

1 Article

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# Waterflooding of Surfactant and Polymer Solutions 3 in a Porous Media Micromodel

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7

8 **Abstract:** In this study, we examine microscale waterflooding in a randomly close-packed porous  
9 medium. Three different porosities are prepared in a microfluidic platform and saturated with  
10 silicone oil. Optical video fluorescence microscopy is used to track the water front as it flows  
11 through the porous packed bed. The degree of water saturation is compared to water containing  
12 two different types of chemical modifiers, sodium dodecyl sulfate (SDS) and polyvinylpyrrolidone  
13 (PVP), with water in the absence of a surfactant used as a control. Image analysis of our video data  
14 yield saturation curves and calculate fractal dimension, which we use to identify how morphology  
15 changes the way an invading water phase moves through the porous media. An inverse analysis  
16 based on the implicit pressure explicit saturation (IMPES) simulation technique uses mobility ratio  
17 as an adjustable parameter to fit our experimental saturation curves. The results from our inverse  
18 analysis combined with our image analysis show that this platform can be used to evaluate the  
19 effectiveness of surfactants or polymers as additives for enhancing the transport of water through  
20 an oil-saturated porous medium.

21 **Keywords:** Porous Media; Optical Video Microscopy; Microfluidics; Waterflooding; Surfactants;  
22 Polymers

23  
2425 

## 1. Introduction

26 Understanding multiphase flows in porous media is critical for enhancing the recovery of oil  
27 from the porous bedrock [1]. When a reservoir is tapped through a wellbore in the bedrock for the  
28 first time, a pressure differential between the reservoir and the wellbore can be used as a primary  
29 form of recovery. Once the pressure differential reaches hydrostatic equilibrium, secondary forms  
30 of recovery such as waterflooding (i.e., water injection) can be used to extract the remaining oil [2].  
31 Approximately 40% of the total available oil is extracted using these two methods.[3]

32 Chemical methods, including the addition of surfactants, polymers or alkali to the water, are  
33 used to enhance the recovery of oil beyond the 40% limit encountered with hydrostatic pressure  
34 and water [4]. Surfactants in water reduce the interfacial surface tension between the water and the  
35 oil, which also reduce the capillary forces and enhance the oil displacement efficiency [5,6].  
36 Polymers act as viscosifying agents, which reduce the viscosity and density mismatch between the  
37 water and oil phases. A reduction in the relative difference between viscosity and density, known  
38 as mobility, allows for increased oil displacement [7,8]. A combination of chemical methods are  
39 proposed as an effective method for enhancing oil recovery [9].

40 Understanding how these mechanisms act in isolation to each other and how they can be  
41 combined is critical for improving oil displacement efficiency. However, transport through oil-  
42 bearing porous media occurs at a rate of 1 linear foot per day [10] and the direct observation of

43 large-scale oil displacement phenomena can take weeks [11], which makes study of multiphase  
44 processes slow and difficult. The slow rate of observation is a direct result of transport through the  
45 interconnected network of grains that make up the porous media.[12] Micromodels based on lab-  
46 on-a-chip platforms offer one possible approach to experimentally investigating multiphase  
47 processes in porous media micromodels at shorter time scales.[13]

48 Micromodels enable direct observation of flow through porous media. In this approach, an  
49 optically transparent flow cell is constructed with a uniform distribution of glass or quartz beads  
50 dispersed inside to act as the porous grain structure and direct visualization of the flow is then  
51 performed using optical microscopy techniques.[14,15] Although advances in microfabrication  
52 technology allow for manufacturing complex pore structures[16–18], most micromodels used to  
53 study multiphase fluid flow through pore media have been done in rectangular pore bodies and  
54 throats.[19–25] Computer-aid design of microchannels can be used to mimic heterogeneous porous  
55 media structure [26,27].

56 This article presents a microfluidic platform for evaluating chemical methods to enhance oil  
57 recover through the waterflooding process. The platform consists of a 750  $\mu\text{m}$  wide microfluidic  
58 channel into which glass beads are dispersed in silicone oil and packed to form a random porous  
59 bed. Optical fluorescence microscopy is used to track the introduction of an aqueous fluorescent  
60 dye to the main channel through a side channel. Tracking the dye enables us to evaluate of the  
61 saturation of the aqueous phase relative to the oil phase. The injection of pure water is compared to  
62 injection of water containing two different kinds of chemical modifiers, sodium dodecyl sulfate  
63 (SDS) and polyvinylpyrrolidone (PVP). SDS is an anionic surfactant and PVP is a polymer. Our  
64 analysis based on optically tracking the invasion of the aqueous phase demonstrate that chemical  
65 modifiers significantly improve the displacement of oil from the microfluidic channel, although  
66 image analysis of fractal dimension morphology illustrate differences in aqueous phase invasion.

67 Micromodels offer qualitative information on flow characteristics, but quantitative tools for  
68 comparison to experiment are not well-developed [28]. To address this gap in quantitative data  
69 evaluation, we introduce an inverse analysis based on implicit pressure explicit saturation (IMPES)  
70 to determine the mobility of our surfactant and polymer phases. The analysis presented here offers  
71 an approach to interpreting two-phase flow data in a porous microfluidic channel and obtaining  
72 parameters such as saturation and mobility that can be used to compare effectiveness of different  
73 chemical methods for enhancing oil recovery. Optical measurements of waterflooding can also  
74 guide the assessment of other multiphase flow problems, such as the transport of sequestered  
75 carbon dioxide in porous bedrock [29], filtration of contaminants [30,31], and the additive  
76 manufacturing of complex fluid networks [32] or thermal management [33].

