INFLUENCE OF NANOPORES ON THE TRANSPORT OF GAS AND GAS-CONDENSATE IN UNCONVENTIONAL RESOURCES

A DISSERTATION
SUBMITTED TO THE DEPARTMENT OF ENERGY RESOURCES ENGINEERING AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Maytham I. Al Ismail
April 2016
I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

(Roland N. Horne) Principal Co-Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

(Mark D. Zoback) Principal Co-Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

(Anthony R. Kovscek)

Approved for the Stanford University Committee on Graduate Studies
Abstract

Shale gas and liquid-rich shales have become important energy sources in the US and other parts of the world. Unlike conventional oil and gas reservoirs, unconventional shale resources contain a very heterogeneous pore system. The pore size varies between micro-, meso- and macroscales (<2 nm, 2-50 nm and >50 nm). The mineral composition of shale rocks varies widely as well from clay-rich to calcite-rich. The nanoscale nature of the pores, coupled with rock mineral heterogeneity, makes the "conventional" understanding of fluid transport in conventional reservoirs no longer suitable to explain and predict accurately the flow behavior in unconventional resources. The research work aimed to bridge the gap in the understanding of the fluid flow behavior of unconventional resources by applying various experimental and molecular simulation tools. Specifically, this research work studied how the rock (i.e. permeability), the fluid (i.e. composition and phase behavior) and the fluid-rock interactions (i.e. adsorption) all behaved with depletion in nanoporous rock formations.

Several laboratory experiments and molecular simulation techniques were applied in this research work. Laboratory experiments included a gas-condensate coreflooding experiment, permeability measurements and adsorption measurements. In the core-flooding experiment, a real gas-condensate mixture obtained from the Marcellus shale play was injected into a Marcellus shale core at in-situ conditions and the composition of gas samples collected along the core was monitored during flow. To investigate the effect of rock mineralogy and pore structure on the transport mechanisms in nanoporous shale reservoirs, the permeability of Utica, Permian and Eagle Ford shale samples were measured using argon as a nonadsorbing gas and CO\textsubscript{2} as an adsorbing gas. In addition, CO\textsubscript{2} adsorption experiments were conducted on different
shale samples in order to investigate the role of shale mineral constituents in adsorption. Moreover, molecular simulation techniques were applied to model the selective adsorption of binary hydrocarbon mixtures in carbon-based slit-pores and to estimate the shift in the critical properties of hydrocarbons due to confinement in nanometer-size pores. The molecular simulation techniques included the grand canonical Monte Carlo (GCMC) and the Gibbs ensemble Monte Carlo (GEMC).

This research work revealed that clay content in shale reservoirs played a significant role in the stress-dependent permeability. For clay-rich samples, higher pore throat compressibility was observed which in turn led to higher permeability reduction with increasing effective stress compared to calcite-rich samples. Numerical simulation results showed that failing to account for stress-dependent permeability in clay-rich shale reservoirs may lead to overestimating the cumulative gas recovery by a factor of two after ten years of production. Permeability measurements with CO$_2$ indicated that CO$_2$ permeability decreased in comparison with the non-adsorbing gases by as high as an order of magnitude due to a combination of CO$_2$ adsorption, sorption-induced swelling and molecular sieving effects. CO$_2$ adsorption measurements indicated that adsorption was controlled mainly by the clay content. Clay-rich shale samples showed higher adsorption capacity compared to clay-poor shale samples. The predominant clay mineral in those shale samples was illite. The platy shape of illite provided the surface area for enhanced adsorption capacity.

This study concluded that in gas-condensate systems of liquid-rich shales, the produced gas becomes leaner during production and significant volumes of condensates, which contain predominantly heavy components, are left behind in the reservoir. The gas-condensate core-flooding experiment showed that composition of the flowing mixture below the dew-point pressure contained less heavy components along the direction of flow. Molecular simulations revealed that the change in gas composition was not only due to condensate dropout and relative permeability effects, but also due to the preferential adsorption of heavy hydrocarbons over methane. This means that initial production from shale reservoirs contain both methane and other heavy components from the free phase. However, as reservoir pressure decreases, methane from the adsorbed phase starts to desorb preferentially and the adsorption sites where
methane molecules used to reside start to accept heavier components.

In addition, molecular simulations conducted at subcritical conditions to estimate the vapor and liquid densities of pure hydrocarbons inside 5 and 10-nm pores revealed that rock-fluid interactions in the form of adsorption caused the critical pressure and temperature of the confined molecules to decrease. This was observed clearly for methane and ethane. The decrease in the critical properties was affected by the size of the pores. For example, the estimated critical pressure and temperature of methane in 5-nm pore were lower than the critical pressure and temperature in 10-nm pore.
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<th>Description</th>
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Chapter 1

Introduction

The U.S. Energy Information Administration (EIA) has shown in a recent report that the total hydrocarbon liquid production (oil and condensates) from tight and shale formations has increased by sevenfold during the past five years. During January 2010, the total tight and shale oil production rate was 0.6 million barrels per day. Five years later during January 2015, the total oil production rate increased to 4.4 million barrels per day. Figure 1.1a shows the total oil production rate for various tight and shale formations in the US. The significant oil output was driven mainly by Eagle Ford and Bakken developments which have benefited greatly from the advancement in horizontal hydraulic fracturing methods.

A similar story can be drawn for US shale gas production. Figure 1.1b plots the total US shale gas output from January 2000 to August 2015. The figure shows that the US shale gas production rate has more than tripled during the past five years. During January 2010, the total US shale gas production rate was 12 billion cubic feet per day. During January 2015, the gas production rate totaled 40 billion cubic feet per day. The Marcellus shale play has been the biggest contributor to the latest shale gas boom. The gas production rate from the Marcellus was 15 billion cubic feet per day which accounted for more than 35% for the total US shale gas output during January 2015. Other major shale gas contributors include Eagle Ford, Haynesville and Barnett shales.

A common feature among all the tight oil, shale oil and shale gas plays that have
Figure 1.1: US hydrocarbon liquids and natural gas production rates from tight and shale resources since year 2000 as reported by EIA (2015).
been contributing significantly to the US energy sector during the last five years is the nanometer sized pores. Unlike the conventional oil and gas reservoirs, the pore size in those unconventional plays could be as low as one nanometer (Chalmers et al., 2012a) as will be discussed further in the next section. The aim of this research project has been to investigate the impact of nanosize pores on the transport mechanisms of gas- and liquid-rich hydrocarbons (i.e. condensates) in tight and shale formations.

1.1 Literature Review

The literature review will first focus on the sedimentary geology of shale rocks with an emphasis on the nanoporous structure. Then, a review of permeability experiments conducted at various research institutes on nanoporous rocks will be presented. After that, a review of gas-condensate systems in conventional reservoirs will be discussed. The results of previous experimental work conducted to investigate compositional change of binary gas-condensate mixtures due to liquid dropout in the core scale will also be presented. Finally, a review of previous efforts; not necessarily related to oil and gas, to understand the fluid properties in the nanopores and how they are compared with fluids in the macropores will be discussed.

1.1.1 Geology overview

Shale sedimentary geology

Mudrocks are siliciclastic sedimentary rocks composed largely of silt-sized and clay sized particles (Prothero and Schwab, 2004). The cut-off between silt-sized particles and clay-sized particles is approximately 0.004 mm, above which the particles are silt-size and below which, they are clay-size (Greensmith, 1989).

Depending on which particle size predominates, mudrocks are divided into two lithologies: siltstone with 50% or more silt-sized particles and claystone with 50% or more clay-sized particles (Greensmith, 1989). Shales are claystones with fissility which is defined according to Dietrich and Skinner (1979) as the tendency to split along closely spaced, roughly planar surfaces that are essentially parallel to bedding.
A picture of shales with fissility is shown on Figure 1.2. Without fissility, the claystone is then identified as mudstone.

Figure 1.2: The dark beds with fissiles are shales and the light beds are limestone (www.neb.gc.ca).

The most abundant minerals in mudstones and shales are clay minerals, fine-sized micas, quartz and feldspars. Minor quantities of other minerals could also be present including zeolites, iron oxides, heavy minerals, carbonates, sulfates and sulfides, in addition to fine-size organic matter (Boggs, 2009). The average weight content for the organic matter in shale rocks is about 2.1 weight percent (Degens, 1965). However, black shales and other organic-rich shales contain 3 to 10 (or even more) percent by weight of organic matter. More organic matter could also be found in oil shales where it ranges to 25 percent or more (Boggs, 2009).

Boggs (2009) argues that the organic matter found in shales is not the same as the original matter deposited in the parent mud. Complex diagenetic processes involving
Table 1.1: Degradation processes of hydrocarbon generation, adapted from Tissot and Welte (1984)

<table>
<thead>
<tr>
<th>Process</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diagenesis</td>
<td>Thermally immature kerogen with little hydrocarbon generation</td>
</tr>
<tr>
<td>Catagenesis</td>
<td>- Zone of oil generation</td>
</tr>
<tr>
<td></td>
<td>- Cracking zone for wet gas generation with increasing proportion</td>
</tr>
<tr>
<td></td>
<td>of methane</td>
</tr>
<tr>
<td></td>
<td>- Zone of oil-associated gas</td>
</tr>
<tr>
<td>Metagenesis</td>
<td>Dry gas zone</td>
</tr>
</tbody>
</table>

chemical and biochemical degradation modified the original organic material yielding an insoluble organic material called kerogen. Kerogen is considered the precursor material of petroleum hydrocarbons. Tissot and Welte (1984) discussed three successive steps that the kerogen goes through to form petroleum hydrocarbons at different depths of burial. A summary of each step is shown in Table 1.1.

The various processes result in different types of fluids at different depths of the formation. The increase in thermal maturation with burial causes the liquid hydrocarbons to transform to gaseous hydrocarbons. Therefore, dry shale gas is found downdip of the formation, while shale oil is found updip of the formation. Gas-condensate is located between the two phases. Figure 1.3 shows the petroleum windows for the Eagle Ford shale play. The oil window is located in the shallower northern part of the play at 4,000 ft depth and the dry gas window is located in the deeper southern part of the play at 14,000 ft depth. The gas-condensate window is located at around 10,000 ft depth.

**Pore size distribution**

Studying the pore structure of shale rocks has received a lot of attention lately because shale rocks have emerged as major hydrocarbon reservoirs. The possibility to produce gas and light liquid hydrocarbons from shale rocks that had previously been considered seals to conventional reservoir rocks necessitated a more thorough understanding of the pore structure of the nanodarcy permeability rocks. Several papers investigating the pore networks of prominent North American shale plays have been
published, including Jarvie et al. (2007), Loucks et al. (2009), Nelson (2009) and Chalmers et al. (2012a). In this section, the major conclusions that are most relevant will be highlighted.

First and foremost, the pores contained in shale reservoirs are much smaller than the pores contained in conventional carbonate and sandstone reservoir rocks. The pores within the shale reservoirs are at nanometer scale, whereas the pores within the conventional reservoirs are at micrometer scale (Nelson, 2009). The International Union of Pure and Applied Chemistry (IUPAC) has adopted three categories of pore sizes: macropores (> 50 nm), mesopores (2-50 nm) and micropores (< 2 nm). Several methods are used to characterize the nanometer-scale pore systems and to define the pore size distribution including mercury porosimetry and gas adsorption analyses.
1.1. LITERATURE REVIEW

(Chalmers et al., 2012a).

Chalmers et al. (2012a) plotted the pore size distribution for rock samples obtained from drill cuttings in several shale plays in North America. Figure 1.4 plots the pore size distribution by mercury porosimetry analyses. Due to injection pressure limitation to 60,000 psi, the mercury porosimetry cannot detect pore diameters less than 3 nm. Therefore, mercury porosimetry cannot be utilized to characterize micropores.

Unlike mercury porosimetry, the low pressure gas adsorption analyses using nitrogen and carbon dioxide probe gases is able to measure micropores. Figure 1.5 shows that the low-pressure gas adsorption analyses were able to identify micropores (< 2 nm) within the investigated shale samples. These results indicate that pores in siliceous mudstones (i.e. shale rocks) are dominantly nanometer in scale. To put things in perspective, Figure 1.6 plots the pore sizes for shales and compares them with rocks with higher pore sizes such as sandstones and tight sandstones. The plot also compares the pore sizes of shales with oils, water and the molecule size for three gases (helium, nitrogen and methane). Clearly, the diameter of oils and gases could be just an order of magnitude lower than the porous medium through which they flow.

Loucks et al. (2009) concluded that most nanopores are within grains of organic matter. Thermal decomposition of organic matter during hydrocarbon generation caused nanopores to form within the organic matter. Their study was based on SEM images obtained for various samples from the Barnett. Large and small nanopores were identified in organic grains of all sizes as shown on Figure 1.7. The figure also indicates that the nanopores come in different shapes, i.e. elliptical, angular or rectangular.

1.1.2 Shale permeability

Many efforts have been made to study the permeability of shales and tight rocks. Vermyleen (2011) and Heller et al. (2014) studied the matrix permeability of shale samples obtained from Barnett, Eagle Ford, Montney and Marcellus over a range of
effective stresses and pore pressures. Their results showed that the matrix permeability of gas shales is more sensitive to changes in confining pressure than changes in pore pressure. Kwon et al. (2001) and Kwon et al. (2004) studied permeability anisotropy and the effect of clay content of illite-rich shale recovered from the Wilcox formation. They concluded that Wilcox shale permeability was anisotropic at low effective pressures $p_e = p_c - p_p$ (3 MPa). However, permeabilities measured at high effective stresses (10-12 MPa) showed little dependence on flow direction. In addition, the authors concluded that at similar porosity, the permeability of high clay content (65%) specimens was smaller than the permeability of the low clay content (40%) specimens. Chalmers et al. (2012b) investigated controls of matrix permeability for Devonian gas shales from the Horn River and Liard basins in northeastern British Columbia, Canada. They concluded that the pore aperture distribution impacts the permeability of the shale samples. Greater flow rates (i.e. permeabilities) were found for samples containing interconnected pathways with macropore apertures higher than 16 $\mu$m and containing balanced ratio of micro-, meso- and macropores. The permeability of samples characterized with interconnected macropore apertures

---

Figure 1.4: Pore size distribution defined by porosimetry analyses (Chalmers et al., 2012a).
of less than $8 \, \mu m$ were found to be relatively low.

Ghanizadeh et al. (2013), Ghanizadeh et al. (2014a) and Ghanizadeh et al. (2014b) studied the influence of lithological factors on matrix permeability of organic-rich shale samples from European Scandinavian Alum and Posidonia formations using different permeating fluids. They observed that the permeability of the samples measured using helium was up to five times higher than the permeability measured using argon and methane under similar experimental conditions. Permeability measurements with water were up to three orders of magnitude lower than helium and methane permeabilities. The stress-dependent permeability analysis showed nonlinear reduction in permeability with increasing effective stress. They were able to describe the stress dependence of permeability with an exponential relationship. The stress-dependent permeability was further investigated for unconsolidated sands (Davies and Davies, 2001), coalbed methane (Pan et al., 2010; Meng et al., 2011; Gensterblum et al., 2014) and shale samples (Pathi, 2008).
1.1.3 Gas-condensate systems in conventional reservoirs

In this part of the literature review, the behavior of gas-condensate fluids in conventional reservoirs will be visited. The results of previous work on gas-condensate reservoirs will also be presented.

Gas-condensate systems

At the original reservoir conditions, a gas-condensate is a single-phase fluid. Usually, the fluid consists predominantly of methane (C1) and other short-chain hydrocarbons. The fluid also may contain small amounts of long-chain hydrocarbons (heavy ends). The methane content in gas-condensate systems ranges from 65 to 90 mol%, whereas in crude oil systems, methane content ranges from 40 to 55 mol%. On the other hand, lower heptanes-and-heavier (C7+) content is reported for gas-condensate systems.
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Figure 1.7: Nanopores found in organic matter in the Barnett shale (Loucks et al., 2009).

than for crude oil systems. Figure 1.8 compares the composition of gas-condensate systems with other categories of hydrocarbon systems. Typical compositions for the various hydrocarbon categories are compared on Table 1.2.

Most known conventional gas-condensate reservoirs are discovered in formation pressures and temperatures in the ranges of 3,000 to 8,000 psi and 200 to 400°F, respectively (Moses and Donohoe, 1962). These wide ranges of pressures and temperatures, along with the wide composition ranges, provide a large variety of conditions for gas-condensate phase behaviors. This increases the challenge for reservoir engineers when studying the gas-condensate systems to achieve the optimum development and operation plans.

At pressures below the dew-point pressure and at certain conditions of temperature, retrograde condensation will occur in the single-phase fluid and the fluid system will separate into two phases: a gas phase and liquid phase. The liquid phase is richer.
in heavy ends and the gas phase is depleted of heavy ends. As the pressure continues
to decrease, more liquid phase is dropped out of solution up to a maximum volume.
Then, liquid volume starts to decrease as illustrated in the pressure-temperature (p-
T) diagram (Figure 1.9). Typically, a gas-condensate system yields from about 30 bbl
of condensate per MMSCF of gas for lean gas-condensate to 300 bbl of condensate
per MMSCF of gas for rich gas-condensate (Kamath, 2007).

**Gas-condensate flow behavior**

The flow behavior of a gas-condensate reservoir depends on the phase envelope of the
fluid system and the reservoir conditions. The phase envelope consists of the bubble-
point line and the dew-point line meeting at the critical point. During isothermal
expansion, the first bubble of gas vaporizes from the liquid at the bubble-point line.
In contrast, the first droplet of liquid condenses from vapor at the dew-point line. At
Table 1.2: Typical composition of different hydrocarbon categories from Wall (1982).

