental conditions of 3400 psia and 120 °C, dodecane is single contact miscible with CO_2 and forms a single phase. In this case, parameters based on three phase surface energy balance, including the entering and spreading coefficients are not applicable in explaining the antifoaming effect of oil. Alternatively, the effect of addition of dodecane to the nonaqueous phase on foam apparent viscosity can be understood in terms of the intermolecular interactions between the nonaqueous phase and the surfactant tail [20]. As the dodecane concentration increases, the intermolecular interactions between the tail and the nonaqueous phase gradually increase and reach a maximum in the absence of CO_2. For $C_{12-14}N(EO)_2$ and pure dodecane, the tail interactions are extremely strong due to the similar size of the surfactant hydrophobe and the oil molecule. According to regular solution theory, the enthalpy of mixing of the surfactant tail and oil is at minimum when the ACN (alkane carbon number) of the oil to the length of the surfactant hydrophobe is close to 1 [62]. As a result of the increase in the nonaqueous phase - tail interactions (A_{Tc}) as the dodecane concentration is increased, the HCB decreased from a value where foam can be generated in the absence of dodecane and shifted towards the balanced point where emulsions/foams are unstable. This reduction in HCB towards the balanced point is further supported by the low IFT for the surfactant at the dodecane-water interface (0.5 mN/m) which is an order of magnitude lower that of pure CO_2–water at the same conditions (Table 5). A similar rationale was adopted by McFann and Johnston to explain the change of phase behavior and type of emulsion of a nonionic surfactant from with the increase in ACN [62]. It was argued that with the increase in ACN above hexane, the oil–tail interactions decreased from its optimum and changes the phase behavior.

In contrast, the addition of crude oil destabilized the foam more profoundly than dodecane, as the apparent viscosity of the foam decreased to 3 cP when the fractional flow of oil was only 0.18 (Fig. 6). Under multiple contact, crude oil is partially miscible with CO_2 which indicate that three phases are present and the destabilization may be examined in terms of entering, spreading and lamellae numbers as shown in Table 5. First, lamellae numbers calculated from interfacial tension measurements between CO_2 – water and crude oil – water are greater than unity (Table 5) indicating that the capillary pressure at the

plateau border is sufficient to pinch off very small oil droplets that can enter the lamellae [49]. Also, the positive entering coefficient suggests spontaneous replacement of a CO_2 – water and oil – water interfaces by an oil water interface (Table 5). Once the droplets enter the pseudoemulsion film, the oil droplet with low $\gamma_o g$ spreads over the lamellae causing it to rupture. Similar results were observed previously by Kuhlman [31] and Wellington et al. [34] where CO_2 foams were more stable at miscible conditions and less stable at immiscible conditions. The same hypothesis can be used to explain these results where at miscible conditions, only changes in the HCB can occur which is insufficient to greatly destabilize the foam. Whereas at immiscible conditions, further destabilization occurs as oil enters and spreads at the CO_2–water interface.

Another possible destabilization mechanism for C/W foams generated by $C_{12-14}N(EO)_2$ in the presence of oil is an accelerated Ostwald ripening where smaller CO_2 bubbles are transferred to bigger ones by the difference in Laplace pressure. The rate of Ostwald ripening is determined by the product of the solubility of the discontinuous phase in the aqueous phase and the diffusion coefficient. Therefore, the presence of oil in micelles increases the solubility of CO_2 in the micelles and causes faster transport of CO_2. Binks et al. showed that the rate of Ostwald ripening of decane is controlled by the solubility of oil in the micellar solution (micelles acting as carriers of decane) rather than simply molecular transport of decane [63].

