Direct Measurement of Minimum Miscibility Pressure of Decane and CO₂ in Nanoconfined Channels

Bo Bao,* Jia Feng, Junjie Qiu, and Shuangliang Zhao*

ABSTRACT: Determining gas and oil minimum miscibility pressure (MMP) plays a vital role in the enhanced oil recovery. Injecting gases above the MMP into oil reservoirs leads to a relatively high oil recovery ratio. For conventional reservoirs, the fluid bulk MMP is measured by lab techniques such as the rising bubble approach. However, for the increasingly important tight and shale reservoirs, oil is confined in nanoscale pores. Nanoscopic MMP remains largely unknown from experiments and relies heavily on theoretical predictions. To close this gap, we developed a nanofluidic device to determine the MMP down to 50 nm by measuring the fluorescence intensity change in a nanoconfined channel. CO₂ and decane are used as the working fluids, with 1% fluorescent dye for characterization. At the isothermal condition, the fluorescence intensity in decane reduces with the injecting CO₂ pressure increasing, and the maximum fluorescence intensity reduction at certain CO₂ pressure indicates the MMP being reached. We measured and compared CO₂ and decane MMP at the bulk scale (5 μm) and nanoscale (50 nm). The experimental results align well with literature data and theoretical predictions. Importantly, our nanofluidic approach provides a promising strategy to determine the nanoscopic fluid MMP and is readily applicable in assisting the enhanced tight/shale oil recovery.

1. INTRODUCTION

Injection of miscible gas especially CO₂ has been proven to be one of most efficient and effective enhanced oil recovery (EOR) approaches in petroleum industry.1,2 From the pore-scale perspective, when the interfacial tension (IFT) between the oil phase and injected gas phase approaches zero, the two phases become miscible, leading to a homogeneous mixture, and reservoir oil is achieved when the IFT between two phases vanishes to zero after multiple contacts.3 Precise determination of MMP plays a vital role in successful implementation of miscible gas injection. A variety of approaches to determine the MMP have been developed by both the industry and academia in the previous decades, which can be categorized as theoretical or experimental methods.

Theoretical methods provide cost-effective and fast predictions of MMP. In the portfolio of theoretical approaches, equation of state (EOS) is one of the cornerstone techniques.4−10 Given the oil composition data, MMP can be calculated numerically using an appropriate EOS assuming that the system reaches equilibrium. It is noteworthy that EOS’s reliability is highly dependent on the quality of the oil composition data.11 In addition to EOS, empirical correlation is another widely adopted approach predicting the MMP based on adequate data of gas and oil properties, including but not limited to temperature, oil composition, gas composition, and initial gas−oil ratio.11−16 Furthermore, molecular simulation is another powerful approach to determining the MMP by simulating the interactions between oil and gas molecules.17 Beneficial from the rapid development in computer science, a variety of data processing algorithms have been developed and applied to calculate the MMP, such as group method of data handling,18 support vector machine,19,20 and support vector regression,21 fuzzy modeling,22,23 genetic programming,24−28 and artificial neural network.29−32 In summary, theoretical methods are effective and powerful tools in determining MMP values and have gained increasing attention. It is equally important to validate these theoretical models by reliable experimental data.

Direct measurement of MMP using experimental apparatus is essential in providing valuable first-hand data and validating theoretical models. During the past few decades, researchers and engineers have made great efforts in inventing various MMP experimental tools and methods, including the slim tube test, rising bubble apparatus (RBA), vanishing interfacial test
(VIT), and other approaches. The slim tube test method has been widely accepted and served as the standard measurement method in the petroleum community. The fundamental principle of the slim tube test is to establish a one-dimensional flow of gas into a long coiled tubing packed with porous materials and saturated with oil, by which the MMP is determined by the measured oil recovery factor, injected pore volumes, and pressures. The drawbacks of slim tube tests are as follows: relatively high cost and time-consuming. The RBA test, another extensively recognized MMP measurement approach, has been invented for more than three decades and adapted for different applications. The RBA test is a protocol to determine the MMP by visualizing and investigating the behavior of a gas bubble rising in a vertical thin column filled with oil according to the bubble shape, size, color, and increasing height. Additionally, the third technology widely used is the vanishing interfacial test (VIT), which was invented in 1997 and has derived to numerous modified versions. The key concept is to investigate the IFT behavior between gas and oil as a function of pressure in a PVT cell and obtain the MMP by extrapolating the observed curve of IFT vs pressure when the IFT approaches to zero. It is noteworthy that neither RBA nor VIT methods can capture the mass transfer mechanism of combined condensing and vaporizing processes. Furthermore, MMP can be determined by investigating the oil swelling factor vs equilibrium pressure, namely, swelling/extraction test. Conventionally, the miscibility process or IFT properties can be characterized via measurement of pressure, volume, temperature, composition, etc., as well as optical imaging by cameras. In recent years, novel sensing techniques, such as X-ray CT, magnetic resonance imaging, and acoustics, have been developed as complementary approaches to conventional methods.

In a recent study, a microfluidic-based method was developed to allow direct visualization of gas–oil multiphase flow in microchannels and measurement of MMP via fluorescence microscopy. Specifically, at pressures below the MMP, distinct gas–oil interfaces were observed as the slug flow of gas/oil moves forward. At pressures above the MMP, the IFT between gas and oil decreases to zero and the two phases appear indistinguishable as the slug flow moves, indicating the miscibility status. This microfluidic method was partially attributed to the giant progress in fabrication and sealing/packaging techniques of microfluidic devices compatible with high-pressure reservoir conditions. Compared to macroscale methods, the microfluidic approach demonstrates unique advantages in ultrafast measurement, rapid heat and mass transfer, in situ visualization, and potential for multiplexing. Consequently, microfluidic-based tests have been progressively developed and applied to visualize and investigate pore-scale mechanisms of EOR processes such as carbon sequestration, reservoir fluid propagation, flooding, fracturing, and emulsification. In addition to MMP determination, microfluidic approaches also demonstrate success in characterizing other phase properties and behaviors of petroleum reservoir fluids, including dew point, bubble point, critical point, phase diagrams, solubility, diffusivity, and precipitation.

