

Transient Foaming Behavior of CO₂-soluble, Viscoelastic Surfactant in Microfluidic Model, Sand Pack and Limestone Core

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ABSTRACT

Aqueous foam has been demonstrated through laboratory and field experiments as an effective conformance control technique for gas enhanced oil recovery. The use of polymer in an aqueous foam is a common practice to increase the viscosity of the foam liquid phase. Such viscosification improves foam performance by increasing the apparent gas viscosity and reducing the rate of foam coalescence. This study explores the use of worm-like micelles (WLM) as an alternative viscosifying agent to polymer. We utilized a cationic, amine-based surfactant; whose micelles transform from spherical to worm-like conformation at elevated salinity. We found evidence that the presence of WLM could accelerate strong foam generation. The WLM structures also allowed for strong foam generation in a heterogeneous limestone core at high-temperature (120°C) and high-salinity (20 wt.% NaCl).

Keywords: Enhanced oil recovery, CO₂ soluble surfactant, viscoelasticity, foam, mobility control, high salinity, microfluidics.

1 INTRODUCTION

One of the challenges in gas enhanced oil recovery (EOR) is the mobility control of the low viscosity injected gas. The main mobility issues include gas fingering through reservoir liquids (i.e. water and oil) due to a vast contrast in viscosity, gravity override due to the low density of the gas, and gas channeling caused by reservoir heterogeneity. Aqueous foam has been proven to alleviate some of the mobility issues both in laboratory and field settings [1,2].

An aqueous foam is a dispersion of a gas in a continuous liquid phase. In porous media, foam is generated through the following three mechanisms [3]:

1. *Snap off*, where a long gas bubble breaks apart when the gas flows through pore constrictions.
2. *Lamellae-division*, where a gas bubble stretches and divides around a branch point in a flow path.
3. *Leave-behind*, where an aqueous lens is formed as two gas menisci invade adjacent liquid-filled pore bodies and converge downstream.

In porous media, the ability of a fluid to flow from one pore to another is dependent upon overcoming the capillary forces imposed by the pore constrictions. Foam generation is typically more robust in the higher permeability porous media due to the lower critical capillary forces for foam generation [3]. Foam improves gas mobility control by

increasing the apparent gas viscosity [4]. In addition, once generated, a foam may become immobile. This fraction of “trapped” foam could occupy up to 65% of total pore volume [5]. Trapped foam severely reduces the effective permeability of gas moving through a porous medium by reducing the number of conduits through which the foam can flow [3].

Foam stability requires the presence of surfactant to lower the interfacial tension (IFT) between its gaseous and liquid phases. Water soluble polymers have also been used with a foaming surfactant to enhance foam performance. The addition of polymer is known to increase the gas apparent viscosity by increasing the viscosity of the foam liquid phase. This increased viscosity also reduces the occurrence of foam bubble coalescence [6]. Despite these benefits, the addition of polymer includes several drawbacks: instability in high-temperature high-salinity environment, irreversible polymer shear degradation, and severe polymer retention by filtration in low permeability formations. In this study, we explored a novel CO₂ foam concept that could alleviate these issues.

N,N,N'-trimethyl-N'-tallow-1,3-diaminopropane (DTM) is an amine-based pH-switchable surfactant. DTM exhibits reversible interconversion between nonionic and cationic forms as illustrated in Figure 1.

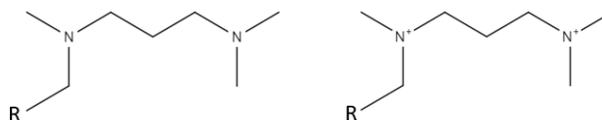


Figure 1 Chemical structure of DTM surfactant head in non-ionic form (left) and cationic form (right).

