

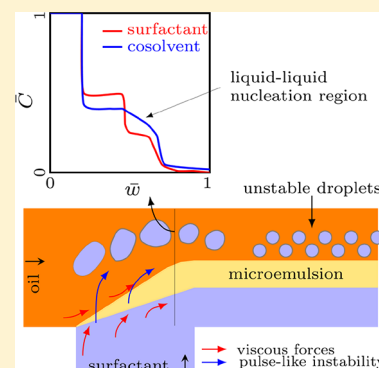
# Spontaneous and Flow-Driven Interfacial Phase Change: Dynamics of Microemulsion Formation at the Pore Scale

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## Supporting Information

**ABSTRACT:** The dynamic behavior of microemulsion-forming water–oil–amphiphiles mixtures is investigated in a 2.5D micromodel. The equilibrium phase behavior of such mixtures is well-understood in terms of macroscopic phase transitions. However, what is less understood and where experimental data are lacking is the coupling between the phase change and the bulk flow. Herein, we study the flow of an aqueous surfactant solution–oil mixture in porous media and analyze the dependence of phase formation and spatial phase configurations on the bulk flow rate. We find that a microemulsion forms instantaneously as a boundary layer at the initial surface of contact between the surfactant solution and oil. The boundary layer is temporally continuous because of the imposed convection. In addition to the imposed flow, we observe spontaneous pulsed Marangoni flows that drag the microemulsion and surfactant solution into the oil stream, forming large (macro)emulsion droplets. The formation of the microemulsion phase at the interface distinguishes the situation from that of the more common Marangoni flow with only two phases present. Additionally, an emulsion forms via liquid–liquid nucleation or the Ouzo effect (i.e., spontaneous emulsification) at low flow rates and via mechanical mixing at high flow rates. With regard to multiphase flow, contrary to the common belief that the microemulsion is the wetting liquid, we observe that the minor oil phase wets the solid surface. We show that a layered flow pattern is formed because of the out-of-equilibrium phase behavior at high volumetric flow rates (order of 2 m/day) where advection is much faster than the diffusive interfacial mass transfer and transverse mixing, which promote equilibrium behavior. At lower flow rates (order of 30 cm/day), however, the dynamic and equilibrium phase behaviors are well-correlated. These results clearly show that the phase change influences the macroscale flow behavior.



## INTRODUCTION

Microemulsions are macroscopically homogeneous mixtures of water, oil, and amphiphile(s), which show a rich phase behavior depending on the mixture composition<sup>1</sup> as well as the temperature<sup>2</sup> and salinity.<sup>3,4</sup> In equilibrium, the phase behavior is well-understood in terms of macroscopic phase transition (e.g., *Type-I* → *Type-III* → *Type-II environment*) and internal microstructures.<sup>5–7</sup> In comparison, the behavior in non-equilibrium situations is much less explored. For instance, it is not clear whether the water–oil–amphiphile(s) mixture forms a microemulsion or an emulsion or both during the flow. Furthermore, the correlation of dynamic and static phase behaviors (equilibrium vs nonequilibrium) and its dependence on the flow is unknown. The purpose of this study is to answer these questions and investigate the dynamics of phase change with the flow in porous media when interfacial tension (IFT) is ultralow.

Phase change in porous media is a broad subject and encompasses the gas, liquid, or solid phases occupying the pore space.<sup>8</sup> Here, “phase change” means the formation of microemulsion, that is, a thermodynamically stable phase, when an aqueous surfactant solution and oil come in contact. Such a phase change is believed to occur in enhanced oil recovery (EOR) processes where an aqueous surfactant

solution is injected into subsurface porous rocks to lower the IFT and mobilize the capillary-trapped oil.<sup>9,10</sup> Near the advancing displacement front in the porous media, the surfactant solution would solubilize a portion of the oil to form a surfactant-rich microemulsion that would coflow with the excess oil and the surfactant-depleted water.<sup>11,12</sup> In other words, the mixture of water–oil–surfactant would be in *Type-III* conditions and would separate to three phases, including a surfactant-rich microemulsion. Because the viscosity of the microemulsion differs from those of water and oil,<sup>13</sup> the resulting three-phase flow and surfactant transport are coupled. However, the coupling of the mass transfer (by diffusion and film instabilities), phase change, convection, and mechanical mixing in porous media have never been clearly demonstrated before.

Micromodels are particularly useful laboratory tools for direct visualization and quantitative description of pore-scale mechanisms controlling the flow and transport phenomena in subsurface porous rocks with micrometer pores and throats. As such, microfluidics have been used to study the flow dynamics

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and transport properties in porous media that may involve single phase flow of Newtonian<sup>14</sup> and non-Newtonian fluids,<sup>15</sup> multiphase flow,<sup>16–20</sup> droplet formation/coalescence,<sup>21–25</sup> and physicochemical interactions at the fluid–matrix interface.<sup>26–29</sup> Despite this, the potential of microfluidics to study the dynamical behavior of water–oil–amphiphile(s) mixtures that form microemulsions is relatively unexplored. Unsal et al.<sup>30</sup> coinjected *n*-decane and an aqueous solution of olefin sulfonate surfactant in a *T*-junction capillary geometry to compare the equilibrium and dynamic phase behaviors of the mixture when the phase environment is *Type-I–III–II*. The authors observed that (i) the microemulsion was formed during the flow on timescales several orders of magnitude faster than the equilibration times (seconds vs hours to days) and (ii) the dynamic phase behavior correlated well with the static one; nevertheless, the nonequilibrium features of the flow arising from hydrodynamic instabilities remained throughout the experiments. Xu et al.<sup>31</sup> used a micromodel to study the displacement of *n*-decane by a surfactant solution {*Type-III* conditions at an interstitial velocity of  $2.43 \times 10^{-5}$  m/s [6.9 feet per day (ft/d)]}. The authors observed (i) a clear front between the invading solution and the displaced oil, suggesting a lag in emulsification compared to the flow, (ii) trapping of oil as the residual wetting phase, upstream of the invading front despite the ultralow IFTs, and (iii) solubilization of the trapped oil by the surfactant solution to form the microemulsion that coflowed with the surfactant solution.