## 77 **2. Materials and Methods**

### 78 *2.1 Device Fabrication*

79 Our device is designed using AutoCad and printed as a mask onto a transparent plastic sheet  
80 (CAD/Art Services). The channel consisted of main channel (750  $\mu\text{m}$  wide and 17 mm long) along  
81 with a side channel (20  $\mu\text{m}$  wide and 3 mm long) for injection of the fluorescent dye. The porous

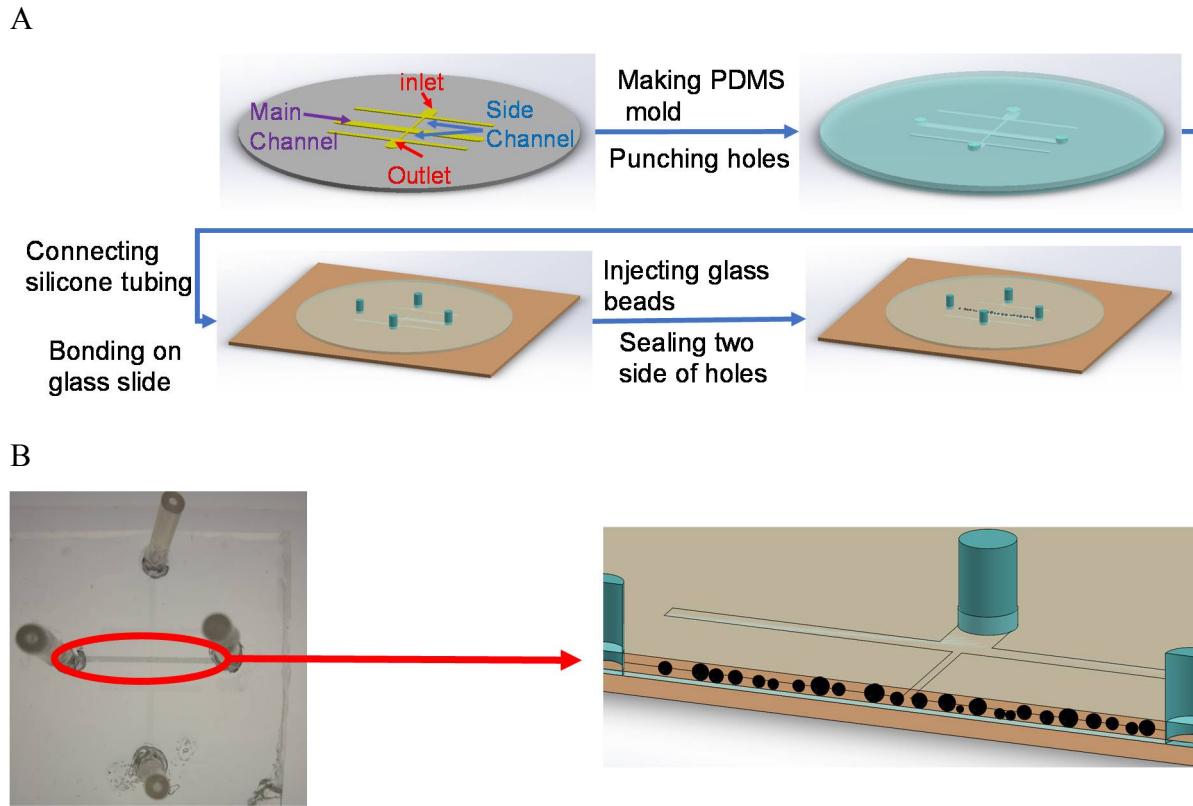


Figure 1 – A) The design of the microfluidic device used in this work along with the procedures used to fabricate the channel. B) A photograph of the microfluidic device with a schematic that illustrates how where glass beads are packed in to form a porous structure.

82 media is assembled from a glass beads packed within the main channel. The fabrication process,  
 83 shown in Figure 1A, begins with conventional photolithography used to transfer the pattern from the  
 84 mask to a 4-inch silicon wafer (University Wafer) using photoresist (SU8 2050, Microchem). The  
 85 photoresist thickness is approximately 54  $\mu\text{m}$  based on profilometry measurements.

86 Once the pattern has been produced onto a silicon substrate through photolithography, it is  
 87 transferred to a polystyrene petri dish into which polydimethylsiloxane (PDMS, Sylgard 184, Dow  
 88 Corning) is poured to form a mold. The PDMS is mixed with a ratio of 10:1 monomer to curing agent  
 89 by weight. After pouring the uncured PDMS over the pattern, the mold is placed in a desiccator,  
 90 where air bubbles are removed from the mold using a vacuum pump. The mold is placed into an  
 91 oven to cure for 2 hours at 60°C. The cured mold is then removed from the silicon master using a  
 92 razor, and 3 mm diameter holes are opened at the channel ends with a biopsy punch to create  
 93 injection points for the fluids.

94 The PDMS microfluidic device is bonded to a microscope slide (Fisher Scientific, Catalog# 12-  
 95 550C) that is washed in acetone and methanol to remove organic debris, after which the solvent is  
 96 washed off the slide with deionized water (ARIES High Purity Water System, Aries Filterworks) and  
 97 the slide is dried with nitrogen. Dust debris is removed from the PDMS using adhesive office tape,  
 98 after which the microscope slide and the PDMS are placed inside a plasma cleaner (Harrick Plasma,  
 99 PDC-32G) and treated for 2 minutes. The PDMS and the microscope slide are then placed in contact  
 100 with one another before being heated at 60°C for around 2 hours to improve sealing. The microfluidic

101 device is then removed from the oven and silicone tubing (Saint-Gobain, Version SPX-50,  
102 Product#ABX00001) is inserted through the 3 mm holes, with a small amount of PDMS placed around  
103 the tubing perimeter to ensure a firm seal. The device is finally placed back in the oven for 1 hour to  
104 cure.

105 The porous media is formed using randomly close-packed soda lime glass microspheres  
106 (P2050SL-2.5 35-45 $\mu$ m - 1kg, Cospheric). Sieves with 38  $\mu$ m, 45  $\mu$ m and 63  $\mu$ m meshes are used to  
107 separate the glass microspheres and achieve a diameter range of ~48-63  $\mu$ m after several rounds of  
108 sieving. Since the diameter of our microspheres is larger than the side channels used to inject our  
109 aqueous phase, we expect the microspheres to remain in place. A laboratory scale (LW  
110 Measurements, Model# HRB224) is used to weigh samples of 0.15 grams of glass microspheres, which  
111 are dispersed in 20 mL of DI water and pumped into the large microchannel using a syringe pump  
112 (GenieTouch, Kent Scientific) until the channel is filled with glass microspheres. After introducing  
113 the glass microspheres, the device is placed in an oven for 8 hours to evaporate excess water, making  
114 it ready for use. The device was weighed both before and after the injection process to determine the  
115 amount of glass microspheres injected into the device. This mass measurement is used with an  
116 estimate for the average microsphere radius (~55.5  $\mu$ m) to calculate the total volume occupied by the  
117 glass microspheres. This measurement provides an estimate for the porosity of the structure formed  
118 by the packed glass microspheres which we found to be comparable to calculations of porosity based  
119 on image analysis. The porosity value that we obtain from these two values only has 5% different  
120 between both measurements.

