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The impacts of solubilized and dispersed crude oil on foam in a porous medium

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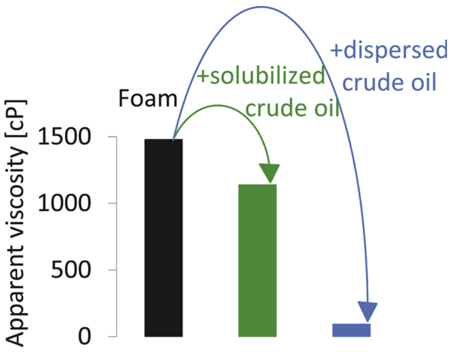
GRAPHICAL ABSTRACT



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ABSTRACT

Dispersed and solubilized oil can impact bulk foam stability differently. Though aromatic components are more soluble in water than straight-chain aliphatic components, solubilized aromatics do not necessarily impact the stability of foam in bulk or porous media, whereas straight-chain aliphatic components can have a detrimental impact (Bergeron et al., 1993; Lee et al., 2013). However, to our knowledge there is no published research on the impact of a solubilized crude oil on foam, as distinct from a separate oil phase, in a porous medium.

To investigate whether the behaviour of steady-state foam with crude oil can be explained by solubilized oil components, we perform foam-flooding experiments with surfactant solution previously equilibrated with crude oil. Furthermore, we conduct foam-flooding experiments with hexane solubilized in the surfactant solution, to determine whether straight-chain aliphatic components can explain the behaviour of the solubilized crude oil on steady-state foam mobility, in the same way that they impact bulk foam in the literature.

The impact of crude oil, as a separate, dispersed oleic phase, is studied here by co-injection of crude oil, surfactant solution and gas in core-floods, focusing on steady-state mobility, captured by the pressure gradient within the core. In our experiments crude oil, as a separate oleic phase, reduces the pressure gradient within the core up to a factor of twenty compared to the case without oil. Nonetheless, this pressure gradient is about a factor three greater than we observe by co-injecting crude oil, water without surfactant, and gas. With a simplified model we fit our three-phase co-injection experimental data by increasing the viscosity of both the gas and water, indicating that some weak foam and emulsion is generated. Neither effect by itself can fit the data.

In contrast, with crude oil or hexane solubilized in the surfactant solution, the pressure gradient is of the same

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order of magnitude as for co-injection gas and surfactant with or without solubilized oil. These results indicate that solubilized crude oil does not reduce foam mobility as much as does the crude oil as a separate oleic phase. Furthermore, the effect of solubilized crude on foam is not due only to straight-chain aliphatic components such as hexane: our experiment with solubilized hexane showed a less-significant impact on foam mobility.

The major result of our work is that we find that both gas and oil mobility are reduced when co-injecting oil, gas and surfactant solution in a porous medium. Another result is that the solubilized crude oil slightly reduces foam mobility, but does not explain the much-larger detrimental impact of crude oil in a separate phase on foam in a porous media.

Nomenclature

f_α	fractional flow [-]
k	permeability [m^2]
$k_{r,\alpha}$	relative permeability to phase α [-]
$k^{o}{}_{r,\alpha}$	end-point relative-permeability [-]
n_α	Corey parameter [-]
∇P	pressure gradient [bar/m]
S_α	saturation of phase α [-]
$S_{r,\alpha}$	residual saturation of phase α [-]
u	total superficial velocity [m/s]
μ	apparent viscosity of foam (Eq. (1)) [cP]