In the recent decade, fluid phase behaviors including MMP in nanoconfinement have gained increasing attention due to the boom of unconventional oil and gas productions. The pores in unconventional reservoirs are ranging from few to hundreds of nanometers, bringing in uncertainties to fluid phase behaviors and thus necessitating a fundamental understanding of these unique phase behaviors. The phase behaviors of the injection phase and initial oil phase in nanopores involve in a complex interplay of nanoscale mechanisms such as wetting, adhesion, surface tension, and capillarity, all of which are dominated by a strong interfacial effect in the nanoconfined. All of these nanoscale mechanisms lead to a significant deviation of phase behaviors from the bulk state. The nanoconfinement effect in fluid phase behaviors has been investigated by theoretical models and simulations based on EOS density functional theory and molecular simulation. Theoretical models predicting the MMP in nanoconfined have been developed using different principles. Theoretical models can use the EOS coupled with multiphase cell algorithm, perturbed-chain statistical associating fluid theory EOS with VIT technique, modified vapor/liquid equilibrium considering capillary pressure effects and critical property shifts, EOS with interfacial thickness, EOS with thermodynamic solubility parameter, EOS with thermodynamic free energy of mixing and modified CO$_2$–oil MMP correlation considering pore radius, and critical property shift. All these studies demonstrate that the MMP decreases significantly in nanoconfinement compared to the bulk state. Interestingly, different studies cover different ranges of nanopore sizes and indicate that reduction in MMP occurs at nanopores at 4 nm, less than 10 nm, and less than 100 nm. One of these studies even predicted that the MMP keeps decreasing in a broader range, i.e., from 1 mm (infinite) to 4 nm. The decrease in MMP in nanoconfinement could be explained by capillarity, electrostatic force, and van der Waals forces as a result of molecular interactions between the fluid and nanopore wall.

In contrast to theoretical perspectives, experimental efforts investigating nanoconfined phase behaviors and MMP require a series of expensive nanofabrication equipment, complicated and precise nanofabrication protocols, and sharp optical imaging systems. Beneficial from the state-of-art nanofluidic technology, researchers began overcoming these challenges and gradually developed a series of silicon/glass-made nanofluidic devices embodied with nanoconfined channels (nanoscale in channel depth and microscale in channel width), nanopores, nanoporous networks, and nanopacked beds to investigate fluid phase behaviors such as evaporation, condensation, and boiling in nanoconfined for EOR purposes. Specifically, evaporation of alkanes in 100 nm nanoconfined channels was observed by optical microscopy. Using a similar design, condensation of hydrocarbon in nanoconfined channels was investigated and it is found that condensation pressure in pores <50 nm is below the bulk saturation pressure. Interestingly, another experimental study on hydrocarbon phase behaviors pointed out that 50 nm confinement effect is negligible. This disagreement actually implies the complexity of nanoconfinement experiments and unknown fundamentals behind them. More experiments with different nanoconfinement geometries and dimensions were designed and carried out, aiming to obtain a better understanding. A following experimental study indicates that condensation condition of alkane in 70 nm nanoconfined channels deviates from the bulk conditions, caused by vapor flow and interface resistances. Furthermore, another experimental study on condensation in packed beds with 15
nm pore throats indicates that pore geometry and surface wettability play an important role in capillary condensation in nanoconfinement.\textsuperscript{93} More recent nanofluidic experiments provide solid evidences supporting that phase behaviors can be affected by nanoconfinement. For example, boiling conditions of hydrocarbons in 88 nm nanoconfined channels was found differing from bulk conditions and predicted classical nucleation theory.\textsuperscript{70} Similarly, evaporation in sub-10 nm nanoporous media reveals that the evaporation pressure is 11\% lower than predictions from the Kelvin equation.\textsuperscript{94} Condensation of hydrocarbons in 8 nm channels shows that phase change conditions were found significantly deviated from bulk conditions.\textsuperscript{95}

All these experiments provide valuable insights into the continuous efforts understanding various nanoconfined phase behaviors of evaporation, condensation, and boiling. However, nanoconfined miscibility has not been measured directly by nanofluidic experiments, even though it is of high importance for both petroleum industry and academia community. To this point, if we propose a "MMP determination quadrant plot" divided by categories of "theoretical" or "experimental", "bulk", or "nanoconfined", it is found that the combination of "experimental" and "nanoconfined" is the only blank quadrant left behind. Hereby, we design and conduct this nanofluidic experiment to directly measure the MMP in nanoconfinement, filling the blank in the quadrant plot.

2. EXPERIMENTAL SECTION

2.1. Nanofluidic Setup. The experimental apparatus including a nanofluidic chip, a chip manifold, and other necessary equipment are shown in Figure 1a. The nanofluidic chip design embodies two microchannels (chip A/B: 100 \( \mu \)m deep \( \times \) 100 \( \mu \)m wide) and two dead-end channels (chip A: 5 \( \mu \)m deep \( \times \) 10 \( \mu \)m wide, chip B: 50 nm deep \( \times \) 5 \( \mu \)m wide), and each dead-end channel perpendicularly intersects in the middle of each microchannel. The width of nanoconfined channel is designed to be 5 \( \mu \)m to guarantee that the channel is wide enough for clearly visualizing fluid phases given the optical microscope settings and also narrow enough to avoid channel to collapse during the chip bonding process.\textsuperscript{96} The pattern of dead-end nanoconfined channels and microchannels were fabricated by two rounds of photolithography and reactive ion etching on the silicon substrate, which was then bonded with a glass wafer. This hybrid silicon-glass chip can sustain high pressure and temperature, and the detailed protocol can be found in our previous study.\textsuperscript{70} A customized chip manifold was designed and built to connect the chip and tubing with sealing O-rings (up to 10 MPa). The manifold was then integrated with a circulator bath and a temperature sensor to control and detect the chip temperature (278.15\textdegree - 373.15 K). A high-pressure pump (Teledyne ISCO 100DX) was used for CO\(_2\) injection at target pressures and a syringe pump (Chemyx Fusion 6000) was used to inject decane into the chip. An optical microscope (Nikon NI-U) was equipped with 20X objective lens and a CMOS camera (PCO Panda) for
Figure 2. (a) Fluorescence visualization of decane and variation of relative intensity in the 5 μm dead-end microchannel at 293.15 K and pressures below, at, and above the MMP. (b) Fluorescence visualization of decane and variation of relative intensity in the 5 μm dead-end microchannel at 303.15 K and pressures below, at, and above the MMP. Variation of relative intensity over time at MMP in the (c) 5 μm-deep dead-end microchannel at 293.15 K, 5.4 MPa and (d) 5 μm dead-end microchannel at 303.15 K, 6.4 MPa.

visualizing and capturing real-time images (resolution at 0.25 μm/pixel) of phase behaviors in the nanofluidic chip. The physical nanofluidic chip and the assembled nanofluidic system are shown in Figure 1b and c, respectively. In this study, decane (99.8%, Collins) was used as a representative oil sample, and a fluorescent dye (TP3400 Fluoro-Lite 5 OEM) was added to decane at the ratio of 1:100 to enable fluorescence imaging. Research grade CO₂ (99.99%, PRAXAIR) was used as the working gas.

