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Carbon Dioxide-in-Water Foams Stabilized with a Mixture of Nanoparticles and Surfactant for CO₂ Storage and Utilization Applications

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Abstract

Synergistic interactions between appropriately designed surface-modified nanoparticles and surfactants are shown to stabilize foams of CO₂ bubbles/droplets dispersed in water at elevated temperature and pressure typical of subsurface formations for enhanced oil recovery or geologic storage of CO₂. The foams are sufficiently viscous to mitigate or eliminate the instability associated with CO₂ displacement of fluids resident in the oil reservoir or brine aquifer. This technology therefore has the potential to increase the efficiency of oil recovery and the efficiency of pore space utilization for storage.

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1. Introduction

Viscous CO₂-in-water (C/W) foams[1, 2] are of interest for subsurface applications including CO₂ utilization for enhanced oil recovery (EOR) and geologic CO₂ storage (GCS). For EOR applications, foams provide mobility/conformance control during CO₂ flooding of hydrocarbon reservoirs. The low viscosity and density of CO₂ leads to poor volumetric sweep of reservoirs. The volumetric sweep efficiency can be improved by creating high viscosity foams, which reduce viscous fingering and channelling of CO₂ through high permeability regions of the

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reservoirs. The result is more efficient placement of CO₂ in the oil-bearing regions of a reservoir.

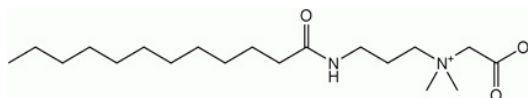
The same mechanisms apply to GCS, since CO₂ is about seven times less viscous than brine and two thirds as dense. Injected CO₂ will therefore displace the resident brine with poor sweep efficiency, leading to CO₂ plumes traveling farther than planned and complicating the design and monitoring of a strategy for secure containment. Increasing the viscosity of the CO₂ with minimal additives could significantly improve the robustness and cost-effectiveness of GCS. High quality (large gas volume fraction) foams are an attractive candidate for this purpose, especially if brine from the storage formation can be used as the continuous phase.

Traditionally, foams are stabilized with surfactants, but recent work suggests that adding nanoparticles to the surfactant solutions can synergistically improve foam viscosity and stability.[3, 4] The design of surfactants for CO₂ foams is based on the concept of hydrophilic/CO₂-philic balance (HCB),[5] which is very similar to the concept of hydrophilic/lipophilic balance (HLB) used to describe surfactant behavior in oil-water systems. The HCB was developed to describe the balance of surfactant and solvent interactions, which influences the interfacial properties of an amphiphile. Key properties which are affected by the surfactant's HCB include the preferred curvature of the CO₂-water interface and the efficiency of the surfactant for lowering the interfacial tension. Recently, the concept of HCB was extended to design nanoparticles for C/W foams.[6] A significant difference between nanoparticles and surfactants as foam stabilizers is the difference in adsorption energy at the fluid-fluid interface. Surfactants typically have an adsorption energy on the order of 1 kT, and thus can dynamically adsorb and desorb from the interface. However, properly designed nanoparticles can have adsorption energies of over 10⁶ kT, causing them to irreversibly adsorb to the interface. The irreversible adsorption can lead to increased stabilities of foams as the particles provide a physical barrier to bubble coalescence.

In this study, viscous CO₂-in-water foams were generated in a lab-scale apparatus with a mixture of silica nanoparticles and lauramidopropyl betaine zwitterionic surfactant without added salt. The synergy between the nanoparticles and the surfactant will be investigated with the goal of increasing the foam viscosity through the addition of nanoparticles. With nanoparticles and surfactant present, CO₂-in-water foams with viscosities of over 50 cP in a 22 darcy beadpack (over 20 cP in capillary tube) and over 100 cP in a 1.2 darcy beadpack (over 16 cP in capillary tube) were generated, compared with viscosities of less than 3 cP when surfactant was not present. The synergy raises the prospect of less expensive methods of conformance control for CO₂ floods and efficient use of aquifer volume for GCS, both in terms of materials costs and logistics.

