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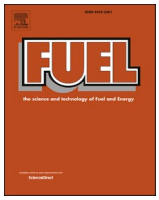

Full Length Article

How does surfactant aid the displacement of oil by water in nanoscale cracks?

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ABSTRACT

The displacement of oil by water is the central concern in enhanced oil recovery. In this paper, we present an experimental study of the displacement of oil by water in a nano-scale, glass channel. The channel was 100 nm thick, composed of hydrophilic glass, and was closed at one end. Displacement was examined under zero applied pressure. Three surfactants were examined for their ability to aid displacement of oil: sodium dodecylsulfate (SDS), an anionic surfactant; Aerosol OT (AOT), an anionic surfactant; and dodecyltrimethylammonium bromide (DTAB), a cationic surfactant. AOT was the only surfactant that caused displacement of oil within 12 h. AOT is also the only one of the three surfactants that can form reverse micelles in the oil phase, and we attribute the oil displacement to the delivery of water to the hydrophilic glass by reverse micelles. We support this conclusion with experiments showing (a) lesser displacement with fewer reverse micelles and (b) that the water phase is discontinuous. The latter implies transport of water through the oil phase. Therefore, the conclusion of this work is that the surfactant aids oil recovery from a hydrophilic channel by enhancing transport of water through oil. The delivered water can adsorb at the solid and continued transport can spontaneously grow a bulk water phase, thereby displacing the oil.

1. Introduction

The displacement of oil from natural reservoirs is the fundamental objective of oil recovery. After drilling an oil well, oil will spontaneously flow out due to the pressure applied from the overlying rock or can be removed by pumping. But only 10 to 25% of original oil in place (OOIP) can be recovered this way [1]. Following the primary recovery, water, saline solutions, or CO_2 is pumped into the well to displace the oil. This secondary recovery can recover another 15 to 25% of OOIP leaving more than 50% OOIP trapped in small cracks and fissures [1]. Enhanced oil recovery (tertiary recovery) techniques are used to mobilize oil in these confined spaces and significantly improve the production of oil [2–6]. Chemicals are frequently used for tertiary recovery, for example, polymers can be used to increase the viscosity [1]. Additionally, surfactants are used in enhancing oil recovery [7–15], with nanoparticles deployed to improve the delivery of surfactants to oil–water interface [16,17].

Experience in the oil industry shows that surfactants can aid oil recovery and two main mechanisms have been suggested: reduction of the oil–water interfacial tension and changes in wettability [14]. If surfactant adsorbs at the oil–water interface, then the adsorption will reduce the Laplace pressure required to move oil–water interfaces, thereby allowing trapped oil globules to be more easily moved through the reservoir [1,4,18]. The wettability of oil reservoir determines the thermodynamics for water to displace oil from the rock. Surfactants can aid the displacement of oil by decreasing the water–rock interfacial tension or hinder the process by decreasing the oil–rock interfacial tension. For example, Stadnes et al showed that an aqueous solution of cationic surfactant (C_nTAB), both decreases the water contact angle on carbonate reservoir rock compared to pure water and increases oil recovery [6,19]. Surfactants also aid in the formation of oil in water emulsions [20–24]. The emulsified droplets can be carried in the water phase and recovered, and in some cases block pores, leading to changes in oil mobility. Finally, some studies suggest surfactants can also facilitate oil recovery by forming a foam [25].

The aim of this work is to distinguish mechanisms for the role of surfactant in the spontaneous displacement of oil by water. As background, we briefly describe the thermodynamics of this process to determine when the process is spontaneous, i.e., when $\Delta G < 0$. When water displaces oil from a crack, three interfaces are involved: oil–water, oil–solid, and water–solid (Fig. 1). With no pumping, the energy of

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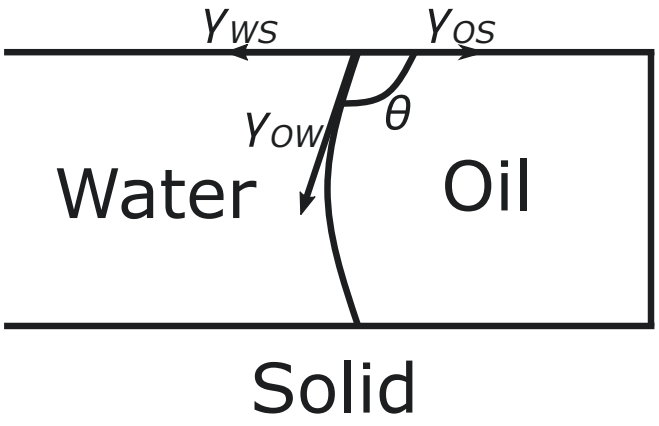

