Experimental Investigation of Confinement Effect on Phase Behavior of Hydrocarbons using Lab-on-a-chip Technology

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Abstract:
The study of phase behavior of hydrocarbons inside shale rock has garnered significant attention in contemporary literature. The present work focused on experimental techniques for addressing this challenge. To this end, lab-on-a-chip technology was integrated with high-resolution imaging techniques (inverse confocal microscopy equipment) for investigating the phase behavior of hydrocarbons inside nanoscale capillaries (nanochannels). Experiments were performed to measure the bubble point temperature of pure hydrocarbons inside nanochannels to study the confinement effect. The novel method of employing a nanofluidic chip enabled the visualization of fluid behavior inside nanoscale channels. The method was found to be highly promising for experimental investigation of the phase behavior in nano-scale pores, which has always been one of the biggest research challenges. The experimental results revealed that for nanochannel depth of 50 nm, the confinement effect in the form of wall–molecule interactions is almost negligible. Additionally, the Peng–Robinson equation of state (PR-EOS) with and without capillary pressure was used for modeling the hydrocarbon phase behavior. Experimental validation of numerical predictions obtained from these thermo-physical models describing the effect of phase behavior for confined fluids were performed in this study.

Keywords: Phase behavior, hydrocarbon, lab-on-a-chip technology, confinement effect, nanofluidic device

Introduction
Concerns about mitigating the world’s energy demands are definitely not new. The ever-increasing global population and subsequent mounting energy demands for limited conventional resources has resulted in a more acute situation. New technical advances (e.g., horizontal drilling, hydraulic fracturing, and state-of-the-art reservoir characterization methods) have enabled the development of “unconventional resources”, especially organic-rich shale, as economically viable alternatives. Despite the promising potential of these
unconventional resources, their consideration as energy sources has presented a number of new challenges related specifically to shale rock media. The phase behavior and pressure-volume-temperature (PVT) properties of fluids confined in tiny pores of unconventional oil reservoirs have always been important research topics. Unlike conventional petroleum reservoirs, shale matrix consists of small mesopores with sizes of 2–50 nm. In mesopores of such sizes, the size of hydrocarbon molecules is slightly smaller than the pore diameter. As a result, wall–fluid interactions play dominant roles in defining the fluid’s behavior [1]. Owing to its predominant effect on the estimation of reserves, the accuracy of simulated PVT properties of unconventional reservoir fluids has always been a challenge in the petroleum industry.

Micro/Nanofluidic devices are used in various fields such as biomedical science, electrical engineering, fluid mechanics, and pharmaceutical science for both fundamental and applied research [2-6]. Such devices also provide methods to directly visualize fluid phase behavior. The resolution of this imaging process can be as low as the size of a single protein molecule [7]. Such nanochannel devices are fabricated by standard semiconductor manufacturing processes [8]. Recent studies have shown that nanofluidic devices can be used to directly visualize fluid flow and fluid phase behavior in 100-nm channels [9, 10].

Several models and simulations have been targeted at predicting the properties of confined fluids; three from among such methods have garnered the most attention from researchers: (1) equation of state–based models [11-17], (2) density functional theory [18], and (3) molecular simulation [19-21]. Among the various modeling and simulation techniques available, the equation of state with capillary pressure modification has attracted the most interest for the simulation of shale reservoirs [22-25]. This reveals the importance of investigating the validity of this technique. Although several modeling and simulation studies have been conducted on this topic, robust studies involving experimental investigation of the confinement effect on the hydrocarbon phase behavior has been lacking in the literature.

In this paper, we present an experimental study of this effect by using a lab-on-a-chip approach. The rest of this paper is organized as follows. We first present the experimental methodology including the design and fabrication steps of our nanofluidic device, as well as the procedure for temperature control, visualization, and data acquisition. Then, we present our experimental and modeling results. We developed a numerical model for the phase behavior of a fluid confined in a nanochannel by combining the equation of state with the capillary pressure effect and performed experimental measurements to validate the predictions from the model. We end the paper with concluding remarks.
Methodology

Lab-on-a-chip technology

Lab-on-a-chip technology is employed to facilitate the integration of multiple laboratory functions in a small micro/nanofluidic chip. Devices fabricated by this technology are designed to handle fluid volumes metered to values as low as a few picoliters to femtoliters inside tiny narrow channels. The motivation behind the present work was to use lab-on-a-chip devices to mimic shale rock media and to be able to investigate the phase behavior inside nanometer-sized pores of shale rock. The device that was used in this work was a nanofluidic chip made of glass, which consisted of several parallel channels fabricated by photolithography.