## 121 2.2 Image Capture and Processing

122 Experimental observations of water injection are accomplished using an Olympus IX70  
123 microscope with a 10X objective lens. A scientific CMOS camera (Optimos, QImaging) is used to  
124 record video and capture images (480 x 270) for porosity analysis. An LED light source (wLS,  
125 QImaging) is used to illuminate the sample and excite the fluorescent dye. Video of the dye being  
126 injected into the fluid is captured at a rate of 5 frames per second. The scale for these images is 3.7281  
127 microns per pixel.

128 After capturing experimental videos, we use ImageJ to crop the videos and retain the main  
129 channel where the oil displacement occurs. These videos are then analyzed using a program written  
130 in MATLAB to track changes in fluorescence due to aqueous phase invasion. The program applies a  
131 boxcar filter to reduce the image noise. A threshold value for each frame of the video is calculated to  
132 retain the area occupied by the fluorescent dye. This area is compared to unoccupied area to obtain  
133 the degree of water saturation. This result is also used to obtain the fractal dimension of the aqueous  
134 phase.

## 135 2.3 Device Characterization

136 MATLAB code [34,35], initially developed to measure porosity and pore radius for thin rock  
137 samples, was adapted to provide a more accurate measure of porosity. Before performing an  
138 experiment, an optical image was taken of the point where the main channel meets with the dye  
139 injection port (Figure 2, top-left). After the image is converted to black and white (Figure 2, top-right),  
140 the MATLAB algorithm draws a series of test lines across the image to determine the average sizes  
141 of pore space (white) and grain size (black), with the ratio of empty pore space to total image area  
142 representing the porosity for a thin sample. The average porosity measured within the device is

143 consistent with measurements made by  
 144 weighing the device. The observed pore size  
 145 is 20  $\mu\text{m}$  for the test sample, while the  
 146 distribution of pore sizes is shown in Figure  
 147 2. The average porosities for all of our packed  
 148 beds were 0.063, 0.113 and 0.143.

149 *2.4 Experimental Details*

150 The experiments utilized silicone oil ( $\nu_{\text{oil}}$   
 151 = 5 cSt,  $\rho_{\text{oil}} = 0.913 \text{ g/mL}$ ) as a defending fluid.  
 152 After porosity measurements are completed,  
 153 silicone oil (product # 317667, Sigma Aldrich)  
 154 is injected into the main channel before the  
 155 main channel is sealed with PDMS to prevent  
 156 leaks. Deionized water ( $\nu_{\text{water}} = 1 \text{ cSt}$ ,  $\rho_{\text{water}} =$   
 157 0.99 g/mL), used as the invading fluid, is  
 158 injected into the microfluidic device through  
 159 a side channel using a syringe pump  
 160 (Chemex Fusion 100). The mobility ratio,  
 161 defined as the ratio of dynamic viscosities ( $M$   
 162 =  $\nu_{\text{oil}} \rho_{\text{oil}} / \nu_{\text{water}} \rho_{\text{water}}$ ), is a measure of the ease with which an invading fluid flows in the presence of a  
 163 defending fluid [36], with lower mobility allowing the invading fluid to flow through the porous  
 164 media and recover more oil than a mobility is higher.

165 The capillary number [37] is  $\text{Ca} = \nu_{\text{oil}} \rho_{\text{oil}} v_{\text{inj}} / \gamma$ , where  $v_{\text{inj}}$  is the average velocity of the invading  
 166 fluid during injection and  $\gamma$  is the surface tension between the two fluid phases. The characteristic  
 167 injection velocity is  $v_{\text{inj}} = Q / b \cdot d$ , where  $Q$  is the injection rate,  $b$  is the gap thickness of the device (~54  
 168  $\mu\text{m}$ ) and  $d$  is the median pore-throat size (~15  $\mu\text{m}$ ). The injection rate for all experiments in this article  
 169 was fixed at 0.1 mL/hr using a syringe pump. Initial experiments were conducted using deionized  
 170 water containing 0.1875 mM of Rhodamine B dye sourced from ARCOS Organics. The surface tension  
 171 at the silicone oil-water interface was 24.35 mN/mm based on measurements described in the  
 172 literature [38]. We estimate the characteristic capillary number is approximately  $6 \times 10^{-6}$ .

173 Experiments conducted with water injection into the oil-saturated porous medium were  
 174 compared to experiments in which a surfactant was introduced to reduce surface tension. Two  
 175 chemical modifiers, sodium dodecyl sulfate (SDS, Sigma Aldrich, Product#75746) and  
 176 polyvinylpyrrolidone (PVP, Alfa Aesar, MW 40,000, Product #J62417), were selected for comparison  
 177 based on their use in the petroleum industry for enhancing oil recovery [39,40]. The fluorescent dye  
 178 solution is prepared as previously described, and a surfactant or polymer with a concentration of 0.1  
 179 wt% added to this solution. Since our injection flow rate is slow, we expect that swelling of the PDMS  
 180 will not influence the results [41]. The injection experiments were conducted in a manner similar to  
 181 those described for water alone.

182 **3. Theory and Simulation**

183 Modeling two-phase fluid flow in porous media requires a coupled system of nonlinear, time-  
 184 dependent partial differential equations.[42] We use an approach known as the implicit pressure,

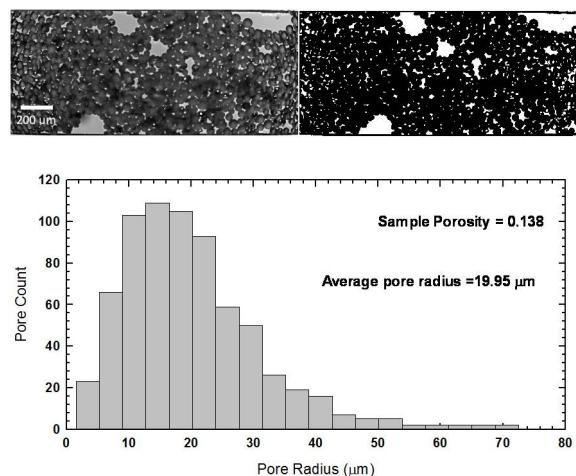


Figure 2 – A representative image of our porous structures (top, left) and a black and white image (top, right) generated during our measurement of the porosity. A sample distribution (bottom) of the pore radius for a representative image.

185 explicit saturation (IMPES) model [43] to simulate the transport of the invading water phase in our  
 186 device. The model relies on an implicit formulation of conservation of mass and momentum to reduce  
 187 the computational cost of the simulation [44].