Fig. 1. Schematic for oil/water inside a close-end capillary. Note that the contact angle is measured through the oil.

displacement, ΔG_D, depends on the sum of the changes in surface energy:

$$\Delta G_{\mathrm{D}} = (\Delta G_{\mathrm{WS}} + \Delta G_{\mathrm{OS}}) + \Delta G_{\mathrm{OW}} \quad (1)$$

where WS is the water–solid interface, OS is the oil–solid interface, and OW is the oil–water interface. We write the two solid terms together in parentheses because this is the energy of displacement of oil at the solid. Each free energy is the product of the interfacial tension, γ, and the change in area, ΔA:

$$\Delta G_{\mathrm{D}} = (\gamma_{WS}\Delta A_{WS} + \gamma_{OS}\Delta A_{OS}) + \gamma_{OW}\Delta A_{OW}. \quad (2)$$

When water displaces oil, the changes in their areas are equal and opposite. Additionally, the surface tensions are related by the Young Equation:

$$\gamma_{WS} = \gamma_{OS} + \gamma_{OW}\cos\theta, \quad (3)$$

where θ is the contact angle through the oil (See Fig. 1).

Thus,

$$\Delta G_{\mathrm{D}} = \gamma_{OW}(\Delta A_{WS}\cos\theta + \Delta A_{OW}). \quad (4)$$

Here we see the dependence of spontaneous displacement on the oil–water interfacial tension and the wettability that is the basis of efforts to use surfactants to lower the oil–water interfacial tension and increase the contact angle of oil. Note that adsorption of surfactant to decrease the oil–water interfacial tension does not directly change the process from non-spontaneous to spontaneous (it affects both terms equally), but if the process is non-spontaneous, adsorption can reduce the work required to displace the oil. But if the surfactant also adsorbs to the oil–solid interface, this will have a detrimental effect by decreasing the contact angle (Eq. (3).

When a uniform diameter channel connects two macroscopic reservoirs containing oil and water, $\Delta A_{OW} = 0$. If the channel is also hydrophilic ($\cos\theta < 0$) displacement of oil by the water is spontaneous. If the oil is in a crack is in a dead-end crack (Fig. 1), then a new oil–water interface will form, and the displacement will only be spontaneous if the wetting term is sufficiently negative.

As discussed above, there are a variety of possible mechanisms for the action of surfactants. Our aim here is to examine the effect of surfactant in a situation where we can directly observe the movement of the oil microscopically and therefore test hypotheses directly. There is much empirical knowledge and considerable application of surface chemical concepts, but by direct observation, we expect to be able to differentiate between hypotheses. We use a simple well-defined geometry, pure glass surfaces and pure water and surfactants to obtain a well-defined system.

In this manuscript, we focus on spontaneous displacement of oil trapped inside a dead-end nanoscale channel, that is, an oil-filled pore that is closed at one end and open at the other to allow exchange of water for oil as shown in Fig. 1. The channel has dimensions 100 nm × 100 μm × 2 mm and is fabricated from glass. Glass is similar to silicate minerals, and the transparency of glass enables high resolution optical imaging In our work, the oil is not pushed out of the channel by application of pressure, instead we consider whether the oil can be removed spontaneously. All the surfactants adsorb to the oil–water interface and so decrease γ_{OW}.

We consider three hypotheses for the mechanism of surfactant: displacement of oil is facilitated by:

1. Lowering the oil–water interfacial tension, leading to an increase in θ and therefore to the wetting term in Eq. (3) becoming more negative.
2. Transport of oil in emulsion droplets in the aqueous phase.
3. Transport of water droplets to the solid–oil interface.

In Mechanisms 2 and 3 the surfactant lowers the oil–water interfacial tension, and thereby increases the number of oil droplets in water (2) or water droplets in oil (3). By droplets, we mean droplets of micrometer–nanometer size, which contrasts with the interface between oil and water considered in (1). We do not distinguish between micelles, oil-swollen micelles, and emulsion droplets or between reverse micelles and larger water droplets coated in surfactant. Water in oil emulsions [26], and the transport of water in oil have been discussed previously [27]. Our main contribution here is that we consider transport of water in oil, the implications of which have not been frequently discussed for oil recovery.