These findings demonstrate a clear link between the phase behavior and flow, yet they raise further questions as to how the phase change and emulsification relate to the flow patterns. To examine this relation, we studied the phase behavior and flow of a microemulsion-forming mixture of an aqueous surfactant solution and oil at the pore scale using a micromodel. The mixture was selected based on an extensive phase behavior study reported elsewhere.<sup>32</sup> The flow rate and the mixture ratio were varied to investigate the mechanisms of microemulsion formation and the equilibrium and nonequilibrium multiphase flow. The multiphase flow was investigated in a micromodel that is a 2.5D representation of subsurface porous rocks with micrometer pores and throats. We used a novel etching method to etch throats (3  $\mu$ m depth) less deeply than the pores (>20  $\mu$ m depth), thus creating pores and throats with a nonuniform depth in both lateral and longitudinal directions. The resulting porous medium is an improved representation of the rocks' pore structure and is more realistic with regard to the dynamics of flow and transport. Because with micromodels, the fluid topology is explicitly resolved at the pore scale, the wettability state at ultralow IFT conditions was investigated as well.

## METHODS

**Materials.** Anionic surfactants, tridecyl alcohol propoxy sulfate (TDA; C<sub>13</sub>-13PO-SO<sub>4</sub>) and internal olefin sulfonate (IOS; C<sub>20–24</sub>IOS), were obtained from Stepan Chemical Company. Both surfactants are polydisperse commercial blends. Phenol-2EO was provided by Harcros Chemicals. Sodium chloride with 99.9% purity was purchased from Fisher Scientific. Deionized water was obtained from a Millipore Direct-Q 5 system, with a minimal resistivity of 18.2 M $\Omega$ ·cm. A light crude oil (density = 0.86 g/cm<sup>3</sup>, molecular weight = 263 g/mol, and viscosity = 13.5 mPa·s) filtered through a 0.45  $\mu$ m filter paper was used.

**Determination of the Phase Diagram.** To determine the phase diagrams, desired amounts of water, surfactant, and cosolvent were weighed in glass ampoules and thoroughly mixed using a vortex centrifuge to attain homogeneity. Oil was then added, and ampoules

were sealed. Samples were then gently mixed and incubated at 24 °C. The surfactant mixture contained TDA and IOS with a fixed mass ratio of 2.75:1. The phase boundaries were determined with increasing brine salinity. From the equilibrated system, the number and appearance of the phases were determined visually by inspection in scattered and transmitted light. The overall composition of the mixtures are given by the volume fraction of oil in the water–oil mixture

$$\alpha = \frac{V_o}{V_{H_2O} + V_o} \quad (1)$$

and the mass fraction of the surfactants and cosolvent

$$\beta = \frac{m_{TDA} + m_{IOS}}{m_{H_2O} + m_{TDA} + m_{IOS} + m_c} \quad (2)$$

$$\delta = \frac{m_c}{m_{H_2O} + m_{TDA} + m_{IOS} + m_c} \quad (3)$$

where *m* and *V* denote the mass and volume, respectively, and subscript c stands for the cosolvent.

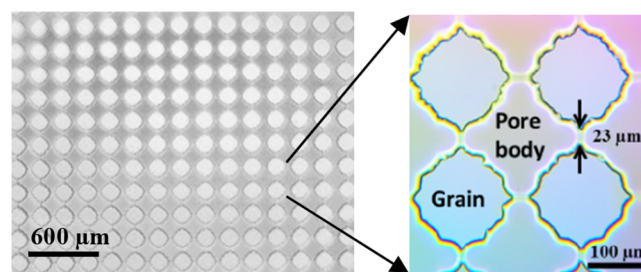
The solubilization ratios, defined as the oil and brine volume divided by the surfactant volume in the microemulsion phase, are given by

$$\sigma_o = \frac{\nu_o \rho_s}{\beta(1 - \alpha)V\rho_{H_2O}} \quad (4)$$

$$\sigma_w = \frac{\nu_w \rho_s}{\beta(1 - \alpha)V\rho_{H_2O}} \quad (5)$$

*V* stands for the total volume of oil and water mixture;  $\rho_{H_2O}$  and  $\rho_s$  denote water and surfactant densities, respectively. Equations 4 and 5 assume a negligible surfactant concentration in excess phases(s). The oil fraction in the microemulsion,  $\phi$ , is calculated by  $\phi \cong \sigma_o/(\sigma_o + \sigma_w)$ . The balanced microemulsion is defined by equal solubilization of oil and water.

**Micromodel and Injection Scheme.** The silica glass micromodel (Figures 1 and S1) was fabricated using a novel approach that allows



**Figure 1.** 2.5D micromodel with a shallower throat, obtained by isotropic hydrofluoric etching.

for creating controlled 3D features.<sup>31</sup> This method applies the isotropic hydrofluoric etching to two neighboring “pores” in the 2D blueprint, which are close enough such that the maximum horizontal etching distance at the top is larger than half of the minimum distance between two designed “pore edges”. This creates a throat that is not only horizontally narrower than the pore body but also vertically shallower than the pore body. The variable depth allowed for retaining the pore and grain connectivity throughout the porous media. Table 1 summarizes the properties of the 2.5D micromodel. The micromodel was set horizontally and first saturated by the equilibrium single-phase microemulsion—which appeared light-yellow in color under the microscope—using a syringe pump (Harvard PHD 22/2000). It was also confirmed that the microemulsion remained single phase (i.e., no phase separation) during and 24 h after the flow. This enabled us to elicit the genuine features of the multiphase flow during the