1. Introduction

Gas can be injected into an oil field as an Enhanced Oil Recovery (EOR) process. However, gas suffers from poor sweep efficiency. Foam EOR can be used to reduce gas mobility, and partially compensate for the effect of permeability heterogeneity [1,2]. Phase mobility quantifies the ease with which the phase flows through the porous medium; it is defined as the ratio of the phase relative-permeability to the phase viscosity. For field application, foam must be able to withstand the presence of crude oil to some degree. If foam is generated near the well in a region of low oil saturation, it still might not propagate to the production well. Thus the feasibility of foam generation far from an injection well is an important issue. With the distance between the injection well and production well usually more than 1200 ft. (366 m) [3], and an interstitial velocity of 2 ft./day (0.6 m/day), the injected surfactant equilibrates with the crude oil in the reservoir for more than 600 days. This leads to the question whether foam can be created in situ if the surfactant has equilibrated with the crude oil (i.e. has solubilized crude-oil components). In porous media, foam without oil shows two flow regimes: a high-quality regime, which reflects foam instability at a limiting water saturation or capillary pressure, and a low-quality regime, with strong shear-thinning behaviour as a function of gas superficial velocity [4]. We define the foam quality as the gas fraction of the combined water and gas superficial velocities. There are various ways to characterize foam stability in the presence of oil, including column tests with “bulk” foam and core-flood tests, often with foam displacing an initial resident oil saturation, such as conducted by Simjoo et al. [5]. Jones et al. [6] and Meling and Hanssen [7] relate foam behaviour in column tests to foam in porous media. They find a strong correlation between column and core-flood experiments conducted in the absence of oil, but poor correlation with the experiments in presence of oil. The impact of different pure oils, in dispersed and solubilized form, on foam has been investigated by various researchers. Bergeron et al. [8] conducted foam core-flooding experiments with foam without oil, pre-equilibrated with an alkane (dodecane), and pre-equilibrated with an aromatic (tetralin). They find that foam with solubilized dodecane achieves a lower pressure gradient, and foam with a solubilized aromatic tetralin achieves a higher pressure gradient, compared to foam without oil. These experiments indicate that different solubilized oils can impact foam in different ways. Meling and Hanssen [7] speculate that the impact of n-alkanes (n-octane, n-dodecane and n-hexadecane), dispersed as a separate phase, on foam in bulk and in porous media can be predicted by the impact of solubilized molecules on the interfacial properties between the gas and water phases. Lobo et al. [9] report that bulk foam is destabilized by solubilized and dispersed dodecane and octane. Similarly, Lee et al. [10] see the same impact of n-dodecane on foam when introduced as a dispersed phase and solubilized in the aqueous phase. From this they deduce that the observed impact of n-dodecane on bulk foam is solely caused by solubilized n-dodecane. However, when conducting the same experiments with an aromatic hydrocarbon (toluene), they report foam destabilisation occurs with toluene in dispersed form and not in solubilized form, similar to what was observed by Vikingstad et al. [11] with bulk foam. These findings indicate that the weakening of foam by a dispersed phase of short-chained alkanes can be attributed in part to solubilized oil molecules. In contrast they find that aromatic hydrocarbons weaken foam only in dispersed form and have no impact on, or can even strengthen, foam when in solubilized form. In this paper, we investigate the impact of a crude oil on foam, comparing solubilized oil and a dispersed oil phase, and determine the impact of the crude oil that can be attributed to solubilized components. To investigate the impact of solubilized crude oil, we conduct core-flood experiments with surfactant solutions pre-equilibrated with oil, where we co-inject gas and surfactant at different ratios but fixed total interstitial velocity: i.e., a foam-quality-scan. To gain a better understanding of which components within the crude oil impact the foam in porous media, we also conduct experiments with the surfactant solutions pre-equilibrated with hexane, to understand the impact of solubilized short alkanes from the crude oil. Furthermore, we conduct steady-state co-injection experiments with crude oil, gas, and water (with and without surfactant) to investigate the impact of crude oil as a separate phase on foam. To gain an understanding of how relative permeability, emulsification, and foam impact the total mobility with three-phase co-injection, we model our experiments using a simplified representation of the separate effects of three-phase flow, emulsification and foam.

2. Materials and procedures

The core used in our experiments is a Bentheimer sandstone, which has been described in previous work [12]. The porosity is 0.248 ± 0.019 and the measured permeability, k, of the core is $2.6 \pm 0.2 \times 10^{-12}$ m^2. The core length is 17 cm, with a diameter of 1 cm, mounted vertically. The cores are coated in epoxy resin, which results in an effective core diameter of 0.94 cm, and are mounted in aluminium core-holders, as done by Jones et al. [13,6]. The experiments are conducted at a temperature of 30 °C and a back-pressure of 20 bars. The three fluids are injected from the bottom of the core, through relatively narrow tubes and connections, with an inner diameter of 0.75 mm, in order to minimise the droplet size of the entering phases. Gas injected into the core is nitrogen with a purity of 99.98%, supplied from a 200-bar gas cylinder. Synthetic seawater solution is used for the brine; see Table 1 for the composition. The crude oil used has a viscosity of 2.8 ± 0.03 cP and a density of 0.84 ± 0.01 g/cm^3, measured at 20 °C. The anionic surfactant, $C_{14\text{-}16}$ alpha olefin sulfonate

Table 1
Synthetic seawater composition.

Salts	Grams / litre
NaCl	**25.4**
KCl	**0.673**
$MgCl_2$.6H2O	**10.2**
$CaCl_2$.2H20	**1.47**
Na_2SO_4	**3.83**

(Witconate, supplied by AkzoNobel), is used as received and is set to 0.5 wt% in all the surfactant solutions. The critical micelle concentration is roughly 0.003 wt% at 23 °C [13]. In the simplified modelling described below, we assume the viscosity of the surfactant solution to be roughly equal to that of the seawater solution, 0.85 ± 0.01 cP at 30 °C [14]. To satisfy adsorption, the core is flooded with more than 10 pore volumes of surfactant solution before starting the foam-quality-scan experiments.