2. Materials

Covalently modified colloidal silica nanoparticles (EOR-5XS, Lot No. LB130204, Nissan Chemical Co., USA) were received as a 20% aqueous dispersion. The surface modification was performed by the manufacturer and is proprietary. The nanoparticle dispersions received from the manufacturer also contained ~10% ethylene glycol, and thus a typical dispersion containing 1% EOR-5XS particles also contains ~0.5% ethylene glycol. Lauramidopropyl betaine (LAPB) was a gift from Rhodia (Mackam DAB-ULS, LOT: UP1J13X04). Per the information provided by the manufacturer, the solution was ~24% lauramidopropyl betaine, ~9.5% myristamidopropyl betaine, ~1% palmitamidopropyl betaine, <1% capramidopropyl betaine, and <0.5% NaCl. The NaCl is a byproduct of the betaine synthesis.[7] A concentration of 35% actives (referred to as "LAPB") was assumed for calculations in this study, based on the typical concentration per the manufacturer. The structure of lauramidopropyl betaine (LAPB) is given in Scheme 1.



Scheme 1. Structure of lauramidopropyl betaine (LAPB).

HCl (1N solution, Fisher Scientific, USA), NaOH (1N solution, Fisher Scientific, USA), and CO₂ (Coleman-grade, 99.99% purity, Matheson, USA) were used as received. Deionized (DI) water (Nanopure II, Barnstead, Dubuque, IA) was used for all experiments.

3. Methods

3.1. Determination of surfactant isoelectric point

Titration was used to determine the isoelectric point (pI) of the LAPB surfactant as described elsewhere.[3]

3.2. Preparation and characterization of aqueous dispersions.

Dispersions of nanoparticles and/or surfactants were prepared and characterized via dynamic light scattering (DLS) and phase analysis light scattering (PALS) to determine particle size and zeta potential, respectively, as described elsewhere.[3] The zeta potential is reported using the Smoluchowski model. All nanoparticle and surfactant concentrations are given as % w/v in the aqueous phase. The NaCl from the stock LAPB solution added a maximum of 0.0006 % NaCl (ca. 0.1 mM NaCl) to the nanoparticle dispersions for a surfactant concentration 0.04 %. The nanoparticle and surfactant mixtures were pH~9 before CO₂ was added.

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed to determine the organic content of the nanoparticles due to the surface modification, following a procedure described elsewhere.⁸ A sample of EOR-5XS particles without added ethylene glycol was obtained from Nissan Chemical Co. for TGA measurements.

3.4. Surface tension measurements

Axisymmetric drop shape analysis of a captive bubble was used to determine the air-water interfacial tension (surface tension, γ) of surfactant solutions with and without 1% EOR-5XS particles, following a procedure described previously.[8]

3.5. Determination of particle stability in CO₂-saturated aqueous phases

The stability of 1% EOR-5XS particle dispersions in DI water and 0.1% LAPB were observed in a variable-volume view cell apparatus modified from previous studies.[9-11] A diagram of the apparatus is shown in Figure 1. First, 10 mL of solution was loaded into the front of the cell. The cell was closed and ca. 5 g of CO₂ was added to the front of the cell. The pressure was controlled by connecting the ISCO pump to the back of the cell. The temperature was controlled with heating tape on the outside of the cell which was controlled by a thermocouple mounted inside the wall of the cell. The sample was stirred with a magnetic stir bar inside the cell and visual observations were made for up to 30 minutes to verify that the dispersions remained transparent, indicating colloidal stability.

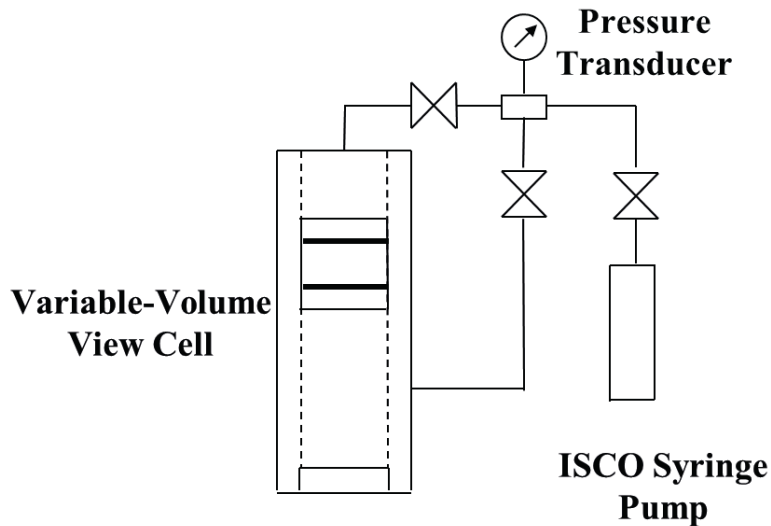


Fig. 1. Variable-volume view cell apparatus for visual observation of nanoparticle dispersions in a CO₂-saturated aqueous phase.