Table 1. Micromodel Properties

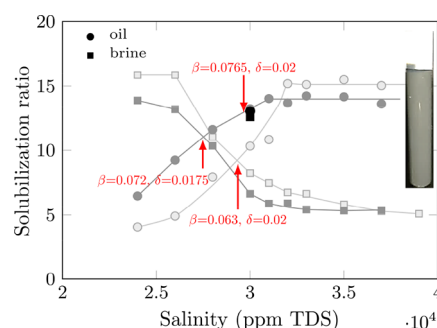
|                                |       |
|--------------------------------|-------|
| length, cm                     | 2.4   |
| width, cm                      | 1.5   |
| porosity                       | 0.565 |
| permeability, mD               | 1026  |
| pore body width, $\mu\text{m}$ | 170   |
| pore body depth, $\mu\text{m}$ | 20.3  |
| throat width, $\mu\text{m}$    | 23    |
| throat depth, $\mu\text{m}$    | 3.2   |

subsequent coinjection of the surfactant solution and oil. At each coinjection test, a minimum of 1 pore volume was injected before making the observations. The injection flow rates expressed as the interstitial velocity (i.e., Darcy velocity divided by the void fraction of porous media) were selected to be around  $\sim 1$  ft/d or 30.48 cm/day, typical of flow and displacements in EOR and groundwater processes.<sup>33–35</sup> At such flow rates, the residence time of the surfactant in porous media is empirically determined to be long enough that the *local equilibrium* assumption is applicable<sup>36–38</sup> and the dispersive mixing transverse to the flow direction is comparable to molecular diffusion.<sup>39,40</sup> *Local equilibrium* implies that the microemulsion forms during the flow and is in equilibrium with excess phases similar to the static conditions. The upper limit of the injection rate was assigned to conditions where convection dominates dynamics, that is, when phase types and flow patterns are relatively unchanged throughout the micromodel. The flow is from the left to the right in all figures (i.e., injector is on the left).

## RESULTS AND DISCUSSION

**Salinity Scans.** Salinity scans were performed at a constant overall composition to determine the evolution of the microemulsion phase type by salinity. Establishing a Winsor-type phase behavior<sup>41–44</sup> is the main purpose here. As such, for anionic surfactants, one would observe oil-in-water (O/W) microemulsions at low salinities, three-phase system at higher salinities that include a middle phase microemulsion in equilibrium with excess water and oil, and water-in-oil (W/O) microemulsions at even higher salinities. In *Type-I* (respectively, *Type-II*) environment, the surfactant bears a stronger affinity for the water (respectively, for oil) phase, whereas in the *Type-III* region, it has a similar affinity for oil and water. With Winsor-type behavior, one can determine the optimum formulation, which is characterized by the (i) minimum interfacial tension between the microemulsion and excess phases, (ii) high solubilization of both water and oil in the microemulsion phase, (iii) balanced affinity for oil and water, and (iv) bicontinuous microstructure.<sup>3,45–47</sup> The optimum formulation is typically used in EOR processes,<sup>10,48</sup> as used here.

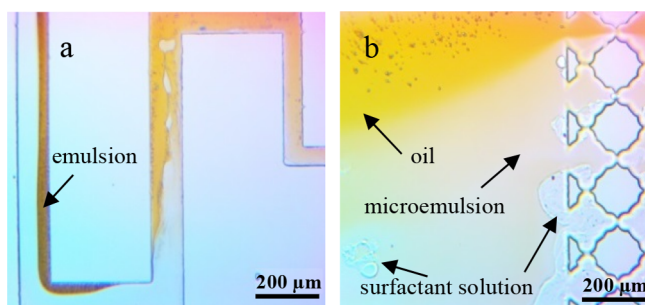
On the basis of the results in Figure 2 and those in ref 32, the “static” (i.e., pipette) composition for the flow study is selected with  $\alpha = 0.5$ ,  $\beta = 0.0765$ ,  $\delta = 0.02$ , and 30 500 ppm NaCl salinity. At equilibrium, the mixture forms a bicontinuous microemulsion close to the invariant point of a pseudoternary diagram in the *Type-III* environment.<sup>32</sup> As we showed previously,<sup>32</sup> the  $\beta/\delta$  ratio controls the composition, volume, and viscosity of the bicontinuous microemulsion. Unlike in pipettes with a constant overall composition, the  $\beta/\delta$  ratio and hence the microemulsion properties may vary under dynamic flow conditions. To evaluate the possible  $\beta/\delta$  ratios that may be observed during the flow, salinity scans were conducted for three  $\beta/\delta$  ratios (Figure 2). These include a case where the “dynamic”  $\beta/\delta$  ( $=3.15$ ) ratio is smaller than the static  $\beta/\delta$  ( $=3.83$ ) ratio (e.g., surfactant adsorption in the porous media)



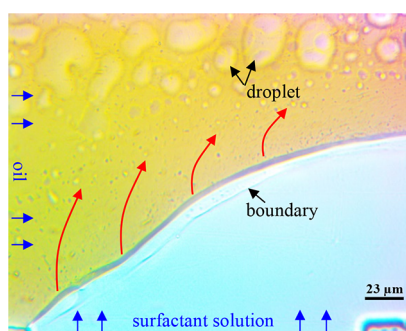
**Figure 2.** Salinity scans at constant overall compositions of the surfactant,  $\beta$ , and cosolvent,  $\delta$ , for three  $\beta/\delta$  ratios. The  $\beta/\delta$  ratio is varied to mimic the possible  $\beta/\delta$  ratios that may be observed during the flow. The oil content is fixed at  $\alpha = 0.5$ , the surfactant is a mixture of  $\text{C}_{13}\text{-13PO-SO}_4$  and  $\text{C}_{20}\text{-24IOS}$  with the mass ratio of 2.75, the cosolvent is phenol-2EO, and the salt is NaCl. The arrows show the balanced microemulsion for each formulation. The inset is a picture of the selected microemulsion in a test tube. The microemulsion viscosity is 52.8 mPa·s.