In its cationic form, DTM surfactants can maintain excellent aqueous solubility under high-temperature and high-salinity conditions as well as potentially having a low adsorption value in the positively charged carbonate reservoirs. A particular feature of cationic DTM is its ability to increase the viscosity of a brine solution at elevated salinity through the formation of worm-like micelles (WLM) [7]. The viscosity of 0.5 wt.% DTM solution at 40°C as a function of salinity is shown in Figure 2. Unlike water soluble polymers, shear-induced degradation of WLM is reversible. WLM filtration in porous media is minimal due to its lower molecular weight.

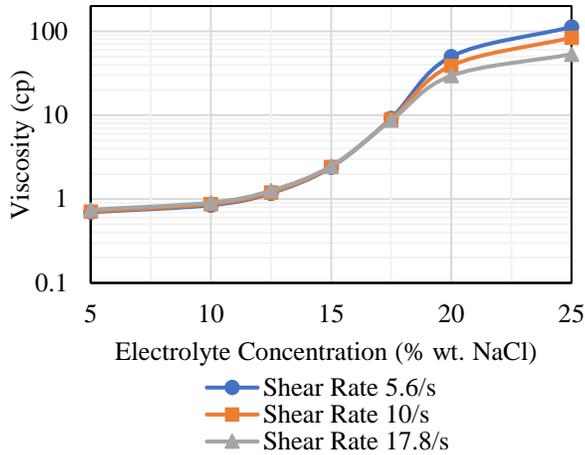


Figure 2 Viscosity of bulk DTM solutions.

The nonionic form of DTM exhibits high solubility in supercritical CO₂. In its application as a foaming agent in foam-assisted gas EOR, DTM could be injected in CO₂. This novel injection strategy could mitigate fluid injectivity loss caused by strong foam formation in the near-wellbore region and reduce surfactant adsorption.

In this study, we investigated the effect of high aqueous DTM solution viscosity and WLM presence on the transient foam behavior in different porous media. The rate of foam propagation was determined for two respective DTM solutions named DTM High (0.5 wt.% DTM, 20 wt.% NaCl) and DTM Low (0.5 wt.% DTM, 15 wt.% NaCl).

2 RESULTS AND DISCUSSION

2.1 Foam Behavior in a Microflow Model

CO₂ and DTM solution were simultaneously injected into a 2.75 Darcy porous permeable microflow model at room temperature. The aqueous phase was injected at a constant rate of 0.6 μL/min and CO₂ was injected at a constant 3 psi pressure difference between the inlet and the outlet of the model. The injection gas rate was measured and used to determine the apparent gas viscosity (μ_f) through the following equation.

$$\mu_f = \frac{k\Delta P A}{QL} \quad (1)$$

k : the porous medium permeability; A : porous medium cross-sectional area; Q : the total volumetric flow rate at a fixed average medium pressure of 60 psi; L : the porous medium length.

The apparent gas viscosity is presented in Figure 3. The microflow model was placed under a microscope and video-recorded throughout the injection period. Top-view images were taken at different points in time throughout the experiment and are presented in Figure 4.

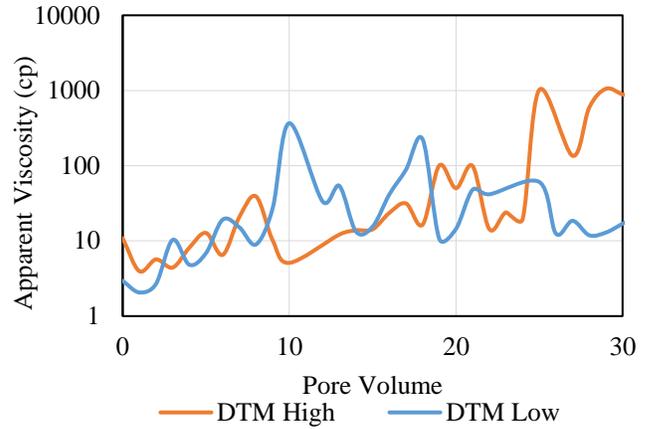


Figure 3 Transient foam viscosity for DTM High and DTM Low during gas-liquid co-injection in the microfluidic porous medium.