Photolithography

Photolithography or optical lithography is the process of fabricating small chips by transferring a geometric pattern from a photomask to a photoresist material. This process consists of several steps (Figure 1). First, a photoresist is applied to the surface of the substrate, and then, a photomask is placed on top of these layers. The photomask, which is typically made of quartz or metal, is used to etch (develop) a specific pattern on the substrate, and the photoresist is then removed to complete the process. The entire surface is subsequently bounded by a layer of glass to form pores inside the chip.
Figure 1-Photolithography process: a, b) a layer of photoresist is spin-coated on the substrate; c) the photomask is mounted and aligned on top of the photoresist; d, e) the pattern of the mask is replicated on the photoresist by illuminating the system; f) the pattern is developed and etched on the substrate (using dry etching or wet etching techniques); and g) the photoresist is removed (stripped). This process can be repeated, along with surface deposition of multiple layers of materials, for obtaining additional surface features until the desired pattern is obtained.
**Nanofluidic chip**

In this work, the lab-on-a-chip technology was employed to design a chip capable of mimicking shale rock media with an acceptable accuracy. To this end, the proposed design consists of a glass substrate in which 20 parallel nanochannels connected to four reservoirs at the corners of the chip are etched using photolithography techniques combined with dry etching techniques (Figure 2). In order to reduce measurement error, we designed equally sized channels all over the chip. The nanochannels were capped by a glass substrate using low temperature glass bonding technique (the fabrication was performed by Klearia Company). Scanning electron microscopy (SEM) was used to image the nanochannels for confirming the desired feature sizes in the nanofluidic chip [26] (Figure 3). Typically the depth of the nanochannels used in this study was 50 nm with ~ 5 microns in width.

*Figure 2-Schematic of nanofluidic chip used in this work (with enlarged sizes)*
Temperature control

Temperature measurements were performed using three SA1XL thermocouples (purchased from OMEGA®). The thermocouples were attached to the chip surface (both on the top and bottom surface in the vicinity of the visualization location of the nanochannels). An Infra-red (IR) camera was used to record the surface temperature of the chip. The IR camera was focused at the center of the chip where the nanochannels are located (Figure 4). In order to accurately measure the temperature at the center of the chip, all the thermocouples were thermally isolated using silicon glue. For calibration purposes, a heating plate was used as the heating source and thermocouples were attached to its surface. In order to heat up the chip and the channels inside it evenly, KHLV flexible string heaters were mounted at the bottom of the chip.

Figure 3-SEM image of fabricated nanofluidic chip for calibration
Visualization and data acquisition

The nanofluidic chip contains four reservoirs that served as the source of the liquid for subsequent injection into the 20 parallel nanochannels, located at the center of the chip. The chip was packaged by bonding (using acrylic glue) Nanoports® (purchased from IDEX Corp.) on top of the four reservoirs. Each Nanoport was then connected to the injection system using PEEK tubing, valves, filters, and syringe pumps. The bubble formation phenomenon was visualized in real time and confirmed using an Olympus IX-81 inverted microscope (Olympus America, Center Valley PA, USA) equipped with a UPLSAPO 20x/0.75 objective, a Rolera XR CCD camera (Qimaging, Surrey BC, Canada), and a Proscan H117 motorized XY stage (Prior Scientific, Rockland, MA, USA) controlled by the μManager freeware (http://www.micro-manager.org). A field lens with 1.6x magnification was used to achieve Nyquist sampling for imaging with the 20x objective. The following fluorescence filter sets (Chroma Technology Corp., Bellows Falls, VT, USA) were used, with the central wavelength and bandwidth of the excitation and emission filters as indicated: 543-nm HeNe laser and 560-nm long-pass filter.

The overall procedure of the experiment consists of mounting the nanofluidic chip under the microscope, injecting hydrocarbons into the channels by using a syringe pump, gradually heating the channels up to the bubble point, and recording the bubble point temperature for each case (Figure 5).