and a case where the “dynamic”  $\beta/\delta$  ( $=4.11$ ) ratio is greater than the static  $\beta/\delta$  (e.g., cosolvent partitions to abundant neighboring oil or when  $\alpha > 0.5$ ). When the dynamic  $\beta/\delta$  is greater than the static one, we observed that the solubilization efficiency reduces, as evident by the reduction in the optimum solubilization ratio from 13 to 9 (Figure 2). This leads to lower microemulsion saturation or equivalently higher oil–water saturations in porous media. In the case where the dynamic  $\beta/\delta$  ratio is greater than the static  $\beta/\delta$ , the solubilization efficiency remains essentially unchanged (Figure 2), but the microemulsion that forms in situ will have a higher oil content and hence a higher viscosity<sup>49</sup> compared to the equilibrium microemulsion. The IFT between the microemulsion and the excess water–oil at optimum salinity is on the order of 0.001  $\text{mN}\cdot\text{m}^{-1}$  using the Huh equation.<sup>50</sup> The viscosity of the middle phase microemulsion is Newtonian and 52.8 mPa·s (Figure S2 in the Supporting Information).

**Mechanism of Microemulsion Formation.** Oil and the selected surfactant solution ( $\beta = 0.0765$  and  $\delta = 0.02$ ) were coinjected at a ratio of  $\alpha = 0.5$  and a total injection rate of 0.8  $\mu\text{L}/\text{min}$  (0.366 ft/d) to investigate the microemulsion formation in porous media. However, it became clear that the microemulsion formed along with a W/O emulsion in the conduits (before reaching the porous medium) rather than in the porous medium. Figure 3 shows a snapshot of the multiphase flow in the conduit (100  $\mu\text{m}$ ) and the chamber before reaching the micromodel. The notable features are as follows: (i) both microemulsion and emulsion form in the conduit; (ii) the flow is unstable partly due to the viscous instabilities at a low IFT<sup>51–53</sup> and partly due to the syringe-pump-induced fluctuation in microfluidic experiments;<sup>54</sup> and (iii) the flow could be stratified in the micromodel because of the parallel phase flow, as seen in the chamber. Despite these interesting features, Figure 3 does not provide unambiguous evidence for how the microemulsion is formed. Figure 4 provides a detailed view of the interface where the streams of oil and the surfactant solution first come in contact. Microemulsion formation as a boundary layer is evident at the contact surface between the surfactant solution and oil (“boundary” in Figure 4). Formation of a middle phase microemulsion upon contact between the aqueous and oil phases is expected based on the equilibrium phase behavior



**Figure 3.** Microemulsion and emulsion both form in the conduits and chamber before reaching the micromodel. (a) The injected oil and surfactant solution flow in the flow-distributor conduit. The surfactant solution is seen as a clear solution, oil is canary-yellow, emulsion is dark (fire)-yellow, and microemulsion is light-yellow. (b) Microemulsion and oil-emulsion separate in the flow chamber before reaching the micromodel. The flow is from the left to the right.



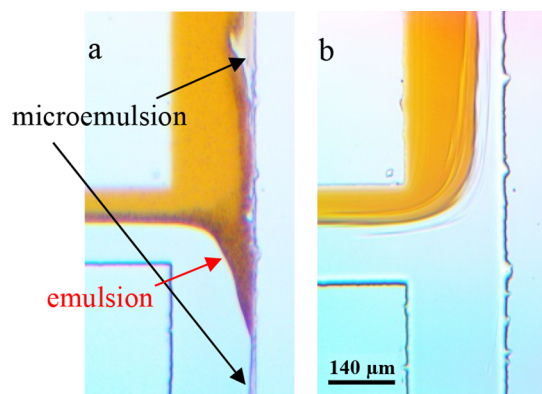
**Figure 4.** Interface where the oil and surfactant solution first come in contact in the conduit. Surfactant solution and oil feed from the bottom and left of the picture (blue arrows), respectively;  $\alpha = 0.5$  and  $v_t = 0.37$  ft/d. Microemulsion (light-colored "boundary" layer) forms initially via diffusion-driven nucleation and film growth at the surface contact of the surfactant solution and oil and later via diffusion at the interface of the emulsion droplets. The nonwetting nature of the microemulsion film at the oil–water interface causes dynamic IFT fluctuations and pulsed Marangoni flows. Red arrows schematically show the magnitude and direction of the pulsed flux. A portion of dragged water forms the microemulsion, whereas the remaining forms a W/O (macro)emulsion (marked by "droplet") in the oil stream, as seen near the north wall. At low flow rates, these giant drops spontaneously emulsify via the *Ouzo* effect.

results, and it has been observed in the absence of a flow in other systems.<sup>55–57</sup> Whether or not convection exists, the mechanism of intermediate phase formation is diffusion-driven nucleation and film growth in the immediate vicinity of the contact surface,<sup>55,58</sup> and its rate of formation is high on initial contact owing to large concentration gradients and surface pressure,  $\pi = \gamma_0 - \gamma$  ( $\gamma_0$  being the bare oil–brine interfacial tension). However, in the absence of convection, the rate decreases considerably over time as the concentration gradients become smaller with diffusion. When the flow is imposed, the rate and extent of formation of the middle phase microemulsion can greatly increase because the flow can produce higher concentration gradients near the interface than those present after the initial short period of rapid diffusion in the absence of a flow. This increased rate can be deduced from the instantaneous and temporally continuous formation of microemulsion as the boundary layer in Figure 4.