3.6. C/W foam formation and apparent viscosity measurement

The C/W foams were formed and characterized in an apparatus modified from previous studies.[3, 6] A diagram of the apparatus used to generate C/W foams is shown in Figure 2. Rather than using one backpressure regulator (BPR) as in our previous studies, two BPRs (Swagelok model SS-4R3A adjustable relief valve, heated to over 75 °C with a water bath) were connected in series for controlling system pressure (reported by the pressure at the upstream BPR) to prevent CO₂ liquid formation. All experiments were done at 2800 psia and 50°C. The system pressure was maintained within 50 psi for all experiments. The pressure gradient caused by the flow of foam through porous media was measured with differential pressure transducers, attached to the upstream and downstream sides of the beadpacks. The beadpacks had permeabilities of 22 D (0.38 cm ID x 11.3 cm long, filled with 180 μm spherical glass beads, porosity of 0.34, pore volume of 0.436 mL) and 1.2 Darcy (1.63 cm ID x 12.42 cm long, filled with 30-50 μm spherical glass beads, porosity of 0.36, pore volume of 9.4 mL). In the 22 D beadpack, a flow rate of 0.5 mL/min gives a superficial velocity of 208 ft/day, a shear rate of 400 s⁻¹, and a residence time of 52 s. In the 1.2 D beadpack, a flow rate of 4.5 mL/min gives a superficial velocity of 102 ft/day, a shear rate of 780 s⁻¹, and a residence time of 125 s. The beadpack superficial velocity used in this study might be found in field applications near an injection well where most foam generation is expected.[1] Per manufacturer's information, the accuracy of the differential pressure reading is ± 0.25% of full scale.

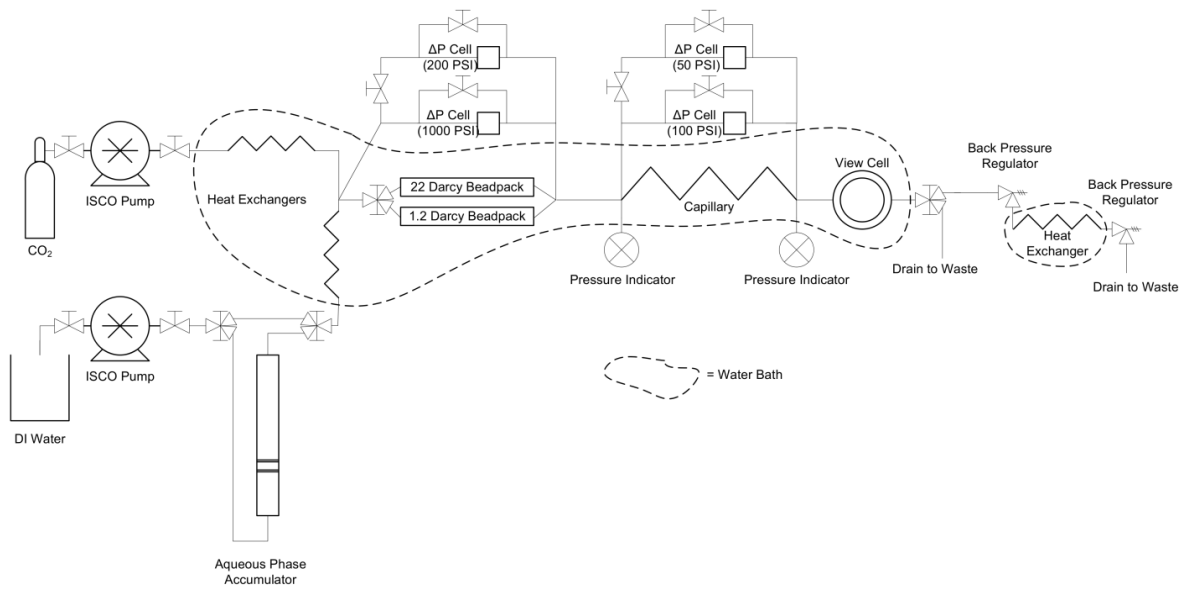


Fig. 2. Diagram of apparatus for C/W foam generation and pressure gradient measurement.