<table>
<thead>
<tr>
<th>Component</th>
<th>Black oil</th>
<th>Volatile oil</th>
<th>Condensate</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>48.83</td>
<td>64.36</td>
<td>87.07</td>
<td>95.85</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.75</td>
<td>7.52</td>
<td>4.39</td>
<td>2.67</td>
</tr>
<tr>
<td>Propane</td>
<td>1.93</td>
<td>4.74</td>
<td>2.29</td>
<td>0.34</td>
</tr>
<tr>
<td>Butane</td>
<td>1.60</td>
<td>4.12</td>
<td>1.74</td>
<td>0.52</td>
</tr>
<tr>
<td>Pentane</td>
<td>1.15</td>
<td>2.97</td>
<td>0.83</td>
<td>0.08</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.59</td>
<td>1.38</td>
<td>0.60</td>
<td>0.12</td>
</tr>
<tr>
<td>C7+</td>
<td>42.15</td>
<td>14.91</td>
<td>3.8</td>
<td>0.42</td>
</tr>
</tbody>
</table>

the critical point, the vapor and liquid phases cannot be distinguished because the composition and all other intensive properties of the two phases become identical.

Gas and gas-condensate reservoirs are determined by the phase envelope in the initial reservoir conditions (Figure 1.9). If the reservoir temperature is above the cricondentherm temperature, the reservoir will follow the A-A’ path during isothermal expansion and the two-phase region will not be entered. Therefore, the reservoir fluid will remain as gas and the fluid composition will remain constant during depletion.

On the other hand, if the reservoir temperature is between the critical temperature and the cricondentherm temperature, the reservoir will follow the B-B’ path during isothermal expansion. Retrograde condensation will start to occur at the reservoir when the B-B’ path crosses the dew-point line. Below the critical condensate saturation, the condensate mobility is zero and only gas will flow. Consequently, the flowing fluid composition will change. As the pressure decreases in the reservoir, more condensate will drop out until the condensate saturation reaches the critical saturation. At this event, condensate will start to mobilize in the reservoir. This phenomenon is captured by the three-zone flow model.

The three-zone flow model was introduced by Fevang (1995). The three flow regions around the wellbore assumed by the model are:

1. a near-wellbore region where condensate and gas are present and mobile,

2. a condensate build-up region where the condensate phase is immobile and only gas is flowing,
3. and, an outer region where only gas is present as shown on Figure 1.10.

The properties of the separated phases in the gas-condensate systems can vary considerably. The C1 content of the gas phase remain high and can vary from 70 to 90 mol%. In addition, the C7+ fractions remain very low at less than one mol%. In contrast, for the liquid phase (condensate), the C1 contents can vary from 10 to nearly 30 mol% and the C7+ contents vary from 40 to 70 mol% (Moses and Donohoe, 1962).

**Gas-condensate core-flooding experiments**

The SUPRI-D research group at Stanford University has previously conducted research to investigate the gas-condensate fluid composition behavior during flow. Additionally, the research group studied how the composition of heavy components of a gas-condensate system change around production wells during depletion. The core-flooding result was then simulated using a compositional simulator.

The gas condensate system that was used in the experiment was a 15% methane and 85% n-butane binary mixture that was prepared in the lab. A schematic of
the core-flooding apparatus is shown on Figure 1.11. Reports documenting the core-flooding results by Shi (2009) and Vo (2010) indicated that the gas-condensate composition varied significantly during depletion. Due to liquid dropout below the dew-point pressure and retention of the liquid at saturations less than the immobile liquid saturation, the flowing gas phase became lighter (i.e. less nC4 concentration) as it flowed from left to right across the core. An example experimental result is shown in Figure 1.12.

### 1.1.4 Gas-condensate systems in unconventional reservoirs

During the discussion of the pore structure of shale rocks, it was shown that in typical shales the pore size varies from 0.5 to 100 nm. In micropores, the properties of confined fluids may shift significantly from those of the bulk fluids due to interaction between the fluid molecules and the solid surface. The shift in the fluid properties becomes even more apparent as the dimensions of the confining space decreases (Hamada et al., 2007; Singh et al., 2009; Travalloni et al., 2010). The fluid properties that could be affected by confinement include: critical temperature and pressure, interfacial tension and capillary pressure, viscosity and Knudsen number.
Critical properties

Estimating the critical properties for fluids confined within nanopores is very important for the development of the fluids thermodynamic models which can then be utilized in the flow modeling (Vishnyakov et al., 2001). Evans et al. (1986a,b) and Ball and Evans (1989) theoretically investigated the phase equilibrium, adsorption and related phenomena for simple fluids confined in model pores, specifically slit-like and cylindrical capillaries. A mean-field density functional theory of inhomogeneous fluids was applied in this problem. One of the outcomes of their investigation was the following approximate relationship:

$$\frac{T_c - T_{cp}}{T_c} \approx \frac{\sigma}{r_p}$$

where $T_c$ is the bulk critical temperature, $T_{cp}$ is the pore critical temperature, $\sigma$ is
Figure 1.12: n-Butane concentration in the flowing mixture generated from Vo (2010). The mixture flowed from left to right.

the Lennard-Jones size parameter and $r_p$ is the pore radius. Morishige et al. (1997) and Morishige and Shikimi (1998) studied the effect of temperature on adsorption isotherms of Ar, N$_2$, O$_2$, C$_2$H$_4$ and CO$_2$ on mesoporous MCM-41 molecular sieves with various pore sizes. The objective of the study was to come up with a quantitative relation between the critical point shift and pore size and molecular properties. The measured critical temperatures at different pore sizes were then used to ascertain the validity of Equation 1.1 by plotting $(T_c - T_{cp})/T_c$ as a function of $d/r_p$ where $d$ and $r_p$ are obtained from the size parameters for the Lennard-Jones potential and the pore radii estimated from X-ray diffraction, respectively. The results indicate that all the data, except for those for CO$_2$, form a straight line passing through the origin as shown on Figure 1.13. Open symbols denote the results for MCM-41 and closed symbols denote results reported for conventional nanoporous adsorbent. The deviation of CO$_2$ was originally believed to be due to a relatively weaker fluid-wall interaction, however, this was refuted later.

Based on their generalized van der Waals equation-of-state (EOS) theory for a
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Figure 1.13: Deviation of critical temperature against the ratio of molecular size to the pore radius (Morishige et al., 1997).

confined Lennard-Jones fluid in a nanopore, Zarragoicoechea and Kuz (2004) derived correlations to estimate the deviation of critical pressure and critical temperature. Adsorption and desorption in the pore was neglected. The derived correlations are:

\[
\frac{T_c - T_{cp}}{T_c} = 0.9409 \frac{\sigma}{r_p} - 0.2415 \left( \frac{\sigma}{r_p} \right)^2 \tag{1.2}
\]

\[
\frac{p_c - p_{cp}}{p_c} = 2 \frac{c_1}{a\sqrt{\pi}} \frac{\sigma}{r_p} - 2 \frac{c_2}{a\pi} \left( \frac{\sigma}{r_p} \right)^2 \tag{1.3}
\]

where \( a = \frac{16\pi}{9} \), \( c_1 = 4.6571 \) and \( c_2 = -2.1185 \). The results of Equation 1.2 were
1.1. LITERATURE REVIEW

compared with the published data of Morishige et al. (1997) presented earlier. The comparison is shown on Figure 1.14. Equation 1.3 could not be calibrated due to the unavailability of experimental data that could be utilized for verification.

![Figure 1.14: Deviation of critical temperature against the ratio of molecular size to the pore radius (Zarragoicoechea and Kuz, 2004).](image)

Singh et al. (2009) applied the grand-canonical transition-matrix Monte Carlo numerical simulation to investigate the behavior of methane, n-butane and n-octane inside nanoscale pore systems. The slit pores were of graphite and mica surfaces and their sizes were between 0.8 to 5 nm. The investigation results revealed that the surface characteristics (mica vs. graphite) and the extent of confinement significantly affect various properties of n-alkanes. The critical temperature of the simple fluid systems was found to be decreasing with increasing confinement. Figure 1.15 shows a plot of the shift in the critical temperature $[\Delta T^* = (T_c - T_{cp})/T_c]$ as a function of the inverse of the slit width ($H$) for methane, n-butane and n-octane in graphite ($G$) slit pores. The shift in the critical pressure $[\Delta p^* = (p_c - p_{cp})/p_c]$ as a function of the inverse of the slit width ($H$) for n-butane and n-octane is shown in Figure 1.16.

Devegowda et al. (2012) used the results of Singh et al. (2009) to estimate the shifts in critical properties of confined pure hydrocarbons as functions of molecular weight. In addition to the results of Singh et al. (2009), Jin et al. (2013) used the data of
Vishnyakov et al. (2001) and Singh and Singh (2011) to develop models to investigate the effects of pore confinement on phase behavior and the critical properties of various hydrocarbon mixtures.

**Interfacial tension and capillary pressure**

Various papers have discussed the effect of nanopore scale on the fluid-wall interfacial tension including Qiao et al. (2006), Hamada et al. (2007) and Qiao et al. (2009). The capillary-gravity equilibrium in porous media introduced by Leverett (1941) indicated that when a mixture of two fluids exists, the interfacial boundary between the fluids is curved and the sharpness of the curvature depends on the pore size. The cause of the curvature is the interfacial tension between the fluids and it gives rise to a pressure differential across the interface, known as capillary pressure. Mathematically, capillary pressure can be estimated by applying the well-known Laplace-Young equation:

\[
p_c = p_g - p_o = \frac{2\sigma_{go} \cos \theta}{r}
\]  

(1.4)
where \( \sigma_{go} \) is the interfacial tension between the liquid and gas phases, \( \theta \) is the wetting angle and \( r \) is the average radius of the contact curvature. Sigmund et al. (1973) concluded that the effect of interfacial tension on phase behavior could be negligible except for scenarios with high curvatures which are typical for nanoporous shales. Therefore, the capillary effect on the phase behavior is not only dependent on the fluid composition and properties, but also on the properties of the formation containing the fluid.

The effect of capillary pressure (interfacial curvature) on phase equilibrium was studied by Bruslovsky (1992). He concluded that when the surface curvature is increased for small pores, the bubble-point pressure decreases and the dew-point pressure increases. Hence, capillary effects have a great impact on the development on shale oil and shale gas-condensate reservoirs. Ping et al. (1996) investigated the effect of capillary pressure and adsorption on the dew point of gas-condensate mixtures in porous media. Recently, work by Du and Chu (2012) and Nojabaei et al. (2013) investigated the effect of capillarity on the bubble-point pressure of Bakkan oil samples. Teklu et al. (2014) applied the shift laws of the critical temperature and pressure...
(Zarragoicoechea and Kuz, 2004) to account for the critical shifts in nanopores in addition to the capillary pressure. Therefore, changes in the phase behavior in the nanopores were due to a combination of capillary pressure effects and critical-shift effects.

**Viscosity**

Fluid confinement in nanopores has a significant effect on the fluid transfer inside the nanoporous medium. Therefore, mass flow rates, pressure drops and shear stresses may not be predicted correctly by the commonly used continuum models of gas transfer (Devegowda et al., 2012). Experimental results obtained by Majumder et al. (2005) indicates that the liquid flow rates in 7-nm diameter nanotubes were four to five orders of magnitude faster than that at the macroscale and with an increase in fluid viscosity, the flow rate did not decrease. Hummer et al. (2001) and Skoulidas et al. (2002) confirmed using molecular dynamics (MD) simulations that the velocity of water or gas was higher inside a carbon nanotube (CNT) than in a classical macroscale tube. Hence, the effects of nanosize channels on fluid viscosity as well as other intrinsic fluid properties need to be investigated at the nanoscale.

Chen et al. (2008) also investigated the transport behavior of water molecules inside a model carbon nanotube using nonequilibrium molecular dynamics (NEMD) simulations. They concluded that the shearing stress between the nanotube wall and the water molecules is an important parameter in estimating the nanofluidic properties. The effective shearing stress is very size-sensitive due to the effect of nanoscale confinement and decreases as the tube size is reduced. Consequently, the nominal viscosity of the confined water decreases as shown in Figure 1.17.

**Knudsen number**

The Knudsen number is defined by Roy et al. (2003) as a measure of the degree of rarefaction of gases encountered in small flows through narrow channels. Mathematically, the Knudsen number is defined as the ratio of the mean free path over the pore diameter, $d_p$ (Javadpour et al., 2007):
$K_n = \frac{\lambda}{d_p}$ \hspace{1cm} (1.5)

where $\lambda$; the mean free path, is defined as (Heidemann et al., 1984):

$\lambda = \frac{k_B T}{\sqrt{2\pi\delta^2 p}}$ \hspace{1cm} (1.6)

where $k_B$ is the Boltzmann constant ($1.3805 \times 10^{-23} J/K$), $T$ is temperature ($K$), $p$ is pressure ($Pa$) and $\delta$ is the collision diameter of the gas molecule.

The Knudsen number is a dimensionless parameter that can be used to determine the appropriateness of the continuum model. The continuum approach involves Darcy flow and is used for flow in micropores (Javadpour et al., 2007). For $K_n < 0.001$, the fluid flow can be considered continuum with no-slip boundary condition as classified by Chambre and Schaaf (1961).
As the Knudsen number increases, rarefaction effects become more important and mass flow rates cannot be predicted by the continuum model alone. As shown in Equation 1.5, the Knudsen number increases as the pore size decreases. In the region \((0.001 < K_n < 0.1)\), the rarefied gas can neither be modeled as a continuous medium nor as a free molecular flow (Karniadakis et al., 2005). Therefore, for nanoporous shales, a combination between Knudsen diffusion with slip flow and pressure forces needs to be considered to model the fluid flux (Javadpour, 2009). A comparison between no-slip flow in micropores and slip flow in nanopores is shown in Figure 1.18.

Figure 1.19 shows the Knudsen number as a function of pressure considering different pore sizes. The pore sizes range from 10 nm to 50 \(\mu\)m. The plot indicates that the Knudsen number decreases by increasing the pressure. Additionally, the Knudsen number increases with smaller pore sizes as discussed earlier.

![Figure 1.18: (a) No-slip flow in micropores vs. (b) slip flow in nanopores (Javadvopour et al., 2007).](image)
1.2 STATEMENT OF THE PROBLEM

The multiphase flow of gas and condensate below the dew-point pressure in shale gas-condensate reservoirs and the multiphase flow of oil and gas below the bubble-point pressure in shale oil reservoirs are not fully understood. The nanoscale nature of the pores in shale rocks, coupled with rock heterogeneity, makes the conventional understanding of multiphase flow in conventional reservoir no longer suitable to explain and accurately predict the flow behavior in unconventional reservoirs. Various phenomena affecting the transport mechanisms of gas-condensate in nanometer sized pores of organic-rich and clay-rich shale come into play such as stress-dependent permeability, multicomponent adsorption and condensate dropout. The aim of this research work was to apply various experimental and computer modeling tools to bridge the gap in the understanding of the behavior of liquid-rich unconventional reservoirs. Three main components were studied: the rock, the fluid and rock-fluid interactions. More precisely, the research work focused on the following parameters:

1. The rock: the characteristics of liquid-rich shales, i.e. porosity, permeability
and pore size distribution.

2. *The fluid:* the compositional behavior of gas-condensate mixtures in shale rocks due to liquid dropout below the dew-point pressure.

3. *Rock-fluid interactions:*

   (a) molecular behavior of gas-condensate mixtures and carbon dioxide in nanometer porous medium, i.e. adsorption,

   (b) the phase behavior and the critical properties of hydrocarbons in the nanopores.

A diagram showing all the components of the research work is provided in Figure 1.20.

As presented in the literature review, efforts have already been made to further understand the fluid flow behavior in unconventional reservoirs. However, this work brings more analysis in areas not fully understood. For example, previous gas-condensate core-flooding experiments had been conducted on Berea sandstone samples using a binary gas-condensate mixture. In this work, the core-flooding experiment was conducted on a shale reservoir sample (Marcellus shale) using a real gas-condensate sample obtained from the field and at in situ conditions. This experiment is unique and to the best of my knowledge, no other lab has tried to conduct such an experiment. In addition, permeability and adsorption measurements in this work were conducted on samples obtained from a single well in the Utica that has not been studied before, and the samples contained a wide range of mineral compositions. Molecular simulations to investigate the competitive adsorption of binary hydrocarbon mixtures in shale have been validated with experimental data published recently. Previous validation efforts have been focused on modeling single component gas adsorption. To the best of my knowledge, this is the first time molecular simulation of binary mixture adsorption in shale has been validated.
1.3 Research Approach

This work contained two phases. In the first phase, experiments were conducted to characterize shale rock samples. The objective of the experiments was to evaluate the pore size distribution, porosity and permeability of the shale core samples. In addition, stress-dependent permeability for shale samples with varying mineral composition was measured. Experiments to estimate the adsorption isotherms of CO$_2$ and CH$_4$ in shale rocks were conducted. A core-flooding experiment to evaluate the compositional behavior of gas-condensate mixture in shale rocks was also carried out.

In the second phase, molecular simulation techniques were employed to explain
some of the experimental observations. Grand canonical Monte Carlo (GCMC) simulation was employed to study the adsorption of single and binary gas-condensate mixtures on carbon models of organic constituents. The pore-size distribution obtained from the previous phase was used as an input parameter for the molecular simulation and the generated adsorption isotherms results were compared with the adsorption experiment in the lab. In addition, Gibbs ensemble Monte Carlo (GEMC) and grand canonical Monte Carlo (GCMC) molecular simulation techniques were employed to estimate the shift in critical properties of hydrocarbons due to confinement in nanometer-size pores.

1.4 Dissertation Outline

The dissertation proceeds as follows. Chapter 2 describes the gas-condensate core-flooding experiment. The experimental apparatus was designed to allow for injection of a gas-condensate mixture at a predetermined upstream pressure and collecting gas samples along the core during flow. Analyses of the compositional behavior of a Marcellus gas-condensate sample across a Berea sandstone sample and Marcellus shale sample are presented.

Chapter 3 describes the permeability experiments of intact Utica and Permian shale samples. The studied shale samples exhibited a wide variation of rock mineralogy. Permeability was measured using the pressure-pulse decay technique. SEM images were collected to aid in the permeability analysis.

Chapter 4 discusses CO$_2$ adsorption shale rocks. Adsorption measurements were conducted on crushed Utica and Permian shale samples. To aid in the CO$_2$ adsorption analysis, pore size distribution (PSD) measurements were conducted using the low-pressure sorption technique. In addition, this chapter discusses the effect of CO$_2$ adsorption on permeability.