2.2. Experimental Procedure. The MMP of decane/CO₂ was measured in the dead-end nanoconfined channel in this study. The nanofluidic chip was thoroughly cleaned in acetone for 30 min and dried in a muffle furnace at 673.15 K for 1 h. Initially, the microchannel and dead-end nanoconfined channel (zoom-in view in Figure 1a) were filled with decane by syringe pump injection. Subsequently, CO₂ was injected into the microchannel to displace the bulk volume of decane. A thin film of decane was formed near the entrance of the dead-end nanoconfined channel during the displacement process due to strong capillary force, which ensures the nanoconfined channel remained being filled with decane. Two sets of experimental temperatures (293.15 and 303.15 K) were selected to carry out the MMP test. The system pressure was stepwise increased at 0.1 MPa intervals and kept constant for a minimum of 50 s under each pressure step in order to reach equilibrium status. The miscibility process in the dead-end nanoconfined channel was captured and recorded as a real-time fluorescence image sequence. The camera frame rate was fixed at 40 fps (exposure time of 25 ms) and 10 fps (exposure time of 100 ms) in 5 μm-deep channel and 50 nm-deep channel, respectively. At each pressure point, a series of 25 fluorescence images were imported into image processing software (ImageJ) to determine the average fluorescence intensity in the nanoconfined channel. The weak fluorescence signal from the captured images was systematically enhanced by linear transformation, Gaussian blurring, and contrast adjustment using ImageJ for a better visual effect. Variation of relative fluorescence intensity as a function of pressure was used to identify the MMP of decane/CO₂. At the MMP, variation of relative fluorescence intensity was plotted as a function of time to indicate the miscibility process between decane and CO₂.

It is noteworthy that this work differs from a previous work using the microfluidic chip determining the MMP in terms of the magnitude of confinement size as well as the motivation. A previous microfluidic work aims to provide a high-throughput testing method to measure the bulk MMP by taking the high mass transfer efficiency of microchannel (250 μm wide × 100 μm deep). This work aims to develop a new method to determine the fluid MMP at the nanoscale (5 μm wide × 50 nm deep) and investigate whether there is any measurable deviation in MMP from the bulk scale. The cross-sectional area here is 10³ times smaller than that in a previous work, yielding much stronger interactions between the channel wall and fluid molecules. Correspondingly, this experimental work is motivated to validate the theoretical claims that nanoconfinement would reduce the MMP while a previous work is driven by developing a bulk MMP measurement tool.

Additionally, this work applies a quasi-static fluid control approach by using a dead-end nanoconfined channel design, instead of a dynamic slug flow approach via a T-junction microchannel design in a previous study. Specifically, CO₂ gradually diffuses into the original oil in the dead-end nanoconfined channel. Such a quasi-static approach is close to the nature of miscibility in terms of thermodynamic...
equilibrium, i.e., the pressure at which the interfacial tension (IFT) between the oil phase and injected gas phase approaches zero, and the two phases become miscible as a homogeneous mixture. Importantly, our quasi-static approach also avoids flow-induced testing errors as the fluid flow introduces a huge pressure drop in the nanochannel. Comparatively, the pressure drop is amplified by ~300 times when the cross-sectional area of the channel is reduced from the microscale (250 μm wide × 100 μm deep)39 to nanoscale (5 μm wide × 50 nm deep). Such a pressure drop leads to a misleading data logging of the design in this work is necessary and shows its advantage over MMP and engineering merit of pressure drop, the quasi-static nanoscopic MMP. In short, given the thermodynamic nature of MMP and engineering merit of pressure drop, the quasi-static design in this work is necessary and shows its advantage over the flowing approach.

3. RESULTS AND DISCUSSION

We first validated the reliability of using a fluorescence signal to identify the MMP at the bulk scale (here we use a 5 μm-deep dead-end microchannel). In our test, when the CO2 pressure in the reservoir is increased, the fluorescence signal intensity in the dead-end microchannel continuously decreases, which indicates CO2 diffusing and dissolving in decane. At each pressure step, we allowed sufficient relaxation (50 s) for the fluorescence signal intensity to reach equilibrium before sampling. When the CO2 pressure is increased to a certain value, the fluorescence signal intensity dramatically reduces. Such a sharp intensity reduction indicates that the fluorescence concentration changes significantly, potentially because CO2 largely mixes with decane in the dead-end microchannel and dilutes the fluorescent dye molecule concentration. It is thus reasonable to assume that, at this pressure, CO2 and decane have reached the minimum miscible condition. This pressure is identified as the CO2-decane MMP in our experiments, which is found to be 5.4 MPa at 293.15 K and 6.4 MPa at 303.15 K (Figure 2a,b). Figure 2c,d shows the fluorescence intensity reduction historical profile at the MMP. The relative intensity curve flattened eventually indicates that the diffusion equilibrium has been reached among CO2, the fluorescent dye, and decane.

We compared the MMP measured through our approach with previous experimental data measured by slim tube or rising bubble methods. We found that the MMP values are close to each other, with a maximum deviation at 4% as shown in Table 1. It is noted that addition of the fluorescent dye at a low concentration (1%) could potentially affect the MMP measurement result because it changes the liquid composition, leading to an unavoidable error. However, such an error is small as seen from the comparison.

We applied the same experimental procedure to measure the decane/CO2 MMP in the 50 nm-deep dead-end nanoconfined channel. The MMP detected through the fluorescence intensity reduction indicates almost the same pressure compared to that in the 5 μm-deep channel (5.4 MPa at 293.15 K and 6.4 MPa at 303.15 K), as shown in Figure 3a,b. Similarly, at the MMP, the fluorescence intensity changing with time is shown in Figure 3c,d. Given many fluid phase properties, such as the boiling and condensation pressures,70 at the nanoscale shift radically from the bulk scale, the MMP measured from our experiments that is consistent from the large scale down to 50 nm is of great theoretical interest.