The effect of temperature for various oil (dodecane) fractional flows is depicted in Fig. 7. The effect of oil fractional flow at each temperature is explained by the above mechanisms. At constant oil fractional flow, an increase in temperature resulted in a noticeable decrease in the foam apparent viscosity. For example, at ~0.05 fractional flow of dodecane, the foam apparent viscosity decreased from 22 cP to 10 cP when the temperature increased from 50 °C to 120 °C. Destabilization effects of increasing temperatures on foams can be explained by the reduction of the viscosity of the continuous aqueous phase, which leads to faster lamellae drainage rates and a decrease in the foam apparent viscosity [37–39]. Furthermore, increasing temperature decreases the density of CO_2 thereby diminishing the solvent strength of CO_2 for the tails of the surfactants. Finally, increasing temperature increases thermal fluctuations and the probability of hole formation given by exp ($-W_h/kT$) [42,43], and W_h is the activation energy.

In EOR applications, the results for C/W foams and O/W emulsions are of great importance for CO_2 mobility control. The surfactant was selective in generating viscous C/W foam at low oil fractions that would be relevant for the case of a small amount of residual oil in the reservoir. In this highly swept part of the reservoir, the foam affords

Table 5
Lamellae number, entering coefficient and spreading coefficient of C/W foam generated by 1 wt% $C_{12-14}N(EO)_2$ in 22% TDS and pH6 (adjusted by HCl) in the presence of crude oil at 3400 psia.

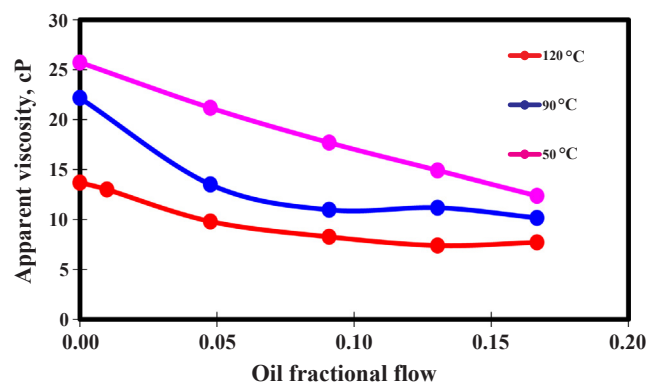|	T (°C)	O-W IFT (mN/m)	C-W IFT (mN/m)	Lamellae number	Entering Coefficient (mN/m)	Spreading Coefficient (mN/m)
Dodecane	24	0.46	3.14	Undefined		
	90	0.36	3.90			
	120	0.42	4.92			
Crude Oil	24	0.65	3.14	0.72	3.79	2.49
	90	0.48	3.90	1.22	4.38	3.42
	120	0.48	4.92	1.53	5.40	4.44

Fig. 7. Oil fractional flow (V_{oil}/V_{total}) on apparent viscosity of C/W foams stabilized with 1 wt%, 22%TDS, $C_{12-14}N(EO)_2$, pH 6 (adjusted by HCl) brine solution under different temperatures, superficial velocity of surfactant solution + CO_2 is 939 ft/day, $V_{CO2}/(V_{CO2} + V_{aq})$ is 0.9 in a 63 Darcy crushed limestone pack at 3400psia. Here, dodecane is used as a model oil. The uncertainty in temperature is ± 1 °C. The errors in apparent viscosity readings are ± 15%.
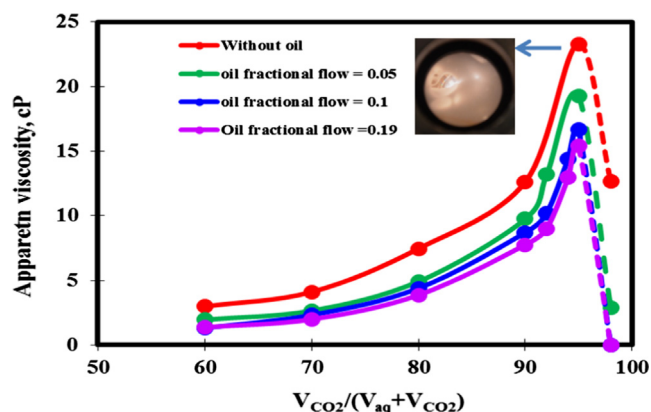
Fig. 8. Effect of $V_{CO_2}/(V_{aq} + V_{CO_2})$ on apparent viscosity of C/W foams stabilized with 1 wt% $C_{12-14}N(EO)_2$, 22%TDS brine pH 6 (adjusted by HCl) solution as a function of oil fractional flow (V_{oil}/V_{total}). The Superficial velocity of CO_2 + surfactant solution is 939 ft/day in a 63 Darcy crushed limestone pack, 120 °C and 3400 psia. Here, dodecane is used as a model oil. The uncertainty in temperature is ± 1 °C. The errors in apparent viscosity readings are ± 15%.