We consider the effect of three surfactants: sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), and sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate (Aerosol OT®, AOT). SDS and AOT are anionic surfactants, whereas DTAB is a cationic surfactant. All surfactants decrease the oil–water interfacial tension so will make the first term in Eq. (3) more negative and therefore test Hypothesis 1. Our model solid is glass, which in common with many reservoir rocks, is anionic, and the model oil is hexadecane. Of the three surfactants, only DTAB is cationic, and it adsorbs to the solid–liquid interface, thereby lowering the oil–solid interfacial tension (decreasing the contact angle), which we expect to hinder displacement of oil by water. SDS, DTAB, and AOT all form regular micelles, which should aid transport of oil droplets (Hypothesis 2). Only AOT forms reverse micelles [28] (which when swollen exist as water in oil droplets), so only AOT should investigate Hypothesis 3. Reverse micelles are formed because AOT is a highly branched anionic surfactant with a high packing parameter [29].

All surfactants were used at 2 × of their respective critical micelle concentrations (CMCs) because the oil–water interfacial tension plateaus at its minimum value near the surfactant CMC. Properties of the surfactant solution at 2 × CMC are listed in Table 1.

Our results show that only AOT causes spontaneous displacement of oil. Therefore decreasing γ_{OW} (Mechanism 1) is not sufficient to displace oil. Not all surfactants that form oil in water micelles displace the oil, so Mechanism 2 is not sufficient. Only the surfactant that formed reverse micelles displaced significant oil, so Mechanism 1 and 3 together were sufficient. The results are consistent with the idea that reverse micelles

Table 1
Properties of aqueous surfactant solutions at 2 × CMC.

Surfactant	None	SDS	DTAB	AOT
CMC (mol/L) [30–32]	N/A	8	14	2.25
Hexadecane–aqueous interfacial tension (mN/m)†	51.4	4.8	8.7	4.5
Oil Contact Angle†	126°	133°	24°	detach*

†Measured in this work. Oil contact angle (measured through the oil) at glass-aqueous interface. Images are in Supplementary Material II).
*The oil droplet detached from the glass.

are important: water was transferred through the oil and deposited at the glass interface, thereby displacing oil.

2. Materials and methods

2.1. Materials

Borofloat® 33 glass wafers were obtained from University Wafer; MICROPOSIT™ S1813® photoresist and MICROPOSIT® MF®-319 developer was obtained from Kayaku Advanced Materials, Inc.; buffered oxide etchant (Buffered HF) 6:1, acetone, hexadecane (99%), sodium dodecyl sulfate (SDS, ≥99.0%), dodecyltrimethylammonium bromide (DTAB, ≥98.0%), and sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate (Aerosol OT®, AOT, ≥97.0%).and isopropyl alcohol were obtained from Sigma-Aldrich; Nanostrip® was obtained from KMG Chemicals; Norland optical adhesive 81 was obtained from Norland Product, Inc. Purified water used was generated with a filtration system in the clean room and a Millipore Reference system otherwise.

3. Fabrication of nanoscale channel.

Nanoscale channels of dimensions, 100 nm × 100 μm × 2 mm (H × W × L), with rectangular cross section were fabricated by adhering two Borofloat glass samples after etching a rectangular groove in one of the wafers using the following MEMS process in a class 100 clean room [33]. Photoresist was spin-coated on a 10 cm diameter glass wafer. A photomask (made by Fineline Imaging, Inc) with 100 μm wide lines spaced by 5 mm was placed over the coated wafer and exposed to UV light (385 nm) for 20 s. After the photoresist was developed, the wafer was immersed into buffered oxide etchant (BOE) 6:1 for 4 min to etch with 100 nm deep channels. After etching, the remaining photoresist on the wafer was removed by sonicating sequentially in acetone, isopropyl alcohol, and DI water. The etched wafer and an unetched wafer were then cleaned in Nanostrip. Wafers were then removed from clean room environment and thermally bonded with in a furnace at 540℃ overnight. The bonded wafers were cut into pieces about 2 mm long. Profilometry showed that the channel height was 100 ± 2 nm.

4. Contact angles

The contact angle of hexadecane on Borofloat® glass in water was measured with a First Ten Angstroms tensiometer. A piece of Borofloat glass was placed in a reservoir of water, and then a droplet of hexadecane was deposited at bottom of the glass. Contact angles in surfactant solution were measured after adding the surfactant to the water phase. All experimental measurements reported in this paper were performed at 22 ± 1 °C and at atmospheric pressure.