Chapter 5 and 6 focus on molecular simulation techniques. Chapter 5 discusses the grand canonical Monte Carlo (GCMC) molecular simulation technique. The GCMC technique was applied to study the competitive adsorption of various binary gas-condensate mixtures that could not otherwise be studied in the lab.
Chapter 6 presents the Gibbs ensemble Monte Carlo (GEMC) molecular simulation technique. The GEMC technique was applied to study the vapor-liquid equilibrium (VLE) of pure hydrocarbons. Additionally, this chapter presents VLE analysis by the GCMC molecular simulation technique.

Chapter 7 summarizes the results of this work and provides concluding remarks.
Chapter 2

Gas-Condensate in Liquid-Rich Shales

2.1 Introduction

Production from the gas-condensate window of the liquid-rich shale plays in the US such as the Barnett, Marcellus and Eagle Ford, has increased dramatically during the past few years. However, there is still a lack of understanding of the flow behavior of gas-condensate in liquid-rich shales when the flowing bottom-hole pressure falls below the dew-point pressure. Condensate dropout below the dew-point pressure leads to variation in the composition of the vapor and liquid hydrocarbons. The phase behavior prediction is complicated further by the nanometer-sized pores of the shale formations where fluid-rock interaction would be significant at the molecular scale.

Shi (2009) and Vo (2010) conducted experiments to investigate the gas-condensate fluid composition behavior during flow through Berea sandstone. During the experiments, a gas-condensate mixture was injected into the core and during the fluid flow, gas samples were collected through sampling ports spaced along the core-holder. Then, the gas samples were characterized using gas chromatography for compositional analysis. The gas-condensate fluid used in the core-flooding experiments was
85%CH$_4$-15%nC$_4$H$_{10}$ binary mixture. Experimental results indicate that the gas-condensate composition varied significantly during depletion. Due to liquid dropout below the dew-point pressure and the retention of the liquid due to relative permeability effects, the flowing gas phase became lighter (i.e. lower n-butane concentration) as it flowed from the upstream side to the downstream side across the core.

Unlike those previous experiments, this work investigated the gas-condensate fluid composition behavior during flow through a Marcellus shale core (and a comparative experiment using a Berea sandstone core). The gas-condensate fluid used in the core-flooding experiment was collected from a well in the Marcellus liquid-rich region and the experiments were conducted at reservoir pressure and temperature. Prior to conducting the experiments, the permeability of the Marcellus shale core and the Berea sandstone core were characterized using the pressure pulse decay technique and the Darcy flow technique, respectively. A general description of gas-condensate systems has been provided in the literature review section of the previous chapter.

### 2.2 Experimental Apparatus

A schematic diagram of the gas-condensate core-flooding apparatus is shown in Figure 2.1. The apparatus contains the following main components:

1. **Piston cylinder**: The piston cylinder contained the gas-condensate mixture and the pressure of the cylinder was controlled by high pressure nitrogen.

2. **Core-holder**: The core-holder was made of titanium with a pressure rating of 5,800 psi. The core-holder contained a rubber sleeve and two end-caps. The 2-inch diameter core was placed inside the rubber sleeve to isolate the core from the confining fluid. Six evenly spaced sampling ports were mounted on the rubber sleeve as shown on Figure 2.2. The sampling ports were connected to sampling valves installed on the core-holder.

3. **Sampling bags**: Tedlar sampling bags were used to collect gas samples. During the flow experiment, the sampling valves were opened to capture the gas samples along the core.
4. **Gas chromatography:** An Agilent 3000C gas chromatograph was used to analyze the collected gas samples. The analysis provided the composition of the collected gas samples.

5. **Data acquisition:** The data acquisition system was employed to monitor the upstream pressure, downstream pressure and the temperature inside the core-holder. The pressures were measured using pressure transducers and the temperature was measured using a thermocouple inserted inside the core-holder through one of the sampling ports.

The procedures to conduct the gas-condensate core-flooding experiment are illustrated in Appendix A.

![Schematic diagram of the core-flooding experimental apparatus](image-url)

**Figure 2.1:** Schematic diagram of the core-flooding experimental apparatus
2.3 Fluid Systems

Two different gas-condensate mixtures were used in the core-flooding experiment: a Marcellus gas-condensate mixture and a synthetic binary methane-butane gas-condensate mixture. In this section, the thermodynamics for each mixture will be discussed.

2.3.1 Binary gas-condensate mixture

The binary gas-condensate mixture contained 85% methane (CH\textsubscript{4}) and 15% n-butane (n-C\textsubscript{4}H\textsubscript{10}) in mole fractions. Methane and n-butane were mixed in the lab by Vo (2010). The phase diagram for the fluid mixture; shown in Figure 2.3, indicates a dew-point pressure of around 1,900 psi at room temperature. During the flow experiment, the upstream pressure was maintained at the dew-point pressure (i.e. 1,900 psi) using a pressure regulator and the downstream pressure pressure was maintained at 1,000 psi using a back-pressure regulator. The binary mixture was then in the two-phase region across the core.
2.3. FLUID SYSTEMS

Figure 2.3: Phase diagram for the binary 85% methane and 15% n-butane gas-condensate mixture obtained from Peng-Robinson equation-of-state (PR-EOS). A-A’ line represents the pressure range during the experiment. A is at the planned upstream pressure of 1,900 psi and A’ is at the planned downstream pressure of 1,000 psi. Blue is the bubble-point line and red is the dew-point line. The black dot represents the critical point of the fluid system.

2.3.2 Marcellus gas-condensate mixture

The Marcellus fluid system that was used in this experiment was collected from a gas-condensate well in the Marcellus shale play. Laboratory fluid pressure-volume-temperature (PVT) data were also provided. The PVT data included constant volume depletion (CVD), constant composition expansion (CCE) and fluid compositional analysis at separator conditions. An equation-of-state (EOS) based compositional simulator (PVTi) was employed to build a fluid model for the gas-condensate mixture. The fluid model was tuned to fit a Peng-Robinson (PR) equation-of-state (EOS) to the observed experimental data.

The first step in the PVT simulation was to define the components that comprise the fluid system. The 11-component Marcellus shale gas-condensate fluid system contained ten well-defined components and one pseudocomponent C7+ (Table 2.1). Extensive splitting of the plus fraction was unnecessary because the capability of the
gas chromatograph was limited to analyzing light hydrocarbons (up to pentanes).

As outlined by Coats and Smart (1986), nonlinear regression was then applied on $\Omega_a$ and $\Omega_b$ of the C7+ fraction. Adjustments of $\Omega_a$ and $\Omega_b$ can be interpreted as an adjustment to the critical pressure and and temperature of the lumped pseudocomponent. $\Omega_a$ and $\Omega_b$ are related to the critical properties by the cubic equation-of-state (EOS) parameters, $a$ and $b$ as shown in the following equations:

$$a = \Omega_a R^2 T_c^2 \frac{\xi}{p_c}$$  \hspace{1cm} (2.1)

$$b = \Omega_b R T_c \frac{T_c}{p_c}$$  \hspace{1cm} (2.2)

where $R$ is the gas constant, $T_c$ is the critical temperature and $p_c$ is the critical pressure.

Sensitivity analysis revealed that the fluid model was very sensitive to the binary interaction coefficients between methane and the plus fractions. Therefore, C1-C7+ binary interaction coefficients were included in the nonlinear regression. Binary interaction coefficients are introduced in order to compensate for the nonsphericity of the heavy hydrocarbons (Pedersen et al., 1989).

Figure 2.4 and Figure 2.5 compare the tuned Peng-Robinson EOS calculations and
2.3. **FLUID SYSTEMS**

the observed PVT laboratory data for the CVD and CCE experiments, respectively. The plots show that a satisfactory agreement between the EOS calculations and the laboratory data was achieved. The observed dew-point pressure was 3,085 psi and it was matched by the fluid model calculations.

![Condensate saturation plot during CVD experiment.](image)

**Figure 2.4:** Condensate saturation plot during CVD experiment.

Compositional data of the separator fluid samples were used to confirm the accuracy of the EOS model. When the fluid model was flashed to separator sampling conditions of 293 psi pressure and 83°F temperature, a good agreement between the measured and calculated compositions for vapor and liquid phases was observed as illustrated in Figure 2.6 and Figure 2.7, respectively.

The fluid phase diagram was generated for the Marcellus gas-condensate system as shown in Figure 2.8. As indicated by the phase diagram, the critical point appeared close to room temperature and conducting the flowing experiment at room temperature would therefore be problematic. Hence, the temperature throughout the apparatus was maintained at the reservoir temperature of 140°F by wrapping the gas cylinder, tubes and core-holder with heating tapes and insulators. At 140°F, the dew-point pressure was approximately 3,000 psi. During the flowing experiment, the upstream pressure was maintained at the dew-point pressure to insure that the fluid system across the core was in the two-phase region.
2.4 Core Characteristics

Prior to performing the gas-condensate core-flooding experiments, experiments were conducted to measure the permeability of the Berea sandstone and Marcellus shale samples.

2.4.1 Berea sandstone

The conventional Darcy flow technique was applied to measure the permeability of the Berea sandstone. The experiment was conducted using nitrogen gas. The gas permeability \( k_{\text{gas}} \) was calculated using the following equation, defined by Scheidegger (1974):

\[
k_{\text{gas}} = \frac{\mu L q}{A} \frac{2p_{\text{down}}}{p_{\text{up}}^2 - p_{\text{down}}^2}
\]  

(2.3)

where \( \mu \) is the gas viscosity, \( L \) is the length of the plug sample, \( q \) is the gas flow rate, \( A \) is the cross-sectional area of the plug sample, \( p_{\text{up}} \) is the upstream pressure and \( p_{\text{down}} \) is the downstream pressure. The intrinsic permeability was determined by the

Figure 2.5: Pressure-volume relation of reservoir fluid during CCE experiment.
Klinkenberg analysis. Klinkenberg (1941) defined the apparent gas permeability as:

\[
k_{\text{gas}} = k_\infty (1 + \frac{b_{\text{slip}}}{p})
\]  \hspace{1cm} (2.4)

where \(k_\infty\) is the intrinsic permeability, \(b_{\text{slip}}\) is the slip factor and \(p\) is the pore pressure during the permeability experiment. Figure 2.9 shows gas permeability as a function of reciprocal pressure. Based on Equation 2.4, the intrinsic permeability \((k_\infty)\) is the y-intercept and the slip factor \((b_{\text{slip}})\) can be determined from the slope of the line. As observed on Figure 2.9, the intrinsic permeability of the Berea sandstone core was approximately 105 md.

The slip factor \((b_{\text{slip}})\) is defined by Klinkenberg (1941) as:

\[
b_{\text{slip}} = \frac{4pc\lambda}{r_p}
\]  \hspace{1cm} (2.5)

where \(c\) is a proportionality factor \((c = 1)\), \(\lambda\) is the gas mean free path and \(r_p\) is the pore radius. The mean free path is defined as the average distance a molecule travels
before it collides with another molecule. In the simplest version of the kinetic theory of gases, molecules that make binary collisions only can be treated as hard spheres of diameter $d$. In this case, $\delta$ in the mean free path formula (Equation 1.6) can just be replaced with the molecular diameter $d$. Equation 1.6 can then be rewritten as:

$$
\lambda = \frac{k_B T}{\sqrt{2\pi d^2 p}}
$$

Equation 2.7 was derived by combining Equation 2.5 and Equation 2.6. Equation 2.7 was then applied to calculate the mean pore throat radius for the Berea sandstone core sample. The mean pore throat radius was estimated to be about 900 nm.

$$
r_p = \frac{4}{b_{slip}} \frac{k_B T}{\sqrt{2\pi d^2}}
$$
2.4. CORE CHARACTERISTICS

2.4.2 Marcellus shale

The Marcellus study area is located in Washington County in Southwest Pennsylvania. The research site contains a multiple well pad from which seven nearly-parallel horizontal wells were drilled in the upper section of the Marcellus shale at true vertical depth (TVD) of approximately 6,500 ft. The Marcellus shale core was collected from a “science” well drilled nearby the research site. The research site location is shown on Figure 2.10.

The Marcellus shale extends throughout much of the Appalachian basin (Figure 2.10) and it is the lowest member of the Devonian age Hamilton group. The Marcellus formation is composed mainly of black shale, and also contains lighter shales and interbedded limestone layers (Ciezobka, 2011). The regional stratigraphy of the Devonian shales and the Marcellus shale formation is shown in Figure 2.11. The Marcellus shale is bounded above by the Mahantango formation and Tully limestone and below by the Onondaga limestone. According to Zagorski et al. (2012), the reserve potential for the Marcellus shale ranges from 50 TCF to more than 500 TCF,
Figure 2.9: Gas permeability of the Berea sandstone core.

making this play a world-class hydrocarbon accumulation.

The pressure-pulse decay technique was applied to study the permeability of the Marcellus shale sample at different effective pressures. The pressure-pulse decay technique was first developed by Brace et al. (1968) to measure permeability of granites. The principle of this technique is to create a dynamically changing flow across the sample and then estimating permeability by fitting the resulting pressure curves to a flow model. During the experiment, a pressure pulse was introduced at the upstream side and maintained constant and the effect of the pressure pulse on the downstream pressure was monitored. Helium gas was used in the experiment to remove adsorption effects and to only test the impacts of effective stress on shale permeability. More details about the experimental apparatus and the pressure-pulse decay technique are presented in the next chapter which provides a thorough discussion of liquid-rich shale permeability.

To compute permeability, the following equations obtained from Brace et al. (1968) were applied:
2.4. CORE CHARACTERISTICS

Figure 2.10: Location of the field data site. Map acquired from Milici (2005).

\[ \Delta p(t) = \Delta p_o e^{-\alpha t} \]  \hspace{1cm} (2.8)

\[ \alpha = \frac{kA}{\beta V_{down} L \mu} \]  \hspace{1cm} (2.9)

where \( \Delta p(t) \) is the pressure difference between the upstream and downstream at time \( t \), \( k \) is the rock permeability, \( A \) is the core cross-sectional area, \( \beta \) is the gas compressibility, \( V_{down} \) is the downstream volume, \( L \) is the length of the core and \( \mu \) is the gas viscosity. By plotting \( \ln(\Delta p(t)/\Delta p_o) \) as a function of time, the slope of the generated line (\( \alpha \)) was used to estimate permeability.

Permeability estimates were obtained at different simple effective stresses. Simple
CHAPTER 2: GAS-CONDENSATE IN LIQUID-RICH SHALES

Figure 2.11: A generalized stratigraphic chart of the Marcellus shale (Zagorski et al., 2012).
effective stress is defined as the difference between the confining pressure and the pore pressure. Mathematically, it is:

\[ p_{\text{eff}} = p_{\text{conf}} - p_p \]  

(2.10)

where \( p_{\text{conf}} \) is the confining pressure and \( p_p \) is the pore pressure. At each effective pressure, permeability estimates were obtained at different pore pressures. Figure 2.12 shows the core permeability as a function of effective stress. The results indicate that the permeability decreased with increasing effective stress. Reduction of permeability at higher effective stresses means the core was deforming and the grains were further pushing against each other (compaction). Over the experimental conditions, the Marcellus shale apparent or gas permeability ranged from 20 nd to 65 nd.

Figure 2.12: Gas permeability of the Marcellus shale core as a function of effective stress.

Similar to the Berea sandstone sample, Klinkenberg analysis was implemented on the Marcellus shale sample. Figure 2.13 plots the gas permeability for the Marcellus
shale sample as a function of reciprocal pressure for 1,000 psi effective stress. The intrinsic permeability of the sample was 37.8 nd. From \(b_{slip}\) analysis, the mean pore throat radius was estimated to be approximately 14.5 nm.

\[
y = 29769x + 37.808 \\
R^2 = 0.961
\]

Figure 2.13: Klinkenberg analysis of Marcellus shale permeability at 1,000 psi effective stress.

### 2.5 Gas-Condensate Flow Experiments

Three gas-condensate flow experiments were conducted in the study as follows:

1. binary (methane-butane) gas-condensate mixture through Berea sandstone core,
2. Marcellus gas-condensate mixture through Berea sandstone core,
3. and, Marcellus gas-condensate mixture through Marcellus shale core.

In each experiment, the gas-condensate mixture was injected into the core at an upstream pressure that was equivalent to the mixture dew-point pressure. The pressure drop across the core insured that the flow occurred in the two-phase region. While the fluid mixture was flowing, gas samples were collected across the core simultaneously through the sampling ports and using the sampling bags. After that, each gas sample was analyzed using gas chromatography.
2.5.1 Binary methane/n-butane gas-condensate mixture across Berea sandstone core

The binary methane/n-butane mixture was injected into the Berea sandstone core sample at an upstream pressure of 1,900 psi which was equivalent to the dew-point pressure. The pressure drop across the 11-inch core was 900 psi. The experiment was conducted at room temperature. Two types of sampling procedures were followed: a noncapture mode and a capture mode. In the noncapture mode, the gas samples were collected when both the upstream valve and the downstream valve were open and the mixture was flowing across the core. In the capture mode, the gas samples were collected when both the upstream valve and the downstream valve were closed. Eventually, the captured condensate in the core was discharged to an empty cylinder to determine its composition.

Figure 2.14 shows n-butane concentration in the collected gas samples along the core during the noncapture mode. The plot indicates that the n-Butane concentration in the vapor phase decreased as the fluid flowed from left (upstream) to right (downstream). The additional pressure drop below the dew point as the fluid was flowing from left to right caused further condensate dropout. As a result, the flowing gas contained lower n-butane concentration and as a result became leaner.

Figure 2.15 shows the n-butane concentration in the collected gas samples during the capture mode. The capture mode started with flowing the gas mixture and collecting samples along the core. As showing on the plot, the compositional behavior of the flowing gas in this step was similar to the behavior of the noncapture mode. Then, the upstream and downstream valves were closed simultaneously and immediately after that, samples were collected across the core at no-flow (i.e. capture) conditions. This step mimics shutting-in a gas-condensate well producing below the dew-point pressure in an attempt to achieve condensate revaporization. The results for the no-flow conditions in Figure 2.15 reveal that revaporization did not occur because the n-butane concentration in the vapor phase did not increase to its initial concentration of 15%. At the end, the fluid inside the core was discharged into a vacated cylinder for compositional analysis. The composition of the discharged fluid
showed a slight increase in n-butane concentration in the vapor phase. The slight increase in the n-butane concentration could be attributed to additional gas evolving from the condensate, which was rich in n-butane, as the core fluid was being discharged to the cylinder and the pressure was decreasing. This means the condensate was behaving similarly to volatile oil.