It is noteworthy that the relative intensity of fluorescence signal could be potentially converted into concentration of CO2 dissolved in the oil phase. However, such conversion pays at a cost of bringing in extra difficulties and errors associated with the calibration test. Specifically, a calibration test is required to quantify the relations between the relative intensity and CO2 concentration in the nanoconfined channels. Given the tiny volume of oil confined in the nanochannel (6.25 × 10⁻³ pL = 25 μm × 5 μm × 50 nm), the maximum dissolved CO2 would be approximately 7.15 × 10⁻¹² mol, assuming that the solubility is on the order of 1.1 mmol/mL.98 Such a trace amount of CO2 would be extremely difficult to be manipulated or measured given the existing injection and characterization system. In addition, the calibration curve is expected to be pressure-sensitive since the refractive index of fluid mixture is also a function of density, which is highly dependent on pressure. In summary, the difficulty in manipulation and measurement of the extremely trace amount of gas and the pressure cross-sensitivity make the "relative intensity–concentration" conversion less feasible or practical than the current method.

The experimental approach we applied here is established on the variation of fluid solubilities. Fundamentally, the three-component Hansen solubility parameter99 can well describe the fluid solubility. For a non-polar substance, such as decane and CO2, the one-component Hildebrand solubility parameter is close to the three-component Hansen solubility parameter100 and is well adaptable for its brevity in math. The Hildebrand solubility parameter (δ) is defined as

\[ \delta = \sqrt{\frac{\Delta U_{\text{vap}}}{v}} \]  

(1)

where \( \Delta U_{\text{vap}} \) is the latent heat of vaporization and \( v \) is the molar volume. From the thermodynamics, \( \delta \) can be further expressed as a function of fluid temperature and pressure,101

\[ \delta = \sqrt{T \left( \frac{\partial P}{\partial T} \right)_v - P} \]  

(2)

Here, we applied the Peng–Robinson equation of state,101 with the critical temperature and pressure modified according to nanopore size to capture the fluid phase property shifting at the nanoscale:102

\[ P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \]  

(3)

where
where $T_c$ and $P_c$ are fluid critical properties at the bulk scale. Combining eqs 1–9, the solubility parameter is a function of fluid temperature, pressure, molar volume, and pore radius, which is suitable to study the confinement effect on the MMP. We take $T = 303.15$ K as an example to show the effect of confinement scale in affecting the CO$_2$–decane MMP. At the isothermal condition, the MMP of two fluids described by the solubility parameter as demonstrated by the previous study is

$$\Delta \delta = |\delta_1 - \delta_2| \leq 3 \text{(cal/cm}^3\text{)}^{0.5}$$

(10)

Here, the CO$_2$–decane MMP is determined by calculating the pressure when the difference between CO$_2$ and decane solubility parameter is at 3 (cal/cm$^3$)$^{0.5}$, as shown in Figure 4.

We calculated the MMP at the bulk (here using pore size of 5 μm), 50 nm, and 5 nm scale for comparison. It is clearly shown that the MMP at the bulk scale is close to the MMP at 50 nm, with the deviation only at ~0.011 MPa (0.17% shift). When the pore size is further reduced to the 5 nm scale, the MMP deviation is ~0.162 MPa (2.5% shift), which is an order of magnitude larger than the 50 nm case and becomes notable.

Figure 3. (a) Fluorescence visualization of decane and variation of relative intensity in the 50 nm dead-end nanoconfined channel at 293.15 K and pressures below, at, and above MMP. (b) Fluorescence visualization of decane and variation of relative intensity in the 50 nm dead-end nanocoffined channel at 303.15 K and pressures below, at, and above MMP. Variation of relative intensity over time at MMP in the (c) 50 nm-deep dead-end nanoconfined channel at 293.15 K, 5.4 MPa and (d) 50 nm-deep dead-end nanoconfined channel at 303.15 K, 6.4 MPa.

Figure 4. CO$_2$–decane MMP at 303.15 K determined by the solubility parameter difference for the bulk, 50 nm, and 5 nm scale.
Theoretically, the pore size influences the critical temperature and pressure in nanopores, which further influence the MMP according to the equations above.

The Lennard-Jones diameter of a fluid plays a key role in determining the critical point shift in the nanopore according to eqs 7–9. For decane, the Lennard-Jones diameter is calculated to be 0.76 nm, and for CO$_2$, the Lennard-Jones diameter is 0.39 nm. When the pore size is at 50 nm, the pore diameter is two orders of magnitude larger than the molecular Lennard-Jones diameter. The critical point shift is small: the CO$_2$ critical temperature shifts from 304.13 to 299.65 K, and the critical pressure shifts from 7.38 to 7.27 MPa (1.5% reduction). The decane critical temperature shifts from 617.70 to 600.25 K, and the critical pressure shifts from 2.10 to 2.04 MPa (2.9% reduction). Such a small critical point shift does not obviously influence the fluid PVT results calculated by the Peng–Robinson equation of state, which is established on the fluid critical properties. The MMP variation due to the pore confinement at 50 nm is thus small and beyond our testing resolution, confirming our experimental results.

When the pore size is further reduced by one order of magnitude (e.g., 5 nm), the difference between the fluid Lennard-Jones diameter and pore size is at one order of magnitude. Theoretically, the confinement effect toward the critical point shift starts to be obvious: the CO$_2$ critical temperature shifts from 304.13 to 260.97 K, and the critical pressure shifts from 7.38 to 6.33 MPa (14.2% reduction). The decane critical temperature shifts from 617.70 to 455.52 K, and the critical pressure shifts from 2.10 to 1.55 MPa (26.2% reduction). In this case, the fluid PVT property at 5 nm changes as a function of the supercritical point, and the supercritical point deviation leads to an obvious shift of the MMP. In general, comparing the fluid Lennard-Jones diameter size and nanocconfinement size gives a reasonable estimation on the thermodynamic equilibria and transport behaviors shift. When the two sizes are close within one order of magnitude, experimental results often deviate from bulk theory predictions and become anomalous. For small molecules such as pentane and CO$_2$ here, sub-10 nm confinement is of crucial importance where classical theory predictions should be reconsidered. Meanwhile, for large molecules such as asphaltene, anomalous transport and thermodynamic behaviors could happen at sub-100 nm or even larger pores.

Experimentally determining MMP at the sub-10 nm scale is challenging. Conventional testing methods require fluid flow and mutual fluid displacement in a sand-packed slim tube or other porous media. However, at the sub-10 nm pore scale, the system permeability with the conventional method is extremely low (nano-Darcy), which leads to an unrealistic experimental duration (months) and an unfavorably low testing repeatability. The nanofluidic approach we developed here is promising to addresses this challenge. In a sub-10 nm nanofluidic channel, detecting the fluorescence signal can be difficult as the dye molecule areal density is an order of magnitude lower than the sub-100 nm channel. However, the fluorescence signal in the nanofluidic device can be enhanced with an additional optical layer, as demonstrated by a previous study. Experimentally determining MMP at the sub-10 nm scale using nanofluidics is of significant interest for our future studies.

