Development of New Surfactants for CO$_2$ Foam Enhanced Oil Recovery

Guanwei* Ren and Quoc P. Nguyen**

*Total E&P R&T USA, guangwei.ren@total.com
**Department of Petroleum and Geosystems
Engineering, The University of Texas at Austin,
Austin, TX, USA,
quoc_p_nguyen@mail.utexas.edu

ABSTRACT

Sweep efficiency in CO$_2$ enhanced oil recovery processes are major problem owing to the unfavorable mobility of CO$_2$. One method of controlling CO$_2$ mobility is through the use of foam. CO$_2$ foam in the past has predominately utilized commercial surfactant formulations, but with mixed results. This work pertains to the development of a new class of surfactants that can be injected with CO$_2$ rather than in water to improve foam performance, surfactant efficiency, and reduce water use. The paper describes the methodology used for designing the surfactants and screening the foaming properties. Surfactant solubility and partitioning between supercritical CO$_2$ (scCO2) and an aqueous phase (brine) were measured as a function of electrolyte concentration and pressure. Foam core flood was conducted to determine foam and surfactant transport. In general, the surfactant solubility in scCO$_2$ increased with pressure. The partitioning of surfactants into scCO$_2$ from brine was almost proportional to pressure, and decreased as temperature increased, where the latter held more sensitivity. Surfactant partition strongly influenced CO$_2$ displacement of brine in sanstone cores. In-situ foam generation during the injection of CO$_2$ with dissolved surfactant was remarkable.

Keywords: Supercritical CO2 foam, CO2 soluble surfactants, oil recovery, mobility control.

1 INTRODUCTION

CO$_2$ flooding is one of the most important methods for enhancing oil recovery (EOR). Miscible CO$_2$ EOR could recover as high as 20% original oil in place (OOIP) depending on the geological specifics [1.]. Within the United States alone, this EOR method produces 260,000 barrels of oil a day (of 280,000 bbl/d worldwide), representing 5.6 percent of U.S. production. The number of CO$_2$ injection projects, particularly for carbonate reservoirs, has continuously increased with the importance of CO$_2$ capture and storage. However, an unfavorable mobility ratio, reservoir heterogeneity and gravity segregation can reduce the macroscopic sweep efficiency. In-situ foaming of CO$_2$ is the method that has the most potential for improving sweep efficiency based on controlling CO$_2$ mobility. A dispersion of CO$_2$ into a surfactant solution has an apparent viscosity several orders of magnitude greater than the viscosity of either phase in the dispersion. In addition, substantial gas trapping in foam can further reduce gas relative permeability as a unique rheological characteristic of dispersed flow in porous media [2,3,4].

Several potential injection strategies for robust foam process have been studied [5,6,7]. Water-alternating-CO$_2$ injection has been most commonly used in field-scale foam process application [8,9], while simultaneous injection of these two phases has been the main injection scheme for lab-scale foam study. This is because the implementation of the latter strategy has encountered some difficulties such as operational constraints and severe reduction of well injectivity. While conventional foaming surfactants only traverse the reservoir in the aqueous phase, we have conducted an extensive experimental and theoretical study of a novel foam process in which the surfactant can partition between the CO$_2$ and the aqueous phases [10]. This novel foaming concept exhibits several advantages over conventional foam, of which lower surfactant adsorption, more in-depth robust foam, and higher injectivity are the most important. In addition, it enables the possibility of continuous injection of CO$_2$ with dissolved surfactant to generate foam in-situ when the injected CO$_2$ mixes with formation brine.

To increase the solubility of surfactant in scCO2, it was necessary to include fluorinated or silicone based hydrophobes to lower the intermolecular interactions of the surfactants. Although these early CO$_2$ soluble surfactants were used successfully in supercritical fluid research, some inevitable drawbacks have impeded their use in commercial applications. Expensive fluorous and silicone-based surfactants have environmental and biological persistence issues [11]. Therefore, efforts have been made to obtain low toxicity and less expensive CO$_2$-soluble hydrocarbon based surfactants, including hydrocarbon polymers [12,13], oxygenated hydrocarbon ionic surfactants [14], and nonionic surfactants [15-18]. Non-fluorinated surfactants is of the most interest.

Previous research has relied almost exclusively on phase behavior, utilizing a stirred high-pressure variable-volume stainless steel view cell [14-17, 19-21], as the standard technique for measuring surfactant solubility. Pressure and temperature induced changes in the turbidity of the solution are noted by visual inspection at each temperature; the phase transition or cloud point pressure is determined by reducing the pressure from a single-phase region until the sample becomes cloudy, i.e., phase separation occurs. This method also does not give any details on the concentration of the solute, thus the conclusions that can be drawn are limited in scope. This article describes an alternative novel method in which the

soluble material was directly sampled and characterized to obatin a much more informative data set. This is an important consideration given that many commercial surfactants contain solvents and impurities. To evaluate the effect of surfactant partitioning between CO_2 and brine on the performance of foam process CO_2 foam core flood experiments were conducted on Berea sandstone with the conventional anionic foaming surfactant (CD 1045) and new non-ionic CO_2 soluble surfactant.