4. Results and discussion

4.1. Surfactant isoelectric point

The lauramidopropyl betaine (LAPB) surfactant was titrated with HCl to find the isoelectric point (pI) of pH \sim 6.4 in DI water, in good agreement with the value of pH \sim 6.1 determined for a similar carboxybetaine (caprylamidopropyl betaine).[3] For the experiments in this study where CO₂ and water are present, the pH will be well below this point and the surfactant will be primarily positively charged (the carboxylate group shown in Scheme 1 will be protonated).

4.2. Dynamic light scattering, thermogravimetric analysis, and zeta potential measurements

A summary of nanoparticle properties is given in Table 1. It is worth noting that the small size of the silica particles is similar to the PEG-coated silica particles investigated in previous studies,[6, 12] and is significantly smaller than the 28 nm diameter bare silica particles used with caprylamidopropyl betaine in a previous study.[3]

Table 1. NP properties.

Particle name	Hydrodynamic diameter by DLS in DI water (nm)	Coating	Organic fraction by TGA (% wt)
EOR-5XS	6.4	Proprietary	10

Zeta potential measurements were made in DI water or a solution of 0.04% LAPB and are reported in Figure 3. The zeta potential of the particles alone is significantly smaller in magnitude than is expected for bare colloidal silica (\sim 30 mV at pH \sim 10), suggesting partial coverage of the nanoparticle by a nonionic or cationic moiety. Interestingly, by adding the 0.04% LAPB, the zeta potential of the particles is negligibly affected, suggesting a very weak interaction between the LAPB and the nanoparticle, even at pH $<$ pI, where the surfactant is primarily positively charged.

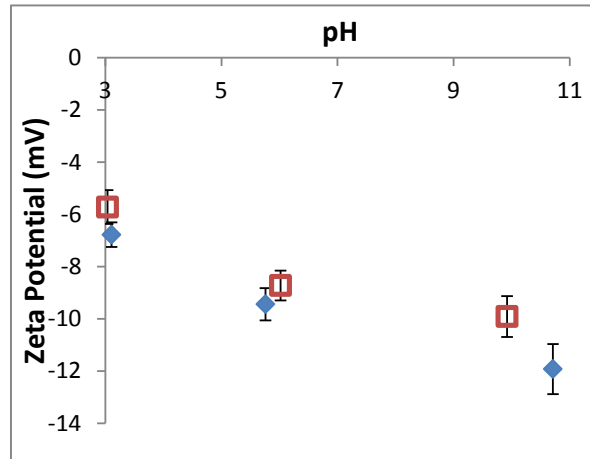


Fig. 3. Zeta potential (Smoluchowski model) as a function of pH of 1% EOR-5XS silica particles in DI water (filled blue diamonds) or 0.04% LAPB solution (open red squares).

4.3. Surface tension measurements

The surface tension (air-water interfacial tension) of LAPB solutions at pH 3 with and without 1% EOR-5XS silica nanoparticles is presented in Figure 4. The addition of 1% EOR-5XS silica nanoparticles did not significantly affect the surface tension or surfactant critical micelle concentration (CMC), which was determined to be $\sim 0.04\%$ at pH 9. The surface tension of 1% EOR-5XS nanoparticles was determined to be ~ 65 mN/m, due to the presence of $\sim 0.5\%$ ethylene glycol. Ethylene glycol in the dispersions may have caused the slight reduction in some surface tension values when the nanoparticles were present. The nanoparticles without added ethylene glycol do not significantly affect the surface tension. The insignificant change in surface tension with added nanoparticles suggests weak interaction between the particles and the surfactant, consistent with the small changes in zeta potential shown in Figure 3. Weak interactions between nanoparticles and surfactants can be favorable because little surfactant is adsorbed on the particle surfaces and remains free in solution to lower the surface tension.[8]