In addition to the imposed flow of the coinjected surfactant solution and oil, we observe spontaneously generated pulselike

flows that drag the microemulsion and surfactant solution drops into the oil stream. This rapid pulselike drag is visible under the microscope (see Figure S3 and Movie S1 in the Supporting Information), and its magnitude and direction are qualitatively shown by red arrows in Figure 4. The spontaneous pulsing flow can be explained as follows. For most surfactant systems near optimal conditions, the middle phase microemulsion does not wet (spread at) the interface but instead rests on that interface as a thin lens (nm scale).<sup>59</sup> This means that  $\gamma_{ow} < \gamma_{om} + \gamma_{mw}$ ,  $\gamma_{ow}$  being the surface tension between oil and water,  $\gamma_{om}$  being the surface tension between oil and the microemulsion, and  $\gamma_{mw}$  being the surface tension between the microemulsion and water.<sup>59–61</sup> Let us say, a perturbation, say an eddy of fresh aqueous solution from the bulk phase to the interface, causes the uniform microemulsion thin film (nm scale) to become slightly thicker at a particular location. This creates a gradient in the disjoining pressure (on the order of  $0.01 \text{ mN}\cdot\text{m}^{-1}$ ),<sup>62–65</sup> which causes a lateral microemulsion flow (i.e., within the film) toward that location, making the film there even thicker. Because the film tension for a nonwetting thin film increases with the film thickness,<sup>66</sup> the local interfacial tension increases at the site of initial perturbation, thereby generating a Marangoni flow from the surrounding area. The formation of the microemulsion phase at the interface distinguishes the situation from that of a more common Marangoni flow with only two phases present.<sup>67,68</sup> Because the spontaneous flow toward the microemulsion film (caused by the disjoining pressure and the size-dependent component of the surface tension) drags the oil along, continuity requires that the flow of the surfactant solution and microemulsion directed toward the bulk oil phase must also arise at the location. Figure 4 shows that such a flow toward the bulk oil phase is strong enough to entrain and carry along the aqueous solution as well; indicating that the volume entrained could well be greater than that of the microemulsion formed at the initial contact surface. As drops of the dragged surfactant solution travel through the oil phase, W/O micro- and macroemulsion drops form by diffusion at the interface. The droplets are most visible near the top of Figure 4. The relatively large size of the water drops suggests that smaller drops coalesce readily. These droplets form the emulsion, seen in Figure 3A, via the *liquid–liquid nucleation or the Ouzo effect*<sup>69,70</sup> (see the next section for more details). In summary, the microemulsion formation can be described as nucleation of the microemulsion at discrete locations on the surface of contact between the surfactant solution and oil. Owing to the nonwetting nature of the new phase, local interfacial tension increases, generating a Marangoni flow toward the microemulsion droplet, which in turn causes a flow toward the bulk oil phase. The formation of the microemulsion phase at the interface distinguishes the situation from that of a more common Marangoni flow with only two phases present.

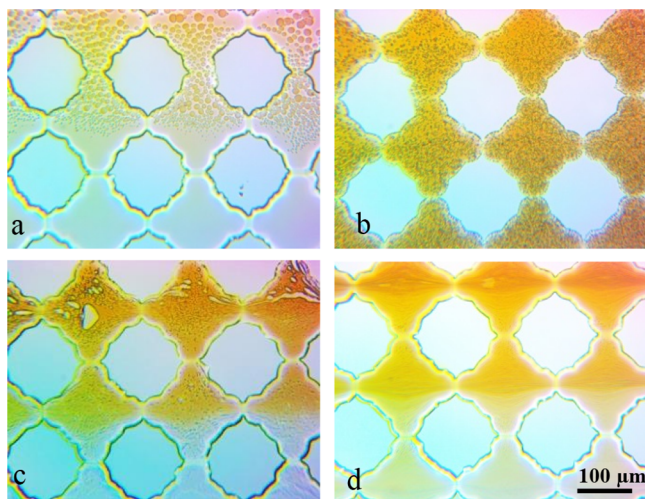
To further emphasize the role of spontaneous pulsed flow rather than convective or mechanical mixing in the formation of the (macro)emulsion droplets, the interstitial velocity was increased from  $1.29 \times 10^{-6} \text{ m/s}$  (0.366 ft/d) to  $3.23 \times 10^{-6} \text{ m/s}$  (9.15 ft/d). Dark emulsion and light-yellow microemulsion can be seen when  $v_t = 0.366 \text{ ft/d}$  (Figure 5A), but the dark emulsion disappears when  $v_t = 9.15 \text{ ft/d}$  (Figure 5B). In addition, no pulselike interfacial mixing was observed at a high convection rate. The lack of a dark emulsion and the pulselike flow suggest that the spontaneous pulsed flow and the occurrence of giant droplets (that eventually form the dark



**Figure 5.** High flow rate suppresses the rapid, pulselike interfacial mixing caused by formation of the microemulsion and responsible for subsequent spontaneous emulsification. Dark emulsion and light-yellow microemulsion (visible at the right wall) are visible at (a)  $v_t = 0.366$  ft/d, but the emulsion disappears at (b)  $v_t = 9.15$  ft/d while the microemulsion is barely visible. The surfactant solution is white and oil is canary-yellow.  $\alpha = 0.5$  in both cases. The incoming flow is from the left.

emulsion) are linked and that the high velocity suppressed both. Regardless of the flow rate, however, a boundary layer microemulsion formed instantaneously when the surfactant solution and oil came into contact, similar to the observation in Unsal et al.<sup>30</sup> The other less-frequent mechanism of microemulsion formation is the occasional bursting of giant O/W droplets in the surfactant-rich stream at low flow rates, similar to the rupture of giant bilayers in the formation of middle phase microemulsions observed elsewhere.<sup>71</sup>

**Emulsification, Emulsion Morphology, and Residence Time.** The previous section shows that an emulsion forms and flows next to the microemulsion as a result of microemulsion formation and small-scale IFT fluctuations at low flow rates. This section aims to establish the mechanism of emulsion formation (mechanical/convective mixing vs spontaneous emulsification). Figure 6 shows the emulsion morphology when the flow rate is varied. The droplet radii decreased from



**Figure 6.** Mixing energy determines the morphology of emulsion, such that the higher the flow rate the smaller is the droplet radii. The total flow rate is (a)  $v_t = 0.183$  ft/d, (b)  $v_t = 0.366$  ft/d, (c)  $v_t = 9.15$  ft/d, and (d)  $v_t = 41.19$  ft/d.  $\alpha = 0.5$  in all cases.