Through the first eight pore volumes injected (PV), 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 a sinusoidal plateauing behavior. Past 8 PV, DTM High continued its μ_f build-up. Over the extended duration of injection, DTM High foam eventually reached higher μ_f value than that of DTM Low foam.

Looking at Figure 4, DTM High foam did not develop as fast as DTM Low foam. At 1 PV, the gas saturation in DTM High is lower, indicating more severe viscous fingering. This outcome is to be expected due to the high viscosity of DTM High liquid phase (Figure 2). After 1 PV, strong foam development for DTM High continued to be slower than that in DTM Low. The strength of a foam in porous media is related to gas saturation and texture (number of lamellae per unit foam volume). DTM Low foam reached its finest texture and highest gas saturation at 10 PV. DTM High, on the other hand, required significantly more time before eventually reaching its finest texture and highest gas saturation at around 30 PV.

This visual result on foam generation indicate that foam generation events occur more frequently in the DTM Low case. A study on foam mobility in periodically converging-diverging channel suggests that a less viscous foam liquid phase may allow for easier passing of foam gas phase through pore constrictions [8]. Such action may lead to higher frequency of snap off induced bubble generation in the lower viscosity liquid phase of DTM Low foam.

At 30 PV, we observed greater μ_f for DTM High, despite the slightly lower gas saturation and coarser foam texture. This result suggests that DTM High foam possessed higher apparent viscosity per individual foam lamella due to its higher viscosity liquid phase.

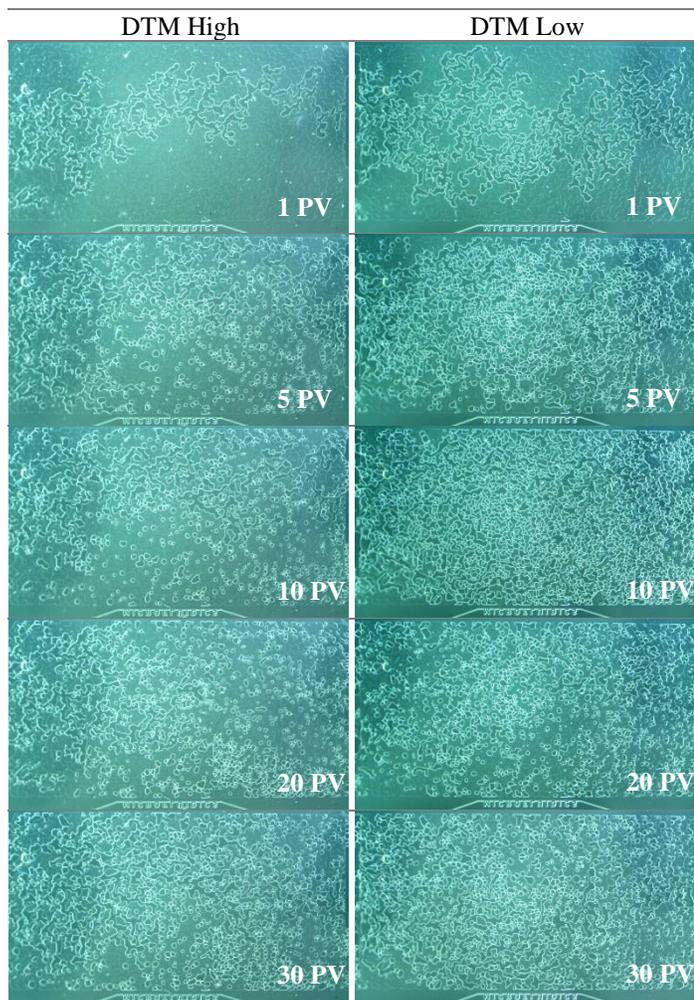


Figure 4 Microfluidic images of Foam Propagation

2.2 Foam behavior in Sand Pack

We sought to translate our findings on foam behavior in microfluidics to foam behavior in an ideal porous medium. We performed a simultaneous injection of CO₂ and brine solution at 10 PV/day into a 3.6 Darcy sand pack at 40°C. The injection foam quality (i.e. volumetric injection rate of CO₂ at 1700 psig over total volumetric injection rate) was 50%. In these experiments, we dissolved the DTM surfactant in CO₂ (0.5 wt.%) at 1700 psig and 40°C. Two respective foam floods were conducted with DTM Low and DTM High. The sand pack was divided into three sections. The sectional as well as the overall apparent viscosities are presented in Figure 5.