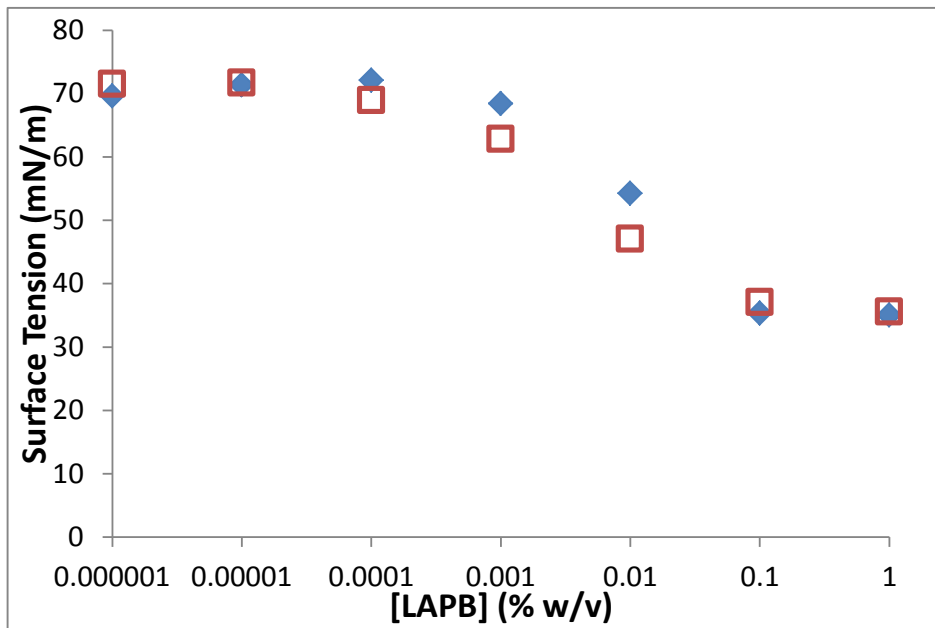


Fig. 4. Surface tension as a function of LAPB concentration of 1% EOR-5XS silica particles in DI water adjusted to pH 3 (filled blue diamonds) or 0.04% LAPB solution adjusted to pH 3 (open red squares). The pH was adjusted by addition of HCl. Note that with 1% EOR-5XS particles, ~0.5% ethylene glycol is present from the stock solution as received from the manufacturer.

Particle stability in CO₂-saturated aqueous phases

In CO₂ saturated aqueous phases, 1% EOR particles dispersions remained transparent for at least 30 minutes in DI water and up to 0.1% LAPB at up to 5000 psia and 90°C. Because the dispersions remained transparent, no significant aggregation of the particles was expected. In a separate study, 1% EOR-5XS dispersions were found to be stable for over 24 h both by visual observation of turbidity and DLS measurements of average particle size at room temperature and atmospheric pressure at pH 9 and 3 with up to 0.1% LAPB. These results indicate that the particles are expected to remain stable for the duration of the foam generation and characterization experiments performed in this study.

4.4. C/W foam formation and apparent viscosity measurements

Apparent viscosities of foams generated in a 22D beadpack at 2800 psia and 50°C are given in Figure 5. Figure 5a indicates that the highest measured foam viscosity without nanoparticles occurred at an injected CO₂ volume fraction (foam quality) of 0.6, while the highest viscosity was measured at 0.8 with added nanoparticles. These results suggest that addition of 1% EOR-5XS nanoparticles to foams stabilized with 0.04% LAPB causes an increase in the phase ratio of CO₂:water that gives the highest foam viscosity (i.e. an increase in the optimum foam quality). Of particular note is the significantly increased foam viscosity at high foam qualities (CO₂ fraction of ≥ 0.8) when nanoparticles were added to the surfactant solution. In the capillary tube, the foams showed a shallow peak in apparent viscosity at a foam quality of 0.8 with only 0.04% LAPB present, but a much more pronounced peak when 1% EOR-5XS particles were added. The visual observations show weak foam which was not very opaque at a quality of 0.6, which became more opaque at a quality of 0.8, and then changed morphology to slugs of foam at a high quality of 0.95.