$\sim 5.8$  to  $\sim 3.2$   $\mu\text{m}$  on increasing the flow rate from 0.183 to 0.366 ft/d. Also, the emulsion volume increased, evident by the increased number of pores occupied by the emulsion (transverse to the flow direction) (as seen in Figure 6B compared to that in Figure 6A at the same spatial location). Further increase in the flow rate,  $v_t = 9.15$  ft/d, makes the droplet radii smaller, but (i) increases the number of emulsion-occupied pores transverse to the flow and (ii) results in incomplete mixing and liquid–liquid slug flow<sup>72,73</sup> as small clusters of the surfactant solution in the emulsion are visible in Figure 6C. At even higher rates, for example,  $v_t = 41.19$  ft/d, the emulsion-occupying pores are smaller (see Figure S4), as is the droplet radii. The reduction in the droplet radius with increased flow rate can be quantified using the droplet breakup dynamics in laminar flow.<sup>74</sup> To break up a droplet of radius  $r$  in a laminar flow field equals  $\eta_c G$ , where  $G$  is the velocity gradient and  $\eta_c$  is the viscosity of the continuous phase. This stress is counteracted by the Laplace pressure, and the ratio gives the Weber number

$$We = \frac{\eta_c Gr}{\gamma} \quad (6)$$

If  $We$  exceeds a critical value  $We_{cr}$  (of the order of 1), the drop bursts. Given the  $\gamma$  and  $G$  values, the breakup of single droplets in the simple shear flow (velocity gradient in the direction normal to that of the flow) at  $We_{cr}$  can be used to obtain an expected droplet radius here.  $G$  in the micromodel porous media can be taken equal to the average shear rate,  $\dot{\gamma}$ , across the throat

$$\dot{\gamma} = \frac{8\bar{c}v_t}{D_h} \quad (7)$$

where  $D_h = 2wd/(w + d)$  is the hydraulic diameter of the pore throat with a width of  $w$  and a depth of  $d$ . Equation 7 assumes a no-flow boundary on the grain surface and calculates the average shear rate at  $\bar{c} = r/R = 0.55$  ( $r/R$  being the distance from the center of the conduit with an equivalent radius  $R$ ) in analogy to the laminar flow in circular pipes. One can also calculate the hydraulic radius of the pore space by  $w\phi/6(1 - \phi)$  because the grains and pores have the same width. The resulting shear rates will be lower than those by eq 7 and are not discussed further. Another method to calculate the expected droplet size in our systems is to use the equivalent shear rate,  $\dot{\gamma}$ , in porous media

$$\dot{\gamma} = \frac{4cv_t}{\sqrt{8k\phi}} \quad (8)$$

where  $k$  and  $\phi$ , respectively, denote the porous media permeability and void fraction (given in Table 1). The coefficient  $c$  is unknown, ranging from 1 for single phase and 4 for multiphase flow,<sup>75–77</sup> and is taken as 1.5 here.

Using  $We_{cr} = 1$ ,  $\eta_c = 13.5$  mPa·s, and  $\gamma = 0.001$  mN·m<sup>−1</sup>, predictions from eq 6 and either eq 7 or 8 for the droplet radius are compared with the experimental data, as shown in Table 2. The calculated droplet radius (eqs 6 and 8) scales as  $r \propto 16/v_t$ , whereas the observed radius scales as  $r \propto \sqrt{16/v_t}$ . Data and predictions agree well at high flow rates, whereas the observed emulsion droplets are an order of magnitude smaller than the prediction at low velocities. The agreement of the calculated and observed droplet radius at a high flow rate confirms that

**Table 2. Comparison of Data and Prediction for Emulsion Droplet Radii as Flow Rate Changes<sup>a</sup>**

| $v_t$<br>(ft/d) | $\dot{\gamma}$ (1/s) | experimental<br>droplet radius<br>( $\mu\text{m}$ ) | droplet radius<br>from eqs 6 and<br>7 ( $\mu\text{m}$ ) | droplet radius<br>from eqs 6 and<br>8 ( $\mu\text{m}$ ) |
|-----------------|----------------------|-----------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
| 0.183           | 0.83                 | 5.8                                                 | 155.7                                                   | 89.0                                                    |
| 0.366           | 1.66                 | 3.2                                                 | 77.8                                                    | 44.5                                                    |
| 9.15            | 41.6                 | 1.3                                                 | 3.1                                                     | 1.8                                                     |
| 41.19           | 187.3                | <1                                                  | 0.7                                                     | 0.4                                                     |

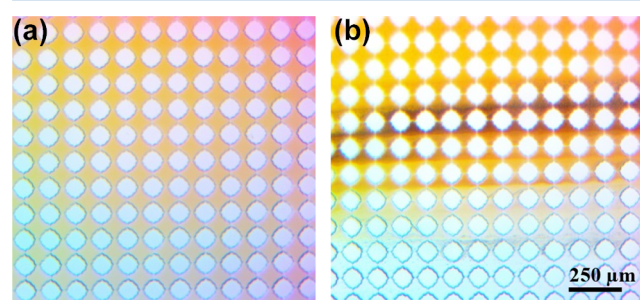
<sup>a</sup>Data and prediction agree at high flow rates, whereas the observed radii are an order of magnitude smaller than the prediction at low velocities.