Figure 4-Image recorded by an IR camera is shown here. The measurements from the IR camera were validated using measurements from the surface mounted thermocouples for performing temperature calibration.
Results and Discussion

Experimental results

We performed experiments on the chip containing 50-nm-deep channels. Hydrocarbons of hexane, heptane and octane with $\geq 99\%$ purity (purchased from Sigma-Aldrich, Table 1) were injected into the channels, and the entire procedure was recorded using the camera connected to the microscope. The experiments were divided into three steps. First, hydrocarbons were injected into the channels. This step should be performed extremely slowly owing to the high pressure drop across the chip. The entire volume of the injected fluid was estimated to be approximately $10^{-5}$ $\mu$L. Second, the fluid inside the channels needs to stabilize in order for the pressure to reach atmospheric pressure. In this step, there should be no fluid movement inside the channels, which means attainment of an equilibrium pressure. Third, after the fluid stabilizes inside the channels, electrical power is supplied to the heater and the temperature is recorded simultaneously. We chose an initial temperature ramp rate of 12 $^\circ$C/min for this process, which was subsequently reduced as the temperature of the chip approached the bubble point temperature.
Table 1 - Specification of Chemical Sample

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Formula</th>
<th>Source</th>
<th>Mole Fraction</th>
<th>Purification Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>CH₃(CH₂)₆CH₃</td>
<td>Sigma-Aldrich</td>
<td>≥0.99</td>
<td>Distillation</td>
</tr>
<tr>
<td>Heptane</td>
<td>CH₃(CH₂)₅CH₃</td>
<td>Sigma-Aldrich</td>
<td>≥0.99</td>
<td>Distillation</td>
</tr>
<tr>
<td>Hexane</td>
<td>CH₃(CH₂)₄CH₃</td>
<td>Sigma-Aldrich</td>
<td>≥0.99</td>
<td>Distillation</td>
</tr>
</tbody>
</table>

Step one: Injection

Figure 6a shows the empty channels before fluid injection. As the fluid injection begins, the channels get partially filled with the hydrocarbon fluid (Figures 6b and 6c). We observed that the process of filling of nanochannels occurred in two different steps. In the first step, the entire set of nanochannels got partially filled with the injected liquid. However, for some of the nanochannels the side-walls were not filled with liquid in this step (Figure 6d). As the injection proceeded, the unfilled parts of the channels began to be occupied by the hydrocarbon fluid (Figure 6e), until all parts of the channels were totally saturated with the liquid (Figure 6f).
Figure 6-Step one: visualization of hydrocarbon injection into the nanochannel network. (a) Empty channels (b) Injection of hydrocarbons starts from the top-left channel. (c and d) As the fluid is pushed further into the channels, the empty bulk volume gets filled with the liquid. (e) With further pushing of the fluid, the parts of the channel wall that are dry get filled. (f) The process continues until the channels are fully saturated.
Step two: Stabilization

In this step, we needed to verify that the pressure inside all of the parallel nanochannels is equilibrated, which is expected to be the same as atmospheric pressure (since there is no flow). A good indicator of pressure difference across the chip is the observation of fluid flow inside the channels. When there is no displacement of fluid inside the nanochannels across the whole chip, we can conclude that equal pressure is attained in the network of nanochannels. From a comparison of Figures 7a and 7b, we could easily see fluid movements inside the injection channels. In these figures, the liquid was observed to be moving inside the left-arm channel.

Figure 7-Step two: stabilization of fluid flow and pressure equilibration inside nanochannels. Before the temperature of the system is increased, pressure should be equilibrated over the entire network of nanochannels. The movement of hydrocarbon fluid inside longer channels was observed in order to confirm that there was no pressure difference along the chip. In these figures, comparing figures a and b, movement of fluid inside top left hand side nanochannel is obvious.
Step three: Evaporation