188 The formulation of the model begins with a mass balance for an incompressible, immiscible two-  
 189 phase flow [45],

190 
$$\frac{\partial(\phi\rho_\alpha S_\alpha)}{\partial t} + \nabla \cdot (\rho_\alpha \mathbf{u}_\alpha) = q_\alpha \quad \alpha = w, o \quad (\text{Eq. 1})$$

191 where  $\phi$  is the medium porosity,  $\rho$  is the fluid density,  $S$  is the saturation,  $\mathbf{u}$  is the volumetric velocity,  
 192  $q$  is the mass flow rate per unit volume, and  $\alpha$  is the phase type (water or oil). Darcy's law is used to  
 193 model the volumetric velocity of the fluid phases as they flow through the porous medium for a thin  
 194 section of negligible depth,

195 
$$\mathbf{u}_\alpha = -\frac{k_{r\alpha}}{\nu_\alpha \rho_\alpha} \mathbf{k} \nabla P_\alpha \quad \alpha = w, o \quad (\text{Eq. 2})$$

196 where  $k_{r\alpha}$  is the relative permeability,  $\mathbf{k}$  is the absolute permeability tensor of the porous medium  
 197 and  $P$  is pressure.

198 Substituting Eq. 2 into Eq. 1 and applying the assumption that porosity does not change with  
 199 time yields [43],

200 
$$-\nabla \cdot [\mathbf{K} \lambda_\alpha(S_\alpha) \nabla P_\alpha] = q_\alpha \quad \alpha = w, o \quad (\text{Eq. 3})$$

201 where the parameter,  $\lambda$ , is referred to as the phase mobility. The saturation of the water phase is  
 202 defined as,

203 
$$\phi \frac{\partial S_w}{\partial t} + \nabla \cdot (f_w(S_w) \mathbf{u}) = \frac{q_w}{\rho_w} \quad (\text{Eq. 4})$$

204 where  $\mathbf{u} = \mathbf{u}_w + \mathbf{u}_o$  is the total velocity of the system and  $f_w = \lambda_w / (\lambda_w + \lambda_o)$  measures the fraction of water  
 205 flowing through the system. Introducing a set of simple analytical expressions allows us to close the  
 206 model presented by Eqs. 3 and 4,

207 
$$\lambda_w(S_w) = \frac{(S^*)^2}{\nu_w \rho_w} \quad \lambda_o(S_o) = \frac{(1 - S^*)^2}{\nu_o \rho_o} \quad S^* = \frac{S_w - S_{wc}}{1 - S_{or} - S_{wc}}$$

208 where  $S_{wc}$  is the water trapped in the pores during the formation of the porous medium and  $S_{or}$  is the  
 209 lowest oil saturation that can be achieved by water displacement. The oil and water phase saturations  
 210 are constrained by  $S_o + S_w = 1$ .

211 The solution to these systems of equations are based on the approach of Aarnes et al. [43] and  
 212 coded in MATLAB. The simulation approach is summarized here. The model simulates a two-  
 213 dimensional representation of the oil-saturated porous medium. The fluid properties (density and  
 214 viscosity) mentioned in the Materials and Methods section are used to estimate the initial mobility  
 215 ratio of the system. The initial oil saturation distribution is assumed to be uniform throughout our  
 216 porous medium. The absolute permeability tensor,  $\mathbf{k}$ , is generated using a random distribution with  
 217 a log-normal profile. As the time step within the simulation advances, the pressure distribution is  
 218 calculated using two-point flux approximation (TPFA) scheme to discretize the pressure equation  
 219 (Eq. 3) along with edge velocities.

220 An explicit finite-volume formulation of the saturation equation (Eq. 4) of the form

221 
$$S_i^{n+1} = S_i^n + (\delta_x^t)_i (\max(q_i, 0) - \sum_j f(S^m)_{ij} v_{ij} + f(S_i^m) \min(q_i, 0)),$$

222 is used to advance the change in phase  
 223 saturation with a dimensionless time step,  
 224  $(\delta_x^t)_i$ . The parameter  $\gamma_{ij}$  is the total flux  
 225 over an edge between two adjacent cells  $\Omega_i$   
 226 and  $\Omega_j$ , and  $f_{ij}$  is the fractional flow  
 227 function at  $\gamma_{ij}$ . The fractional flow function  
 228 is,

$$229 \quad f_w(S)_{ij} = \begin{cases} f_w(S_i) & \text{if } \nu \cdot n_{ij} \geq 0 \\ f_w(S_j) & \text{if } \nu \cdot n_{ij} < 0 \end{cases}$$

230 (Eq.5)

231 The model presented here is used to  
 232 directly compare to experimental results.  
 233 This done by taking the ensemble average of  
 234 the water phase saturation,  $\langle S_w \rangle =$   
 235  $N^{-1} \sum_{i=1}^N S_{w,i}$ , across the simulation  
 236 domain with  $N$  elements (i.e., total numbers  
 237 of grid blocks) as a function of simulation  
 238 time. The results are converted to  
 239 experimental time, which allow for a direct  
 240 comparison to experimental results. The  
 241 ensemble average of experimentally  
 242 observed water saturation is directly  
 243 measured by identifying the area occupied by  
 244 the Rhodamine B dye. We obtain a  
 245 coefficient of determination through water  
 246 phase saturation to determine the goodness of fit for the simulation.

247 If the coefficient of determination (COD) is below a value of  $r^2 = 0.9$ , we run a series of forward  
 248 simulations to try and improve the fit to our data. Mobility is used as an adjustable parameter as a  
 249 way to account for mixing [46] between phases. The mobility for the next forward simulation is  
 250 drawn from a uniform probability distribution,

$$251 \quad M_{i+1} = M_f [1 + (2\xi - 1)\delta]$$

252 where  $M_f$  is the mobility ratio associated with the best COD,  $M_{i+1}$  is the mobility for the next forward  
 253 simulation, and  $\xi$  is a random uniform number that ranges from 0 to 1 and  $\delta$  is a maximum possible  
 254 range parameter, which we set to a value of 0.1. The new COD value is compared to the old COD  
 255 value when the simulation is complete. The factor,  $M_f$ , remains unchanged if the new COD is lower  
 256 than the old COD. Otherwise, we update  $M_f = M_{i+1}$  if the COD value is found to improve.