In addition to precisely defining the confinement size, the silicon-glass micro/nanofluidic device importantly provides a remarkable tolerance of high fluid pressure and temperature that match the shale/tight reservoir conditions. The fluid pressure in the micro/nanochannel can be increased up to 50 MPa$^{106}$ and fluid temperature up to 573 K.$^{107}$ The typical shale/tight reservoir pressure is in the range of 27.52–68.95 MPa (3992–10,000 psi),$^{108,109}$ and the temperature is in the range of 327.59–422.04 K (130–300 °F),$^{108,109}$ which are well or partially falling into the silicon chip temperature/pressure allowance. Importantly, the surface of nanofluidics can be modified with other materials to include varying wettability for studying nanoscale fluid behaviors,$^{103}$ such as the graphene-coated hydrophobic nanochannel for studying ultrafast water transport.$^{110}$ Overall, our nanofluidic device demonstrates a new experimental method in measuring MMP at the nanoscale that is readily applicable to engineering frontiers such as enhanced shale/tight oil recovery. The pressure-resistant and visible nanofluidic confinement device as well as quasi-static operation can be also extended into other phase behavior studies in the nanoscale, including the critical point shift in nanopores as predicted by numerical models$^{7,102}$ and thus validate or improve the models.

The CO$_2$–decane binary system was chosen in this study because the bulk MMP experimental data is available for comparing with our measured data in the nanoconfined channel. It is noted that the complex oil mixture is of interest for industrial applications. Previous numerical studies have predicted MMPs of 3-component oil, 10-component oil, Bakken oil, Pembina live tight oil, and other dead oil in nanopores.$^{77,83–87}$ Theoretically, the fluid phases for the oil mixture in nanopores could potentially deviate from the PR-EOS prediction applied in this work due to pore surface adsorption selectively enriching heavy fluid components.$^{95}$ A modified EOS with molecular simulation methods, such as density functional theory,$^{111}$ is thus needed to accurately predict the fluid mixture phases and MMP in nanopores accordingly. The quasi-static nanofluidic method developed in this work is expected to be vital in determining the nanoscopic MMP of complex oil systems in the future and providing data support to numerical findings.

4. CONCLUSIONS

In this paper, we developed a nanofluidic device to measure the CO$_2$–decane MMP down to the 50 nm scale. The fluorescence intensity reduction in the nanochannel system is used as a reference to determine the MMP. At the isothermal condition, the MMP is taken as the CO$_2$ injection pressure at which the fluorescence intensity in oil after CO$_2$ injection has the maximum drawdown. We first validated this methodology by measuring the CO$_2$–decane bulk MMP in a 5 μm-deep microchannel and found that the results are close to those measured with conventional methods. Using the same strategy, we measured the CO$_2$–decane MMP at 50 nm and found an inconspicuous shift from the bulk MMP at both 293.15 and 303.15 K. Theoretically, we realized that, at 50 nm, the pore size is two orders of magnitude larger than the fluid Lennard-Jones diameter. The confinement effect in influencing fluid supercritical properties is negligible. The CO$_2$–decane MMP shift at 50 nm is only 0.17% from the bulk value, confirming our experimental finding. The theory further predicts that, at the 5 nm pore size, the CO$_2$–decane MMP shift from the bulk value becomes notable. The nanofluidic device is promising in measuring the fluid MMP down to a few nanometers with the method developed here, by combining an optical layer in the...
nanofluidic device to enhance fluorescence signals in the future study.

Overall, this work identifies that a sharp fluorescence intensity reduction in oil during gas injection can be used as a key reference to identify nanoscopic MMP, an important technique innovation. With this new approach, we find that the bulk MMP theory firmly holds down to 50 nm, providing solid evidence to extend the validity of concise classical theories down to the nanoscale. This work further indicates a promising direction of importance, which is to detect the MMP at the sub-10 nm scale using nanofluidics. The current limitation of detecting the MMP at sub-10 nm was discussed, and potential solutions have been suggested as well. We anticipate that the nanofluidic approach combining fluorescence detection to address the engineering challenge of measuring the nanoscopic fluid MMP, with immediate applications in the enhanced shale/tight oil recovery.

AUTHOR INFORMATION

Corresponding Authors

Bo Bao — State Key Laboratory of Chemical Engineering and School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China; Email: bbao@ecust.edu.cn

Shuangliang Zhao — State Key Laboratory of Chemical Engineering and School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China; Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology and School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China; orcid.org/0000-0002-9547-4860; Email: szhao@ecust.edu.cn

Authors

Jia Feng — State Key Laboratory of Chemical Engineering and School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Junjie Qiu — State Key Laboratory of Chemical Engineering and School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c05584

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (no. 21808056) and the generous support from PetroChina Innovation Foundation (2019D-5007-0208).