the mechanical or convective mixing (i.e., droplet breakup by stress due to a velocity gradient) is the primary mechanism for emulsification at such high rates. More importantly, the smaller observed droplet radii at low flow rates support the hypothesis, presented above, that the emulsification of the giant droplets in Figure 4 occurs without having to apply a large external thermal or mechanical energy source. In other words, the giant drops spontaneously emulsify in a manner similar to the liquid–liquid nucleation process or the *Ouzo* effect<sup>69</sup> as follows. The water-immiscible oil flows over the aqueous phase and microemulsion droplets, which contains the cosolvent and surfactant. Droplets or other aggregates in both the microemulsion and surfactant solution become more lipophilic as the cosolvent diffuses into the surrounding oil phase, increasing the solubilization capacity for oil and decreasing that for water, until the saturation limit for water is exceeded. This supersaturation of water leads to droplet nucleation and emulsion formation. Similar to spontaneous emulsification by the *Ouzo* effect, we observe micrometer-sized droplets<sup>70</sup> with a low dispersivity index (being  $\sqrt{\langle r^2 \rangle / \langle r^2 \rangle} - 1$  where  $r$  is the droplet radius)<sup>78–84</sup> of 14% based on 100 droplets. Contrary to the nucleation by the *Ouzo* effect, here, the droplets are unstable and disappear in bulk phases when given enough time. One may note that even without the imposed flow, spontaneous emulsification could occur via a suitable diffusion path<sup>55</sup> to form highly polydisperse droplets, unlike the relatively uniform-size droplets by the liquid–liquid nucleation mechanism.

The presence and nature of emulsion remained a non-equilibrium and unstable phenomenon because the emulsion droplets disappeared by flowing in the porous media, and a stratified (but uniform) multiphase flow (i.e., microemulsions, oil, and water) was observed downstream when  $v_t \leq 9.15$  ft/d. At  $v_t = 41.19$  ft/d, the emulsion did not disappear, and the flow appearance as seen in Figure 6D remained unchanged. These observations confirm the relevance of the residence time and the continuous mass transfer by diffusion at the droplet interface with the surrounding oil–microemulsion and reveal that the nature of mixtures (emulsion vs microemulsion) depends on the Péclet number.

**Dynamic versus Static Phase Behavior.** Regardless of the flow rate, (i) the microemulsion that formed spontaneously had the same appearance (i.e., color and texture) as the equilibrium microemulsion and (ii) there was an entry *mixing and coalescing zone* in the porous media, after which a clear flow of separated bulk phases (microemulsion(s), excess oil, and excess brine) appeared. Yet, at all flow rates, the in situ phase behavior correlated with the local  $\beta/\delta$  ratio rather than the equilibrium  $\beta/\delta$  ratio. For example, an oil-rich (rather than balanced) microemulsion was observed adjacent to all excess-oil

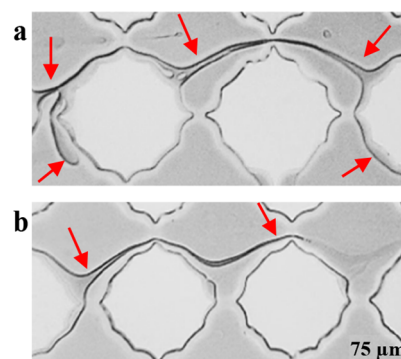
regions, implying that the local  $\beta/\delta$  ratio in porous media was greater than the equilibrium  $\beta/\delta$  ratio in pipettes because of the cosolvent partitioning to oil. At low flow rates where the local  $\beta/\delta$  ratio is relatively uniform and close to the equilibrium one, a good correlation between the dynamic in situ and static phase behaviors was observed. This confirms the validity of *local equilibrium* assumption, evident by the *locally* uniform single-phase flow in Figure 7A. At high flow rates, however, the



**Figure 7.** Top view of the mid-section of the micromodel. The total flow rate is: (a) 0.366 ft/d and (b) 41.19 ft/d.  $\alpha = 0.5$  in both cases. The flow is from the left to the right.

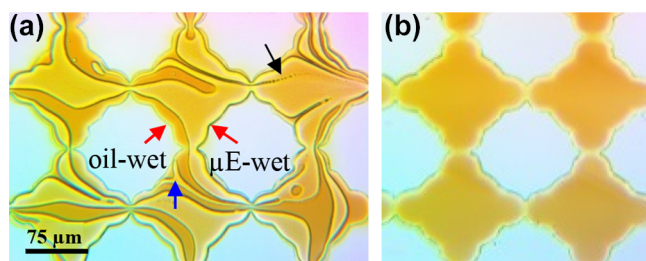
transverse mixing in porous media remained minimal, and thus, the local variation of the  $\beta/\delta$  ratio remained maximal. Even though the balanced microemulsion of equilibrium nature was observed at rates greater than 9 ft/d, out-of-equilibrium phases were dominant (Figure 7B).

**Film Flow.** An interesting and unexpected observation in the two-phase flow of the microemulsion and oil was related to the wetting phase. Compared to both oil and water, it is generally believed that the microemulsion is the wetting phase.<sup>85,86</sup> However, when oil is the minor phase, we observed that oil flows on the solid surface in the form of rivulets. Figure 8A shows an example, where oil is the wetting phase compared to the microemulsion and flows as rivulets with a film thickness of  $\sim 5$ – $11 \mu\text{m}$ . Image is shown in grayscale for better visualization. The image is taken after 2 pore volumes of coinjection to ensure that the initial pore fluids are completely displaced and that the spatial configuration and flow of phases



**Figure 8.** (a) Oil is the wetting phase compared to the microemulsion (i.e., the continuous phase) and flows as rivulets with a film thickness of  $\sim 5$ – $11 \mu\text{m}$ . The wetting phase arcs between two non-neighboring grains. (b) The wetting oil phase flows as rivulets along the flow streamlines over multiple grains and eventually solubilizes in the continuous phase. In both cases, the interstitial velocity is 0.366 ft/d and  $\alpha = 0.33$ . Image is shown in grayscale for better visualization. Red arrows indicate the oil film. The flow is from the left to the right.

are representative of the experimental conditions. The wetting oil phase, surprisingly, arcs between two non-neighboring grains. The film flow seems to arise from the friction drag<sup>87</sup> exerted by the microemulsion on the oil film. Figure 8B shows an example of the wetting oil phase flow as rivulets along the flow streamlines over multiple grains, before disappearing in the continuous phase. The oil stream solubilizes into the major phase, that is, the microemulsion, because of the ultralow IFTs. These results strongly suggest that in microemulsion systems, the wetting phenomena depend not only on the thermodynamics of the systems, best described by the equilibrium contact angles,<sup>88,89</sup> but also on the flow and nonequilibrium phase behavior. Figure 9A shows an example of mixed-wet state