5. Displacement of oil by water

A nanochannel was placed in a flow cell (See Supplementary Material, Figure S-1), and one side of the nanochannel was sealed by Norland optical adhesive 81 (Norland Product, Inc). All microscopy was performed with a Zeiss Imager M2 microscope. A transmission image was recorded before any liquid was injected into the flow cell to locate of the nanochannel, and all subsequent images were recorded at the same position. The images were recorded in the x–y plane where the channel was 100 μm × 2 mm (Fig. 2). The bulk reservoir was about 200 μm from the microscope field of view to reduce the background fluorescence intensity emitted from the bulk solution. The channel is long and thin, so to enable presentation of high-resolution images of the channel, each image shown in this manuscript is a set of high-resolution images of adjacent areas that were automatically captured and stitched together. In some images (e.g., in Fig. 6B) subtle vertical lines appear at the boundary of the original images.

The flow cell was filled with hexadecane that spontaneously wet the channel. After one hour, hexadecane was removed from the channel with a syringe, and an aqueous solution was injected into the flow cell. All aqueous solutions contained a water-soluble fluorescent dye, 5 μM Rhodamine B, to enable detection of the water phase, and the fluorescence intensity at a given pixel should be proportional to the volume of water at that location. Rhodamine B does not dissolve in hexadecane, so the oil-filled region remained dark during fluorescence imaging. One of three test surfactants was added to the water phase. The displacement of oil by water was viewed in Epifluorescence with a filter set composed by an excitation filter of 545 ± 12.5 nm, a beam splitter of 570 nm and an emission filter of 605 ± 35 nm. The experiment was repeated three times for each surfactant condition.

6. Reverse micelles in hexadecane

A series of 10 mL AOT solutions with different concentration and 5 μM rhodamine B was prepared in 20 mL vials, then 3 mL of hexadecane was layered on top of each solution and equilibrated for 24 h to allow transport of the water into the oil and formation of reverse micelles. Then the hexadecane layer was transferred with a syringe from the vial into 1 cm path-length glass cuvettes to perform spectrofluorometry in a Horiba FlouroMax-4 spectrofluorometer. Since rhodamine B is soluble in water but not in pure hexadecane, the hexadecane phase will fluoresce if there are reverse micelles containing water in the hexadecane phase.

7. Results and discussion

7.1. Thermodynamics of wetting

As described in the introduction, we can determine whether wetting is spontaneous from the measured contact angle and the oil–water interfacial tension. The measured contact angle for hexadecane on glass in water was 126 ± 7, i.e., the glass is hydrophilic. See Supplementary Material II Contact Angle Measurements for photographs. When there is no increase in the area of the oil–water interface, then, from Eq. (3), water should spontaneously displace oil from the channel. Our channel

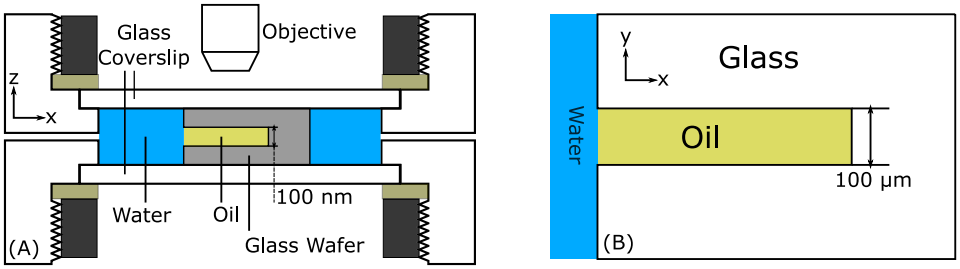

Fig. 2. (A) Schematic of the fabricated channel with a flow cell viewed from the side (Figure S-1 contains a photograph). The channel has a height of 100 nm, is initially filled with oil (yellow color) and its thickness is greatly exaggerated in this schematic for visibility. The bulk oil in the flow cell is then replaced with an aqueous solution (blue). (B) Schematic of the top-down view of the channel. The channel has a width of 100 μm. Schematics are not to scale.

has a uniform cross-section, so thermodynamics predicts displacement. Oil displaced from the channel must go somewhere, and so for predictions for our particular set-up we need to include the energy of the displaced oil. If we assume that the displaced oil forms a spherical droplet in bulk water, then the displacement is still spontaneous (See SM: III. Calculation of Displacement Energy). This is because the channel has a high aspect ratio (100 nm × 100 μm × 2 mm) so the area of the channel is much greater than the area of the droplet. Using the literature value of the interfacial tension of hexadecane–water (55.2 mN/m) [34], the energy of displacement is $\Delta G_D = -1.3 \times 10^{-8}$ J.