Lee et al. [10] find that solubilized n-dodecane can have a stronger detrimental impact on bulk foam (formed with sodium dodecyl sulfate) than the aromatic hydrocarbon toluene. Therefore we choose to conduct our core-flood experiment with a solubilized alkane. We conduct our experiments with hexane (supplied by VWR), because shorter alkanes in the oleic phase cause faster bulk foam collapse with AOS, and hexane in the oleic phase can increase AOS foam mobility in Bentheimer sandstone by almost a factor two [15]. Moreover, the process of oil solubilisation into micelles and resulting swollen micelles is most prominent with shorter alkanes [16]. In some of our experiments surfactant solutions are equilibrated first with the crude oil or with hexane. Surfactant solution and crude oil are mixed as follows: 1029.1 +/− 0.1 g of surfactant solution with 198.9 +/− 0.1 g of crude oil, stirred daily for 11 days. With the surfactant solution with solubilized hexane, 730.8 +/−0.1 g of surfactant solution are mixed with 80.7 +/−0.1 g of hexane for 10 days. The two-phase co-injection core-floods with pre-equilibrated surfactant are conducted in the same way as the foam-quality-scan core-floods. The surfactant solution equilibrated with crude oil is first separated from the crude oil and any separate emulsion layer, then centrifuged at 2000 rpm for 2 h, and finally filtered through a filter paper (Sartorius) with a pore size of 0.45 μm, under a pressure gradient imposed by a vacuum pump. As shown in Fig. 1, all particles in the unfiltered solution have a size smaller than 0.45 μm, and thus we decided not to filter and centrifuge the solution equilibrated with hexane. The surfactant (which is mainly a mixture of $C_{14}H_{27}O_3S^-Na^+$ to $C_{16}H_{31}O_4S^-Na^+$ [17,18]) has a molecular length of about 2.3 nm, assuming carbon-carbon and carbon-sulphur bond-lengths of 1.5 Å and 1.8 Å respectively [19]. This corresponds to a minimum micelle diameter of 4.6 nm. Applying Dynamic Light Scattering (DLS, by Malvern Zetasizer), we determine the micelle-size distribution of the surfactant solution equilibrated with crude oil, and surfactant solution without oil; see Fig. 1. As also reported by Lee et al. [20], the mode of the micelle-size distribution of the surfactant solution increases after equilibration with oil. However, unlike their case, the polydispersity [21] of the micellar aggregates slightly decreases. The surfactant concentration in the surfactant solution equilibrated with crude oil is determined by titration to be 0.37 +/- 0.01 wt%; see Table 2. From Total Oil Content (TOC) measurements (using a Shimadzu TOC analyser and a Skalar Primacs^{SLC} TOC analyser), we deduce that the solubilized crude-oil content is 0.14 +/- 0.03 wt.%. We assume that the surfactant concentration of the pre-equilibrated solution decreases from 0.5 to 0.37 wt % because of surfactant losses to the crude oil and generated emulsion. We do not observe an emulsion when equilibrating the surfactant solution with hexane. We discuss the effect of the loss of this surfactant below.

Table 3 gives the surface-tension for the crude oil, synthetic seawater without surfactant and with 0.5 wt.% AOS. Table 4 gives the relevant interfacial tensions for the crude oil and the aqueous solutions, and the respective entering-, spreading-, and bridging-coefficient values and lamella number [22]. Interfacial-tension (IFT) values of less than 1 mN/m and 18 ± 1 mN/m were measured for crude oil with surfactant solution in synthetic seawater and for crude oil with synthetic seawater, respectively. These measurements were conducted using the Du Noüy–Padday method at room temperature (21 ± 1 °C) and ambient pressure. The measured interfacial tension between crude oil and surfactant solution was below the measuring range of the device (1–350 mN/m). In our calculation of the range of foam-stability-coefficient values we use interfacial tensions of 0 and 1 mN/m. We assume the interfacial tension between crude oil and pre-equilibrated surfactant solution to be equal to that of crude oil and surfactant solution.

All our core-flood experiments were conducted with a total injection rate of 0.1 ml/min, which is equivalent to 6.8 ft./day ($2.4{\cdot}10^{-5}$ m/s) superficial velocity. To minimize any impact of hysteresis while conducting the foam-quality scan, in collecting data we alternated between low and high foam qualities. We define the foam-quality as the gas fraction of the combined gas and water injection rate. The three-phase co-injection experiments without surfactant were conducted after the three-phase co-injection experiment with surfactant. To remove the surfactant from the core, we flooded the core with 190 PV of synthetic seawater to remove the surfactant. We prefer not flooding the core with a solvent (such as alcohol), to avoid the possibility of a solvent altering the core properties or a residual concentration of solvent later impacting oil-water interactions.

3. Results and discussions

We examine three different ways that the crude oil can impact pressure gradient compared to co-injection of gas and surfactant without oil: 1) oil weakening foam when solubilized, 2) oil as a separate phase impacting the three-phase relative permeabilities of water and

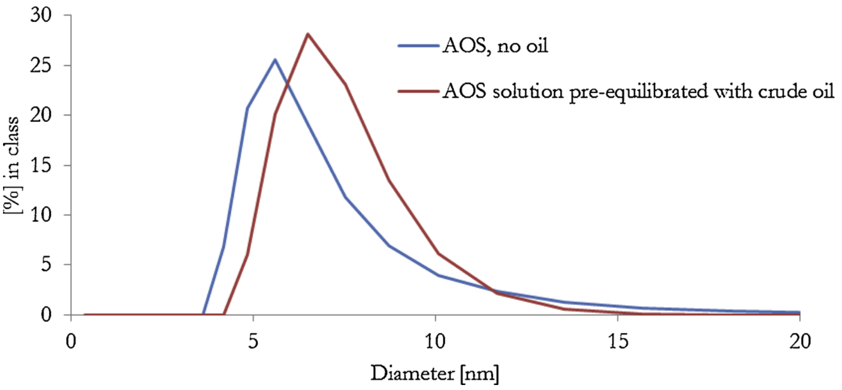


Fig. 1. Size distribution of surfactant micelles, measured with the Malvern Zetasizer.

Table 2
The measured and calculated surfactant and oil content of the surfactant solutions.