REFERENCES

(1) Alvarado, V.; Manrique, E. Enhanced Oil Recovery: An Update Review. Energies 2010, 3, 1529–1575.
(2) Cao, M.; Gu, Y. Oil Recovery Mechanisms and Asphaltene Precipitation Phenomenon in Immiscible and Miscible CO2 Flooding Processes. Fuel 2013, 109, 157–166.
(3) Pedersen, K. S.; Christensen, P. L.; Shakhli, J. A.; Christensen, P. L. Phase Behavior of Petroleum Reservoir Fluids; CRC press, 2006, DOI: 10.1201/9781420018257.
(4) Jaubert, J.-N.; Auvaille, L.; Pierre, C. Is It Still Necessary to Measure the Minimum Miscibility Pressure? Ind. Eng. Chem. Res. 2002, 41, 303–310.
(5) Nasrifar, K.; Mosheghian, M. Application of an Improved Equation of State to Reservoir Fluids: Computation of Minimum Miscibility Pressure. J. Pet. Sci. Eng. 2004, 42, 223–234.
(6) Zhao, G.-B.; Addharma, H.; Towler, B.; Radoss, M. Using a Multiple-Mixing-Cell Model to Study Minimum Miscibility Pressure Controlled by Thermodynamic Equilibrium Tie Lines. Ind. Eng. Chem. Res. 2006, 45, 7913–7923.
(7) Meyberg Nunes Costa, G.; Sergio de Mello Vieira Rocha, P.; Leal Chagas Ribeiro, A.; Roberto Freire de Menezes, P.; Carlos Alves de Lima, R.; Ubriratan Oliveira Costa, P.; de Almeida Rodrigues, E. An Improved Method for Calculating CO2 Minimum Miscibility Pressure Based on Solubility Parameter. J. Pet. Sci. Eng. 2012, 98-99, 144–155.
(8) Haghitalab, A.; Kariman Moghaddam, A. Prediction of Minimum Miscibility Pressure Using the UNIFAC Group Contribution Activity Coefficient Model and the LCVM Mixing Rule. Ind. Eng. Chem. Res. 2016, 55, 2840–2851.
(9) Zhang, K.; Jia, N.; Li, S. Exploring the Effects of Four Important Factors on Oil–CO2 Interfacial Properties and Miscibility in Nanopores. RSC Adv. 2017, 7, 54164–54177.
(10) Haghitalab, A.; Hasannatj, H.; Panah, H. S. Prediction of Minimum Miscibility Pressure of Pure CO2, Carbon Dioxide Gas Mixtures and Polymer-Supercritical CO2 in Oil Using Modified Quadruple Cubic Plus Association Equation of State (MqCPA EoS). Fluid Phase Equilib. 2018, 478, 114–128.
(11) Alomair, O.; Malallah, A.; Elsharkawy, A.; Iqbal, M. Predicting CO2 Minimum Miscibility Pressure (MMP) Using Alternating Conditional Expectation (ACE) Algorithm. Oil Gas Sci. Technol. 2015, 70, 967–982.
(12) Dong, M.; Huang, S.; Dyer, S. B.; Mourits, F. M. A Comparison of CO2 Minimum Miscibility Pressure Determinations for Weyburn Crude Oil. J. Pet. Sci. Eng. 2001, 31, 13–22.
(13) Li, H.; Qin, J.; Yang, D. An Improved CO2 –Oil Minimum Miscibility Pressure Correlation for Live and Dead Crude Oils. Ind. Eng. Chem. Res. 2012, 51, 3516–3523.
(14) ZareNezhad, B. A New Correlation for Predicting the Minimum Miscibility Pressure Regarding the Enhanced Oil Recovery Processes in the Petroleum Industry. Pet. Sci. Technol. 2016, 34, 56–62.
(15) Lai, F.; Li, Z.; Hu, X. Improved Minimum Miscibility Pressure Correlation for CO2 Flooding Using Various Oil Components and Their Effects. J. Geophys. Eng. 2017, 14, 331–340.
(16) Shokir, E. M. E.-M. CO2–Oil Minimum Miscibility Pressure Model for Impure and Pure CO2 Streams. J. Pet. Sci. Eng. 2007, 58, 173–185.
(17) Peng, F.; Wang, R.; Guo, Z.; Feng, G. Molecular Dynamics Simulation to Estimate Minimum Miscibility Pressure for Oil with Pure and Impure CO2. J. Phys. Commun. 2018, 2, 115028.
(18) Hemmati-Sarapardeh, A.; Mohagheghian, E. Modeling Interfacial Tension and Minimum Miscibility Pressure in Paraffin-Nitrogen Systems: Application to Gas Injection Processes. Fuel 2017, 205, 80–89.
(19) Delforouz, F. B.; Khorsand Movaghar, M. R.; Shariaty, S. New Empirical Correlations for Predicting Minimum Miscibility Pressure (MMP) during CO2 Injection; Implementing the Group Method of Data Handling (GMDH) Algorithm and Pitzer’s Acentric Factor. Oil Gas Sci. Technol. 2019, 74, 64.
(20) Shokrollahi, A.; Arabloo, M.; Gharagheizi, F.; Mohammadi, A. H. Intelligent Model for Prediction of CO2 – Reservoir Oil Minimum Miscibility Pressure. Fuel 2013, 112, 375–384.
(21) Zhong, Z.; Carr, T. R. Application of Mixed Kernels Function (MKF) Based Support Vector Regression Model (SVR) for CO2 – Reservoir Oil Minimum Miscibility Pressure Prediction. Fuel 2016, 184, 590–603.
(22) Ahmadi, M.-A.; Ebadi, M. Fuzzy Modeling and Experimental Investigation of Minimum Miscible Pressure in Gas Injection Process. Fluid Phase Equilib. 2014, 378, 1–12.
(23) Mollayi-Berneti, S. Determination of Minimum Miscibility Pressure in CO2-IOR Projects with the Aid of Hybrid Neuro-Fuzzy System. *Fuel* 2016, 180, 59–70.

(24) Emera, M. K.; Sarma, H. K. Use of Genetic Algorithm to Estimate CO2–Oil Minimum Miscibility Pressure—a Key Parameter in Design of CO2 Miscible Flood. *J. Pet. Sci. Eng.* 2005, 46, 37–52.

(25) Rezaei, M.; Eftekhar, M.; Schaffie, M.; Ranbar, M. A CO2 Oil Minimum Miscibility Pressure Model Based on Multi-Gene Genetic Programming. *Energy Explor. Exploit.* 2013, 31, 607–622.

(26) Kaydanli, H.; Najafzadeh, M.; Hajizadeh, A. A New Correlation for Calculating Carbon Dioxide Minimum Miscibility Pressure Based on Multi-Gene Genetic Programming. *J. Nat. Gas Sci. Eng.* 2014, 21, 625–630.

(27) Kamari, A.; Arabloo, M.; Shokrollahi, A.; Gharagehei, F.; Mohammadi, A. H. Rapid Method to Estimate the Minimum Miscibility Pressure (MMP) in Live Reservoir Oil Systems during CO2 Flooding. *Fuel* 2015, 153, 310–319.

(28) Bian, X.-Q.; Han, B.; Du, Z.-M.; Jaubert, J.-N.; Li, M.-J. Integrating Support Vector Regression with Genetic Algorithm for CO2 Oil Minimum Miscibility Pressure (MMP) in Pure and Impure CO2 Streams. *Fuel* 2016, 182, 550–557.

(29) Huang, Y. F.; Huang, G. H.; Dong, M. Z.; Feng, G. M. Development of an Artificial Neural Network Model for Predicting Minimum Miscibility Pressure in CO2 Flooding. *J. Pet. Sci. Eng.* 2003, 37, 83–95.

(30) Dehghani, S. A. M.; Sefiti, M. V.; Ameri, A.; Kaveh, N. S. Minimum Miscibility Pressure Prediction Based on a Hybrid Neural Genetic Algorithm. *Chem. Eng. Res. Des.* 2008, 86, 173–185.

(31) Zendehboudi, S.; Ahmadi, M. A.; Bahadori, A.; Shafei, A.; Bahadagli, T. A Developed Smart Technique to Predict Minimum Miscible Pressure–Eor Implications. *Can. J. Chem. Eng.* 2013, 91, 1325–1337.