After atmospheric equilibrium pressure was achieved throughout the chip, the heating procedure was started. A suitable temperature rise rate was achieved by gradually increasing the voltage from the power supply to the heater. By visually monitoring the nanochannels while the temperature was increasing, we were able to pinpoint the bubble formation. Bubble formation can be clearly seen in Figures 8a–8f. For bubble point determination, we considered the first bubble formed inside the channel as the reference for the bubble point temperature. It is noteworthy that bubbles start to form in a very short period of time as the temperature is increased; this can validate the homogeneity of the fluid-system employed in these experiments.
Figure 8-Step three: visual observation of bubble formation and evaporation of hydrocarbon fluid. (a) Nanochannels are fully saturated with hydrocarbon. (b) The first bubbles form inside the channels as the temperature is increased. (c–e) Further increase in temperature leads to further bubble formation in multiple nanochannels. (f) The liquid inside the channels is fully evaporated.
Modeling of bubble point temperature for confined hydrocarbons

We used a modified version of the Peng–Robinson equation of state (PR-EOS) \[27\] to model the bubble point temperature for pure octane. This technique has been extensively used for modeling of phase behavior \[9, 28-31\]. The technique entails calculation of the surface tension and the corresponding estimation of the capillary pressure. The capillary pressure is then used to correlate the vapor phase pressure, which is later substituted in fugacity calculations. Based on our preliminary design of 50-nm-deep nanochannels, modeling was performed for such channel sizes in this study. The interfacial surface tension in each case was calculated as follows \[1, 32-34\]:

\[
\sigma^{1/4} = \sum_{i=1}^{N_c} P_{\sigma i} \left( \frac{\rho^L_{i}}{MW_L} x_i - \frac{\rho^V_{i}}{MW_V} y_i \right)
\]

(1)

where

\[
\frac{\rho^L_{i}}{MW_L} = \frac{P_L}{Z_L RT}
\]

(2)

and

\[
\frac{\rho^V_{i}}{MW_V} = \frac{P_V}{Z_V RT}
\]

(3)

In these equations, \(P_{\sigma i}\) is the parachor of component \(i\); \(\rho^L\) and \(\rho^V\) are the liquid and vapor densities, respectively; and \(x_i\) and \(y_i\) are the molar fractions of component \(i\) in liquid and vapor, respectively.

Capillary pressure is calculated based on the Young–Laplace equation as follows \[35\]:

\[
P_c = 2 \sigma \cos \theta \left( \frac{1}{d} + \frac{1}{w} \right)
\]

(4)

where \(\theta\) is the contact angle, \(d\) is the nanochannel depth and \(w\) is the nanochannel width.

At vapor–liquid equilibrium, the fugacity of a specific component in the liquid phase should be equal to that in the vapor phase:

\[
f_{iL} = \Phi_{iL} x_i P_L
\]

(5)

\[
f_{iV} = \Phi_{iV} y_i P_V
\]

(6)

Finally, the vapor phase pressure is correlated with the liquid phase pressure and capillary pressure as follows:
\[ P_V = P_L + P_c \]  \hspace{1cm} (7)

The properties used in these calculations were obtained from references [1, 32, 36-38].

Calculations were performed for models considering PR-EOS with capillary pressure modifications and without capillary pressure. The results are shown in Figure 9 and Table 2.
Bubble Point Temperature under Confinement (K)

<table>
<thead>
<tr>
<th>Component</th>
<th>Experiment</th>
<th>PR-EOS model without capillary pressure</th>
<th>PR-EOS model with capillary pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>341.9±0.4</td>
<td>340.7</td>
<td>358.1</td>
</tr>
<tr>
<td>Heptane</td>
<td>373.3±0.2</td>
<td>374.4</td>
<td>391.8</td>
</tr>
<tr>
<td>Octane</td>
<td>398.7±0.3</td>
<td>400.7</td>
<td>419.2</td>
</tr>
</tbody>
</table>

*Table 2- Confined bubble point temperatures measured and modeled for three hydrocarbons. Each measurement was repeated three times to assure the accuracy of the results.*

The resulting bubble point temperature calculated using this model for a 50-nm-deep channel containing hexane, heptane and octane as the hydrocarbon fluid is compared with experimental results obtained from microfluidic chips with the same size. Experiments were repeated three times to ensure validity of the data obtained. It can be drawn from the results obtained that the bubble point temperature measured at 50 nm channel is very close to calculations based on the PR-EOS without accounting for capillary pressure. Therefore, it can be concluded that at pore sizes as small as 50 nm, the commonly used PR with capillary pressure model is not accurate enough.