Description	Total carbon (ppm)	Oil content (wt%)	Surfactant concentration (wt%)
AOS solution without solubilized oil	**2880** ± 140[a,b]	–	**0.50** ± 0.02[a,b]
Solubilized crude oil in pre-equilibrated AOS solution	**3330** ± 140[b]	**0.14** ± 0.02[b,c]	**0.37** ± 0.01[c]; surfactant concentration decreased by 0.13 wt% due to depletion by emulsion, generated while equilibrating.
Solubilized hexane in AOS solution	**27×10^2** ± 2×10^2[d]	Total oil + surfactant concentration: **0.44 – 0.51**	

[a] Values calculated using the active content in the original AOS solution.
[b] Values calculated from Shimadzu TOC analyser values.
[c] Values calculated from the surfactant titration measurement.
[d] Values calculated with the Skalar Primacs^{SLC} TOC analyser values.

Table 3
Surface-tension values measured at ambient conditions.

Surface tension (mN/m)	
Crude oil	**27** ± 1
Synthetic seawater	**73** ± 1
Synthetic seawater with 0.5 wt.% AOS C14-16	**28** ± 1

gas, and 3) oil weakening the foam as a separate phase, possibly as an emulsion. We analyse our data to distinguish these three effects. Our analysis of the core-flood experiments is focused on the measured absolute-pressure data, from which we calculate the pressure gradient, ∇P [Pa/m]. Using the pressure gradient, we calculate the apparent viscosity of foam, μ [Pa·s], as follows:

$$\mu = \frac{k}{u}|\nabla P| \tag{1}$$

where u is the total superficial velocity [m/s] and k is the permeability of the porous medium [m^2]. Eq. (1) gives apparent viscosity [Pa·s]; below we report results in cP (1000 times the value in Pa·s). A benchmark core-flood experiment is conducted without any oil. This produces a relatively strong foam, similar to that reported by Jones et al. [13], who conducted core-flood experiments with the same surfactant and porous medium at similar salinity. The apparent viscosity is presented as a function of the gas fractional flow (foam-quality) in Fig. 2. The shape of the curve at foam qualities between 60% and 95% is similar to what was observed by Jones et al. [13] with the same surfactant (Fig. 3).

3.1. Effect of solubilized oil on foam

In the foam scan with solubilized oil, the maximum apparent viscosity is about 1200 cP with solubilized crude oil and 1600 cP with solubilized hexane, indicating that foam is generated in both cases (Fig. 2). Therefore, we conclude that solubilized oil, whether crude oil or hexane, does not prevent AOS-foam generation. However, the foam-scan results without oil and with solubilized crude oil differ in two aspects: foam in the high-quality regime is weaker, and the shear-thickening behaviour (concave-upward shape of the curve) in the low-quality regime is not observed with solubilized crude oil. At foam qualities 40–60%, surfactant solution equilibrated with hexane shows an apparent-viscosity profile similar to surfactant solution equilibrated with crude oil, and is only 5–10% different from that without any oil. However, as foam quality increases, the apparent viscosities with solubilized hexane and without any oil are almost identical. The maximum apparent viscosity of foam made with surfactant solution equilibrated with crude oil is approximately 20% lower than with surfactant solution without solubilized oil. This is a reflection of weaker foam in the high-quality regime. However, the decrease of apparent viscosity may be caused in part by the decrease of surfactant concentration. The surfactant concentration in the solution with solubilized crude oil is 0.37 wt%, whereas the surfactant concentration in the surfactant solution without oil is 0.5 wt% (Table 2). Jones et al. [13] showed that foam apparent viscosity decreases by about the same fraction for surfactant concentration decreasing from 0.5 wt.% to 0.1 wt %; see Fig. 3. Because, for the experiment with crude oil, both the surfactant concentration changed and some oil was solubilized (see Table 2), it is not clear how much the decrease in surfactant concentration and presence of solubilized oil separately impacted foam apparent viscosities. Nonetheless, it can be said that the observed behaviour of foam equilibrated with hexane cannot explain the major impact of hexane as a separate oleic phase on foam in porous media reported by Tang et al. [15]. The impact of solubilized oil on steady-state foam apparent viscosity is limited in our results and cannot explain the observed three-phase flow (crude oil, surfactant, gas) results described in the next section.

3.2. Effect of 3-phase relative-permeability

Three-phase flow without any foam or emulsion can result in high apparent viscosity, compared to water, due to three-phase relative-permeability effects. Three-phase co-injection experiments without surfactant (using Soltrol 170 as a model oil, composed of C12-C14 iso-alkanes, with a viscosity of 2 cP at 37.8 °C) in Bentheimer sandstone produce apparent viscosities in the range of 100 cP simply through three-phase relative-permeability effects [23]. In our analysis of the steady-state co-injection experiment with surfactant, gas, and 1% fractional flow of crude oil, we assume that the oil saturation is close to the gas-flood residual oil saturation. The results of the three-phase co-injection experiments, Fig. 4, lack the characteristic two foam regimes seen in Fig. 2. Furthermore, the magnitude of foam apparent viscosity with oil as a separate phase without surfactant is lower (maximum 180 cP, Fig. 4) than with foam with solubilized oil (maximum 1500 cP, Fig. 2). Oil fractional flow is also important: apparent viscosity increases with increasing oil fractional flow (and, by implication, increasing oil saturation). This result is somewhat counter-intuitive, since foam is expected to be weaker at higher oil saturation [24]. However, the increase in apparent viscosity with increasing oil fractional flow in Fig. 4 could be due in part to emulsion generation [25] or to three-phase relative-permeability effects at greater fractional flow of oil. Also,

Table 4
Interfacial-tension values measured at ambient conditions, and the calculated entering, spreading and bridging coefficients, and lamella number.