2 MATERIALS AND METHODS

The nonionic surfactant (2EH-PO5-EO9) was gift from The Dow Chemical Company and was used as received. The surfactant contained the same base alcohol 2-ethyl-1-hexanol with a linker of 5 PO and 9 EO units, respectively. Sodium chloride (certified ACS, Fisher) was used as received. Brine was made from deionized (DI) water with 3wt% or desired concentration NaCl. Surfactant was used at 0.2 wt%.. Liquid CO_2 was 99.5% purity, industrial grade.

Solubility test. All 2EH-PO5-EO9 solubilities in CO_2 were measured from 1500 psi to 3500 psi and temperature at 35 ^{o}C. No water was added. For surfactant concentration analysis, surfactant disolved in each CO_2 sample was trasnfered into a fixed volume of DI water. The surfactant concentration in the DI water was measured directly by HPLC (high-performance liquid chromatography) with an evaporative light scattering detector. The HPLC allows for more accurate determination of the concentration of surfactant and can also give useful information about the distribution of molecules and the partitioning between the phases.

Partitioning test. The method for determining 2EH-PO5-EO9 partition coefficients is quite similar to that used for the surfactant solubility test above. The sampling system and procedure, however, were modified to accommodate the presence of the aqueous phase. In a typical experiment, a high pressure cylinder was charged with CO_2. Surfactant solution was then injected into the cylinder. The system was well equilibrated for 24 hours before recording the equilibrium fluid pressure. Surfactant samples were taken from the water phase for concentration analysis. The brine salinity was fixed at 3 wt% in the studies of pressure effect. The surfactant partition coefficient is calculated using Eq. (1)

$$k = \frac{m_{sCO2} / (m_{sCO2} + m_{fCO2})}{m_{sw} / (m_{sw} + m_w)} \qquad (1)$$

where m_{sCO2} is the mass of surfactant in the free CO_2, which is the difference between the initial mass of surfactant injected in brine into the cell and the remaining mass of surfactant in the brine at equilibrium (m_{sw}); m_{fCO2} is the mass of free CO_2 determined based on the initial mass of CO_2 charged into the cell and the solubility of CO_2 in the brine at equilibrium pressure and temperature; m_w is the initial mass of water

injected into the cell. Note that the solubility of water in CO_2 was neglected.

Core flood test. A Phoenix Hassler-type core holder was mounted in the vertical direction and fluids were injected from the top to the bottom. Two backpressure regulators were used in a series to maintain a constant backpressure of 1500 psig during coreflooding. The core was cleaned and dried in a convection oven at 110 °C for 48 hours. It was then wrapped in three layers of aluminum foil and a thin Teflon heat shrink tube. The wrapped core was placed in the core holder and vacuumed for 10 hours before saturating the core with brine (3 wt% NaCl) in order to measure its porosity. The permeability of the brine saturated core was determined based on Darcy's law.

CO_2 and the surfactant solution were alternatingly injected into the core at 0.1 cc/min (1.4 ft/d) and 0.3 cc/min (4.2 ft/d), respectively. Surfactant solution and gas slug size were 0.1 pore volume (PV) and 0.2 PV respectively. Respective pressure drops over the three sections of the core were recorded. All core floods were conducted at 35 ^{o}C and 1500 psi backpressure.

3 RESULTS AND DISCUSSION

The solubility of 2EH-PO5-EO9 increases with increasing pressure (Figure 1) as has been seen with previous cloud point studies. The result suggests that the loss in solvation (CO_2-surfactant interactions) outweighs the benefit gained in decreased surfactant-surfactant interactions, which agrees with previous studies that have shown that the solute-solute interactions are the dominant factor in solubility in CO_2 [22]. This effect becomes more pronounced at higher temperatures and pressures, as the system reaches the limit of compressibility. The EO adds additional polar ether linkages that can increase the solvation by CO_2, however, this is offset by increased interactions between the surfactant molecules. The surfactant-surfactant interactions are not greatly affected by pressure, but are stronger at lower temperatures, whereas the CO_2-surfactant interactions increase with pressure. As a result, the solubility may not significantly decrease at higher pressures as more EO group is added since the CO_2 solvation can compete.