Strong foam generation in these experiments did not occur instantaneously. The onset of strong foam generation in DTM High and DTM Low cases began at 0.9 and 1.5 PV, respectively. The delay in strong foam generation may be attributed to the time required for the surfactant to partition from CO₂ into the brine phase. Once in the brine, the DTM monomers are protonated and convert into a cationic form through an acid-base reaction with carbonic acid.

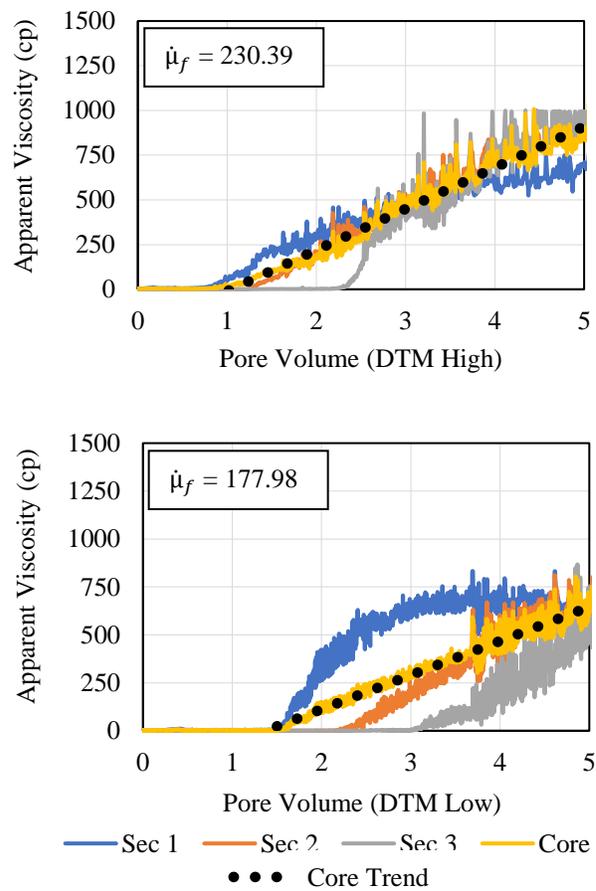


Figure 5 Transient foam viscosity for DTM High (top) and DTM Low (bottom) in sand pack.

The microflow experiment results indicate that foam generation events occur more frequently in the DTM Low foam due to its lower liquid phase viscosity. However, the results from foam sand-pack flood experiments show more robust foam generation for DTM High. It is important to note that the onset of strong foam propagation is not a unique function of foam generation rate. It is also determined by the ability of foam to resist the coalescence (foam stability). Newly created bubbles must be able to resist foam film thinning and rupturing as they move through constricted pores. Otherwise, the foam cannot accumulate fine texture. It can be hypothesized that in large scale foaming experiments (microfluidic pore volume is 2.3 μ L; sand pack pore volume 66.0 mL), foam stability becomes more important factor than foam generation. Therefore, it would be reasonable that the more stable DTM High foam would propagate faster.

We also quantified the rate of foam viscosity build-up ($\dot{\mu}_f$). This foam property was defined as the slope of the linear fit to the apparent viscosity from the onset of strong foam generation to the point of strong foam breakthrough. We observed a 30% increase in $\dot{\mu}_f$ in DTM High case compared to DTM Low. The higher $\dot{\mu}_f$ can be attributed to

higher foam viscosity, a larger portion of foam trapping, and better foam stability as foam propagates through the sand pack.