	Interfacial tension (mN/m)	Entering coefficient	Spreading coefficient	Bridging coefficient	Lamella number
Crude oil / synthetic seawater	**18** ± 1	**64**	**28**	**4870**	**0.6**
Crude oil / synthetic seawater + 0.5 wt.% AOS C14-16	< **1**	**2-3**	**1-2**	**95–96**	**4-∞**

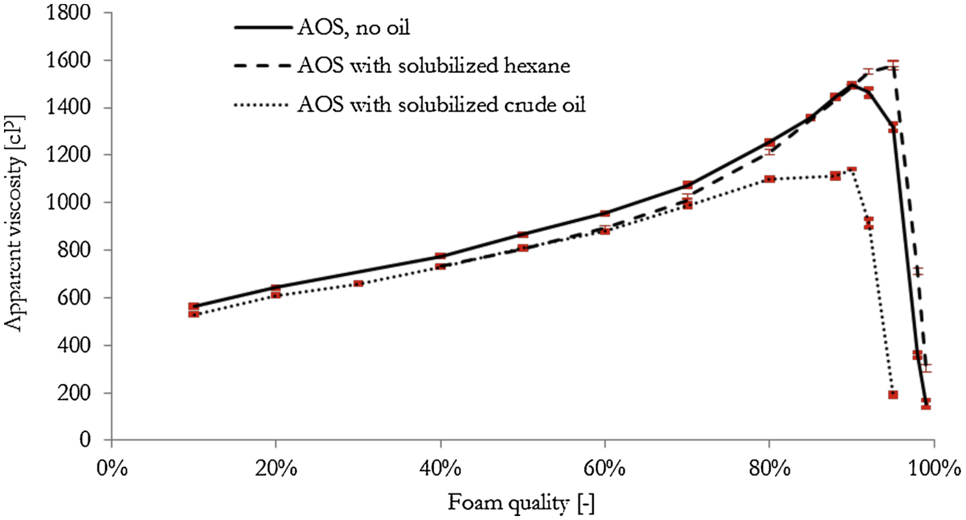


Fig. 2. Foam apparent viscosity as a function of foam quality for foams made without solubilized oil, and with surfactant with solubilized crude oil and with solubilized hexane. The lines are to guide the eye. Bars indicate standard deviation of measurements over time in the given test.

while it is well known that oil forms macroemulsions with water and surfactant, this is not accounted for in foam simulation models, so far as we know. We want to point out this deficiency.

3.3. Effect of emulsification and weaker foam

We observed an emulsion and fast-collapsing foam after shaking a test tube with crude oil and seawater (without surfactant). With surfactant we observed a finer emulsion, and finer-textured foam. We believe that these qualitative observations correspond to the phase interactions in the core. In Fig. 4 the apparent-viscosity curves as a function of foam quality have a similar shape, but differ in magnitude. In the case of three-phase co-injection we observe an increase in apparent viscosity with increasing water fractional flow, whereas in the case of foam injection without oil we observe an increase in apparent viscosity with increasing gas fractional flow. This indicates that the aqueous phase has a reduced mobility in the presence of oil. Moreover, in our three-phase co-injection experiments (with and without surfactant) we observe an emulsion in the effluent. Therefore, the higher apparent viscosity observed with 1% oil fractional flow with surfactant in the aqueous phase, compared to that without surfactant, is likely to reflect, at least in part, a more-viscous emulsion generated with surfactant than without. Similarly, the higher apparent viscosity at higher foam qualities, as observed with foam without oil (see Fig. 2), indicates that the gas phase has a reduced mobility, which indicates stronger foam compared to the case without surfactant. Thus, we hypothesize that the relatively high apparent viscosities achieved with three-phase co-injection is a combined result of relative permeability, effects of emulsification, and weak foam. The relative-permeability effect reduces gas and water mobilities as oil fractional flow increases. Oil emulsification reduces oil mobility and weaker foam leads to increased gas mobility compared to foam without oil.

4. Modelling of laboratory experiments

There are three possible causes of reduced mobility in our experiments; relative permeability, effects of emulsification, and weak foam. To distinguish between them, we compare the data to a very simple model qualitatively incorporating the three effects. We chose to use a simple model with three fitting parameters because fewer fitting parameters means there are fewer solutions, allowing one to make firmer conclusions on which parameters impact the observed behaviour. We model our laboratory experiments with three-phase relative-permeability curves and viscosity-multiplication factors for the