7.2. Displacement of oil by water

In this section we describe microscopic measurements of the exchange of oil for aqueous solutions in a nanoscopic channel. Fig. 3A is a transmission optical image of the channel when it contains air. The channel is open to a reservoir to the left and closed to the right, and the 100 nm dimension is into the page. In contrast to the thermodynamic measurements and analysis, when we performed the experiment where we offered water the opportunity to displace oil inside the channel, there was a very limited amount of displacement after 12 h. Fig. 3B shows an epifluorescence image where the water was stained and appears bright. There is a small amount of water to the left of the channel but essentially the channel remains filled with oil (it is dark). A common opinion is that addition of surfactant molecules into the aqueous phase would reduce the oil/water interfacial tension, thus lowering the energy barrier to improve oil recovery, [1,15] and that will be examined in the following section.

7.3. Displacement of oil by aqueous surfactant solution

We repeated the above experiment but with surfactant molecules in the water phase to test its impact on oil displacement. We first measured the hexadecane–aqueous interfacial tensions at 2 × CMC and these values are shown in Table 1. All three surfactant solutions had an interfacial tension in the range 4–9 $mJ{\cdot}m^{-2}$ which was much smaller than the value of 55 $mJ{\cdot}m^{-2}$ for pure water.

Our first surfactant was DTAB, and the results for exchange are shown in Fig. 4: there is again no displacement of oil. Although DTAB decreases the hexadecane–aqueous interfacial tension, it can also dissociate to form DTA^+, which adsorbs at the glass–water interface by ion-exchange [35] and will lower the glass–water interfacial tension, which will favor displacement of oil. But DTABr or DTA^+ may also adsorb to the oil–aqueous interface, decreasing the contact angle which, from Eq. (3) would raise the barrier to displacing oil. Measurement of the hexadecane contact angle in DTABr solution confirmed this: the contact angle decreased to 24° (See Supporting Information, Fig. S3) indicating that surfactant adsorption had lowered the glass–oil interfacial tension by more than the glass–water interfacial tension.

The exchange experiment for SDS solutions is shown in Fig. 5. There is some exchange at the left edge, but the majority of the channel remains dark after 12 h (Fig. 5B), indicating that oil remains in the channel. The contact angle of the oil in SDS solution remains above 90°, and indicates that exchange is thermodynamically spontaneous. The lack of exchange excludes the possibility that (a) lowering the oil–water interfacial tension alone or (b) emulsification of the oil is sufficient to cause displacement of oil by water.

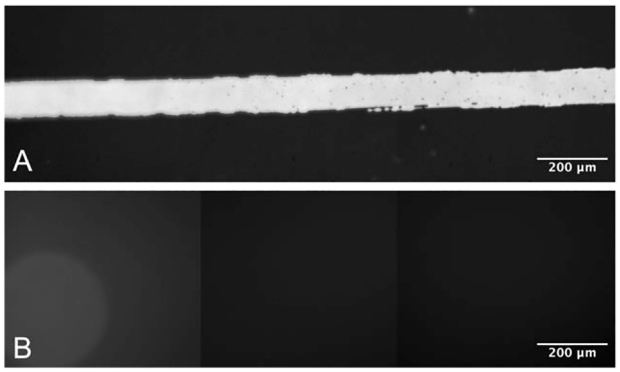

Fig. 4. Light microscopy images of oil displacement by pure water with DTAB. (A) Transmission image of the nanochannel containing air. (B) Epifluorescence image 12 h after adding aqueous 20 mM DTAB + 5 μM Rhodamine B to the reservoir. The absence of fluorescence intensity inside the nanochannel indicates that no oil was displaced by water.

In distinct contrast to the results for water, aqueous DTABr or aqueous SDS, when AOT was present in the water, there was very significant displacement of oil by water (Fig. 6). The majority of the channel became highly fluorescent after 12 h. The high fluorescence intensity suggests that most of the oil originally inside the channel was displaced by water.

We performed image analysis of the photographs to quantify the volume of oil for three repeat measurements. The fraction of displacement was calculated by measuring the emission from a 5 μM Rhodamine B + 20 mM NaCl aqueous solution as a reference to define 100% displacement. NaCl was added to reduce the Debye length of the solution to screen surface electrostatic effects. The results, shown in Fig. 7, reveal that about 60% of the oil was displaced using $AOT_{(aq)}$, while water, $DTAB_{(aq)}$ and $SDS_{(aq)}$ each displace little. Quantitatively, about 22 × as much oil was displaced by the AOT solution compared to water, and a Student's *t*-test showed $p = 0.018$ for the comparison between AOT solution and water.