(32) Tatar, A.; Shokrollahi, A.; Mesbah, M.; Rashid, S.; Arabloo, M.; Bahadori, A. Implementing Radial Basis Function Networks for Modeling CO2–Reservoir Oil Minimum Miscibility Pressure. *J. Nat. Gas Sci. Eng.* 2013, 15, 82–92.

(33) Liao, C.; Liao, X.; Chen, J.; Ye, H.; Chen, X.; Wang, H. Correlations of Minimum Miscibility Pressure for Pure and Impure CO2 in Low Permeability Oil Reservoir. *J. Energy Inst.* 2014, 87, 208–214.

(34) Mogensen, K. A Novel Protocol for Estimation of Minimum Miscibility Pressure from Slimtube Experiments. *J. Pet. Sci. Eng.* 2016, 146, 545–551.

(35) Ghorbani, M.; Gandomkar, A.; Montazeri, G. Describing a Strategy to Estimate the CO2 –Heavy Oil Minimum Miscibility Pressure Based on the Experimental Methods. *Energy Sources, Part A* 2019, 41, 2083–2093.

(36) Elfsharkawy, A. M.; Poettmann, F. H.; Christiansen, R. L. Measuring Minimum Miscibility Pressure: Slim-Tube or Rising-Bubble Method? In *SPE/DOE enhanced oil recovery symposium*; Society of Petroleum Engineers, 1992, DOI: 10.2118/214114-MS.

(37) Zhang, K.; Gu, Y. Two Different Technical Criteria for Determining the Minimum Miscibility Pressures (MMPs) from the Slim-Tube and Corelood Tests. *Fuel* 2015, 161, 146–156.

(38) Moosazadeh, M.; Keshavarzi, B.; Ghobti, C. Investigation of the Minimum Miscibility Pressure for Injection of Two Different Gases into Two Iranian Oil Reservoirs: Experimental and Theory. *Can. J. Chem. Eng.* 2017, 95, 1014–1020.

(39) Christiansen, R. L.; Haines, H. K. Rapid Measurement of Minimum Miscibility Pressure With the Rising-Bubble Apparatus. *SPE Reservoir Eng.* 1987, 2, 523–527.

(40) Aderkunie, O.; Hoffman, B. T. Experimental and Analytical Methods to Determine Minimum Miscibility Pressure (MMP) for Bakken Formation Crude Oil. *J. Pet. Sci. Eng.* 2016, 146, 170–182.

(41) Li, S.; Luo, P. Experimental and Simulation Determination of Minimum Miscibility Pressure for a Bakken Tight Oil and Different Injection Gases. *Petroleum 2017*, 3, 79–86.

(42) Zhang, K.; Jia, N.; Zeng, F. Application of Predicted Bubble-Rising Velocities for Estimating the Minimum Miscibility Pressures of the Light Crude Oil–CO2 Systems with the Rising Bubble Apparatus. *Fuel* 2018, 220, 412–419.

(43) Zhang, K.; Gu, Y. New Qualitative and Quantitative Technical Criteria for Determining the Minimum Miscibility Pressures (MMPs) with the Rising-Bubble Apparatus (RBA). *Fuel* 2016, 175, 172–181.

(44) Rao, D. N. A New Technique of Vanishing Interfacial Tension for Miscibility Determination. *Fluid Phase Equilib.* 1997, 139, 311–324.

(45) Gu, Y.; Hou, P.; Luo, W. Effects of Four Important Factors on the Measured Minimum Miscibility Pressure and First-Contact Miscibility Pressure. *J. Chem. Eng. Data* 2013, 58, 1361–1370.

(46) Shang, Q.; Xia, S.; Shen, M.; Ma, P. Experiment and Correlations for CO2–Oil Minimum Miscibility Pressure in Pure and Impure CO2 Streams. *RSC Adv.* 2014, 4, 63824–63830.

(47) Hawthorne, S. B.; Miller, D. J.; Jin, L.; Gorecki, C. D. Rapid and Simple Capillary-Rise/Vanishing Interfacial Tension Method To Determine Crude Oil Minimum Miscibility Pressure: Pure and Mixed CO2 , Methane, and Ethane. *Energy Fuels* 2016, 30, 6365–6372.

(48) Lashkarbolooki, M.; Eftekhar, M. J.; Najimi, S.; Ayatollahi, S. Minimum Miscibility Pressure of CO2 and Crude Oil during CO2 Injection in the Reservoir. *J. Supercrit. Fluids* 2017, 127, 121–128.

(49) Nobakht, M.; Moghadam, S.; Gu, Y. Determination of CO2 Minimum Miscibility Pressure from Measured and Predicted Equilibrium Interfacial Tensions. *Ind. Eng. Chem. Res.* 2008, 47, 8918–8925.

(50) Saini, D. An Investigation of the Robustness of Physical and Numerical Vanishing Interfacial Tension Experimentation in Determining CO2 + Crude Oil Minimum Miscibility Pressure. *J. Pet. Eng.* 2016, 2016, 1–13.

(51) Zhang, K.; Gu, Y. Two New Quantitative Technical Criteria for Determining the Minimum Miscibility Pressures (MMPs) from the Vanishing Interfacial Tension (VIT) Technique. *Fuel* 2016, 184, 136–144.

(52) Mutuailplu, M.; Jiang, L.; Liu, X.; Liu, Y.; Zhao, J. CO2 and Alkane Minimum Miscibility Pressure Estimation by the Extrapolation of Interfacial Tension. *Fluid Phase Equilib.* 2019, 494, 103–114.

(53) Orr, F. M., Jr.; Jessen, K. An Analysis of the Vanishing Interfacial Tension Technique for Determination of Minimum Miscibility Pressure. *Fluid Phase Equilib.* 2007, 255, 99–109.

(54) Abedini, A.; Mosavat, N.; Torabi, F. Determination of Minimum Miscibility Pressure of Crude Oil–CO2 System by Oil Swelling/Extraction Test. *Energy Technol.* 2014, 2, 431–439.

(55) Abdurrahman, M.; Permadi, A. K.; Bae, W. S. An Improved Method for Estimating Minimum Miscibility Pressure through Condensation–Extraction Process under Swelling Tests. *J. Pet. Sci. Eng.* 2015, 131, 165–171.

(56) Liu, Y.; Jiang, L.; Tang, L.; Song, Y.; Zhao, J.; Zhang, Y.; Wang, D.; Yang, M. Minimum Miscibility Pressure Estimation for a CO2/n-Decane System in Porous Media by X-Ray CT. *Exp. Fluids* 2015, 56, 154.