## 257 4. Results and Discussion

### 258 4.1 Oil displacement efficiency

259 The experimental displacement of silicone oil by waterflooding is illustrated in Figure 3. The  
 260 rhodamine-dyed water initially builds up sufficient pressure at the inlet port to break through into

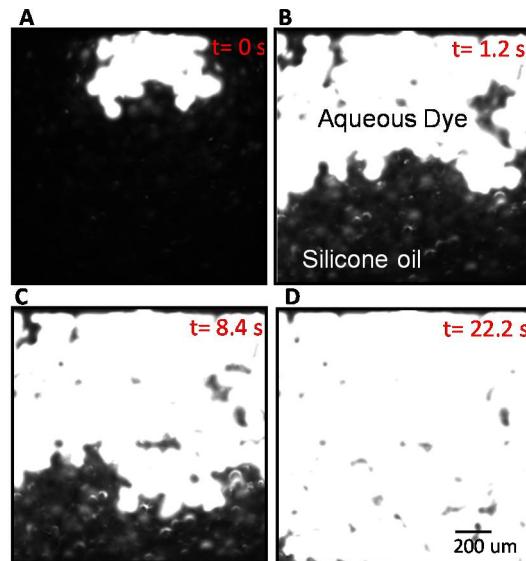


Figure 3 – A representative experiment for water with 0.1% SDS at a porosity of 0.143. Initially (A), the main channel full of silicone oil which is black. When the water phase invades the main channel, rhodamine B is used to track the displacement of silicone oil (B and C) until the whole main channel fluoresces (D). In this figure, the white represents rhodamine B and black represents silicone oil.

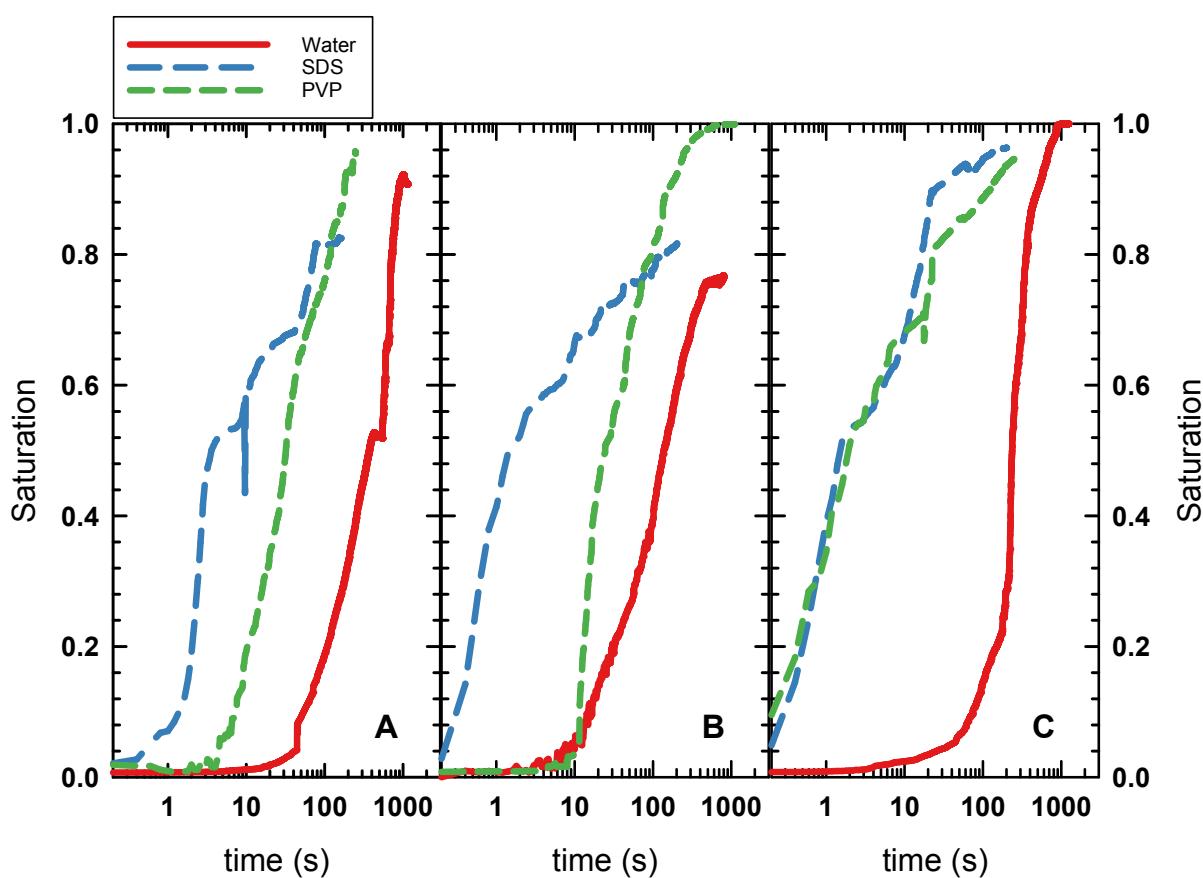


Figure 4 – The relationship between saturation of an invading water phase for three water-based fluids (no surfactant, 0.1% SDS and 0.1% PVP) as they displace oil from a packed bed of glass microspheres with porosity of 0.063 (A), 0.113 (B) and 0.143 (C).

261 the porous media micromodel. As the water displaces silicone oil, some silicone oil still remain in  
 262 voids (Figures 3B and C) and, after approximately 20 seconds, the water reaches the exit port on the  
 263 opposite side of the porous media micromodel (Figure 3D). Observing the porous media micromodel  
 264 after the initial exit of the water, we see a reduction in void size over time as additional silicone oil is  
 265 either displaced by water or shrinks due to the applied pressure of the flow.

266 We performed three separate types of waterflooding experiments similar to the one described  
 267 in Figure 3. The first type of experiment used water mixed only with rhodamine, while the other  
 268 two types of experiments utilized SDS or PVP (Figure 4). A packed bed of glass beads was prepared  
 269 before each experiment and characterized using the previously described protocol. MATLAB image  
 270 analysis code was written to track the area occupied by the rhodamine dye during the experiment,  
 271 allowing estimation of the average water phase saturation defined by  $S_w = A_{\text{dye}} / A_{\text{channel}}$ .