From the AOT experiment, we conclude that the presence of reverse micelles and a decrease in oil–water interfacial tension was sufficient to allow rapid displacement of oil by water in our system. Further research would be needed to determine whether this is a general phenomenon.

7.4. Evidence for the role of transport of water by reverse micelles

So why does the displacement of oil occur with aqueous AOT and not

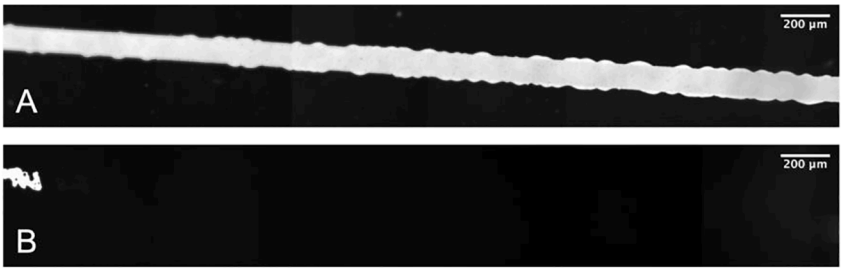

Fig. 3. Light microscopy images of oil displacement by pure water (no surfactant). (A) Transmission image of the nanochannel containing air. The air-filled channel is white, and the glass region is dark. (B) Epifluorescence image 12 h after adding water containing Rhodamine B to the reservoir (on the left). Only a small volume of oil was displaced by water.

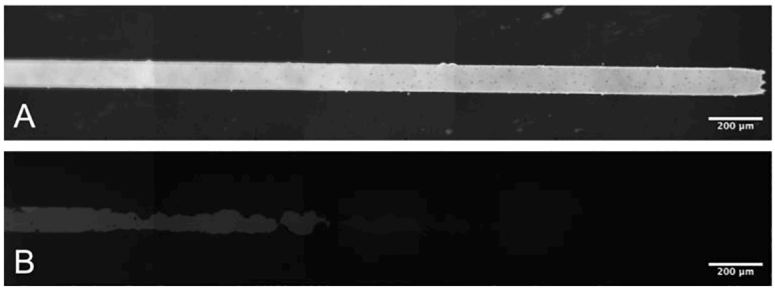

Fig. 5. Light microscopy images of oil displacement by SDS solution (A) Transmission image of the nanochannel containing air. (B) Fluorescence image 12 h after adding 20 mM SDS + 5 μM Rhodamine B. Only a very small displacement of oil is observed with SDS.

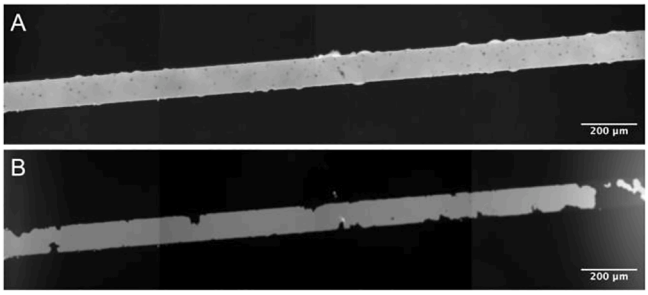

Fig. 6. Microscopy images of the displacement of oil by aqueous solution of AOT. (A) Transmission image of the nanochannel containing air. (B) Fluorescence image 12 h after addition of 5 mM AOT + 5 μM Rhodamine B to the flow cell.

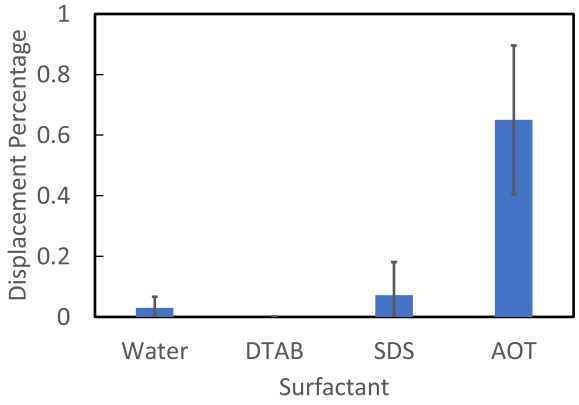

Fig. 7. Displacement percentage of hexadecane by different aqueous solutions. Error bars represent the 95% confidence interval at each condition. About 60% oil displacement was achieved when AOT was present. ANOVA showed an effect of surfactant ($p < 0.001$) and a Student's t-test showed $p = 0.018$ for the comparison between AOT and water.