Fig. 9. Apparent viscosity of C/W foams and O/W emulsions (without CO_2) at 3400 pisa and 120 °C in a 63 Darcy limestone pack and capillary tube with 1 wt %, 22%TDS, $C_{12-14}N(EO)_2$, pH 6 (adjusted by HCl) brine solution with different $V_{oil}/(V_{oil} + V_{aq})$ at total superficial velocity 939 ft/day. In C/W foam experiments, CO_2 fractional flow (V_{CO_2}/V_{total}) was held constant at 0.9. Here, dodecane was used as a model oil. The uncertainty in temperature is ± 1 °C. The errors in apparent viscosity readings are ± 15%.

desired mobility reduction. On the other hand, the foam broke in the presence of large fractions of oil that resembles the displacement front. Here the absence of foam is desirable for enhanced mixing of CO_2 and oil to produce oil.

4.4. Effect of foam quality

The effect of foam quality (fractional flow of CO_2 in the non-dodecane phase $V_{CO_2}/(V_{CO_2} + V_{aq.})$ on foam apparent viscosity in the limestone pack for various dodecane fractional flows is shown in Fig. 8. In the absence of oil, increasing the foam quality from 0.6 to 0.9 resulted in an increase in apparent viscosity from ~ 4 cP to ~ 14 cP. Assuming a constant bubble size, increasing the foam quality increases the lamella density (number of lamellae per unit length) adding more resistance to flow and increasing the viscosity of the foam [11]. Further increase of foam quality to 0.95 caused fluctuations in the pressure drop across the limestone back and visual appearance of coarse foam in the view cell as depicted in the inset in Fig. 8. At 0.95 foam quality, the capillary pressure reached the "limiting capillary pressure" [26] above which the disjoining pressure was insufficient to stabilize the lamellae [64,65] causing coalescence of bubbles and a decrease in the capillary pressure [26]. Upon displacement of the coarse foam, the capillary pressure increases again above the limiting capillary pressure causing lamellae rupture and coalesce. Therefore, the fluctuations in the pressure drop across the limestone pack are caused by continuous cycles of foam formation and coalescence about the limiting capillary pressure [26]. With the addition of dodecane, the foam apparent viscosity as a function of foam quality showed a similar trend but with a slight decrease in foam apparent viscosity. The drop in viscosity can be attributed to an increase in interactions between the nonaqueous phase and the surfactant tail as described above, that drives the system towards the balanced state. Another explanation is that the addition of dodecane increased the total flow rate which can result in a decrease in the apparent viscosity according to the shear thinning model developed by Hirasaki and Lawson [11]. Interestingly, the optimum foam quality (0.9) was constant with the addition of dodecane fractions up to ~0.2. This result is the opposite of the finding by Rong, where the presence of oil shifted the optimum foam quality from 0.97 to ~ 0.8 [66]. This difference in behavior can be explained by the difference in the nature of the non-continuous phases. In Rong's work, air was used as the non-continuous phase and oil (decane) would enter and spread at the interface to thin the lamellae and lower the disjoining pressure. Thus, the limiting capillary pressure (and the optimum foam quality) was lowered. In the present case with CO_2 as the non-continuous phase, which
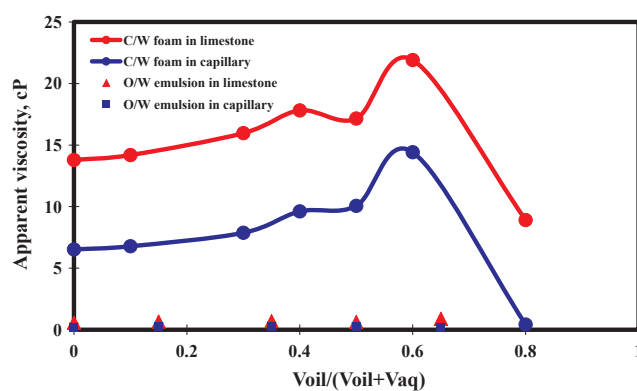
was miscible with dodecane, there was no oil phase to spread at the C-W interface. Therefore, the optimum foam quality did not change with oil.