272 Figure 4 shows the results of our waterflooding experiments, both for the presence and the  
 273 absence of surfactant or polymer. Three separate packed beds of different porosities (0.063, 0.113 and  
 274 0.143) were prepared for each fluid type, and Figure 4A shows the results for a media with porosity  
 275 0.063. The water-bearing SDS initially invades the packed bed faster than either the water-bearing

276 PVP or water alone could do. The SDS reduces the oil-water interfacial tension more significantly  
277 than PVP and water alone, which we illustrate by a contact angle measurement. An image analysis  
278 method was adapted to measure the contact angle at the oil-water interface in our microfluidic  
279 channel [47]. The measured contact angles were  $42.9^\circ \pm 1.4^\circ$  and  $22.3^\circ \pm 0.9^\circ$  for the SDS and PVP  
280 solutions, respectively. Water was measured to have a contact angle of  $11.2^\circ \pm 0.9^\circ$  in the absence of  
281 a surfactant or polymer. The contact angle for water in the microchannel is similar to contact angle  
282 values reported for plasma-treated PDMS surfaces [48–50]. While the SDS solution initially invades  
283 the oil phase at a faster rate in Figure 4A, the PVP solution typically saturates the porous media to a  
284 more significant degree after a longer period of time.

285 The experiment shown in Figure 4B was conducted for a packed bed with porosity 0.113. As in  
286 Figure 4A, the water-bearing PVP solution achieves a higher saturation than SDS or water alone and  
287 invasion by both surfactant solutions occurred faster than for water alone at this porosity. For the  
288 highest porosity value (0.143 in Figure 4C), water alone achieved the highest level of saturation  
289 compared to values at the lower porosities, although its rate of invasion slower than the surfactant  
290 solutions. Both the PVP and SDS solutions invaded at comparable rates at the highest porosity, with  
291 SDS saturating the porous bed to a slightly greater extent than the PVP solution.

#### 292 4.2 *Fractal dimension*

293 We used image analysis to evaluate the fractal dimension of the area occupied by the by the  
294 fluorescent dye in our microfluidic device fluorescent dye in our microfluidic device to better  
295 understand the oil displacement kinetics. A MATLAB code was adapted to evaluate the fractal  
296 dimension using the Hausdorff technique [51], where a series of boxes are drawn within the region  
297 containing the dye. The bright pixels within each box are counted and compared to the total number  
298 of boxes drawn by the code. The values obtained by this analysis provide a measure of the fractal  
299 dimension for the area occupied by the water. The results of the image analysis (Figure 5A-C) show  
300 that water and the PVP solution begin with a fractal dimension of  $D_f \sim 1.2$  or less, representing  
301 structures classified as stringy [52]. At the lowest (0.063, Figure 5A) and highest (0.143, Figure 5C)  
302 porosity levels, it takes about 100 s for the water to occupy an area that morphologically resembles a  
303 fractal ( $D_f \sim 1.6$ ).

304 The only exception to this transition in morphology is the channel with porosity 0.11 (Figure  
305 5C), for which the evolution takes place over a period of time approximately half that of the other  
306 data sets. The SDS solution also exhibits different morphological behavior than the other solutions,  
307 achieving a fractal morphology on a short timescale ( $\sim 1$  s or less), indicating that these solutions  
308 invade oil-saturated pore spaces at a far easier rate than the other solutions. All solutions achieved a  
309 final fractal dimension of  $D_f \sim 1.89$ , indicating that fluid had percolated [53] through the packed bed  
310 in the microchannel.

311 The fractal dimension is connected to the area saturated by the invading fluid through its  
312 radius of gyration [54]. The radius of gyration represents a measure of the extent to which the  
313 invading fluid has displaced the oil in the porous medium and is defined as [55],

$$314 R_g = \sqrt{M_{2x} + M_{2y}}$$

315 where

316

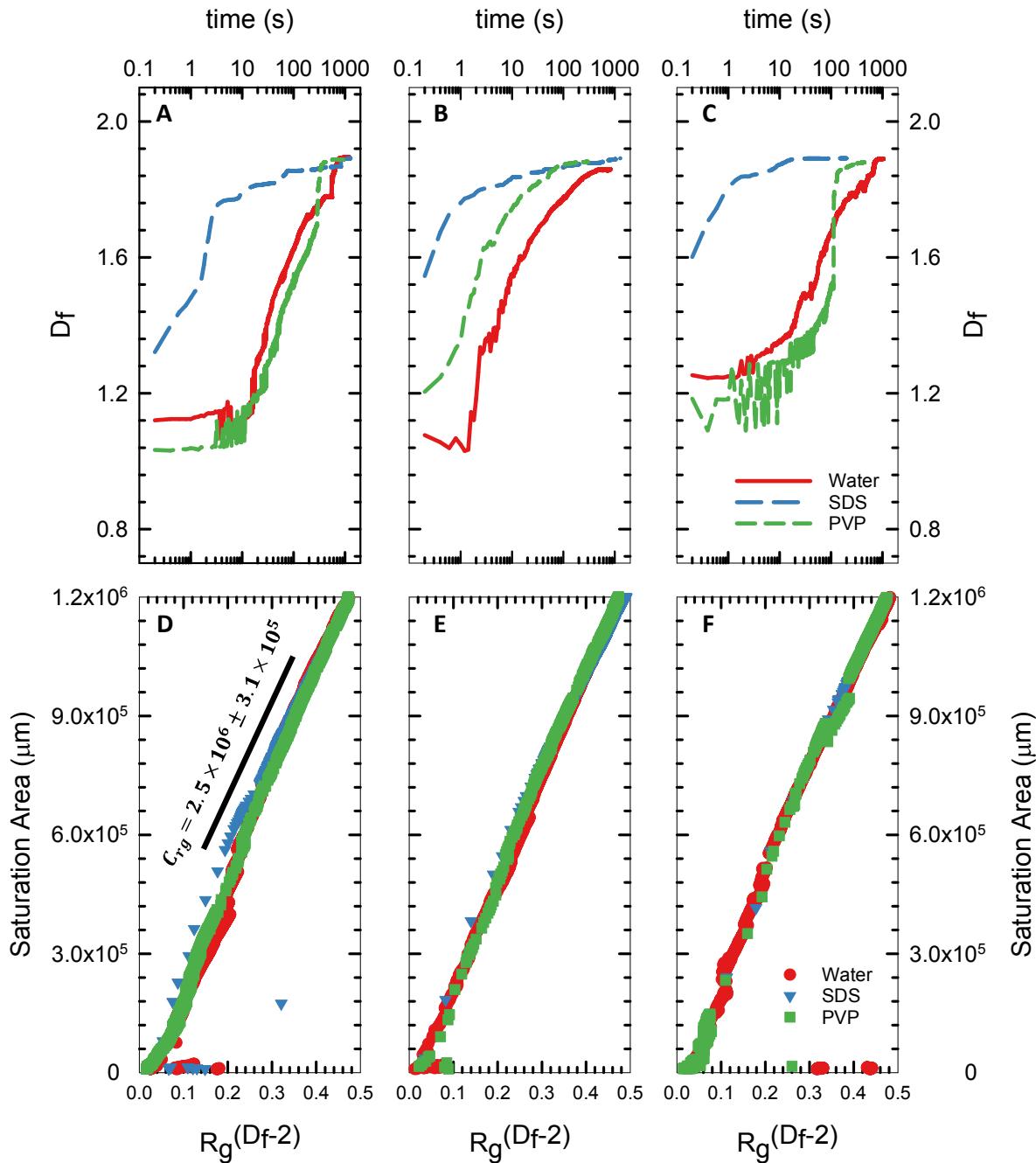


Figure 5 – The Hausdorff fractal dimension (A-C) as a function of time was evaluated using image analysis. The results in A-C show that, while all the samples evolve differently with time, they reach a point where they are topologically similar. Combining the fractal dimension with radius of gyration (D-F) reveal that all samples scale linearly with the saturation area.