2.5.2 Marcellus gas-condensate mixture across Berea sandstone core

The objective of this experiment was to investigate the behavior of actual gas-condensate mixtures in conventional reservoirs. This experiment was conducted by flowing the Marcellus gas-condensate mixture through the 11-in-long Berea sandstone core. As observed on the mixture phase diagram (Figure 2.8), the experiment could not be conducted at room temperature. Therefore, the temperature in the experimental apparatus was elevated to 140°F which is the temperature of the reservoir from which the Marcellus gas-condensate sample was collected. Temperature tapes and insulators were used to raise the temperature of the entire apparatus as shown in
2.5. GAS-CONDENSATE FLOW EXPERIMENTS

Figure 2.15: n-Butane concentration in the vapor phase during binary gas-condensate mixture flow from left to right in the capture mode across Berea sandstone core.

Figure 2.16. The upstream pressure was maintained at the dew-point pressure (i.e. 3,000 psi) and confining pressure was set at 3,300 psi. Due to the limited supply of Marcellus gas-condensate sample, only a noncapture experiment was conducted.

Figure 2.17 shows the propane concentration in the collected gas samples across the core. The propane behavior is evident of condensate dropout as its concentration in the vapor phase was decreasing with the additional pressure drop from left to right. In this experiment, the i-Butane and n-butane concentrations in the vapor phase could not be measured accurately by the gas chromatography because they were extremely low.

2.5.3 Marcellus gas-condensate mixture across Marcellus shale core

The objective of this experiment was to investigate the behavior of actual gas-condensate mixtures in a real reservoir. Initially, the rock sample was vacuumed and the confining pressure was set at 3,300 psi. The temperature throughout the
apparatus was controlled at 140°F. The experiment started by injecting the Marcellus gas-condensate mixture into a 6.5-inch core from Marcellus shale at an upstream pressure of 3,000 psi. Due to the core’s low permeability, steady-state flow condition could not be established. The experiment was then conducted under transient flow conditions.

At the beginning of the experiment, the downstream valve was closed because the goal was to first charge the core with the gas-condensate mixture. Experimental data (upstream pressure, downstream pressure and temperature) were collected during the core-flooding experiment as shown in Figure 2.18. After eight hours of injection, gas molecules reached the downstream side and the downstream pressure started to increase. The gas-condensate injection continued for another 33 hours during which the gas-condensate sample in the cylinder ran out. As a result, the upstream valve was closed and the gas-condensate mixture was left to equilibrate across the sample in a transient mode. The upstream and downstream pressures then were 3,000 psi and 450 psi; respectively. After closing the upstream valve, an upstream sample (US) representative of the initial gas-condensate mixture was collected. A downstream
2.5. GAS-CONDENSATE FLOW EXPERIMENTS

Figure 2.17: Propane concentration in the vapor phase during Marcellus gas-condensate flow from left to right in the noncapture mode across Berea sanstone core. Port 4 was used to insert a thermal couple to monitor the temperature inside the core-holder and therefore, it could not be utilized to collect a gas sample.

sample (DS1) was collected as well. As the gas-condensate mixture was equilibrating, three sets of port samples were collected along the core. The first set of port samples (SS1) contained three samples along the core and were collected when the upstream pressure was 2,530 psi at $t = 44$ hours. The second and third sets of port samples (SS2 and SS3) were collected when the upstream pressures were 1,520 psi ($t = 80$ hours) and 755 psi ($t = 145$ hours); respectively. Toward the end of the experiment at $t = 192$ hours, a second downstream sample (DS2) was collected. The experiment was concluded after 200 hours.

All the collected samples were characterized using the gas chromatograph. The first port sample set (SS1) was not adequate to be characterized. Therefore, while collecting the subsequent port sample sets (SS2 and SS3), the port valves were left open for a longer period of time to allow for more gas to be captured in the sampling bags. Figure 2.19 plots the ethane, propane, i-butane and n-butane concentrations measured by the gas chromatograph for the collected vapor samples. A total of nine samples were analyzed: the initial upstream sample, two samples from each of the three sampling ports and two downstream samples.
2.6 Discussion

2.6.1 Experiment

The experimental results shown in Figure 2.19 indicate that for the port sample set SS2, there was a reduction in ethane, propane, i-butane and n-butane concentrations along the core compared to their concentrations in the injected gas-condensate mixture observed for the upstream sample (US). This reveals that there was a change in the composition of the mixture as it was flowing along the core. Figure 2.20 shows the phase diagram for the injected gas-condensate mixture based on the compositional analysis of the initial upstream sample (US). Port sample set SS2 were collected at an upstream pressure of 1,520 psi. The phase diagram shows clearly that the samples were collected below the dew-point pressure. Therefore, similar to the observations in the Berea sandstone experiments, the change in composition across the Marcellus shale was due partly to liquid dropout below the dew-point pressure. The liquid
Figure 2.19: (a) Ethane (b) propane, (c) i-butane and (d) n-butane concentrations in the vapor phase during the Marcellus gas-condensate core-flooding experiment. The initial sample represents the injected mixture at the upstream side. Downstream sample (DS1) was collected at 41 hours and downstream sample (DS2) was collected toward the end of the experiment at 192 hours. Sample set SS2 and sample set SS3 were collected at different times during the experiment. TC stands for thermocouple and it refers to the port where the thermocouple was inserted. P1, P2 and P3 are port 1, port 2 and port 3; respectively.
Figure 2.20: Phase diagram for the Marcellus gas-condensate sample based on the composition of the injected upstream sample (US). A-A’ line represents the actual pressure range during the injection process. A is at the initial upstream pressure and A’ is at the downstream pressure. Blue is the bubble-point line and red is the dew-point line. The black dot represents the critical point of the fluid system.

Unlike sandstone, preferential adsorption of species in shale could also lead to compositional variation in the flowing gas-condensate mixture. This process, referred to as gas chromatographic separation (CS), appears in shale rocks because gas molecules flowing in shales tend to move individually rather than in bulk (Rezaveisi et al., 2014). In this experiment, molecules in the gas-condensate mixture heavier than methane had higher affinity to the pore walls relative to methane. Hence, as the gas-condensate mixture was flowing across the shale core, heavy molecules adsorbed and became immobile yielding a leaner flowing vapor phase containing lower concentrations of heavy components.

Freeman et al. (2012) analyzed production and compositional data of five wells in a North American shale gas play. Based on the well data, the authors observed that the relative composition of heavy components declined over time. They also observed that the decline of relative composition of the heavier components was greater than that of lighter components. In this experiment, similar observations have been made.
Hydrocarbon concentrations for sample set SS2 (Figure 2.19) indicate that the relative composition of the lighter components (i.e. ethane and propane) declined by approximately 53% at sampling port P2 compared to sample port P1, whereas the relative composition of the heavier component (n-butane) declined by approximately 77%.

Compositional analysis of port sample set SS3 collected at an upstream pressure of 755 psi reveals that there was a change in the mixture composition. The additional pressure drop led to more condensate dropout. In turn, more heavy components in the flowing vapor phase dropped to the liquid phase. This is especially evident at sampling port P1 where the composition of all four components in the vapor phase decreased. At sampling port P3, the relative increase of ethane and propane concentrations in sample set SS3 compared to sample set SS2 is indicative of condensate revaporization in the core at low pressure which falls at the bottom part of the phase envelope (Figure 2.20). However, the concentrations of i-butane and n-butane did not increase with the revaporization due to their higher affinity of the pore walls which prevented them from evolving to the vapor phase from the adsorbed phase.

The downstream samples were collected at low pressure conditions as well. The first downstream sample (DS1) was collected at a downstream pressure of 450 psi and the second downstream sample (DS2) was collected at a downstream pressure of 100 psi. The phase diagram (Figure 2.20) indicates that downstream sample DS1 was collected at the bottom boundary of the two-phase region and downstream sample DS2 was collected below the two-phase boundary in the single-phase (gas) region. Accordingly, as observed in sampling port P3, revaporization of the liquid phase occurred causing the composition of the heavy components in the vapor phase to increase (Figure 2.19).

The second downstream sample (DS2) was collected at a lower pressure compared to the first downstream sample (DS1). Hence, additional heavy components revaporized and this caused their compositions in the vapor phase to increase. Revaporization of heavier components (i.e. i-butane and n-butane) was more pronounced than that of lighter components (i.e. ethane and propane). At sample DS2, the relative composition of the lighter components increased by 5% compared to the initial
compositions of the injected mixture. On the other hand, the relative composition of the heavier components increased by 42% for i-butane and by 27% for n-butane. Unlike the samples collected at port P3, the downstream samples were collected from the downstream dead volume and therefore, i-butane and n-butane were free to revaporize from the liquid phase (i.e. condensate). In other words, i-butane and n-butane in the downstream dead volume were not adsorbed to limit their revaporization with the additional pressure drop.

### 2.6.2 Numerical simulation

Numerical simulation was applied to model the Marcellus gas-condensate experiment using the compositional simulator ECLIPSE 300. The core was modeled in a Cartesian coordinate system. The core was divided into grid blocks in the x-direction only. The cross-section of the grid block was square. The area of the square was equal to the cross-sectional area of the cylindrical core. Figure 2.21 shows grids of the core in the x-direction. In the numerical simulation, the vapor samples were collected via wells that were opened to simulate capturing a sample and then shut. A fluid model based on the actual mixture composition of the upstream gas-condensate sample was included in the numerical simulation.

Figure 2.21: Core grid blocks in the x-direction. Gas-condensate flow was simulated from left (US) to right (DS). Port samples and downstream samples were collected in the simulation via wells penetrating grid blocks corresponding to the actual sampling points of the Marcellus experiment.
Figure 2.22 shows a comparison of the ethane, propane, i-butane and n-butane concentrations in the vapor phase between the actual vapor port samples (SS3) and the compositional simulator ECLIPSE 300. In the numerical simulation, the samples were collected at similar upstream pressure conditions as samples SS3 (i.e. \( p_{US} = 1,520 \text{ psi} \)). The reported concentrations from the numerical simulator were obtained from the vapor composition of the produced gas from each well representing the sampling ports. The results indicate that the numerical simulator overestimated the concentrations of all components in the vapor phase especially at sampling ports P2 and P3. At sampling port P1, the results show that the difference between the numerical simulation and experiment was small for all components except n-butane.

Figure 2.23 plots the condensate saturation across the core estimated by the numerical simulation at the time step during which sampling set SS2 was being collected.
The plot shows clearly that numerical simulation was able to model liquid dropout below the dew-point pressure. This however led to only small reduction in the estimated concentrations of the heavy components in the vapor phase. Therefore, in the experiment gas chromatographic separation (CS) must have played a significant role in retaining heavy hydrocarbons in the adsorbed phase. The impact of adsorption in general on permeability was investigated experimentally in work described in Chapter 4. Additionally, ECLIPSE 300 is not capable of simulating the gas chromatographic phenomena and therefore, it was studied further using molecular simulation techniques in work described in Chapter 5.

![Figure 2.23: Condensate saturation along the core estimated by numerical simulation time step of SS2 sampling. Gas was flowing from left to right.](image)

2.7 Summary

The gas-condensate flowing experiments showed that in gas-condensate systems, the gas composition varies along the direction of flow during depletion. In conventional sandstone, the change in gas composition was due to a combination of condensate dropout and relative permeability effects. In the Marcellus shale experiment, preferential adsorption appeared to also cause significant variation in gas composition. Therefore, in liquid-rich shales, the produced gas becomes leaner with depletion and the condensate left behind is rich in heavy components in the adsorbed phase.
Chapter 3

Permeability of Liquid-Rich Shales

3.1 Introduction

Understanding the transport mechanisms in shale reservoirs is essential for a number of applications including reservoir characterization, production forecasting and field development. Shale reservoirs are complex and heterogeneous geologic systems. The mineralogy, total organic carbon (TOC) content, and the texture of the organic-rich shales are highly variable even across a single well. In this research, we investigated the lithological controls on matrix permeability of Utica and Permian shale samples. The mineralogy of the shale samples varied from clay-rich to calcite-rich. The TOC content ranged between 1.0 and 5.9%. Permeability measurements were conducted using a nonadsorbing gas (argon) at effective stresses ranging between 500 psi (3.45 MPa) and 4,000 psi (27.6 MPa). The effects of mineralogy and TOC on the intrinsic permeability and the stress-dependent permeability were studied. Permeability measurements were also conducted using an adsorbing gas (CO$_2$) to investigate the effect of CO$_2$ adsorption on permeability. The CO$_2$ permeability measurements will be discussed in the next chapter.
3.2 Sample Descriptions

Permeability experiments were conducted on four intact Utica shale samples and two intact Permian shale samples of varying mineral composition. The samples were collected from two different wells drilled in the Utica and Permian shales. The ternary diagram (Figure 3.1a) shows the mineral composition of all the Utica shale samples that were collected across the horizontal lateral. The plot indicates that the shale mineral composition varied with depth. At the top of the formation, the shale was clay and quartz-rich and at the bottom, the shale was calcite-rich. Four sample sets containing both horizontally-oriented samples and vertically-oriented samples were received. The mineral composition of the received samples varied widely as shown in Figure 3.1b.

Figure 3.2a shows the mineral composition for all the samples collected from the Permian well. Similar to the Utica samples, the plot indicates that the shale mineral composition varied with depth. Five vertically oriented samples were received. The mineral composition of the received samples is shown in Figure 3.2b.
3.2. SAMPLE DESCRIPTIONS

Figure 3.2: Ternary plot representations of the shale mineral compositions of the Permian samples. The ternary plot on the left is for all the samples. Colors represent depth of sample retrieval, dark blue represents the top of the formation and red represents the bottom. The plot indicates that the shale mineral composition varies significantly. The ternary plot on the right is for the five received samples for permeability measurements.

Table 3.1 lists the results of vitrinite reflectance, TOC and X-Ray Diffraction (XRD) analyses for the Utica samples. The analyses were not conducted on the actual received samples, but were obtained from other analyzed samples 1 to 3-ft deeper or shallower than the actual received samples. The received samples were organic-rich (1.7-3.3 wt% TOC). Their thermal maturity ranged between 0.99 and 1.18% $R_o$. The clay content varied from 11 wt% at the bottom of the formation (sample U4) and 49 wt% at the top of the formation (sample U1). Illite was the predominant clay mineral (7-34 wt%). The carbonate content ranged between 12 and 80 wt% with calcite as the predominant carbonate mineral (7-78 wt%). The quartz content ranged between 7 and 28 wt%. Feldspars ranged between 0 and 3 wt%. Finally, the pyrite content was consistent across the received samples at 1 wt%.

Table 3.2 lists the results of vitrinite reflectance, TOC and X-Ray Diffraction (XRD) analyses for the Permian samples. Similar to the Utica samples, the analyses were not conducted on the actual received samples, but were obtained from other analyzed samples 1 to 3-ft deeper or shallower than the actual received samples.
CHAPTER 3. PERMEABILITY OF LIQUID-RICH SHALES

Table 3.1: Summary of vitrinite reflectance (% $R_o$), TOC (wt%) and XRD analysis (wt% without TOC) for the Utica samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth ft</th>
<th>$R_o$</th>
<th>TOC</th>
<th>Clays</th>
<th>Carbonates</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>6281.2</td>
<td>0.99</td>
<td>2.4</td>
<td>49</td>
<td>12</td>
<td>28</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>U2</td>
<td>6444.2</td>
<td>1.02</td>
<td>1.7</td>
<td>41</td>
<td>26</td>
<td>26</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>U3</td>
<td>6491.0</td>
<td>1.07</td>
<td>3.3</td>
<td>20</td>
<td>55</td>
<td>19</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>U4</td>
<td>6529.0</td>
<td>1.18</td>
<td>2.1</td>
<td>11</td>
<td>80</td>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.2: Summary of vitrinite reflectance (% $R_o$), TOC (wt%) and XRD analysis (wt% without TOC) for the Permian samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth ft</th>
<th>$R_o$</th>
<th>TOC</th>
<th>Clays</th>
<th>Carbonates</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>9910.3</td>
<td>1.16</td>
<td>5.9</td>
<td>27.0</td>
<td>27.8</td>
<td>35.4</td>
<td>6.5</td>
<td>3.3</td>
</tr>
<tr>
<td>P2</td>
<td>10134.3</td>
<td>0.89</td>
<td>1.0</td>
<td>5.5</td>
<td>68.8</td>
<td>17.5</td>
<td>7.2</td>
<td>1.0</td>
</tr>
<tr>
<td>P3</td>
<td>10233.8</td>
<td>1.28</td>
<td>4.2</td>
<td>31.6</td>
<td>13.1</td>
<td>39.1</td>
<td>13.7</td>
<td>2.5</td>
</tr>
<tr>
<td>P4</td>
<td>10354.5</td>
<td>-</td>
<td>0.8</td>
<td>53.0</td>
<td>7.9</td>
<td>25.3</td>
<td>11.1</td>
<td>2.7</td>
</tr>
<tr>
<td>P5</td>
<td>10364.4</td>
<td>-</td>
<td>0.8</td>
<td>41.8</td>
<td>8.9</td>
<td>35.2</td>
<td>12.5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The received samples were organic-rich (0.8-5.9 wt% TOC). Their thermal maturity ranged between 0.89 and 1.28% $R_o$. The clay content varied from 5.5 wt% at the top of the formation (sample P2) and 53 wt% at the bottom of the formation (sample P4). The clay types were illite (2.7-21.9 wt%), mixed layer smectite/illite (2.8-19.2 wt%) and chlorite (0-15.3 wt%). The carbonate content ranged between 7.9 and 68.8 wt%. The carbonate was calcite (3.8-24.2 wt%) and dolomite (2.6-44.6 wt%). The quartz content ranged between 17.5 and 39.1 wt%. Feldspars ranged between 6.5 and 13.7 wt%. Finally, pyrite content was low, ranging between 1.0 and 3.3 wt%.