Figure 2 shows the partition coefficient of 2EH-PO5-EO9 as a function of pressure. The result shows that the surfactant was actively transported to the CO_2 phase. Although an increase in CO_2 density modestly raises the solubility of CO_2 in water, this effect has not been found to influence the solvation of the surfactant in the water phase [23].
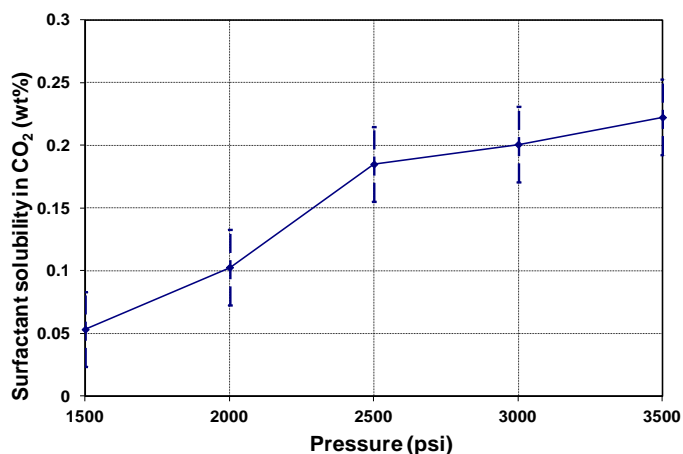
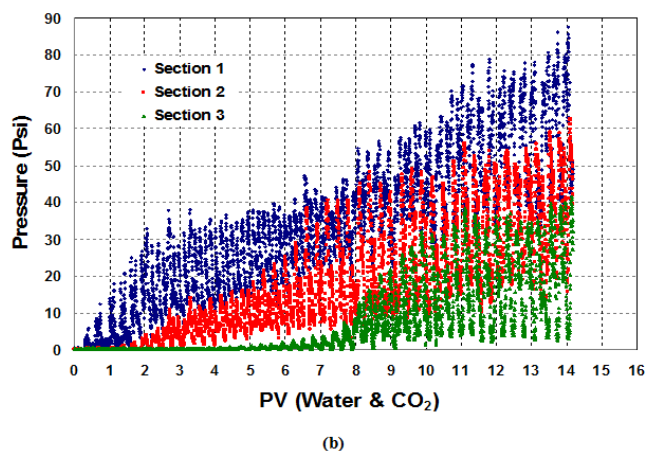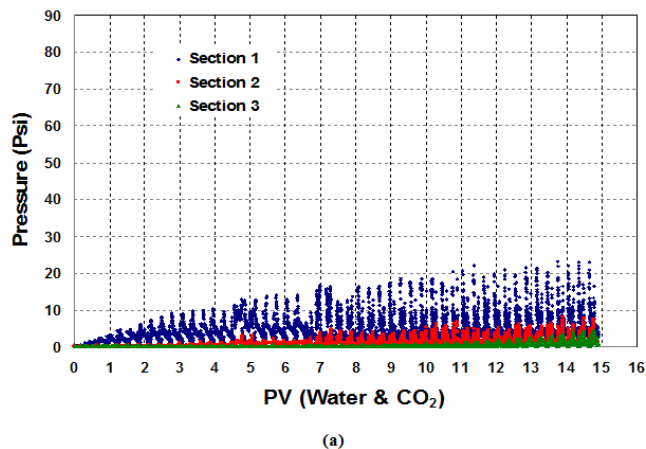Figure 1: Solubility of 2EH-PO5-EO9 in CO_2 as a function of pressure at 35°C.

Figure 2: Partition coefficient of 2EH-PO5-EO9 in a CO_2-bine system with 3wt% NaCl at 35°C.

(a)

(b)

Figure 3: Pressure drop during surfactant alternating gas injection for (a) anionic surfactant CD 1045, and (b) nonioninc surfactant 2EH-PO5-EO9.

Figure 3 shows the sectional pressure drops for 2EH-PO5-EO9 and the anioninc surfactant CD 1045. For both cases, the pressure drops build up during liquid injection and decrease in the chasing gas injection. They tend to fluctuate from cycle to cycle. The fluctuation in pressure drop magnitude becomes more obvious as foam propagates. For 2EH-PO5-EO9, it only took one injected pore volume (IPV) for foam to propagate into Section 2 and then 5 IPV to reach Section 3. On the contrary, a double amount of fluids are required for CD 1045 stabilized foam to yield a significant pressure drop response. It is important to note that CD 1045 and 2EH-PO5-EO9 exhibit almost the same level of adsorption in sandstone. Therefore, the higher foam robustness with 2EH-PO5-EO9 is attributed to the better surfactant transport during gas injection cycle owing to the partitioning of surfactant between CO_2 and water. The magnitude of pressure drop (or CO_2 mobility reduction) for 2EH-PO5-EO9 stabilized foam is 5 to 10 times higher than that for CD 1045.

4 CONCLUSIONS

The solubility of 2EH-PO5-EO9 in CO_2 at 35°C increases up to 0.2 wt% as pressure increases above 2000 psi. The partitioning of the surfactants between CO_2 and water phases increased almost linearly with pressure. The partition coefficient was very sensitive to surfactant impurity (i.e. distribution of EO and PO groups).

Several measurements of surfactant partition coefficient were conducted at 35 °C and 3500 psi with salinity changes up to 9wt% NaCl. The results show little or no effect of electrolyte concentration on the partition coefficient.

Surfactant partitioning strongly affects foam performance in sandstone cores. CO_2 soluble surfactant does improve foam propagation and injectivity. Alternating injection also strenthens the advanatges of CO_2 soluble surfactant stabilized foam with respect to quicker and stronger foam generation. This is attributed to the improved surfactant transport during alternating injection owing to

surfactant partitioning between CO_2 phase and aqueous phase.

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