317  $M_{2x} = \frac{1}{S} \sum_{i=1}^N (x_i - M_{1x})^2 \quad M_{2y} = \frac{1}{S} \sum_{i=1}^N (y_i - M_{1y})^2 \quad \text{and} \quad M_{1x} = \frac{1}{A_w} \sum_{i=1}^N x_i \quad M_{1y} = \frac{1}{A_w} \sum_{i=1}^N y_i$

318 where  $A_w$  is the measured area occupied by the invading water phase,  $N$  is the number of pixels  
 319 making up the pattern as recorded by the CMOS camera, and  $x_i$  and  $y_i$  are the coordinates of each  
 320 pixel in the observed pattern. We find that the relationship between area and radius of gyration is  
 321 well described by  $A_w = C_{rg} R_g^{(D_f-2)}$ , where  $D_f$  is a function of time, as shown in Figures 5A-C. The

	Water		0.1% SDS		0.1% PVP	
	$A_{\max} (\mu\text{m}^2) / 10^6$	$t_c$ (s)	$A_{\max} (\mu\text{m}^2) / 10^6$	$t_c$ (s)	$A_{\max} (\mu\text{m}^2) / 10^6$	$t_c$ (s)
Porosity	0.063	1.266	86.2	1.105	17.6	1.253
	0.11	1.059	111.1	1.241	11.0	1.209
	0.143	1.258	357.1	1.269	2.1	1.209
						10.4

Table 1 – Fitting parameters for  $A_{\max}$  and time constant of the three water-based fluid systems examined in this work.

322 relationship between area, radius of gyration and fractal dimension proposed here is similar to  
 323 previously proposed models for diffusion limited viscous fingering in porous media [56]. By  
 324 comparing data from all nine porosities examined in this work, we find that the data collapses to a  
 325 single curve when  $C_{rg} = 2.5 \times 10^6 \pm 3.1 \times 10^5$ , where  $A_w$  and  $R_g$  are in units of microns (see Figure 5 D-F).

326 While the fractal dimension can help us identify morphological differences in the way an  
 327 invading fluid phase spreads, and we would also like to observe differences in rate of invasion  
 328 ( $dA_w/dt$ ). Numerical calculation of the rate of invasion from image analysis data is challenging since  
 329 noise in the data can create artifacts that suggest unrealistically large fluctuations in invasion rate.  
 330 To minimize the effect of such artifacts, we chose to fit the area data to a model,  $A_w =$   
 331  $A_{w,max}(1 - e^{-t/t_c})$ , that is consistent with expected behavior of oil recovered through water injection  
 332 into porous reservoirs.[57] The parameter,  $A_{w,max}$ , is the maximum area occupied by the water during  
 333 the experiment and  $t_c$  is the time constant of the experiment.

334 Table 1 summarizes the results of fitting an exponential rise to a maximum for our area data  
 335 as a function of time. The average value of the area parameter is  $A_{w,max} = 1.208 \times 10^6 \pm 7.5 \times 10^4 \mu\text{m}^2$ ,  
 336 with the small standard deviation indicating that there is no significant difference between samples  
 337 based on maximum area occupied by the invading water phase. We do find that there are  
 338 significant differences in time constants for  
 339 the samples we examined, with the water  
 340 samples exhibiting more than a 4-fold  
 341 increase in time constant with increasing  
 342 porosity. The time constants for SDS and  
 343 PVP-bearing solutions exhibit an opposite  
 344 trend, i.e., a decrease in time constant with  
 345 increasing porosity. This suggests that the  
 346 polymer and surfactant solutions make it  
 347 easier to fill larger void volumes when  
 348 compared to water alone.

#### 349 4.3 IMPES

350 We implemented an inverse IMPES  
 351 simulation to be compared to our  
 352 experimental results. Figure 6 shows a  
 353 sample simulation result for 0.1% SDS,

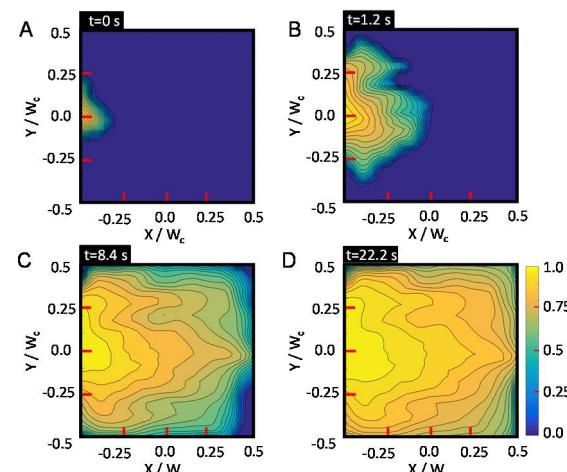


Figure 6 – An IMPES simulation for the case with 0.1% SDS in water. Snapshots are taken at intervals that correspond to Figure 3. The color bar shows the value for the local saturation.