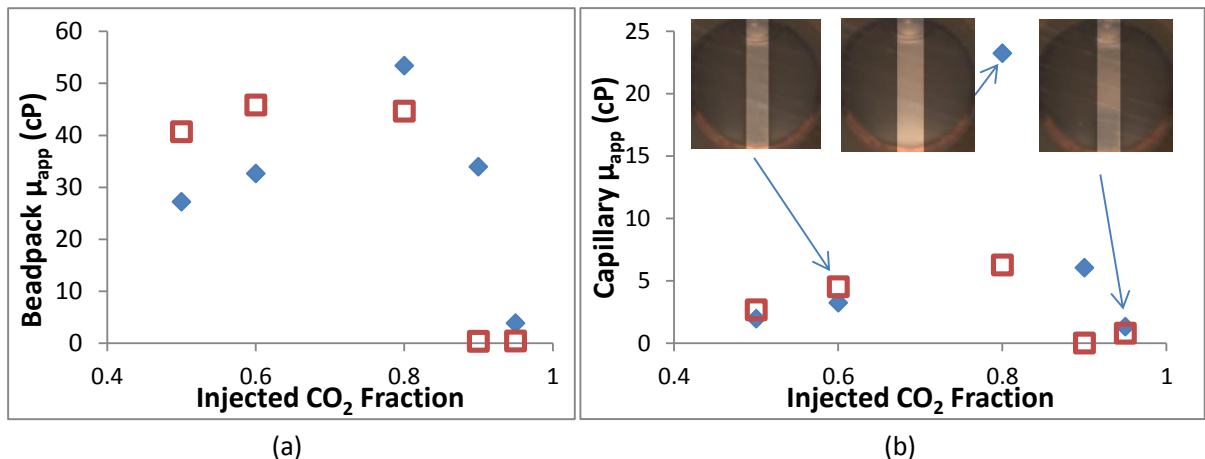


Fig. 5. Apparent viscosity of C/W foams generated in a 22 D beadpack at 2800 psia and 50°C, stabilized with 0.04% LAPB (open red squares) and mixture of 1% EOR-5XS and 0.04% LAPB (filled blue diamonds). Panel (a) gives the apparent viscosity in the beadpack and panel (b) gives the apparent viscosity in the capillary tube. The superficial velocity in the beadpack was 200 ft/day. The capillary tube shear rate is $\sim 200 \text{ s}^{-1}$. Examples of C/W foams stabilized with 1% EOR-5XS with 0.04% LAPB in the view cell are given as insets in (b), with arrows indicating the associated viscosity measurement. Foam is visible in the center of the window in the vertical channel between Teflon spacers. The Teflon spacers have been darkened with photo editing software to highlight the channel. Dark regions in the channel indicate absence of foam. Window diameter is 1.4 cm and visual path length is 0.8 cm. Note that the viscosity of a CO₂-water mixture without surfactant is less than 3 cP, with or without nanoparticles present.

Figure 6 gives apparent viscosity results of foams generated in a 1.2 D beadpack at the same temperature and pressure as in Figure 5. Figure 5a shows the addition of 1% EOR-5XS particles increasing the viscosity at all injected CO₂ volume fractions investigated. As in Figure 5a, it appears that the addition of nanoparticles increased the optimum foam quality. It is noteworthy that the apparent viscosities reported in Figure 6a are the highest known for C/W foams containing nanoparticles. The high viscosities may be due to the low superficial velocities investigated, where foams may shear thin at higher velocities (note the lower viscosities in Figure 5 where the superficial velocity is double that in Figure 6). In the capillary tube, the results for 0.04% LAPB only do not indicate the existence of a pronounced optimum in foam quality, but the addition of 1% EOR-5XS caused a pronounced peak at a quality of 0.8 (as in Figure 5b) to become apparent. The visual observations indicate foam with excess aqueous phase present at a quality of 0.4, then a cell completely filled with opaque foam at a quality of 0.8, then a weaker and less opaque foam at a quality of 0.9. Interestingly, the apparent viscosity values in the capillary tube were similar in both Figure 5b and 6b, despite different foam generators and shear rates at which the measurements were taken, suggesting that the foams are robust and can be generated and utilized at a wide range of conditions.