**Figure 9.** (a) Dynamic mixed-wet state in the two-phase flow of oil and microemulsion. Oil is seen as dark canary-yellow, and the microemulsion ( $\mu E$ ) is lighter in color. Red arrows show the spatial variation of wettability as two adjacent grids are wetted by oil and the microemulsion, whereas the blue arrow shows the variation of wettability with time as the initial microemulsion wetting film is displaced by the wetting oil phase. Black arrow shows the film miscibility. (b) Two-phase flow becomes homogenous further downstream of the flow. The interstitial velocity is 0.183 ft/d and  $\alpha = 0.33$ . The flow is from the left to the right.

in an oil–microemulsion two-phase flow that is dynamic both spatially and temporally. Figure 9B shows further downstream of the flow at the same width. Because wetting, relative permeability, and trapping are well-correlated;<sup>90–99</sup> further studies are required to define the implications of our findings.

## CONCLUSIONS

On the basis of the salinity scans, a mixture of water + crude oil + TDA + IOS + phenol-2EO with the overall composition of  $\alpha = 0.5$ ,  $\beta = 0.0765$ , and  $\delta = 0.02$  was selected to study the phase change and the resulting multiphase flow involving microemulsions. The mixture formed a bicontinuous microemulsion in equilibrium. The surfactant solution and oil mixture was coinjected into a 2.5D micromodel, and the coupling of microemulsion phase formation and flow patterns was analyzed. Regardless of the bulk flow rate, it was observed that a microemulsion was formed that correlated well with the equilibrium phase. The microemulsion formed in the first place by diffusion-driven nucleation of the microemulsion film at discrete locations on the initial surface of contact between the surfactant solution and oil and later via continuous interfacial mass transfer on emulsion droplets. The former is instantaneous compared to the flow, whereas the latter is slow and diffusive. Both mechanisms are adversely affected by the bulk flow rate, which minimizes the first and prolongs the second because of minimal transverse mixing. In addition to the imposed flow, spontaneous pulselike Marangoni flows into the oil stream were observed at the initial surface contact of the surfactant solution and oil. The pulsed flow could be attributed

to the nonwetting nature of the microemulsion phase at the water–oil interface, which creates gradients in the disjoining pressure and surface tension, thus generating a Marangoni flow. The formation of the microemulsion phase at the interface distinguishes the situation from that of a more common Marangoni flow with only two phases present.

An emulsion formed and flowed next to the microemulsion at all bulk flow rates. The mechanism of emulsion formation was, however, flow-rate-dependent. The droplets' size in low flow rates does not fit the prediction of shearing-based mechanisms, which implied that shearing is not the origin of droplets in low flow rates. The emulsion was monodisperse at low flow rates with droplet radii of 3–6  $\mu m$  (depending on the flow rate), an order of magnitude smaller than those predicted by the droplet breakdown theory in a simple shear flow. These results suggest that the giant droplets (that originated from the microemulsion formation mechanism at low flow rates) spontaneously emulsify at low flow rates in a manner similar to the liquid–liquid nucleation process or the *Ouzo* effect. Contrary to this, at high bulk flow rates, the emulsification occurred via mechanical or flow mixing. The number of emulsion-occupied pores in the direction transverse to the flow first increased (because of mechanical mixing) and then decreased (because of stratified flow) with the bulk flow rates. The emulsion is unstable, however, and disappears while flowing in the porous medium, except when the bulk flow rate is very high (>9.15 ft/d here). These results reveal that the phase change, for example, the formation of microemulsion, influenced the flow patterns, and the flow patterns affected the characteristics of the phases. The out-of-equilibrium phase behavior resulted in layered flow patterns when the volumetric flow rate was large, whereas at lower flow rates, the dynamic and equilibrium phase behaviors were well-correlated. Thus, the *local equilibrium* assumption is applicable in EOR processes with the typical frontal velocity of 1 ft/d.

Although microemulsion wetted the solid in most cases, the wetting state also showed/had non-homogeneous and non-equilibrium characteristics. In some cases a mixed wettability behavior was observed where adjacent grains were respectively wetted by oil and microemulsion. In other cases, oil as the minor phase wetted the solid surface. These observations disprove the common assumption that the microemulsion is the wetting phase compared to oil and water and suggest that it may be misleading to rely on the equilibrium or quasi-equilibrium characterization of wetting by contact angles. The wetting oil flowed as rivulets with a film thickness of  $\sim 5$ –11  $\mu m$  that either arcs between two non-neighboring grains (i.e., skipped the middle grain) or moved along the flow streamlines over multiple grains before disappearing in the continuous microemulsion phase.

As present results show, the behavior of microemulsion-forming water–oil–amphiphile(s) mixtures in flow fields is a paradigmatic example for the richness of dynamic phenomena out of equilibrium. Further studies are needed to fully characterize such multiphase flow problems where the timescales involved in phase change and bulk flow are comparable. In addition, using micromodels that represent complex geometries of heterogeneous rocks, such as the multiple-scale pore sizes<sup>17,100</sup> and fractures,<sup>101</sup> is highly encouraged.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.7b02856](https://doi.org/10.1021/acs.langmuir.7b02856).

Structure of the 2.5D micromodel using an optical profilometer, steady shear and complex viscosities of the microemulsion, time-lapse image of the surfactant–oil interface, and wide view of the micromodel showing the emulsion volume at flow rates (a) 9.15 ft/d and (b) 41.19 ft/d ([PDF](#))

Pulsed spontaneous flow at the surfactant–oil interface ([MPG](#))

Oil as the wetting phase flows as rivulets with a film thickness of  $\sim 5\text{--}11\ \mu\text{m}$  ([MPG](#))

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### Notes

The authors declare no competing financial interest.

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