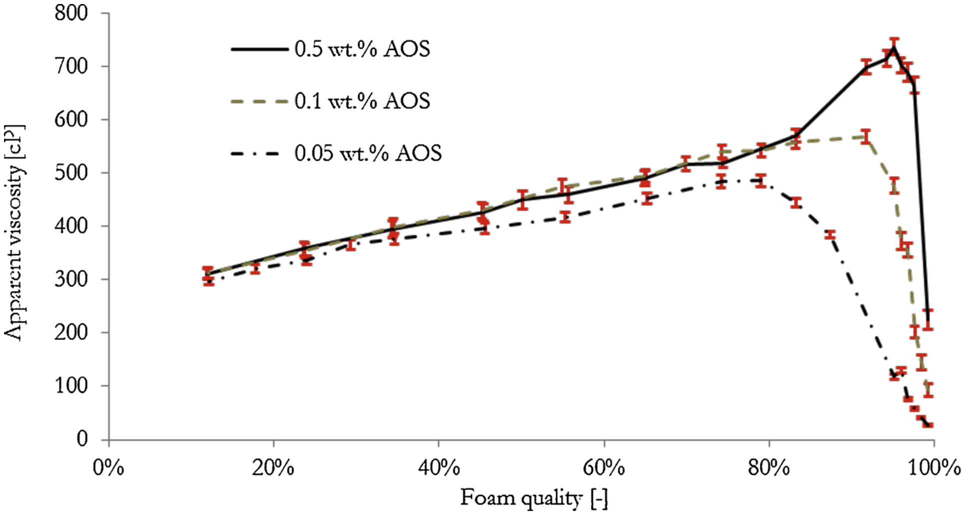


Fig. 3. Foam apparent viscosity as a function of foam quality at various surfactant concentrations, from Jones et al. [13], with no oil present. The lines are to guide the eye. Bars indicate standard deviation of measurements over time in the given test.

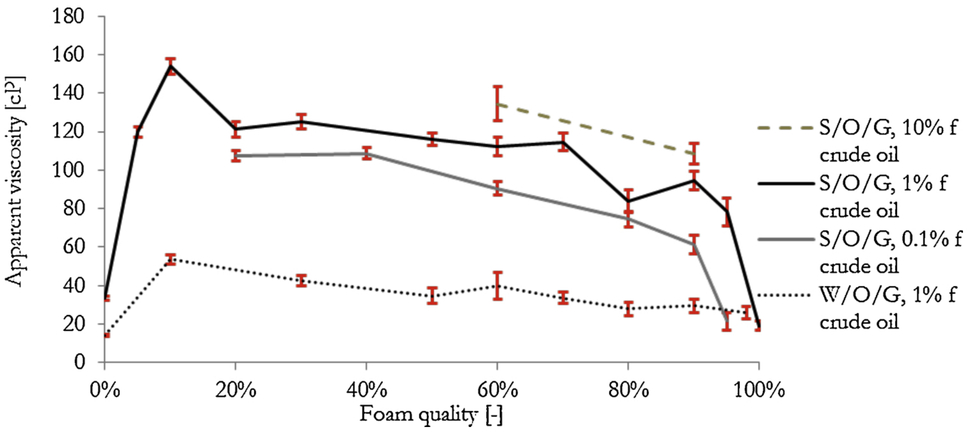


Fig. 4. Foam apparent viscosity as a function of foam quality for three-phase co-injection experiments. The foam quality is defined as the gas fraction of the gas- and aqueous-phase volumetric injection rate. The line is to guide the eye. S is aqueous surfactant solution, W brine without surfactant, O oil, G gas and f is total volume % oil in the injected fluids. Bars indicate standard deviation of measurements over time in the given test.

Table 5

Corey-parameter values for the relative-permeability functions for each phase.

	Water	Oil	Gas
n_α	3.5	4	3.8
$s_{r,\alpha}$	0.089	0.108	0.24
$k^o_{r,\alpha}$	0.1	0.35	0.6

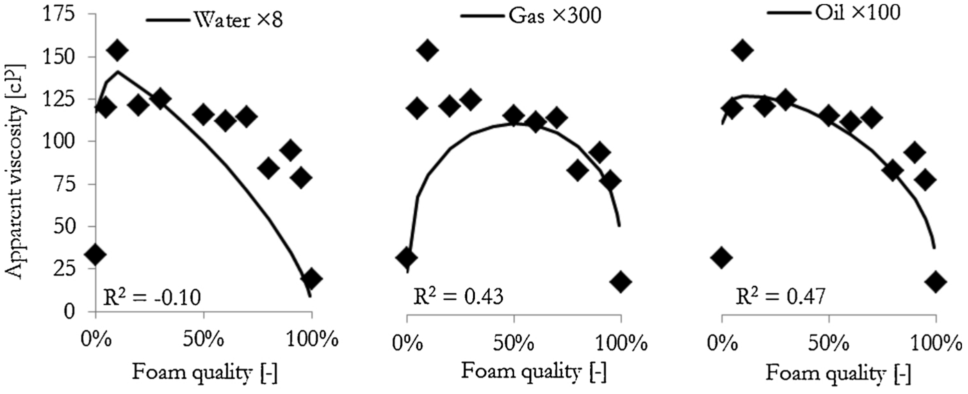
different phases. We use the three-phase relative-permeability data of Alizadeh and Piri [23] and a Corey-style relative-permeability relationship as in Eq. (2). In this relationship, n_α is the Corey exponent, $S_{r,\alpha}$ the residual saturation, and $k^o{}_{r,\alpha}$ is the end-point relative-permeability of phase α. See Table 5 for our Corey parameter values, based on a fit to the data of Alizadeh and Piri [23]. Thus we assume that the residual saturations in our case are equal to those measured without surfactant in the aqueous phase and with a model oil. Moreover, we foam-flooded the core before conducting the three-phase co-injection experiments, therefore we assume there is trapped gas in the porous medium, even when gas fraction-flow is zero. The water, oil, and gas relative-permeability fits to the experimental data are shown in Fig. A1 -a, b, and c in Appendix A.

$$k_{r,\alpha} = k^o_{r,\alpha} \times \left(\frac{S_\alpha - s_{r,\alpha}}{1 - s_{r,o} - s_{r,g} - s_{r,w}} \right)^{n_\alpha} \tag{2}$$

