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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

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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]

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

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

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