In the capillary pressure calculations, the surface tension of the confined hydrocarbons is estimated by neglecting the curvature effect. Furthermore, the parachor factors are based on a simplistic model that can be applied only to larger-sized channels.

**Conclusion**

Nanofluidic chips with channels of 50-nm depth and 5-μm width were fabricated for this study. The goal of this research was to investigate the confinement effect on the bubble point temperature of hydrocarbons.
using a novel method of lab-on-a-chip and to evaluate the validity of using the Peng–Robinson equation of state with and without capillary pressure modeling of nanopores. High tech lab-on-a-chip devices were fabricated, tested and employed for investigation of phase behavior of hydrocarbons. Pure hydrocarbons of hexane, heptane and octane were used as the hydrocarbon fluid, and the bubble point temperature measured on the nanofluidic chip was found to be almost equal to the bulk bubble point temperature. A model based on the Peng–Robinson equation of state, which has mostly been used in reservoir simulations, was applied as a typical model. It can be concluded from these measurements that at a channel size of 50 nm, the confinement effect on the bubble point temperature is almost negligible, which is in good agreement with the results reported in [1]. Additionally, a comparison of the experimental results with those of the model reveals that at pore sizes as small as 50 nm, the capillary-pressure-based models fail to describe the phase behavior of hydrocarbons inside confined media and such models cannot be used for accurate reservoir simulations.

Acknowledgement

The use of facilities at the Microscopy and Imaging Center (MIC) and the Material Characterization Facility (MCF) at Texas A&M University is acknowledged. We would like to thank the Crisman Institute for Petroleum Research for funding and supporting our project. We would also like to thank Klearia Company for fabrication of the chips. Lastly, we would like to thank Dr. Stanislav Vitha at the Texas A&M MIC and Dr. Amanda Young at the Texas A&M MCF for their help and support.
### Nomenclatures

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>(1)</td>
<td>Surface tension (N/m)</td>
</tr>
<tr>
<td>$\rho^L$</td>
<td>(1)</td>
<td>Liquid density (kg/m$^3$)</td>
</tr>
<tr>
<td>$\rho^V$</td>
<td>(1)</td>
<td>Vapor density (kg/m$^3$)</td>
</tr>
<tr>
<td>$P_{ei}$</td>
<td>(1)</td>
<td>Parachor factor</td>
</tr>
<tr>
<td>$N_c$</td>
<td>(1)</td>
<td>Number of components</td>
</tr>
<tr>
<td>$MW_L$</td>
<td>(1)</td>
<td>Liquid molecular weight (gr/mol)</td>
</tr>
<tr>
<td>$MW_V$</td>
<td>(1)</td>
<td>Vapor molecular weight (gr/mol)</td>
</tr>
<tr>
<td>$Z_L$</td>
<td>(2)</td>
<td>Liquid compressibility factor</td>
</tr>
<tr>
<td>$P_L$</td>
<td>(2)</td>
<td>Liquid Pressure (Pa)</td>
</tr>
<tr>
<td>$R$</td>
<td>(2)</td>
<td>Gas Constant (m$^3$ Pa K$^{-1}$ mol$^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>(2)</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>$Z_V$</td>
<td>(3)</td>
<td>Vapor compressibility factor</td>
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<tr>
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<td>(3)</td>
<td>Vapor Pressure (Pa)</td>
</tr>
<tr>
<td>$P_c$</td>
<td>(4)</td>
<td>Capillary pressure (Pa)</td>
</tr>
<tr>
<td>$d$</td>
<td>(4)</td>
<td>Channel depth (m)</td>
</tr>
<tr>
<td>$w$</td>
<td>(4)</td>
<td>Channel width (m)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>(4)</td>
<td>Contact angle (rad)</td>
</tr>
<tr>
<td>$f_{iL}$</td>
<td>(5)</td>
<td>Liquid fugacity (Pa)</td>
</tr>
<tr>
<td>$f_{iV}$</td>
<td>(6)</td>
<td>Vapor fugacity (Pa)</td>
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<td>Vapor fugacity coefficient</td>
</tr>
<tr>
<td>$x_i$</td>
<td>(5)</td>
<td>Mole fraction of component $i$ in liquid</td>
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<tr>
<td>$y_i$</td>
<td>(6)</td>
<td>Mole fraction of component $i$ in vapor</td>
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</table>
References