3.3 Experimental Apparatus

Permeability experiments were conducted in a hydrostatic pressure vessel. A photo of the hydrostatic permeability system is shown in Figure 3.3. The three main components of the system were the pressure vessel that holds the core, the pore pressure controller, and the confining pressure controller. The pressure vessel was a Temco HCH biaxial hydrostatic core-holder. The pore pressure was controlled by a Quizix QX1500 pump, which was connected to the gas cylinder and which includes two
independently controlled motor-driven pistons. One piston was connected to the up-
stream side of the core-holder and the other piston was connected to the downstream
side. The pump can operate in different operating modes including constant pressure
or constant flow rate. The pressures and flow rates were measured by the Quizix
system at an accuracy of ±0.01% and ±0.1%, respectively. The confining pressure
was controlled using an Isco pump. A Heise DXD pressure transducer was used to
measure the confining pressure at an accuracy of ±0.1%.

![Diagram of experimental apparatus]

Figure 3.3: The hydrostatic permeability system inside the thermal isolation chamber.

All experiments were conducted at a temperature of 38°C with only ±0.1°C tem-
perature fluctuation over testing periods lasting several months. Temperature stabil-
ity was achieved by enclosing the hydrostatic permeability system within a thermal
isolation chamber and installing a heat control system. The heat control system con-
sisted of a heat generator and a fan. The heat generator turned on and off within
the intended temperature window using a feedback algorithm implemented via Lab-
View. The fan was always kept on during the experiment to circulate the air and
keep temperature constant in the thermal isolation chamber.
3.4 Methodology

Permeability measurements for each sample were conducted at different pore pressures and confining pressures. Figure 3.4 illustrates the permeability measurement program with argon and CO$_2$. The program contains several loading and unloading cycles. During a single loading and unloading cycle, the pore pressure was maintained constant and the confining pressure was increased step-wise to the maximum effective stress and then decreased step-wise. At each step, a single permeability measurement was conducted using the pressure-pulse decay technique.

As shown in Figure 3.4, the sequence of a set of permeability experiments consisted primarily of several argon cycles followed by a CO$_2$ cycle that was followed by a single argon cycle. Before introducing a new pore fluid, the system including the sample were vacuumed overnight. Then, the pore fluid was injected at the target pore pressure and the sample was left to saturate for 24 hours prior to the argon cycle or 48 hours prior to the CO$_2$ cycle. The purpose of the argon cycles was to study Klinkenberg effects and to investigate stress-dependent permeability. The permeability during one of the cyclic loadings with argon was also used as a reference point to compare with the CO$_2$ permeability obtained from the CO$_2$ cycle. The purpose of the CO$_2$ cycle was to investigate the effect of CO$_2$ adsorption on permeability. The last argon cycle was included in the testing program to investigate permeability recoverability. This chapter will focus on discussing the initial argon cycles (pre-CO$_2$). CO$_2$ permeability analysis will be discussed in the following chapter.

3.4.1 Pressure-pulse decay technique

In the pressure-pulse decay technique, a pressure step was introduced at the upstream side, while the pressure response on the downstream side was measured. Pressure transducers in each cylinder of the Quizix pump were used to measure the pressure in the upstream and downstream reservoirs. To generate the upstream pressure step, the equilibrium pore pressure was increased by nearly 10%.

The model by Brace et al. (1968); described briefly in the previous chapter, was used to estimate the permeability of the shale samples. First, the natural logarithm
3.4. METHODOLOGY

Figure 3.4: Pore pressures and confining pressures during cycles of permeability measurements with Argon and CO\textsubscript{2} for the Utica and Permian samples. Ar Pp and Ar Pc are the pore pressure and confining pressure, respectively, during permeability measurements with argon. CO\textsubscript{2} Pp and CO\textsubscript{2} Pc are pore pressure and confining pressure, respectively, during permeability measurements with CO\textsubscript{2}.

of the difference between the upstream and the downstream pressure was plotted as a function of time. The pressure difference follows an exponential decay:

\[ \Delta p(t) = \Delta p_o e^{-\alpha t} \]  

(3.1)

where \( \Delta p(t) \) is the difference between the upstream pressure and the downstream pressure at time \( t \), \( \Delta p_o \) is the difference in pressure at time \( t = 0 \), \( t \) is time and \( \alpha \) is the decay exponent. Then, the slope of the linear trend between the logarithm of pressure difference and time (i.e. the decay exponent, \( \alpha \)) was used to compute permeability using the following equation:

\[ \alpha = \frac{kA}{\mu \beta L \left( \frac{1}{V_{up}} + \frac{1}{V_{down}} \right)} \]  

(3.2)

where \( k \) is the sample permeability, \( A \) is the sample cross-sectional area, \( \mu \) is the gas
viscosity at the given temperature and pressure conditions, $\beta$ is the gas compressibility, $L$ is the length of the sample, $V_{up}$ is the upstream volume and $V_{down}$ is the downstream volume. An example of an upstream pressure pulse generated to measure the permeability of a shale sample at 300 psi pore pressure is shown in Figure 3.5. The generated upstream pressure pulse was maintained constant creating an infinite upstream reservoir volume. Therefore, Equation 3.2 can be reduced to:

$$\alpha = \frac{kA}{\mu \beta LV_{down}}$$

(3.3)

Figure 3.5: An example of a pressure pulse generated to measure the permeability at 300 psi pore pressure.

### 3.4.2 Klinkenberg analysis

Klinkenberg (1941) discovered that slip flow occurs when the pore diameter of a porous medium approaches the mean free path of the flowing gas molecules. This results in an increase in the frequency of collisions between the gas molecules and the rock walls, leading to an additional flux at the wall surface that enhances the flow rate. This phenomena is called the Klinkenberg effect and it is expressed as follows:
3.4. METHODOLOGY

\[ k_{\text{gas}} = k_{\infty}(1 + \frac{b_{\text{slip}}}{p}) \]  

(3.4)

where \( k_g \) is the gas or apparent permeability, \( k_{\infty} \) is the intrinsic or Klinkenberg-corrected permeability, \( b_{\text{slip}} \) is the Klinkenberg slip factor and \( p \) is the pore pressure during the permeability experiment. A plot of measured gas permeability as a function of reciprocal mean pore pressure should reveal a straight line that can be analyzed to calculate the Klinkenberg-corrected permeability and the Klinkenberg slip factor. The Klinkenberg-corrected permeability is calculated from the y-intercept and the Klinkenberg slip factor is calculated from the slope of the straight line. The following expression by Klinkenberg (1941) relates the Klinkenberg slip factor \( b_{\text{slip}} \) to the mean free path \( \lambda \) and the pore radius \( r \):

\[ b_{\text{slip}} = \frac{4pc\lambda}{r} \]  

(3.5)

where \( c \) is a proportionality factor \( (c = 1) \). The mean free path is defined as the average distance a molecule travels before it collides with another molecule. Mathematically, the mean free path is defined as (Heidemann et al., 1984):

\[ \lambda = \frac{k_B T}{\sqrt{2\pi\delta^2p}} \]  

(3.6)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \delta \) is the collision diameter of the gas molecule and \( p \) is the pressure. In the simplest version of the kinetic theory of gases, molecules that make binary collisions only can be treated as hard spheres of diameter \( d \). In this case, \( \delta \) in the mean free path formula (Equation 3.6) can just be replaced with the molecular diameter \( d \). Equation 3.6 can then be rewritten as:

\[ \lambda = \frac{k_B T}{\sqrt{2\pi d^2p}} \]  

(3.7)
By combining Equation 3.5 and Equation 3.7, a mean pore throat radius can be calculated from the Klinkenberg plot using the following expression:

\[ r = \frac{4 k_B T}{b_{slip} \sqrt{2\pi d^2}} \]  

(3.8)

3.4.3 Stress-dependent permeability

Porous media deform under stress causing the permeability to change. Thus, permeability is a function of effective stress. Many researchers have reported that shale permeability decreases with increasing effective stress (Ghanizadeh et al., 2013, 2014a,b; Heller et al., 2014; Gensterblum et al., 2015). In this work, the stress-dependent permeability was determined by measuring the permeability of the samples over a range of effective stresses. The stress dependence of permeability can be described according to the following exponential function (Pathi, 2008; Chalmers et al., 2012b; Gensterblum et al., 2014, 2015):

\[ k_\infty = k_o e^{-c_m \sigma_{eff}} \]  

(3.9)

where \( k_\infty \) is the Klinkenberg-corrected permeability, \( k_o \) is the permeability at zero effective stress, \( c_m \) is the slope of the line and is a measure of pore throat compressibility and \( \sigma_{eff} \) is the effective stress. The effective stress \( (\sigma_{eff}) \) is the simple effective stress and it is defined as the difference between confining pressure and pore pressure:

\[ \sigma_{eff} = p_{conf} - p_p \]  

(3.10)

3.5 Results and Data Processing

As shown previously on the testing program (Figure 3.4), the characterization of the samples consisted of a number of cyclic loadings of permeability measurements. Each step in the loading phase and unloading phase represents a single permeability
3.5. RESULTS AND DATA PROCESSING

measurement by the pressure pulse decay technique. Figure 3.6 shows the apparent argon permeability (bedding-parallel) as a function of effective stress for the Utica samples U1, U2, U3 and U4. The plots indicate that as the effective stress increases, the apparent permeability decreases due to pore compaction. Additionally, the plots indicate that as the pore pressure decreases, the apparent permeability increases due to slippage effects. The highest apparent argon permeability (2.05 $\mu d$) was observed for U3 at 200 psi (1.38 MPa) pore pressure and 500 psi (3.45 MPa) effective stress. The lowest apparent argon permeability (0.036 $\mu d$) was observed for Sample U2 at 900 psi (6.21 MPa) pore pressure and 2000 psi (20.7 MPa) effective stress.

Argon permeability measurements were conducted on samples P2 and P4 from the Permian samples. The permeability measurement for sample P1 was aborted because its permeability was too low causing the testing program duration to be too long (weeks). Sample P3 was preserved for future tests. Sample P5 was severely broken. Consequently, a plug could not be prepared for permeability measurements.

Figure 3.7 shows the apparent argon permeability (bedding-perpendicular) as a function of effective stress for Permian samples P2 and P4. The permeability behavior was similar to the apparent permeability behavior observed for the Utica samples. Pore compaction at higher effective stresses caused the apparent permeability to decrease and slip effects at low pore pressures caused the apparent permeability to enhance. In addition, the apparent permeability of sample P2 was higher than the apparent permeability of sample P4. The highest apparent permeability measured for samples P2 and P4 at 200 psi (1.38 MPa) pore pressure and 500 psi (3.45 MPa) effective stress were 6.24 $\mu d$ and 1.34 $\mu d$, respectively.

Klinkenberg analyses were carried out for the Utica and Permian samples. The apparent argon permeability was plotted as a function of reciprocal mean pore pressure for the six samples (Figure 3.8). For each sample, the permeability versus reciprocal mean pore pressure plot was generated for different effective stresses. Slippage effects are clearly observed for all the samples. As the pore pressure decreases ($1/p_{\text{mean}}$ increases on the Klinkenberg plot), the apparent permeability is enhanced. The plotted data were fitted linearly with a straight line. The slope and y-intercept of the best-fit straight lines are shown on Table 3.3. From Equation 3.4, the slope and y-intercept
FIGURE 3.6: Apparent argon permeability as a function of effective stress for the bedding-parallel Utica samples. The legend indicates the pore pressures at which the permeability measurements were conducted.

can be defined as:

\[ \text{slope} = k_\infty b_{\text{slip}} \]  \hspace{1cm} (3.11)

\[ y_{\text{intercept}} = k_\infty \]  \hspace{1cm} (3.12)

3.6 Discussion

Two parameters were obtained from the Klinkenberg plots: the Klinkenberg slip factor \(b_{\text{slip}}\) and the Klinkenberg-corrected permeability \(k_\infty\). The Klinkenberg parameters for the Utica and Permian samples are tabulated in Table 3.3. The Klinkenberg parameters were used to investigate the effect of shale mineralogy on permeability,
### Table 3.3: Data obtained from the Klinkenberg analysis plots for all samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{eff}$, psi</th>
<th>Slope, $\mu d$.psi</th>
<th>y-Intercept, $\mu d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>118.4</td>
<td>0.706</td>
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<td>1500</td>
<td>61.6</td>
<td>0.306</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>54.2</td>
<td>0.183</td>
<td></td>
</tr>
<tr>
<td>U2</td>
<td></td>
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<tr>
<td>500</td>
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<tr>
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<tr>
<td>2000</td>
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<td>3000</td>
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<td>0.257</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>31.5</td>
<td>0.247</td>
<td></td>
</tr>
<tr>
<td>U4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>11.7</td>
<td>0.126</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>10.7</td>
<td>0.094</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>9.8</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>9.0</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>315.3</td>
<td>4.679</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>392.1</td>
<td>4.193</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>377.7</td>
<td>4.133</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>366.4</td>
<td>4.027</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>363.7</td>
<td>3.871</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>67.9</td>
<td>1.005</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>99.6</td>
<td>0.541</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>72.7</td>
<td>0.296</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>50.3</td>
<td>0.174</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>29.5</td>
<td>0.173</td>
<td></td>
</tr>
</tbody>
</table>
to characterize the pores of the shale samples and to evaluate the stress-dependent permeability. Additionally, scanning electron microscopy (SEM) and low-pressure gas sorption analysis were employed to aide in the pore structure characterization.

### 3.6.1 Effect of shale mineralogy on matrix permeability

The Klinkenberg-corrected permeability values obtained from the y-intercept of the Klinkenberg plots are plotted against effective stress on Figure 3.9. The results indicate that the Klinkenberg-corrected permeability of the Utica and Permian samples varied. At 500 psi effective stress, sample U3 was the most permeable Utica sample \( k_\infty = 0.937 \mu d \) and sample U2 was the least permeable \( k_\infty = 0.107 \mu d \). Sample P2 was the most permeable Permian sample \( k_\infty = 4.679 \mu d \) and sample P1 was the least permeable sample \( k_\infty = 0.0029 \mu \). Sample P1 is not shown on Figure 3.9b because only one data point of Klinkenberg-corrected permeability was obtained (at 500 psi effective stress). Figure 3.9 also shows that as the effective stress increases, the permeability of the shale samples decreases. This clearly indicates that rock deformation/compaction at higher effective stresses impacts permeability. Further discussions about the stress-dependent permeability will be presented later.

Figures 3.10a and 3.10b plot the Klinkenberg-corrected permeability at 500 psi effective stress as a function of total organic content (TOC) for the Utica and Permian samples. Figure 3.10a shows that there is a positive correlation between TOC and
3.6. DISCUSSION

Figure 3.8: Apparent permeability as a function of reciprocal mean pore pressure for the Utica and Permian samples plotted for the Klinkenberg analysis. The legend indicates the effective stress at which the permeability measurements were conducted.
Figure 3.9: Klinkenberg-corrected permeability as a function of effective stress for the Utica and Permian samples.
permeability. However, this relationship between TOC and permeability was not observed in the measurements of the Permian samples. Although sample P1 had the highest TOC (5.9 wt%), it showed the lowest permeability. Previous studies by Loucks et al. (2009), Curtis et al. (2010), Sondergeld et al. (2010) and Sone and Zoback (2013a) have shown that pore volume resides in the solid organics. Therefore, samples with higher TOC are expected to have higher porosity which may lead to higher permeability. However, as observed with the Permian samples, the higher permeability with higher TOC is not always guaranteed because permeability is also a function of how well the pores in the kerogen are connected.

Figures 3.10c and 3.10d plot the Klinkenberg-corrected permeability at 500 psi effective stress as a function of clay content for the Utica and Permian samples. Based on both plots, there is no clear relationship between clay content or mineralogy and permeability. Therefore, shale mineral composition did not have an impact on the magnitude of the Klinkenberg-corrected permeability of the studied Utica and Permian samples.

### 3.6.2 Pore shape

Using the Klinkenberg analysis results of the argon permeability measurements of the Utica and Permian samples, the logarithm of Klinkenberg $b_{slip}$ factor was plotted as a function of the Klinkenberg-corrected permeability $k_\infty$ as shown in Figure 3.11. This method was introduced by Heid et al. (1950) to study sandstone samples.

The best-fit straight line for the $b_{slip}$ versus $k_\infty$ dataset from Heid et al. (1950) had the following equation:

$$
    b_{slip} = 0.777 k_\infty^{-0.39}
$$

(3.13)

where $b_{slip}$ and $k_\infty$ are in atm and md; respectively. According to Heid et al. (1950), for ideal cases consisting of a parallel capillary bundle, the exponent would be -0.5 because in the parallel capillary bundle case, $b_{slip}$ should inversely vary with the square root of permeability. The -0.39 slope was considered to be corresponding to
Figure 3.10: The effect of TOC and clay content on Klinkenberg-corrected permeability of the Utica and Permian samples.
the ideal case. Jones and Owens (1980) conducted permeability experiments on tight gas sands and produced the following best-fit straight line relation:

\[ b_{slip} = 0.86k_\infty^{-0.33} \]  \hspace{1cm} (3.14)

where \( b_{slip} \) and \( k_\infty \) are in atm and md; respectively. According to Jones and Owens (1980), the -0.33 slope is related to Lamb’s expression (Lamb, 1932; Jones, 1975); a cube root relation for flow through narrow ducts. Therefore, Equation 3.14 suggests that flow in the tight gas sands was controlled by slit-like apertures rather than round pores. This procedure was also followed by Davies and Davies (2001) to study cemented sandstone samples. They observed that as rock type changed, so did the Klinkenberg slip factor.

The extrapolation of the best-fit straight lines from Heid et al. (1950) and Jones and Owens (1980) (Equations 3.13 and 3.14) are plotted on Figure 3.11. As shown in the figure, the Utica and Permian shales measurements are scattered closely around the extrapolation lines but each sample appears to have its own trend. Figure 3.12 shows the best-fit straight lines for only the clay-rich samples (samples that contained
CHAPTER 3. PERMEABILITY OF LIQUID-RICH SHALES

clay content higher than 40 wt%).

\[ y = 116.8x - 0.407 \]
\[ R^2 = 0.7446 \]

Figure 3.12: Klinkenberg \( b_{\text{slip}} \) factor as a function of Klinkenberg-corrected permeability \( k_\infty \) for the clay-rich samples U1, U2 and P4.