with the other surfactants? The key feature of AOT, which is a highly branched surfactant, is that it can form reverse micelles in oil. Prior research showed that when the alkane carbon chain is longer than 9 carbon atoms, as is the case here for hexadecane, AOT is mostly distributed in aqueous phase [36], but AOT is known to form reverse micelles [28]. Since reverse micelles are key to our argument, we provide evidence that AOT did form reverse micelles in this in this particular case by testing for a water domain within the hexadecane-rich phase.

Although the water content in reverse micelles within hexadecane is too dilute to measure in the 100 nm thick channel using our microscope, it is routine to measure fluorescence in centimeter-pathway samples in a commercial fluorimeter with 1 cm pathlength [24] we performed the following experiment: 3 mL of hexadecane was placed in contact with 10 mL aqueous solutions containing 5 μM Rhodamine B and each of a series of AOT concentrations. The fluorescence emission from the hexadecane phase was measured in the range 560–600 nm in a fluorimeter. For all concentrations, the fluorescence in AOT was greater than for water (Fig. 8), indicating that the dye has been solubilized in the hexadecane-rich phase, and therefore there is significant water in the hexadecane-rich phase, presumably in reverse micelles. A control experiment using SDS instead of AOT showed a slight reduction in fluorescence. We, therefore, conclude that reverse micelles containing water form within hexadecane in the presence of AOT, but not in SDS, and that there is a significant increase in the water content between 1 and 2.5 mM AOT.

An alternative hypothesis for our displacement experiments is that rather than water displacing the hexadecane, the fluorescence emission that we use as an indicator for the water phase simply arises from water within reverse micelles within the hexadecane-rich phase. To test this hypothesis, we placed hexadecane that had been equilibrated with 5 mM AOT aqueous solution into the flow cell (the exact hexadecane that was used for the data in Fig. 7). Once the hexadecane filled the entire nanochannel, we observed no fluorescence intensity within the nanochannel. This result indicates that the fluorescence emission that we reported in Fig. 6 does not originate from water within reverse micelles; it is from bulk water.

There was much more water in hexadecane equilibrated with 5 mM AOT solutions than when equilibrated with 1 mM AOT solution, so this

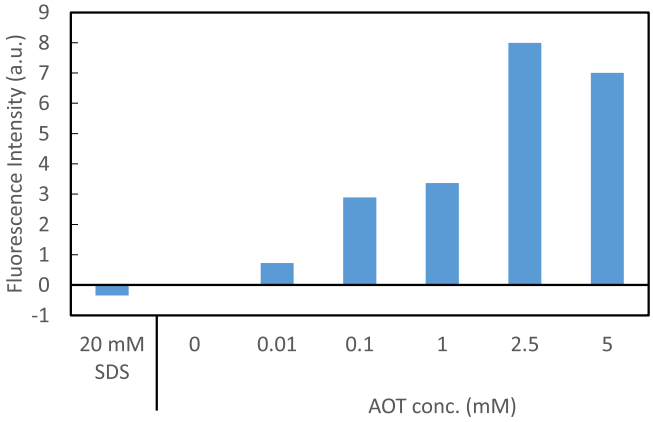

Fig. 8. Spectrofluorometry of Rhodamine B in hexadecane after contact with an aqueous solution of 5 μM Rhodamine B and different AOT concentrations as labelled on the horizontal axis. Fluorescence intensity was the sum of the emission in the range 560–600 nm measured through a 1 cm path length. The excitation wavelength was 525 nm, and the background of the pure water emission was subtracted from each value. The emission of Rhodamine B indicates the presence of a water phase within the hexadecane-rich phase. A large increase in fluorescence was observed when the AOT concentration was above 2.5 mM.

offered the opportunity to test whether the displacement of oil is correlated with the amount of water present in the oil phase. We measured the displacement of oil in the nanochannel 12 h after using a 1 mM AOT solution and then again after an additional 12 h exposure to a 5 mM AOT solution. The result is shown in Fig. 9. For the 1 mM AOT, there is very little displacement of water whereas for the 5 mM AOT a large fraction of water entered the channel. Thus, there is a correlation between the water content within the hexadecane phase and the extent of exchange of water for hexadecane in the channel. This experiment is not completely decisive on its own because the difference in AOT concentration also changes the interfacial tension: we measure the interfacial tension to be 19.6 mN/m at 1 mM AOT and 4.5 mN/m at 5 mM AOT. But our other experiments using SDS showed that interfacial tension is not the primary determinant of displacement of the oil. Thus, we conclude that not only is the transport of water within the hexadecane the requirement for displacement of oil by water in this system, the extent of the displacement depends on the concentration of water in the hexadecane phase.