The effect of increasing the dodecane fraction in the liquid non-CO_2 phase, $V_{oil}/(V_{oil} + V_{aq})$, on foam apparent viscosity or O/W emulsion viscosity (absence of CO_2) at 120 °C and 3400 psia is shown in Fig. 9. In these experiments, the total superficial velocity was held constant at 939 ft/day (0.331 cm/s). Experiments in the presence of CO_2 were conducted at constant CO_2 fractional flow of 0.9 (845 ft/day). Counterintuitively, the increase in oil fraction in the liquid phase to 0.65 caused a gradual increase in the apparent viscosity of the foam despite the antifoaming effect of dodecane. Increasing the dodecane to aqueous phase ratio causes a slight increase in foam quality $V_{CO_2}/(V_{CO_2} + V_{aq.})$ from 0.9 in the absence of dodecane to ~ 0.96 which increases the foam apparent viscosity as explained above. Beyond this point, the sudden decrease in the foam apparent viscosity can be attributed to either the insufficient surfactant concentration in the total fluid to stabilize lamellae (very low V_{aq}) or the increase in the capillary pressure above the limiting capillary pressure. In Fig. 9, it is noticeable that the viscosities of O/W emulsions (0.5–1.0 cP) generated in the absence of CO_2 are an order of magnitude lower than those of the C/W foam at oil fractions up to 0.6. The instability of the O/W emulsions can be attributed to HLB values close to the balanced point as explained above. This behavior confirms that the apparent viscosity observed in the presence of CO_2 is due to the presence of C/W foams and not O/W emulsions. To further explain the results of the instability of O/W emulsions in the limestone pack, periodic images of emulsions generated by hand mixing equal volumes 1 wt% $C_{12-14}N(EO)_2$ and dodecane were taken and observed (Fig. 10) at room temperature. The results show that the emulsions separate into two clear phases within 30 min indicating highly unstable emulsions.