The best-fit straight line for the clay-rich samples is:

\[ b_{\text{slip}} = 116.8k_\infty^{-0.407} \] (3.15)

where \( b_{\text{slip}} \) and \( k_\infty \) are in psi and \( \mu d \), respectively. The -0.407 slope indicate that the shape of the pores that provide the flow conduits in the clay-rich samples is pore system is similar to flow through a bundle of tubes (circular).

Figures 3.13 and 3.14 show scanning electron microscopy (SEM) images from the clay-rich Utica and Permian shale samples; respectively. The SEM images suggests that the dominant conduits to fluid flow in the Utica samples are pores within the kerogen (Figure 3.13). Pores were also observed within the clay material. This observation explains the positive correlation between the Klinkenberg-corrected permeability and TOC shown on Figure 3.10a. In the Permian samples, the SEM images indicate that the dominant conduits to flow are interconnected pores between the grain particles. In both samples, the size of the pores was between 100 and 200 nm.
3.6. **DISCUSSION**

Figure 3.13: SEM images obtained from the Utica shale samples. As seen on the images, the pores are mainly developed within the kerogen with some pores found within the clay.
Figure 3.14: SEM images obtained from the Permian shale samples. As seen on the images, the dominant conduits to flow are mainly interconnected pores between the grain particles.
3.6.3 Pore size

Equation 3.5 was applied to estimate the mean pore radius of a porous medium assuming the porous medium contains a number of capillary tubes. Equation 3.5 was then applied to calculate the mean pore radius for the Permian and Utica samples at different effective stresses. Argon molecule diameter \((d)\) used in the calculation was 0.358 nm. Figure 3.15 plots the mean pore radius for the Permian samples as a function of effective stress. Pore compaction at increasing effective stress caused the mean pore radius to decrease as observed on the plot. Overall, the mean pore size of the Permian samples was in the order of 10s of nanometers.

The plot also suggests that the reduction in the mean pore radius varied between the two Permian samples. At 3,000 psi effective stress, the mean pore radius of sample P2 decreased by approximately 25%, whereas the mean pore radius of sample P4 decreased by nearly 75%. Compared to sample P2, sample P4 contained more clay content (53 wt%). Sone and Zoback (2013b) investigated the mechanical properties of various shale gas reservoir rocks and observed that the creep deformation in samples with higher clay content was generally more pronounced. Therefore, higher creep deformation for sample P4 caused the pore to further compact which in turn led to significant reduction in the mean pore radius.

Figure 3.15: Mean pore radius as a function of effective stress for the Permian samples.

Figure 3.16 plots the mean pore diameter for the Utica samples as a function of effective stress. As observed on the plot, the Utica samples behaved similarly
to the Permian samples. As the effective stress increased, the mean slit-pore width decreased. The mean pore diameter was also in the order of tens of nanometers. However, the magnitude of pore size reduction with increasing effective stress for the four samples was comparable even though their mineral composition (i.e. clay content) varied significantly. This could be attributed to the orientation of the samples. Unlike the Permian samples, the Utica samples were oriented parallel to bedding (horizontal). Therefore, the confining pressure was acting in the bedding-perpendicular direction. As pointed out by Sone and Zoback (2013b), in addition to mineral composition, the direction of loading with respect to the bedding plane strongly affects creep deformation. In the Utica samples, deformation due to bedding-perpendicular loading may have masked the deformation of the soft components of the shales (clay and kerogen). This led to rather comparable pore compaction among the four samples.

![Figure 3.16: Mean slit-pore diameter as a function of effective stress for the Utica samples.](image)

Figure 3.16: Mean slit-pore diameter as a function of effective stress for the Utica samples.

Figure 3.17 shows Klinkenberg-corrected permeability as a function of mean pore throat diameter for the Utica and Permian samples. The plot indicates that there is a log-linear relationship between mean pore throat diameter and permeability for the studied samples. This is observed in the vertically-oriented samples (Permian) and horizontally-oriented samples (Utica). This relationship clearly illustrates the impact of effective stress increase on the porous media. As the effective stress increases, the porous media deform causing the size of the pores to decrease (Figures 3.15 and 3.16). As a direct consequence, the permeability of the porous media goes down. Assuming
a porous medium of a bundle of capillary tubes, a relationship between pore radius and permeability was derived by applying Darcy’s and Poiseuille’s laws as follows (Kozeny, 1927; Carmen, 1937):

\[ k_\infty = \frac{\phi r_p^2}{8\tau^2} \]  

where \( \phi \) is porosity and \( \tau \) is tortuosity. Equation 3.16 indicates that a log-log plot of permeability as a function of pore radius should have a slope of two. A line with a slope of two is drawn in Figure 3.17 and the measured data are scattered around it. It is true that in this case the mean pore throat diameter calculation was dependent on the Klinkenberg-corrected permeability (Equations 3.8 and 3.11). However, pore sizes estimated independently by the SEM at ambient conditions (Figures 3.13 and 3.14) were equivalent (100-200 nm in diameter). Therefore, the observations of Figure 3.17 is plausible and confirms that the flow conduits for the shale samples are circular.

3.6.4 Stress-dependent permeability

The Utica and Permian samples showed a nonlinear reduction in Klinkenberg-corrected permeability with increasing effective stress (Figure 3.9). The exponential relationship (Equation 3.9) describes the stress-dependent permeability well. Figure 3.18
Table 3.4: Data obtained from the best-fit lines of the stress-dependent permeability analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>(k_o), (\mu_d)</th>
<th>(c_m), (-1/\text{MPa})</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>1.1655</td>
<td>0.132</td>
</tr>
<tr>
<td>U2</td>
<td>0.1298</td>
<td>0.061</td>
</tr>
<tr>
<td>U3</td>
<td>1.0604</td>
<td>0.060</td>
</tr>
<tr>
<td>U4</td>
<td>0.1424</td>
<td>0.049</td>
</tr>
<tr>
<td>P2</td>
<td>4.578</td>
<td>0.006</td>
</tr>
<tr>
<td>P4</td>
<td>1.030</td>
<td>0.078</td>
</tr>
</tbody>
</table>

shows the Klinkenberg-corrected permeability of the Utica and Permian samples as a function of effective stress on a semilog plot.

![Semilog plot of Klinkenberg-corrected permeability as a function of effective stress for the Utica and Permian samples.](image)

Figure 3.18: Semilog plot of Klinkenberg-corrected permeability as a function of effective stress for the Utica and Permian samples. The best-fit lines are shown on the plot.

The permeability data for each well were fitted with an exponential line. The slope of the line (\(c_m\)) represents the pore throat compressibility and the y-intercept (\(k_o\)) represents the permeability at zero effective stress. Data from the best-fit lines are tabulated in Table 3.4.

Figure 3.19 plots the slope of the line (\(c_m\)) as a function of clay content. The plot indicates that there is a positive relationship between clay content and sample’s sensitivity to effective stress. As the clay content increases, the sensitivity of shale’s
3.6. DISCUSSION

permeability to variation in effective stress increases. Among the six samples, the highest sensitivity to effective stress \((0.132 \text{ MPa}^{-1})\) was observed for sample U1 which contained 49 wt\% clay. The lowest sensitivity to effective stress \((0.006 \text{ MPa}^{-1})\) was observed for sample P2 (5.5 wt\% clay) even though sample P2 showed the highest permeability measurement. According to Chalmers et al. (2012b), it is more likely to observe greater sensitivity to changes in effective stress in samples that have higher permeability coefficients. This, however, was not observed here indicating that stress-dependent permeability was greatly influenced by the rock mineralogy; particularly clay content.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{cm_vs_clay_content}
\caption{\(c_m\) as a function of clay content.}
\end{figure}

ECLIPSE 300 compositional simulator was utilized to assess the significance of including stress-dependent permeability in reservoir simulation. A single-layer, radial grid model consisting of 30 cells in the radial direction was constructed. The model included a vertical well in the center grid. the cell sizes increased logarithmically away from the wellbore (Figure 3.20). The Marcellus gas-condensate fluid model (Table 2.1) was included in the compositional simulation. Reservoir properties are tabulated in Table 3.5.

The stress-dependent permeability was captured in ECLIPSE 300 compositional simulator by including transmissibility multipliers at different pore pressures. Three cases of pore throat compressibility \((c_m)\) were simulated representing low clay content
Table 3.5: Reservoir parameters for the radial model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial reservoir pressure ($p_i$)</td>
<td>5,000 psi</td>
</tr>
<tr>
<td>Reservoir temperature ($T$)</td>
<td>140 °F</td>
</tr>
<tr>
<td>Reservoir permeability ($k$)</td>
<td>5 $\mu$d</td>
</tr>
<tr>
<td>Reservoir porosity ($\phi$)</td>
<td>10 %</td>
</tr>
<tr>
<td>Reservoir thickness ($h$)</td>
<td>200 ft</td>
</tr>
</tbody>
</table>

$c_m = 0.01/\text{MPa}$, moderate clay content ($c_m = 0.05/\text{MPa}$) and high clay content ($c_m = 0.1 \text{ MPa}$). The transmissibility multipliers for each case of $c_m$ are shown in Table 3.6.

Figure 3.21 shows the normalized cumulative gas production for ten years of continuous production at 1,000 psi well bottom-hole pressure (WBHP). The three cases of pore throat compressibility were normalized by a base case in which stress-dependent permeability was not considered (i.e. $c_m = 0$). The reservoir simulation results indicate that failing to account for stress-depending permeability resulted in overestimating the cumulative gas production during the simulated period. For example, when comparing the high clay content case ($c_m = 0.1/\text{MPa}$) with the base case ($c_m = 0$), Figure 3.21 shows that neglecting stress-dependent permeability caused the cumulative gas production to be overestimated by a factor of two.
Table 3.6: Transmissibility multipliers assumed for different pore throat compressibility factors.

<table>
<thead>
<tr>
<th>Pressure, psi</th>
<th>$c_m = 0.01/\text{MPa}$</th>
<th>$c_m = 0.05/\text{MPa}$</th>
<th>$c_m = 0.1/\text{MPa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>4,500</td>
<td>0.966</td>
<td>0.842</td>
<td>0.708</td>
</tr>
<tr>
<td>4,000</td>
<td>0.933</td>
<td>0.708</td>
<td>0.502</td>
</tr>
<tr>
<td>3,500</td>
<td>0.902</td>
<td>0.596</td>
<td>0.356</td>
</tr>
<tr>
<td>3,000</td>
<td>0.871</td>
<td>0.502</td>
<td>0.252</td>
</tr>
<tr>
<td>2,500</td>
<td>0.842</td>
<td>0.422</td>
<td>0.178</td>
</tr>
<tr>
<td>2,000</td>
<td>0.813</td>
<td>0.356</td>
<td>0.126</td>
</tr>
<tr>
<td>1,500</td>
<td>0.786</td>
<td>0.299</td>
<td>0.090</td>
</tr>
<tr>
<td>1,000</td>
<td>0.759</td>
<td>0.252</td>
<td>0.063</td>
</tr>
</tbody>
</table>

3.7 Summary

Laboratory experiments were conducted to study the effect of shale mineralogy on permeability of liquid-rich shale samples. Permeability measurements indicated that shale mineralogy did not show a clear effect on the magnitude of permeability. High permeabilities were observed for both clay-rich and calcite-rich samples. Permeability measurements also showed that there was a positive correlation between permeability and TOC in the horizontal Utica samples. SEM images obtained for Utica samples confirmed that pore resided primarily in the kerogen. SEM images obtained for the Permian samples showed that their flow conduits were interconnected pores between grain particles. The size of the pores in the Utica and the Permian samples were in the order of tens of nanometers. Stress-dependent permeability analysis showed that the sensitivity of shale permeability to variations in effective stress is influenced by rock mineralogy. As the clay content increases, shale permeability becomes more sensitive to effective stress (higher pore throat compressibility). In shale reservoirs, effective stress measured as the difference between overburden stress and pore pressure increases with hydrocarbon production. Therefore, to achieve more accurate reservoir simulations and production forecasting, stress-dependent permeability should be considered especially for clay-rich shale reservoirs.
Figure 3.21: Normalized cumulative gas production at 1,000 psi well bottom-hole pressure (WBHP).
Chapter 4

CO\textsubscript{2} Adsorption in Shale

4.1 Introduction

Unconventional reservoirs, such as shale formations, are known to hold abundant amounts of hydrocarbons. However, extremely low intrinsic permeability is a common characteristic of all unconventional shale reservoirs. Therefore, advanced technologies that enable operators to develop and produce hydrocarbons commercially from those low permeability reservoirs are necessary. Among the enabling technologies is hydraulic fracturing. During hydraulic fracturing operations, large volumes of water are commonly used. This becomes a challenge in areas where water resources are scarce. Hence, a proposed supplement for water in hydraulic fracturing of shale reservoirs is hydraulic fracturing with CO\textsubscript{2}. Among the benefits of using CO\textsubscript{2} in hydraulic fracturing is less flow-back water that needs to be treated or disposed of. In addition, shale formations are known to adsorb CO\textsubscript{2} preferentially over CH\textsubscript{4} as noted by several researchers (Kang et al., 2011; Gasparik et al., 2014; Heller and Zoback, 2014). Thus, another promising application for CO\textsubscript{2} is CO\textsubscript{2} injection for enhanced oil recovery. Understanding the transport mechanism of CO\textsubscript{2} in high organic nanoporous shale reservoirs is therefore essential. The objective of the study described in this chapter was to investigate the effect of CO\textsubscript{2} adsorption on the transport mechanisms in shale reservoirs and how the amount of CO\textsubscript{2} adsorption is affected by shale mineralogy. This work involved three different experiments: permeability measurements,
adsorption measurements and pore-size distribution (PSD) analysis. Three sample sets were used in the experiments: Utica samples, Permian samples and Eagle Ford samples.

### 4.2 Sample Description

The descriptions of the Utica and Permian samples have already been presented in the previous chapter (Figures 3.1 and 3.2). The Eagle Ford sample set contained two samples: a vertical sample (EF-V) and a horizontal sample (EF-H). Figure 4.1 shows the ternary diagram of the mineral compositions of the two samples. Both samples were composed predominantly of carbonate (70-85 wt%) which is typical for the Eagle Ford shale. The clay content for both samples was 8.2-10.5 wt% and the TOC content was approximately 2 wt%. The quartz concentration varied between 4 wt% for EF-V and 13 wt% for EF-H. The amount of feldspar and pyrite in both samples were minor.

![Ternary diagram showing the mineral composition of the two Eagle Ford samples (vertical and horizontal)](image)

Figure 4.1: Ternary diagram showing the mineral composition of the two Eagle Ford samples (vertical and horizontal)

The permeability experiments were conducted on intact samples. On the other hand, the adsorption experiments and PSD measurements were conducted on crushed
samples. Crushed samples were preferred over intact samples for adsorption experiments because the time required for intact samples to reach equilibrium would be prohibitively long (Heller and Zoback, 2014). For each adsorption experiment, approximately 30 g of sample was used. The crushed samples had a particle size between 50 and 250 microns. After crushing, the samples were dried inside a vacuum oven at 40°C. At near vacuum conditions, 40°C is above the boiling point of water.

4.3 Experimental Apparatus

Three different apparatuses were used in this study. The permeability measurements were conducted in the hydrostatic pressure vessel described in the previous chapter (Figure 3.3). The adsorption experiments were conducted using a fixed-volume adsorption apparatus (Heller and Zoback, 2014) and the PSD analysis was performed using low-pressure sorption in a Quantachrome Autosorb iQ (Quantachrome, 2014).

4.3.1 Adsorption apparatus

Figure 4.2 shows the apparatus for the fixed-volume adsorption experiment. The apparatus consisted of four main components: a reference cell, a sample cell, a pressure transducer and a temperature bath. The reference cell was connected to the gas cylinder. The crushed sample was loaded into the sample cell. To accommodate varying sampling sizes, the volume of the sample cell was adjusted using aluminum spacers. The reference cell and the sample cell were separated by a valve. The gas pressure inside the reference cell and the sample cell was monitored using Heise pressure transducers with ±0.02% accuracy. The temperature of the system was controlled using a temperature bath. The reference cell, the sample cell and the tubings connecting them were all submerged into the oil bath. The temperature of the oil bath was set using a temperature controller.
4.3.2 Low-pressure sorption apparatus

The PSD measurements were carried out using a low-pressure sorption in the Quantachrome Autosorb iQ. Similar to the adsorption experiments, the samples used in the analysis were crushed samples. The Quantachrome Autosorb iQ contained two stations: a degassing station and an analysis station.

First, approximately 100 mg of crushed sample was loaded into a glass cell. Then, the glass cell was installed in the degassing station. At the degassing station, the sample was vacuumed for four hours. A heating jacket was used to maintain the temperature at 50°C during the vacuuming process. After degassing the samples, the glass cell was transferred to the analysis station. The analysis station contained a dewar bottle of liquid nitrogen at -196.15°C. The liquid nitrogen is used to ensure the vapor pressure of the probe gas is 1 atm. At the analysis station, an adsorption isotherm was generated by injecting the probe gas (in this case it was N₂) at preprogrammed pressure steps to a relative pressure, \( p/p_0 = 1 \). Then, a desorption isotherm was generated by decreasing the pressure from \( p/p_0 = 1 \) at preprogrammed pressure steps. The adsorption and desorption isotherms were then used to generate the pore size distribution (PSD). As recommended by Quantachrome (2014), the desorption
branch of the isotherm is more appropriate to evaluate the PSD because the desorption branch exhibits a lower relative pressure, resulting in a lower free energy state. Therefore, the desorption branch is closer to the true thermodynamic equilibrium.