Our final evidence for the importance of reverse micelles in the oil phase for delivering water into the channel is that the water domain is discontinuous, as shown in Fig. 9 and with a time series in Fig. 10. In Fig. 10, the water phase to the right of the image grows in size without being in contact with the bulk water phase that is to the left of the image. There are in fact two breaks in the water phase (Fig. 10) across which water was transported. From our video, we cannot rule out the possibility of a very thin (nm) connecting channel, but we consider this very unlikely. All our evidence is consistent with this transport though oil being the critical factor is enabling displacement of oil by water in a hydrophilic channel, and the transport being aided by reverse micelles.

Our focus in this paper has been on the role of reverse micelles to deliver water into a thermodynamically preferred state in a nanochannel. We also note that our results show that the resulting water-rich phase sometimes does not have a minimized surface area (e.g., Fig. 10). This suggests that there is considerable surfactant at the interface to lower the energy. Thus, the reverse micelles help by transporting surfactant as well as water.

8. Conclusion

We studied spontaneous displacement of oil by water in dead-end hydrophilic-glass nanochannels with no applied pressure. Although water is thermodynamically favored to displace oil in the nanochannel, the displacement was not observed after 12 h, which indicates the presence of an activation barrier. With the assistance of Aerosol OT, a surfactant that can form reverse micelles in oil phases, water can displace oil in a nanochannel in 12 h. Reverse micelles play the role of a carrier to deliver water into the channel. The delivered water can adsorb at the solid, and continued transport of water can spontaneously grow a bulk water phase, thereby displacing oil. Other surfactants such as SDS and DTAB, which do reduce the oil–water interfacial tension but do not form reverse micelles, do not result in substantial displacement of oil by water. Thus, we conclude that reducing the oil–water interfacial tension is not sufficient for water to displace oil in the nanochannel. The results from SDS and DTAB also suggest that emulsification of oil into micelles in the water-rich phase does not enable rapid exchange. In summary, oil displacement in our experiments is not driven by a reduction in surface tension or by emulsification of oil in water. It is driven by transport of water through the oil. Reverse micelles provide the means of transportation to achieve the thermodynamically preferred state. The surfactant that is delivered in the reverse micelles should also help by decreasing the oil–water interfacial tension for the water-rich phase that is delivered into the channel. Our evidence for the role of transportation via reverse micelles includes images that show that the water phase is discontinuous and a correlation between the amount of water phase within the oil and the amount of water that is displaced. It may be advantageous for future work on enhanced oil recovery to deliberately examine surfactants that form reverse (water in oil) micelles, for example by selecting surfactants with a high packing parameter.

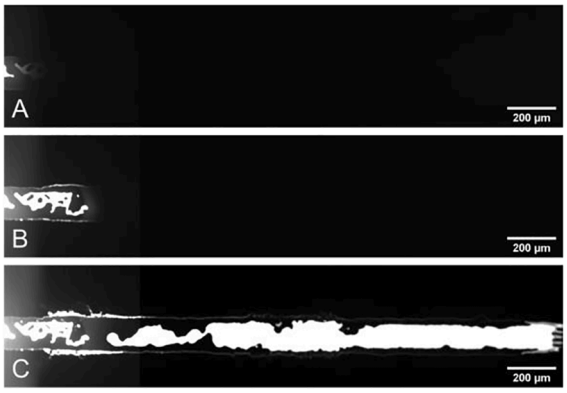

Fig. 10. Time series of discontinuous displacement in a nanoscale channel. (A) 30 min, (B) 150 min, (C) 12 h.

9. Author statement

Zechen Zhang did all the experiments, William Ducker obtained the funding. All other aspects were done by both authors.

Fig. 9. (A) Fluorescence image after 12 h in contact with 1 mM AOT + 5 μM Rhodamine B. (B) Fluorescence image after 12 h displacement with 5 mM AOT + 5 μM Rhodamine B. When there is much more water in the hexadecane phase (5 mM AOT vs 1 mM AOT), then more hexadecane is exchanged for water.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.128248.

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