5. Conclusions

As shown previously [23], $C_{12-14}N(EO)_2$ stabilized viscous CO_2/water foams at 120 °C and 3400 psia. The effects of a first contact miscible hydrocarbon (dodecane) and multiple contact miscible crude oil on CO_2 foam apparent viscosity were contrasted upon increasing the hydrocarbon volumetric fractional flow (decreasing CO_2 fractional flow) at a constant aqueous surfactant solution volumetric fractional flow and total flow rate. When dodecane volume fraction in the nonaqueous phase was increased from 0 to 0.8, the apparent viscosity of the foam gradually decreased from 14 cP to 5 cP. Since dodecane and CO_2 are first contact miscible at the experimental conditions entering and
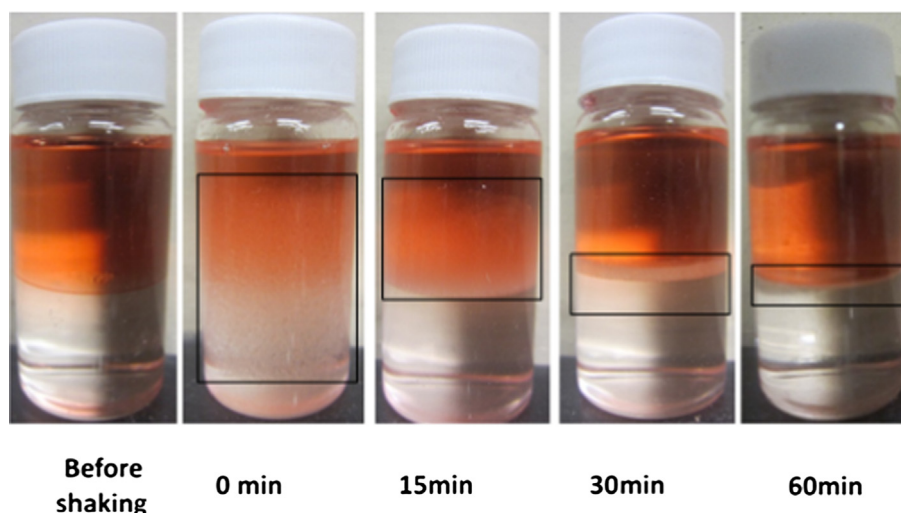
Fig. 10. Images of emulsions generated by hand mixing equal volumes of 1 wt%, 22%TDS, $C_{12-14}N(EO)_2$, pH 6 (adjusted by HCl) and dodecane (dyed red) at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spreading coefficients are not applicable for explaining the weakening of the foam. Therefore, a new mechanism was proposed where the foam lamellae are destabilized as the surfactant tail interactions with the CO_2 - dodecane solution increase, as this shifts the HCB close to the balanced state. Furthermore, oil droplets and oil dissolved in micelles within the lamellae will dissolve CO_2 and may enhance the destabilization by Ostwald ripening.

Relative to dodecane, for the case of crude oil – which is multiple contact miscible with CO_2, the foam apparent viscosity decreased more rapidly and reached 3 cP when the fraction of oil in the nonaqueous phase was only 0.1. The rapid destabilization of foam suggests the presence of additional foam destabilization mechanisms such as entering and spreading of the immiscible portions of the crude oil into the CO_2–water interface as confirmed by positive entering and spreading coefficients. These coefficients were calculated from interfacial tension measurements between CO_2 – water and crude oil – water at high temperatures and pressures.

In the absence of CO_2, viscosities of the emulsions generated by $C_{12-14}N(EO)_2$ with either dodecane or crude oil are an order of magnitude lower than those of the C/W foams. The low apparent viscosity of the O/W emulsions, when compared to C/W foams, is attributed to the low stability of the emulsion system. Here, the oil–water interfacial tension (0.5 mN/m) was an order of magnitude less than that of the CO_2–water interfacial tension in the presence of surfactant, indicating that the O/W emulsion system may be approaching the three phase region (balanced state) where emulsions are unstable. Thus, the surfactant was preferentially selective towards formation of stable C/W foams and not oil water emulsions. This selectivity is beneficial in CO_2 EOR, whereby the C/W foams are stable in the presence of small amounts of oil as in the case of residual oil but break at the displacement front where the amount of oil is large.

The effects of other parameters such as concentration, temperature and CO_2 volume fractional flow were studied. In the presence of residual dodecane in the limestone pack and surfactant concentration below 0.2 wt%, no foam was generated. At such low surfactant concentrations, lamellae are less stable and more susceptible to oil destabilization effects. The lower stability of the lamellae may be attributed to fewer micellar layers, which results in a less effective structural disjoining pressure. Also, when temperature was increased, foam apparent viscosity decreased in the absence and presence of oil as the viscosity of the continuous phase decreased and the probability of thermal fluctuations in the curvature of the lamellae increased. Furthermore, it was found that the presence of dodecane up to fractional flow of 0.2 had little effect on the optimum CO_2 volume fraction

(quality) indicating that minimal change occurred in the limiting capillary pressure.

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