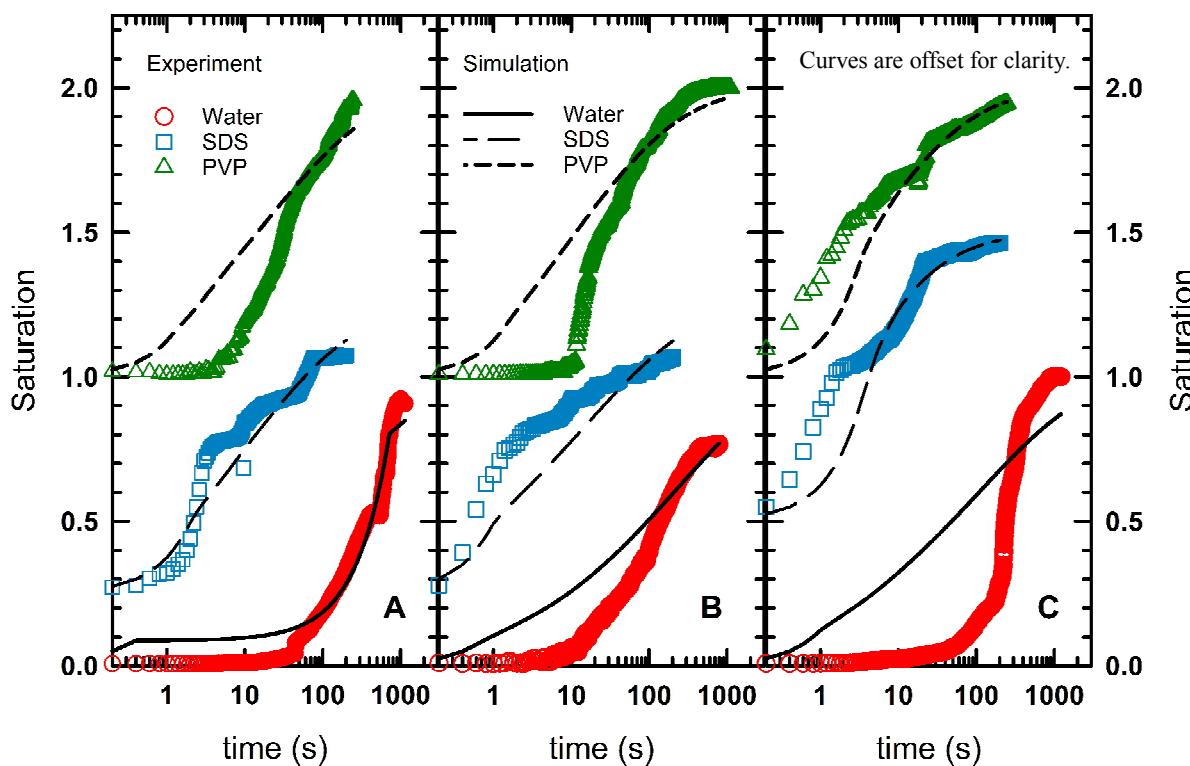


Figure 7 – A comparison of our experimental results to an IMPES simulation of oil displacement by an invading water phase in a medium with porosity of 0.063 (A), 0.113 (B) and 0.143 (C). The saturation curves are offset from each other for better clarity.

354 matching the conditions observed in Figure 3. The key differences between results of our simulations  
 355 and the experiment is that the simulation results show the invasion initially occurring at a slightly  
 356 slower rate than in the actual experiment (Figures 6A and 6B), and near the midpoint of the simulation  
 357 (Figure 6C), the invading phase breaks through and occupies a wider region than that at the  
 358 comparable experimental time (Figure 3C). We attribute these differences to the way our IMPES  
 359 simulation models do not count interface tension effect. To mimic the structure of the randomly  
 360 packed spheres, we modeled the permeability using values drawn from a log-normal distribution  
 361 [43], although the procedure is designed to model porous rock rather than a packed bed of spheres.

362 Despite these differences, the average saturation curves obtained by simulation closely match  
 363 our experimental curves (Figure 7) with high coefficients of determination for most of these curves  
 364 (Table 2). The mobility ratios that best fit the data exhibit decreases with increasing porosity both  
 365 for water and 0.1% PVP, indicating that these phases move through the porous packed bed easier at  
 366 higher porosities. The mobility ratios for 0.1% SDS deviate from this trend; at a porosity of 0.113, the  
 367 0.1% SDS appears to have a mobility of 33.3. While the coefficient of determination was low for this  
 368 case, the simulation did capture the general saturation trend as a function of time. Overall, our  
 369 simulations do show that the addition of SDS or PVP improves the mobility of the water phase as it

	Water			SDS			PVP		
Porosity	0.063	0.113	0.143	0.063	0.113	0.143	0.063	0.113	0.143
Mobility	255.8	114.7	87.2	11.2	33.3	1.9	18.2	12.5	4.6
R <sup>2</sup>	0.95	0.87	0.54	0.87	0.29	0.88	0.8	0.79	0.87

Table 2 – The mobility ratio that best fit the experimental data and the coefficient of determination (R<sup>2</sup>) associated with each fit.

370 invades an oil-saturated medium, and except for the 0.113 case, SDS exhibits lower mobility ratios  
 371 than PVP for the experiments conducted here.

372 **5. Conclusions**

373 We developed a microfluidic platform by which the waterflooding of an oil-saturated porous  
 374 structure is investigated through optical fluorescence microscopy. Where the characterization of bulk  
 375 porous media is rate limited [10,11], our microfluidic platform is able to characterize the invasion of  
 376 a water phase into an oil-saturated medium within a relatively short amount of time. The flexibility  
 377 of this platform allows us to rapidly analyze chemical modification techniques that are commonly  
 378 used in the petroleum industry [39,40] to enhance the recovery of oil. Observations of our device  
 379 using optical fluorescence microscopy enables us to track the invasion of a water phase into an oil  
 380 saturated phase and evaluate parameters such as saturation [58–60], fractal morphology [52,54,61],  
 381 temporal evolution of flow patterns [62,63] and invasion rate [64,65] that are important for evaluating  
 382 the effectiveness of different types of surfactants used for waterflooding. A simulation based on the  
 383 IMPES approach [42,43,45] for modeling two-phase flow in porous media was implemented in  
 384 MATLAB [43] to perform an inverse analysis of our experimental data to estimate the mobility of the  
 385 invading phase. The results of our inverse analysis demonstrate a significant decrease in mobility for  
 386 water bearing a polymer or surfactant.

387 The analysis performed in this article will form the basis of future work aimed at characterizing  
 388 the effect surface tension has in our microfluidic platform. Our IMPES model will be adjusted by  
 389 using closure expressions [66] for saturation curves that incorporate surface tension as it influences  
 390 capillary pressure. We also aim to control the porosity of our system through photolithography  
 391 techniques [13,26]. The approach we have used here can be used to evaluate other enhanced oil  
 392 recovery systems, including other types of polymers or surfactants [67], nanoparticles [68,69], and  
 393 foams [70,71]. Our platform can also be applied to other porous media situations that involve  
 394 diffusion and transport in biomedical systems [32,72], carbon sequestration [73,74] and additive  
 395 manufacturing of complex fluid networks [33,75,76].

396

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