Fig. 5 shows three model fits, each with only the water, gas, or oil viscosity increased (increased by 8×, 300× and 100×, respectively). These figures indicate that the apparent-viscosity trend as a function of foam quality cannot be modelled with an increased gas viscosity only, as is usually done when modelling foam in the presence or absence of oil [26]. Reducing water mobility alone misses the high-quality data and has a negative R^2 because the sum of the discrepancy between the data and the curve is larger than the sum of the discrepancy between the data and a horizontal line equal to the average of the data. A model for reduced gas mobility with foam misses the data at low foam quality. Increasing oil viscosity alone does a somewhat better job, but it is hard to identify a mechanism for reducing oil mobility by such a large factor and without affecting gas or water mobility. Moreover, after shaking a test tube with crude oil and surfactant solution we observed foam and an emulsion. These test-tube experiment indicate that modelling three-phase co-injection requires increasing both gas and liquid viscosity.

Fig. 6-a shows the model fits with a single viscosity multiplier for all the three-phases (4.5×); Fig. 6-b with only the water and gas viscosities increased (by 3× and 90×, respectively); and Fig. 6-c with only the oil and gas viscosities increased (by 13× and 90×, respectively). These figures illustrate that no adjustment to a single phases mobility fits the data. More-complex, even mechanistic, foam models still could not improve the fit in Fig. 5-b by adjusting gas mobility alone, since the biggest deviation is at low foam quality. Thus, we believe this experiment should be modelled by increasing both gas and either water or oil viscosity (Fig. 6-c).

Fig. B1 -a in Appendix B shows the model fit for the three-phase co-injection data with 1% oil fractional flow and without any surfactant in the aqueous phase. Fig. B1 -b shows the model fit for the three-phase co-injection data with 0.1% oil fractional flow with surfactant in the aqueous phase. These figures illustrate that the proposed model can capture our observed three-phase flow behaviour with different fractional flows, with and without surfactant. However, further work needs to be conducted to assess the sensitivity of the viscosity multipliers to the oil and water fractional flows. Our results show that complete and predictive flow modelling for this foam-oil combination requires a more-detailed model for both foam and emulsification. Specifically, Fig. 6-b and c show that to model three-phase flow with such an oil, an increased oil viscosity or increased water viscosity needs to be included in the model to account for emulsification.



a b c

Fig. 5. The apparent viscosities achieved at different foam qualities in the three-phase co-injection experiments, with surfactant in the aqueous phase and 1% crude oil fractional flow. Figure a, b, c, show the modelled apparent viscosity vs foam quality with an increased water (×8), gas (×300), or oil (×100) viscosity, respectively.

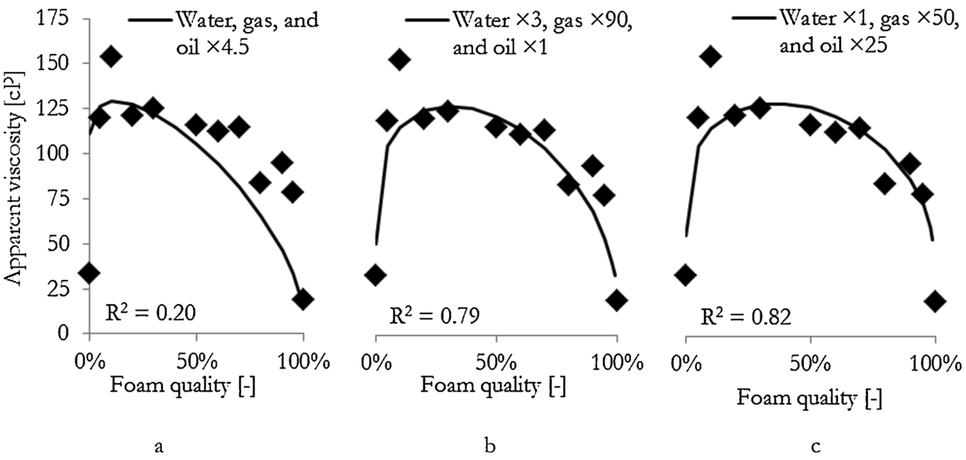


Fig. 6. The apparent viscosities achieved in the three-phase co-injection experiments with surfactant, gas and 1% oil fractional flow, modelled with three sets of apparent phase-viscosity multipliers.

5. Conclusions

Solubilized crude-oil experiments (pre-equilibrating our surfactant solution with crude oil or hexane) show that the impact of our solubilized crude oil on AOS foam is limited, and does not explain the behaviour we observe with three-phase co-injection. We do not observe significant impact of solubilized hexane on AOS foam in porous media, indicating that the large impact of dispersed hexane on AOS foam [15] cannot be accounted for by solubilized hexane.