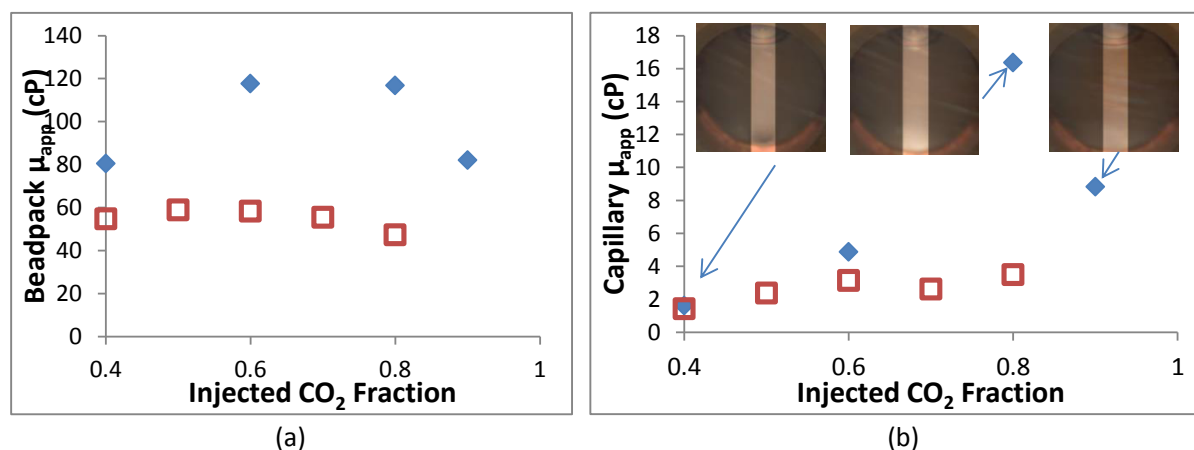


Fig. 6. Apparent viscosity of C/W foams generated in a 1.2 D beadpack at 2800 psia and 50°C, stabilized with 0.04% LAPB (open red squares) and mixture of 1% EOR-5XS and 0.04% LAPB (filled blue diamonds). Panel (a) gives the apparent viscosity in the beadpack and panel (b) gives the apparent viscosity in the capillary tube. The superficial velocity in the beadpack was 100 ft/day. The capillary tube shear rate is $\sim 1700 \text{ s}^{-1}$. Examples of C/W foams stabilized with 1% EOR-5XS with 0.04% LAPB in the view cell are given as insets in (b), with arrows indicating the associated viscosity measurement. Foam is visible in the center of the window in the vertical channel between Teflon spacers. The Teflon spacers have been darkened with photo editing software to highlight the channel. Dark regions in the channel indicate absence of foam. Window diameter is 1.4 cm and visual path length is 0.8 cm. Note that the viscosity of a CO₂-water mixture without surfactant is less than 3 cP, with or without nanoparticles present.

5. Conclusions

In this study, viscous CO₂-in-water foams were generated in a lab-scale apparatus with a mixture of surface-modified silica nanoparticles and lauramidopropyl betaine zwitterionic surfactant. The nanoparticles weakly interact with the surfactant molecules, as indicated by zeta potential and surface tension measurements. Foam apparent viscosity was measured in both a beadpack and a capillary tube according to Darcy's law and the Hagen–Poiseuille equation, respectively. In some cases, strong synergy was observed where the mixture of nanoparticles and surfactant produced significantly more viscous foams than either nanoparticles or surfactant alone. With nanoparticles and surfactant present, CO₂-in-water foams with viscosities of over 50 cP in a 22 darcy beadpack (over 20 cP in capillary tube) and over 100 cP in a 1.2 darcy beadpack (over 16 cP in capillary tube) were generated, compared with viscosities of less than 3 cP when surfactant was not present. Data collected in both beadpacks suggests that the addition of nanoparticles increases the optimum foam quality, allowing the formation of more viscous foams at higher qualities than with surfactant alone. The synergy raises the prospect of less expensive methods of conformance control for CO₂ EOR and efficient use of aquifer volume for GCS, both in terms of materials costs and logistics.

Acknowledgements

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