2.3 Foam behavior in Limestone Core

The final part of this work was to investigate DTM foaming in a natural porous medium. We performed a simultaneous injection of CO₂ and DTM solution into a 70 md Indiana Limestone at 120°C, 50% injection foam quality, and 1 PV/day. Since DTM solubility in CO₂ decreases as temperature increases at 1700 psig, we injected the DTM surfactant in the aqueous phase for both DTM High and DTM Low. The sectional as well as the overall apparent gas viscosities are presented in Figure 6.

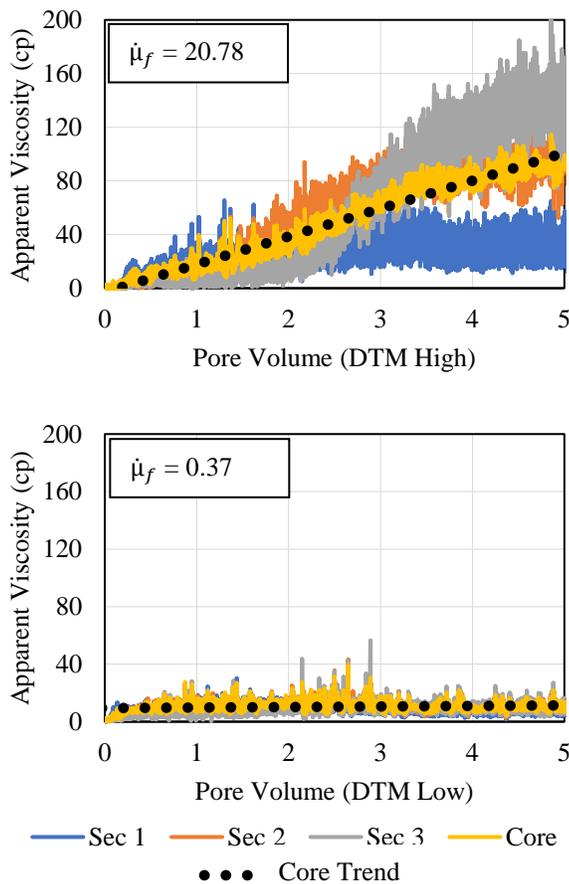


Figure 6 Transient foam viscosity for DTM High (top) and DTM Low (bottom) in limestone

In the DTM High case, strong foam generation began immediately and continued at a buildup rate of 20.78 cp/PV. A strong foam was not observed in the DTM Low case. We suspect that the lack of foam generation for DTM Low is due to the ultra-low viscosity of the aqueous phase at 120°C leading to a very unstable foam. In addition, the heterogeneity of limestone core required a sufficiently high foam viscosity to impede gas flow in the highest permeability channels. The

high viscosity liquid phase of DTM High foam enabled for a stable foam with a high enough apparent viscosity to divert gas from the high permeability channels and trigger foam generation in other gas unprocessed regions of the limestone core.

3 CONCLUSION

In this study, we investigated the effect of WLM and the associated increase of aqueous phase viscosity on the transient foam behavior in porous media by using DTM solutions at low and high salinities. Through microflow model experiments, it was found that foam generation may be impeded in the high salinity case (high viscosity environment), which could be pronounced for small pore networks. It was also found that higher DTM salinity resulted in greater individual lamella viscosity. For larger and macroscopically homogeneous pore networks such as the sand pack, the onset of strong foam propagation was dependent more on foam stability than foam generation rate. This was also observed through transient foam behavior in limestone core, where strong foam propagation was obtained at 120°C and 20 wt.% NaCl by increasing foam stability and apparent viscosity. This work is part of our development of a novel CO₂ foam process with CO₂ soluble and viscoelastic surfactants for improving sweep efficiency in CO₂ EOR in high temperature, high salinity carbonate reservoirs.

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