(57) Liu, Y.; Jiang, L.; Song, Y.; Zhao, Y.; Zhang, Y.; Wang, D. Estimation of Minimum Miscibility Pressure (MMP) of CO2 and Liquid n-Alkane Systems Using an Improved MRI Technique. *Magn. Reson. Imaging* 2016, 34, 97–104.

(58) Czarnota, R.; Janiga, D.; Stopa, J.; Wojnarowski, P. Determination of Minimum Miscibility Pressure for CO2 and Oil System Using Acoustically Monitored Separator. *J. CO2 Util.* 2017, 17, 32–36.

(59) Nguyen, P.; Mohaddes, D.; Riordon, J.; Fadaei, H.; Lele, P.; Sinton, D. Fast Fluorescence-Based Microfluidic Method for Measuring Minimum Miscibility Pressure of CO2 in Crude Oils. *Anal. Chem.* 2015, 87, 3160–3164.

(60) Marre, S.; Adamo, A.; Basak, S.; Aymonier, C.; Jensen, K. F. Design and Packaging of Microreactors for High Pressure and High Temperature Applications. *Ind. Eng. Chem. Res.* 2010, 49, 11310–11320.
2012 Opportunities in Flow-through Chemistry and Materials Science. What Can We Expect from It? Eng. Manuf. Applications. Fabrication on Glass Materials for Microfluidic Devices. Anal. Chem. of State for CO₂ Minimum Miscibility Pressure Prediction in Pressure for Enhanced Oil Recovery (EOR). Fundamentals, Fabrication, and Functions. Anal. Chem. Partial Phase Behaviour and Miscibility of Confined Fluids in Nanopores. In Nanoporous Model for Unconventional Natural Gas. Langmuir 2016, 32, 4499−4499. (94) Jatukaran, A.; Zhong, J.; Persad, A. H.; Xu, Y.; Mostowfi, F.; Sinton, D. Direct Visualization of Evaporation in a Two-Dimensional Nanopore Model for Unconventional Natural Gas. ACS Appl. Nano Mater. 2018, 1, 1332−1338. (95) Zhong, J.; Zhao, Y.; Lu, C.; Xu, Y.; Jin, Z.; Mostowfi, F.; Sinton, D. Nanoscale Phase Measurement for the Shale Challenge: Multi-component Fluids in Multiscale Volumes. Langmuir 2018, 34, 9927−9935. (96) Li, H.; Zhong, J.; Pang, Y.; Zandavi, S. H.; Persad, A. H.; Xu, Y.; Mostowfi, F.; Sinton, D. Direct Visualization of Fluid Dynamics in Sub-10 Nm Nanochannels. Nanoscale 2017, 9, 9556−9561. (97) Yong-Chen, S.; Ning-Jun, Z.; Yu, L.; Jia-Fei, Z.; Wei-Guo, L.; Yi, Z.; Yue-Chao, Z.; Lan-Lan, J. Magnetic Resonance Imaging Study on the Miscibility of a CO₂-n-Decane System. Chin. Phys. Lett. 2011, 28, 096401. (98) Xolile, P. M. Physical Solubility of Carbon Dioxide in Decane (C₄H₁₀) Solvent from a CO₂/CH₄ System. Universiti Teknologi Petronas 2013. (99) Hansen, C. M. 50 Years with Solubility Parameters—Past and Future. Prog. Org. Coat. 2004, 51, 77−84. (100) Hildebrand, J.; Scott, R. Evaluation of Solubility Parameters. The Solubility of Nonelectrolytes. New York: Reinhold Publishing Corporation 1950, 424. (101) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. Ind. Eng. Chem. Fundam. 1976, 15, 59−64. (102) Zagorodnechea, G. J.; Kuz, V. A. Critical Shift of a Confined Fluid in a Nanopore. Fluid Phase Equilib. 2004, 220, 7–9. (103) Zhong, J.; Alibakhshi, M. A.; Xie, Q.; Riordon, J.; Xu, Y.; Duan, C.; Sinton, D. Exploring Anomalous Fluid Behavior at the Nanoscale: Direct Visualization and Quantification via Nanofluidic Devices. Acc. Chem. Res. 2020, 53, 347−357.
(104) Adel, I. A.; Tovar, F. D.; Schechter, D. S.; others. Fast-Slim Tube: A Reliable and Rapid Technique for the Laboratory Determination of MMP in CO\textsubscript{2}-Light Crude Oil Systems. In SPE Improved Oil Recovery Conference; Society of Petroleum Engineers, 2016.

(105) Zhong, J.; Talebi, S.; Xu, Y.; Pang, Y.; Mostowfi, F.; Sinton, D. Fluorescence in Sub-10 Nm Channels with an Optical Enhancement Layer. Lab Chip 2018, 18, 568–573.

(106) Gothsch, T.; Schilcher, C.; Richter, C.; Beinert, S.; Dietzel, A.; Büttgenbach, S.; Kwade, A. High-Pressure Microfluidic Systems (HPMS): Flow and Cavitation Measurements in Supported Silicon Microsystems. Microfluid. Nanofluid. 2015, 18, 121–130.

(107) Cheng, X.; Ooms, M. D.; Sinton, D. Biomass-to-Biocrude on a Chip via Hydrothermal Liquefaction of Algae. Lab Chip 2016, 16, 256–260.

(108) Cho, Y.; Eker, E.; Uzun, I.; Yin, X.; Kazemi, H. Rock Characterization in Unconventional Reservoirs: A Comparative Study of Bakken, Eagle Ford, and Niobrara Formations. In SPE Low Perm Symposium; use Bakken, Eagle Ford, and Niobrara; Society of Petroleum Engineers: Denver, Colorado, USA, 2016.

(109) Hosseininoosheri, P.; Hosseini, S. A.; Nuñez-López, V.; Lake, L. W. Impact of Field Development Strategies on CO\textsubscript{2} Trapping Mechanisms in a CO\textsubscript{2}–EOR Field: A Case Study in the Permian Basin (SACROC Unit). Int. J. Greenhouse Gas Control 2018, 72, 92–104.

(110) Xie, Q.; Alibakhshi, M. A.; Jiao, S.; Xu, Z.; Hempel, M.; Kong, J.; Park, H. G.; Duan, C. Fast Water Transport in Graphene Nanofluidic Channels. Nat. Nanotechnol. 2018, 13, 238–245.

(111) Zhao, Y.; Wang, Y.; Zhong, J.; Xu, Y.; Sinton, D.; Jin, Z. Bubble Point Pressures of Hydrocarbon Mixtures in Multiscale Volumes from Density Functional Theory. Langmuir 2018, 34, 14058–14068.