Experiments with crude oil co-injected with gas and water show that co-injection of crude oil, gas, and water (with and without surfactant) resulted in similar trends in apparent viscosity as a function of foam-quality. With our simplified model, the apparent viscosities in three-phase-flow cannot be modelled with reduced gas mobility only; it requires reduced liquid (either water or oil) mobility as well. Furthermore, the apparent viscosity increases with increasing oil fractional flow (from 0.1% to 10%), which could be explained by the three-phase relative-permeability effects and emulsions generation in the core. Lastly, we did not observe foam in the effluent, though we did observe fast-collapsing foam when shaking a test-tube with crude oil and water (with and without surfactant).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

To model foam-free relative permeabilities in our three-phase co-injection experiments we use the experimental data of Alizadeh and Piri [23]. They conducted three-phase co-injection experiments in Bentheimer sandstone with a model oil (Soltrol 170), nitrogen and water without surfactant, and thus did not generate a foam or emulsion as in our experiments. They determined phase saturations using dual-energy computed tomography. Fig. A1 (a, b and c) show the relative-permeability data as a function of the phase saturations from Alizadeh and Piri [23], and our modified Corey-

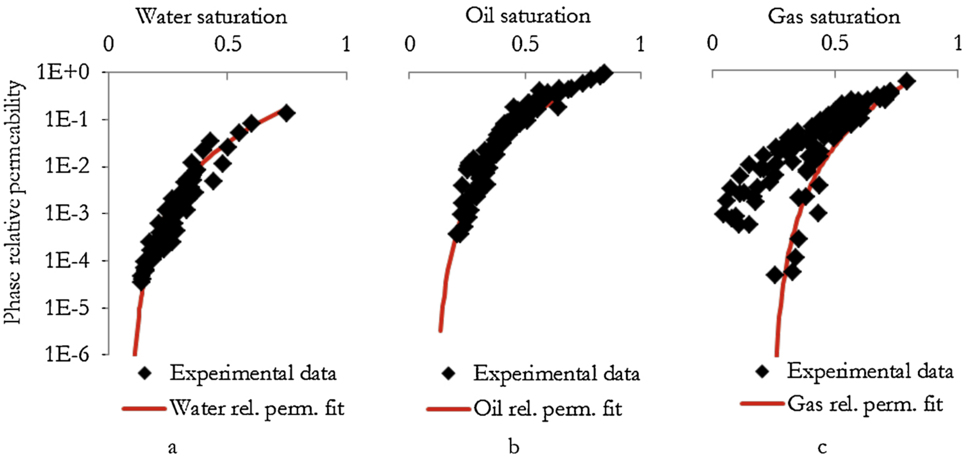

Fig. A1. Three-phase relative-permeability experimental data, after Alizadeh and Piri [23], and fit according to the parameters in Table 5. Note that we fit the gas relative-permeability trend from the data for decreasing gas saturation.

model fits using to the parameters in Table 5. Alizadeh and Piri observe two gas relative-permeability relationships (Fig. A1 -c), one for increasing gas saturation and one for decreasing gas saturation, where there is some trapped gas in the porous medium. Because in our experiments we have foam in our porous medium, and thus trapped gas, we use the trend of decreasing gas saturation. Though the experiments of Alizadeh and Piri were also conducted with Bentheimer sandstone, our relative-permeability relationships might differ due to a different interfacial-tension (and wettability) between our crude oil and Bentheimer sandstone compared to their model oil and Bentheimer sandstone. To model our experiments we first calculate the relative-permeability ratios of the different phases from the fractional-flow values; see equations Eq. (A1) and Eq. (A2). We then infer the phase saturations from the relative-permeability functions of the three phases, $k_{r,\alpha}$. We then calculate the three-phase mobilities and apparent viscosity using the relative-permeability values and viscosities of the phases, μ_α.

$$\frac{\frac{k_{r,\alpha}}{\mu_\alpha}}{\sum \frac{k_{r,i}}{\mu_i}} = f_\alpha \tag{A1}$$

$$\frac{f_\alpha \times \mu_\alpha}{\sum f_i \times \mu_i} = \frac{k_{r,\alpha}}{\sum k_{r,i}} \tag{A2}$$

Appendix B

Fig. B1 -a shows the model fit for the co-injection of water (without surfactant), gas, and crude oil (1% fractional-flow) and Fig. B1-b shows the model fit for the co-injection of surfactant, gas and oil (0.1% fractional-flow). These figures are shown to illustrate that the proposed model can capture our observed three-phase flow behaviour with different fractional flows, with and without surfactant.

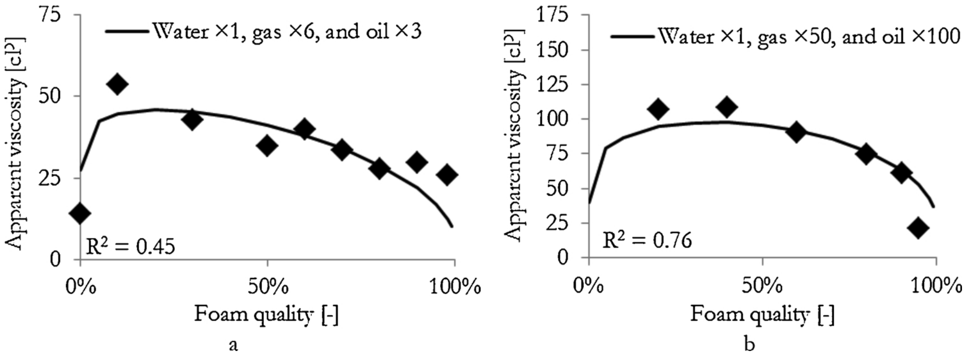

Fig. B1. Apparent viscosities at different foam qualities in the three-phase co-injection experiments and their model fits. Figure a shows the experimental data obtained without surfactant in the aqueous phase, and 1% crude oil fractional flow, and the model fit with increased oil (×3) and gas viscosities (×6). Figure b shows the experimental data obtained with surfactant in the aqueous phase, and 0.1% crude oil fractional flow, and the model fit with increased oil (×100) and gas viscosities (×50).

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