4.4 Methodology

4.4.1 Permeability measurements

CO$_2$ permeability measurements were conducted on the Utica samples and the Eagle Ford samples using the pressure-pulse decay technique described in the previous chapter. The CO$_2$ permeability of the Permian samples was not measured. The testing program for the Utica samples is shown in Figure 3.4. As discussed in the previous chapter, the testing program for the Utica sample involved measuring the permeability in multiple cycles: first with Argon in five cycles, then a single cycle with CO$_2$, and finally a single cycle with argon. For this chapter, the permeability from the CO$_2$ cycle was estimated and compared with pre- and post-CO$_2$ argon cycles as shown in Figure 4.3a. The pore pressure during the CO$_2$ permeability measurement was determined based on mean free path calculations. The aim was to achieve similar mean free path for argon and CO$_2$.

The testing program for the Eagle Ford samples was slightly different than the testing program for the Utica samples but both shared a similar objective; determining the effect of CO$_2$ adsorption on permeability. Figure 4.3b illustrates the testing program for the Eagle Ford samples. Helium gas was used instead of argon as the nonadsorptive gas. Klinkenberg analysis was not included in the testing program. The pore pressures for helium and CO$_2$ achieved the same mean free path.

4.4.2 Mean free path

A discussion about the mean free path definition and formulation was presented in the previous chapter (Equation 3.7). The molecular diameters ($d$) for argon, helium and CO$_2$ used in Equation 3.7 were obtained from the CRC Handbook of Chemistry
Figure 4.3: (a) Pore pressures and confining pressures during cycles of permeability measurements with argon and CO$_2$ for the Utica samples. The data obtained for the first two cycles of permeability measurements (gray) were not included in the investigation of the impact of CO$_2$ adsorption on permeability. (b) Pore pressures and confining pressures during cycles of permeability measurements with helium and CO$_2$ for the Eagle Ford samples.
Table 4.1: Molecular diameters obtained from Haynes (2014)

<table>
<thead>
<tr>
<th>Gas</th>
<th>d, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.358</td>
</tr>
<tr>
<td>He</td>
<td>0.215</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.453</td>
</tr>
</tbody>
</table>

and Physics (Haynes, 2014) as shown on Table 4.1. Figure 4.4 plots the calculated mean free path as a function of pressure for the three gases.

Table 4.2 shows the estimated mean free path for CO$_2$ during the CO$_2$ permeability measurements, as well as for the pre- and post-CO$_2$ permeability measurements with argon (Utica samples) and helium (Eagle Ford samples). As shown on the table, the estimated mean free path for the three gases was comparable. Therefore, any deviation of CO$_2$ permeability from argon or helium permeability was solely due to the adsorptive nature of CO$_2$. In one case with a Utica sample (sample U1), the pre- and post-CO$_2$ permeability cycles with argon were conducted at 700 psi pore pressures. Accordingly, the pore pressure during the CO$_2$ permeability cycle was increased to 437 psi. This resulted in a mean free path of approximately 1.575 nm for both gases.

![Figure 4.4: The mean free path for argon, helium and CO$_2$ as a function of pressure.](image-url)
Table 4.2: The calculated mean free path (MFP) for different gases and pore pressures.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Pore pressure, psi</th>
<th>MFP, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar (pre-CO$_2$)</td>
<td>600</td>
<td>1.837</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>375</td>
<td>1.836</td>
</tr>
<tr>
<td>Ar (post-CO$_2$)</td>
<td>600</td>
<td>1.837</td>
</tr>
<tr>
<td>Eagle Ford</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He (pre-CO$_2$)</td>
<td>2000</td>
<td>1.764</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>377</td>
<td>1.826</td>
</tr>
<tr>
<td>He (post-CO$_2$)</td>
<td>2000</td>
<td>1.764</td>
</tr>
</tbody>
</table>

4.4.3 Adsorption isotherms

CO$_2$ adsorption measurements were performed on the Utica and Permian samples. For each sample, the uptake of gas was measured by successively transferring the sorptive gas from the reference cell to the sample cell and monitoring the drop in pressure at each gas transfer step. Figure 4.5 shows the raw pressure data of a CO$_2$ adsorption measurement. CO$_2$ was transferred successively from the reference cell to the sample cell. At each step, additional gas was charged into the reference cell as indicated by the pressure increase. Then, the valve separating the reference cell and the sample cell was opened to allow the gas to transfer to the sample cell as indicated by the pressure drop. At pressure equilibrium, the valve between the sample cell and reference cell was closed. Then, additional gas was charged into the reference cell to increase its pressure to a value higher than the pressure of the previous step and the above process was repeated.

The pressure drop that occurred whenever the valve separating the reference cell and the sample cell was opened was not only due to gas expansion into the sample cell but also due to adsorption. Basically, the adsorbed molecules do not contribute to the gas phase pressure because the adsorbed molecules are bound and therefore have no kinetic energy (Heller and Zoback, 2014). The amount of excess adsorption can be calculated using the following equation:

\[ n_{\text{excess}}^{\text{ads}} = n_{\text{total}} - n_{\text{free}} \]
where $n_{total}$ is the total number of moles originally in the system before the valve is opened and gas is allowed to expand to the sample cell and $n_{free}$ is the number of moles in the free phase after gas expansion. With no gas adsorption, $n_{free}$ should be equivalent to $n_{free}$ resulting in zero excess adsorption. However, gas adsorption causes $n_{free}$ to be lower than $n_{total}$ and the difference between $n_{total}$ and $n_{free}$ is controlled by how many gas molecules are adsorbed. At the first step ($i = 1$), $n_{total}$ and $n_{free}$ can be calculated as follows:

$$n_{total} = \frac{p_1 V_R}{Z_1 R T_1} \quad (4.2)$$

$$n_{free} = \frac{p_2 (V_R + V_S)}{Z_2 R T_2} \quad (4.3)$$

where $p_1$ is the pressure at the reference cell, $V_R$ is the volume of the reference cell,
$T_1$ is the temperature before opening the valve, $Z_1$ is the compressibility factor at $p_1$ and $T_1$, $R$ is the universal gas constant, $p_2$ is the equilibrium pressure after opening the valve, $V_S$ is the volume of the sample cell, $T_2$ is the temperature after opening the valve and $Z_2$ is the compressibility factor at $p_2$ and $T_2$. In the subsequent steps ($i > 1$), $n_{\text{total}}$ should include the moles of gas in the sample cell from the previous step in addition to the total moles in the reference cell after charging it to a higher pressure. Mathematically, this can be expressed as:

$$n_{\text{total}} = \frac{p_{1,i} V_R}{Z_1 RT_1} + \frac{p_{2,i-1} V_S}{Z_2 RT_2}$$  \hspace{1cm} (4.4)$$

where $p_{1,i}$ is the pressure of the reference cell after pressurizing and $p_{2,i-1}$ is the pressure of the sample cell before opening the valve. The volume of the reference cell and the sample cell ($V_R$ and $V_S$) were determined by using a nonadsorbing gas (helium). First, the reference cell was charged with Helium to a certain pressure and the total number of moles in the reference cell was calculated using Equation 4.2. After opening the valve, the pressure drop was only due to void volume filling in the sample cell (no adsorption). The void volume of the sample cell was then calculated as follows:

$$V_S = \frac{n_{\text{total}} Z_2 RT_2}{p_2} - V_R$$  \hspace{1cm} (4.5)$$

Equation 4.1 was used to obtain the excess adsorption. To estimate the absolute adsorption, the following equation was used:

$$n_{\text{absolute}}^{\text{ads}} = \frac{n_{\text{excess}}^{\text{ads}}}{1 - \frac{\rho_{\text{gas}}}{\rho_{\text{ads}}}}$$  \hspace{1cm} (4.6)$$

where $\rho_{\text{gas}}$ is the gas phase density and $\rho_{\text{ads}}$ is the adsorbed phase density. $\rho_{\text{gas}}$ was obtained from the National Institute of Standards and Technology (Lemmon et al., 2015). $\rho_{\text{ads}}$ was estimated using the hard sphere term, $b$, in the Soave-Redlich-Kwong equation of state. The term $b$ is equivalent to the density of the adsorbed phase (Lin, 2010). Thus, $\rho_{\text{ads}}$ can be estimate as follows:
\[ \rho_{ads} = \frac{0.08664RT_c}{p_c} \]  

where \( T_c \) and \( p_c \) are the critical temperature and critical pressure, respectively.

### 4.5 Results and Data Processing

#### 4.5.1 CO\(_2\) permeability

Figure 4.6 shows the apparent helium permeability (pre-CO\(_2\) and post-CO\(_2\)) and the apparent CO\(_2\) permeability as a function of effective stress for the Eagle Ford samples. The permeability with helium was measured at 2,000 psi pore pressure and the permeability with CO\(_2\) was measured at 377 psi pore pressure. The vertical sample EF-V (Figure 4.6a) showed a permeability range of 0.014 µd to 0.010 µd in the first cycle with helium. The corresponding effective stress ranged from 1,000 psi to 4,000 psi. Hysteresis was observed in the permeability measurements because permeability rebounded to only 0.012 µd after unloading. This phenomena was an indication of permanent change to the pore structure.

In the CO\(_2\) cycle, the results show an order of magnitude reduction in permeability measurements. The permeability measurements ranged from 0.001 µd to 0.0004 µd. However, permeability was recovered when helium gas was applied again in the post-CO\(_2\) permeability cycle. The effect of permanent compaction is apparent here as the permeability measurements did not fully recover to the original values observed for the pre-CO\(_2\) cycle.

The horizontal sample EF-V (Figure 4.6b showed a permeability range of 1.31 µd to 1.13 µd in the first cycle with helium (pre-CO\(_2\)). This permeability range is two orders of magnitude higher than the permeability range of the vertical sample. In the next cycle, the CO\(_2\) permeability was slightly lower than the preceding helium permeability but it was recovered when CO\(_2\) was substituted with helium during the post-CO\(_2\) cycle. One important observation from the post-CO\(_2\) permeability measurements with helium for EF-H sample was that helium permeability during the
third cycle was higher than helium permeability during the first cycle. Another important observation was the hysteresis behavior of CO\textsubscript{2} permeability measurements. Unlike the hysteresis behavior of helium permeability measurements, CO\textsubscript{2} permeability during the unloading phase was higher than the permeability during the loading phase. Both observations will be discussed further in the next section.

Figure 4.7 shows the apparent argon permeability (pre-CO\textsubscript{2} and post-CO\textsubscript{2}) and the apparent CO\textsubscript{2} permeability as a function of effective stress for the Utica samples. The permeability with argon was measured at 600 psi pore pressure and the permeability with CO\textsubscript{2} was measured at 375 psi pore pressure except for sample U1 which was measured at 700 psi and 437 psi argon and CO\textsubscript{2} pore pressures, respectively. Figures 4.7a and 4.7c indicate that samples U1 and U3 exhibited similar behaviors of argon and CO\textsubscript{2} permeabilities. The CO\textsubscript{2} permeability measurements slightly decreased compared to the preceding argon permeability measurements. In both samples, the permeability was recovered during the post-CO\textsubscript{2} cycle with argon.

Figure 4.7b shows that the apparent permeability with CO\textsubscript{2} was an order of magnitude lower than than the apparent permeability with argon. The permeability range with argon was between 0.15 \(\mu\)d at 500 psi effective stress and 0.066 \(\mu\)d at 3,000 psi effective stress. The permeability range with CO\textsubscript{2} was between 0.011 \(\mu\)d at 500 psi effective stress and 0.0063 \(\mu\)d at 1,500 psi effective stress. The post-CO\textsubscript{2} cycle was aborted due to technical issues with the experimental apparatus.

Figure 4.7d shows that the apparent permeability with CO\textsubscript{2} was similar to the preceding measurements with argon. In the post-CO\textsubscript{2} cycle with argon, a slight permeability enhancement was observed. During all Utica samples measurements, permeability hysteresis was not observed. That is, the permeability values during the unloading phase always recovered to the original values measured during the loading phase.

### 4.5.2 CO\textsubscript{2} adsorption

Figure 4.8 shows the absolute adsorption of CO\textsubscript{2} as a function of pressure for the Utica and Permian samples. The data were fit to a Langmuir model (Langmuir, 1916). The
4.5. Results and Data Processing

Figure 4.6: Helium and CO\textsubscript{2} apparent permeability as a function of effective stress for the Eagle Ford vertical and horizontal samples.

Figure 4.7: Argon and CO\textsubscript{2} apparent permeability as a function of effective stress for the Utica samples.
Figure 4.8: CO$_2$ adsorption isotherms measured on the Utica and Permian samples.

Langmuir model is the most common model used to describe an adsorption isotherm (Heller and Zoback, 2014). The model is formulated as follows:

$$V_p = \frac{V_L p}{p_L + p} \quad (4.8)$$

where $V_p$ is the adsorbed volume at pressure $p$, $V_L$ is the Langmuir volume and $p_L$ is the Langmuir pressure. The Langmuir volume $V_L$ is the total adsorbed volume at infinite pressure and the Langmuir pressure $p_L$ is the pressure at which half the Langmuir volume is adsorbed. The Langmuir parameters used to fit the experimental data of the CO$_2$ adsorption measurements are shown on Table 4.3. The results indicate that the CO$_2$ adsorption capacity for the samples varied. The Langmuir volumes $V_L$ for the Utica samples ranged between 27.0 SCF/ton and 152.3 SCF/ton. The Permian samples showed a wider range (60.4 SCF/ton to 641.8 SCF/ton). For the most part, the fitted Langmuir volumes for the Utica and Permian samples were within the same range as the results obtained by Heller and Zoback (2014) for CO$_2$ adsorption experiments conducted on Barnett, Eagle Ford, Marcellus and Montney shales. The only exception is Permian sample P5 which exhibited an unusually high Langmuir volume at approximately 640 SCF/ton.
Table 4.3: TOC (wt%), clay content (wt%) and Langmuir isotherm parameters $p_L$ and $V_L$ used to fit the experimental data of the Utica and Permian CO$_2$ adsorption measurements.

<table>
<thead>
<tr>
<th></th>
<th>U1</th>
<th>U2</th>
<th>U3</th>
<th>U4</th>
<th>P1</th>
<th>P2</th>
<th>P5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC, wt%</td>
<td>2.4</td>
<td>1.7</td>
<td>3.3</td>
<td>2.1</td>
<td>5.9</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Clay, wt%</td>
<td>49.0</td>
<td>41.0</td>
<td>20.0</td>
<td>11.0</td>
<td>27.0</td>
<td>5.5</td>
<td>41.8</td>
</tr>
<tr>
<td>$p_L$, psi</td>
<td>795.3</td>
<td>703.2</td>
<td>1175.2</td>
<td>255.3</td>
<td>980.6</td>
<td>1040.2</td>
<td>1004.9</td>
</tr>
<tr>
<td>$V_L$, scf/ton</td>
<td>152.3</td>
<td>119.6</td>
<td>99.3</td>
<td>27.0</td>
<td>171.1</td>
<td>60.4</td>
<td>641.8</td>
</tr>
</tbody>
</table>

Table 4.4: Pore volumes and surface areas for the Utica and Permian samples as obtained from the low-sorption analysis.

<table>
<thead>
<tr>
<th></th>
<th>U1</th>
<th>U2</th>
<th>U3</th>
<th>U4</th>
<th>P1</th>
<th>P2</th>
<th>P5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume, cc/g</td>
<td>0.013</td>
<td>0.011</td>
<td>0.011</td>
<td>0.010</td>
<td>0.004</td>
<td>0.017</td>
<td>0.044</td>
</tr>
<tr>
<td>Pore surface area, m$^2$/g</td>
<td>3.279</td>
<td>3.180</td>
<td>3.042</td>
<td>2.943</td>
<td>6.113</td>
<td>1.193</td>
<td>24.271</td>
</tr>
</tbody>
</table>

4.5.3 Pore-size distribution

Pore size distribution analysis was conducted on the Utica and Permian samples used in the CO$_2$ adsorption analysis. Figure 4.9 plots the pore size distribution for both sample sets. The pore volume in cc/nm/g was plotted as a function of pore diameter in nm. The results show that the size of the pores accessed by the low pressure sorption analysis was mostly below 10 nm for both shales. Additionally, the results indicate that the pore volume in cc/nm/g varied between the samples. However, the variation among the Utica sample was narrower compared to the Permian samples as indicated by Figure 4.9a (Utica) and Figure 4.9b (Permian). The pore volume in the pore size distribution of the Permian samples varied by an order of magnitude. For example, the pore volume in Permian samples P2 and P5 were 0.004 cc/g and 0.044 cc/g; respectively. The pore volumes and surface areas obtained from low-pressure sorption analyses are shown on Table 4.4.
4.6 Discussion

4.6.1 Permeability anisotropy

The Eagle Ford samples exhibited a significant amount of permeability anisotropy as observed in the vertical and horizontal permeability measurements. Using helium gas, the permeability of the horizontal sample was two orders of magnitude higher than the permeability of the vertical sample as shown on Figure 4.10a, which plots the helium permeability as a function of effective stress during loading cycles. The results indicate that fluid transport in the vertical sample was limited to flow through connected pores, whereas fluid transport in the horizontal core was dominated by flow through microcracks along the bedding planes. Additionally, the permeability measurements suggest that the magnitude of permeability anisotropy was affected by CO$_2$ adsorption. Using CO$_2$ gas, the permeability of the horizontal sample was three orders of magnitude higher than the permeability of the vertical sample as shown in Figure 4.10b. Therefore, permeability anisotropy with CO$_2$ was higher than permeability anisotropy with helium.
4.6. DISCUSSION

4.6.2 Effect of CO₂ adsorption on permeability

Eagle Ford samples

The effect of CO₂ adsorption on permeability varied between the two Eagle Ford shale samples. The CO₂ permeability of the vertical sample was an order of magnitude lower than the helium permeability (Figure 4.11a) while the CO₂ permeability of the horizontal sample was only 20% lower than the helium permeability (Figure 4.11b). As mentioned earlier, fluid transport in the vertical sample was limited to flow through connected pores. CO₂ adsorption then led to further narrowing or even blocking of those small pores. Consequently, CO₂ permeability of the vertical sample was substantially lower than helium permeability. On the other hand, CO₂ adsorption in the horizontal sample slightly reduced the size of the dominant pathways for pore fluids. The CO₂ permeability of the horizontal sample was therefore slightly lower than the helium permeability.

Molecular sieving effects also cause permeability measurements with helium to be higher than the permeability measurements with CO₂ (Cui et al., 2009). The kinetic diameter of helium is lower than the kinetic diameter of CO₂. Therefore, the small pore throats of the fine-grained shale effectively acts as a molecular sieve yielding a lower permeability with CO₂.
Utica samples

Similar to the observations in the Eagle Ford samples, the effect of CO₂ adsorption on permeability varied between the four Utica samples. As shown on Figure 4.7, the apparent CO₂ permeability of Utica sample U2 was lower than the prior argon permeability by an order of magnitude whereas the apparent CO₂ permeability of Utica sample U4 was comparable to the prior argon permeability. In the Eagle Ford samples case, the variation in the permeability response to adsorption was attributed to the size of the fluid flow conduit and the orientation of the samples. In the Utica samples case, all the samples were horizontal. Yet the permeability response to CO₂ adsorption varied. This could be attributed to the size of the pores and the effect of mineral composition on CO₂ adsorption. The latter will be discussed later in the CO₂ adsorption analysis section.

In the results described in the previous chapter, the pore sizes for the Utica samples were estimated using the Klinkenberg analysis of argon permeability measurements. Klinkenberg analysis of CO₂ permeability measurements was also conducted by measuring the CO₂ permeability at two additional pore pressures at 500 psi effective stress. Figure 4.12 shows the apparent permeability as a function of reciprocal mean pore pressure as measured with argon and CO₂. From the Klinkenberg analysis, the Klinkenberg-corrected permeability ($k_\infty$) and the mean pore diameter ($d_p$) were estimated for the CO₂ measurements and compared with the argon measurements as
Figure 4.12: The apparent argon and CO$_2$ permeability as a function of reciprocal mean pore pressure for the Utica samples. The effective stress during all measurements was 500 psi.

The results in Table 4.5 indicate that the Klinkenberg-corrected permeability estimates obtained for the same sample using argon and CO$_2$ were different. Civan (2010) and Civan et al. (2011) argued that the Klinkenberg-corrected permeability or the intrinsic permeability does not depend on the type of fluid used for its determination because it is a property of the porous medium. However, as observed here and as reported by other researchers (Sinha et al., 2013; Ghanizadeh et al., 2014a,b; Gensterblum et al., 2014), different Klinkenberg-corrected permeability estimates were obtained for the same sample using different gases. The main reason for this discrepancy is the adsorbed layer of CO$_2$. The Klinkenberg analysis does not account for the adsorbed layer. The “stationary” adsorbed layer is therefore treated as part of the solid surface. This leads to narrower pore sizes as estimated for the Utica
samples. However, the magnitude of the pore size reduction exceeded the size of an adsorbed multilayer of CO$_2$. Specifically, the narrowing of the pore size after CO$_2$ adsorption should not exceed 1-4 nm assuming the size of a single adsorbed layer of CO$_2$ is approximately 0.453 nm (Table 4.1). This indicates clearly that there is an additional factor that influences the permeability of CO$_2$ in shale rocks and it could be sorption-induced swelling.

Sorption-induced swelling has been investigated extensively in coals (Durucan et al., 2009; Pini et al., 2009; Pan et al., 2010; Chen et al., 2011; Day et al., 2012; Gieisting et al., 2012; Adeboye and Bustin, 2013). They found that adsorption-induced coal swelling caused a significant decrease in permeability measured with CO$_2$ compared to permeability measurements with helium. Heller and Zoback (2014) investigated the volumetric swelling strain resulting from helium, methane and CO$_2$ adsorption on pure mineral samples in a triaxial compression apparatus. The samples included carbon, illite and kaolinite which are part of the main constituents of the shale. They found that helium (nonadsorbing) did not cause a swelling strain. On the other hand, they observed that methane and CO$_2$ caused swelling strain and the magnitude of the swelling strain was dependent on the volume of adsorption.

From this discussion, the hypothesis is that CO$_2$ adsorption and adsorption-induced swelling caused permeability measurements with CO$_2$ to be lower than the permeability measurements with argon. Molecular sieving also affected the permeability of the Utica samples. However, its impact was minimal. Unlike the measurements of the Eagle Ford samples where CO$_2$ permeability was compared with helium permeability, in the case of the Utica samples, CO$_2$ permeability was compared with argon permeability. The molecular diameters of argon and CO$_2$ are larger than the

Table 4.5: Klinkenberg-corrected permeability and pore diameter estimated from argon and CO$_2$ permeability measurements at 500 psi effective stress.

<table>
<thead>
<tr>
<th></th>
<th>Argon</th>
<th></th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_\infty$, $\mu d$</td>
<td>$d_p$, nm</td>
<td>$k_\infty$, $\mu d$</td>
</tr>
<tr>
<td>U1</td>
<td>0.706</td>
<td>67.3</td>
<td>0.339</td>
</tr>
<tr>
<td>U2</td>
<td>0.107</td>
<td>39.7</td>
<td>0.0027</td>
</tr>
<tr>
<td>U3</td>
<td>0.937</td>
<td>47.2</td>
<td>0.344</td>
</tr>
<tr>
<td>U4</td>
<td>0.126</td>
<td>92.7</td>
<td>0.125</td>
</tr>
</tbody>
</table>
molecular diameter of helium. Therefore, the contribution of molecular sieving in decreasing the permeability of the Utica samples when measured with CO₂ was not significant.

4.6.3 Post-CO₂ permeability measurements

The post-CO₂ permeability measurements with helium in the Eagle Ford samples and with argon in the Utica samples indicate that the impact of CO₂ adsorption on permeability was reversible. That is, when the samples were vacuumed post-CO₂ and their permeability was measured again with the nonadsorbing gas, the permeability was recovered to the pre-CO₂ levels for most of the samples as shown in Figures 4.6 and 4.7. However, two samples showed permeability enhancements above the pre-CO₂ levels. The two samples were EF-H and U4. This indicates that the injected CO₂ may have altered the samples affecting their permeabilities.

Mito et al. (2008), Wigand et al. (2008), Kummerow and Spangenberg (2011) and Huq et al. (2012) have investigated the effects of injecting CO₂ into deep saline aquifers or depleted sandstone reservoirs using geochemical techniques. With the presence of pore-waters, CO₂ has been found to be reactive with the rock minerals leading to significant dissolution of calcite and dolomites. Using laboratory experiments, modeling and field monitoring, Czernichowski-Lauriol et al. (2006) observed dissolution reactions close to the CO₂ injection zone in carbonate reservoirs leading to increased porosity. Therefore, the increase in permeability post-CO₂ injection is attributed to possible calcite dissolution. The samples were tested in “as-received” conditions. Hence, bound water may have assisted in the dissolution reactions. One factor that supports this explanation is the dominant mineral composition. Both samples were carbonate-rich. The carbonate content of samples EF-H and U4 were 70 wt% and 80 wt%; respectively.

4.6.4 CO₂ adsorption analysis

The Langmuir parameters obtained from the adsorption experiments of the Utica and Permian samples are shown in Table 4.4. Figure 4.13a shows the Langmuir volume
as a function of clay content for the Utica and Permian samples. Permian sample P5 showed a significantly high Langmuir volume. If it is excluded from the plot, a positive relationship is observed between Langmuir volume and clay content for the Utica and Permian samples as shown in Figure 4.13b.

Unlike the clay content, the organic content (TOC) did not show a clear correlation with Langmuir volume as shown in Figure 4.14a. Permian sample P5 had the lowest TOC, yet it showed the highest Langmuir volume. As for the other Utica and Permian samples (Figure 4.14b), the TOC was on the low end and a clear relationship between Langmuir volume and TOC could not be observed. This does not mean TOC is not contributing to adsorption. Because TOC was low and its variation was narrow for all the samples, a relationship could not be established. Additionally, a relationship could not be established between Langmuir volume and vitrinite reflectance as shown on Figure 4.15.

In a study by Ross and Bustin (2009), the authors observed that methane sorption capacity increased with TOC for Jurassic and Devonian-Mississippian (D-M) shales from northern British Columbia, western Canada. The variation in TOC was wide (up to 38 wt%). However, because of the coexistence of organic matter, their study could not exclusively address the impact of clay minerals on adsorption capacity. Similar observations about the effect of TOC and adsorption capacity have been reported by Zhang et al. (2012). Nuttall et al. (2005) found a positive relationship between CO\textsubscript{2} storage capacity and TOC in Devonian black shales from Kentucky, USA. However, they could not find a correlation with the clay content.

In this work, due to their wide variation across the Utica and Permian samples, the role of clay minerals in adsorption was apparent. Clay minerals played a significant role in the adsorption capacity of the studies samples. The clay mineral provided the surface area for the CO\textsubscript{2} molecules to adsorb. Figure 4.16 shows the relationship between clay content and surface area of the samples. The surface area was obtained from the low-pressure sorption analysis (Table 4.4). The results indicate that as the clay content increased in the sample, the surface area increased as well. The surface area of Permian sample P5 was on order of magnitude higher than the surface area of the other Permian and Utica samples. This explains the significantly high adsorption
4.6. DISCUSSION

Figure 4.13: Langmuir volume as a function of clay content: (a) including Permian sample P5 (b) excluding Permian sample P5

Figure 4.14: Langmuir volume as a function of TOC: (a) including Permian sample P5 (b) excluding Permian sample P5

Figure 4.15: Langmuir volume as a function of vitrinite reflectance: (a) including Permian sample P5 (b) excluding Permian sample P5
Figure 4.16: The relationship between clay content and pore surface area for the Utica and Permian samples

capacity of Permian sample P5 among all the tested samples. Venaruzzo et al. (2002) conducted CO$_2$ adsorption experiments on bentonitic clay samples from Patagonia region, Argentina and found a positive correlation between CO$_2$ adsorption capacity and surface areas of clays.

The predominant clay mineral in the Utica and Permian samples was illite. Busch et al. (2008) reported that illite had higher CO$_2$ adsorption capacity than kaolinite. Illite is platy (Keller et al., 1986). The platy shape provides the surface area for increased adsorption capacity. Figure 4.17a shows an SEM image obtained for clay-rich Utica sample U1. Figures 4.17b, 4.17c and 4.17d show the elemental analysis of three spots on the SEM image using energy-dispersive X-ray spectroscopy (EDS). Figure 4.17d indicates that the green rectangle on the SEM image is drawn over a clay mineral. As indicated by the SEM image, the shape of the clay mineral is platy which provides additional surface area for adsorption between the clay plates.

4.7 Summary

In this chapter, CO$_2$ permeability and adsorption measurements were discussed. The permeability measurements on intact Eagle Ford and Utica shale samples showed that in general CO$_2$ impacted the permeability of the shale samples negatively. The permeability to CO$_2$ in shales decreased in comparison with nonadsorbing gases (helium
Figure 4.17: SEM image using energy-dispersive X-ray spectroscopy (EDS) for the clay-rich Utica sample U1.
or argon) due to CO$_2$ adsorption, sorption-induced swelling and molecular sieving effects. Adsorption measurements conducted on crushed Utica and Permian samples showed that the adsorbed volume was controlled mainly by the clay content. The clay minerals (i.e. illite) provided the surface area for adsorption.
Chapter 5

Competitive Adsorption by GCMC Molecular Simulation Technique

5.1 Introduction

As described in Chapter 2, the gas-condensate flowing experiment performed on the Marcellus shale illustrated the significance of preferential adsorption in the behavior of the gas-condensate composition with depletion. Unfortunately, estimating mixed gas adsorption by laboratory experiments is very challenging. Therefore, molecular simulation techniques were utilized to measure mixed gas adsorption. In this chapter, molecular simulation of the adsorptive behavior of light and heavy hydrocarbon molecules is discussed. Molecular simulation by the grand canonical Monte Carlo (GCMC) technique was applied to generate adsorption isotherms of pure and binary hydrocarbons. The simulations were conducted on a slit-pore model composed of parallel planar graphitic surfaces. To test the model, the adsorption isotherms of pure methane, pure ethane, pure n-butane and binary methane/ethane mixture were compared with experimental data. Then, the adsorption isotherms of various binary hydrocarbon mixtures were simulated and the selectivity relative to methane was determined as a function of pore pressure. The ultimate goal of the work was to understand the effect of preferential adsorption on the compositional behavior of confined multicomponent hydrocarbon mixtures.
5.2 Grand Canonical Monte Carlo Simulation

In this work, the grand canonical Monte Carlo (GCMC) molecular simulation technique was used to study the adsorption of a bulk fluid on a solid adsorbent (Allen and Tildesley, 1987; Frenkel and Smit, 2002). The simulations were carried out at constant chemical potential ($\mu$), volume ($V$) and temperature ($T$). The GCMC method was first implemented by Norman and Filinov (1969) for classical fluids. In the Monte Carlo simulation scheme, a Markov chain of molecular configurations is produced. As explained by Frenkel and Smit (2002), the Markov chain is generated using three trial moves:

1. **Particle displacement:** a randomly selected particle is displaced a predetermined distance. The move is accepted with a probability:

   \[ P = \min[1, \exp\{-\beta[U(s'^{N}) - U(s^{N})]\}] \]  
   \[(5.1)\]

   where $U(s'^{N})$ and $U(s^{N})$ are the potential energy functions of the new and old configurations; respectively. $\beta$ is calculated as follows:

   \[ \beta = \frac{1}{k_B T} \]  
   \[(5.2)\]

   where $k_B$ is the Boltzmann’s constant.

2. **Particle insertion:** a particle is inserted at a random position. The insertion is accepted with a probability:

   \[ P = \min[1, \frac{V}{\Lambda^3(N+1)} \exp\{\beta[\mu - U(N+1) + U(N)]\}] \]  
   \[(5.3)\]

   where $V$ is the volume, $\Lambda$ is the thermal de Broglie wavelength, $\mu$ is the chemical potential and $N$ is the number of molecules inside the framework.

3. **Particle removal:** a randomly selected particle is removed from the system. The
5.2. GRAND CANONICAL MONTE CARLO SIMULATION

(a) Displacement  (b) Insertion  (c) Removal

Figure 5.1: Schematic of the GCMC trial moves: (a) particle displacement, (b) particle insertion and (c) particle removal.

removal of a particle is accepted with a probability:

\[ P = \min[1, \frac{\Lambda^3 N}{V} \exp\{-\beta[\mu + U(N-1) - U(N)]\}] \]  (5.4)

The GCMC molecular simulation technique was applied using the publicly available multipurpose simulation code, Music (Gupta et al., 2003; Chempath et al., 2013). A schematic of the GCMC trial moves is shown in Figure 5.1. For flexible molecules such as n-butane, the configurational-bias Monte Carlo move first introduced by Rosenbluth and Rosenbluth (1955) was applied. The move involved randomly selecting a molecule and then randomly selecting a site of this molecule. From the selected site, the molecule was allowed to regrow. The Rosenbluth scheme was used to accept or reject the regrown molecule (Frenkel and Smit, 2002).

Molecular simulations were conducted to estimate the adsorbed gas density as a function of pressure. At each pressure, 50 million Monte Carlo steps were performed. The initial 40% of the steps were used for equilibration and the remaining 60% of the steps were used to calculate the ensemble averages.

5.2.1 Graphitic slit pores

The molecular simulations were conducted using graphitic slit pores. The slit pores contained two opposing pore walls as shown in Figure 5.2. Each pore wall contained a three-layer perfect graphite slab. The graphitic layers were noninteracting and
only interacted with the simulated molecules inside the slit pores. The dimensions of the slit pores in the $x$ and $y$-directions were 4.272 nm and 4.932 nm; respectively, with periodic boundary conditions. The dimension in the $z$-direction represented the distance between the two opposing graphite slabs (i.e. pore size). By modifying the pore size, gas adsorption isotherms were generated at various pore widths.

![Figure 5.2: Two opposing walls of the graphitic slit pore. The distance between the two walls is the slit pore size.](image)

The carbon or graphite represents the organic matrix (i.e. kerogen) of the shales. An illustration of the three-dimensional molecular structure of kerogen is shown in Figure 5.3. As observed from the three-dimensional molecular structure, a slit pore of graphite can be considered as an approximate of the kerogen pore (Pitakbunkate et al., 2015). A similar approach to model gas adsorption in the organic matter of shales and unmineable coalbeds using graphitic slit pores has been conducted previously by several researchers. Liu and Wilcox (2012) investigated the adsorption of pure CO$_2$ for carbon capture and sequestration applications. Mosher et al. (2013) investigated the adsorption of pure methane (CH$_4$) in shales for enhanced natural gas recovery applications. The adsorption of mixtures including CO$_2$/CH$_4$ and CO$_2$/N$_2$ has also been examined by Liu and Wilcox (2013). In addition to pure CH$_4$ adsorption, this work investigated the adsorption of additional pure and binary hydrocarbon mixtures which were applicable for gas-condensate systems in liquid-rich shales.
5.2.2 Lennard-Jones (LJ) 12-6 potentials

The pairwise-additive LJ potential equation was used to model the interaction energy between each two gas molecules in the simulation cell, as well as between the gas molecules and the carbon atoms comprising the pore surfaces. The LJ potential equation is:

$$U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

(5.5)

where $r_{ij}$ is the separation between atoms $i$ and $j$, $\epsilon_{ij}$ is the LJ well depth and $\sigma_{ij}$ is the LJ size. To illustrate the definition of $\sigma$ and $\epsilon$, Figure 5.4 plots the intermolecular potential as a function of distance for methane. $\sigma$ is the distance at which the intermolecular potential between two particles is zero and $\epsilon$ is the minimum intermolecular potential between two particles and it is a measure of the attraction energy between the two particles.

The LJ parameters were obtained from the TraPPE force field for alkane molecules as described by Martin and Siepmann (1998). A united-atom approach is used in this force field. In this case, each carbon atom and its surrounding hydrogen atoms are considered as one LJ sphere with one set of parameters, such as methane molecules.
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Figure 5.4: Intermolecular potential as a function of distance for a CH₄ molecule (σ = 3.73Å and ϵ/k_B = 148K.

Table 5.1: LJ parameters for TraPPE force fields

<table>
<thead>
<tr>
<th>Pseudoatom</th>
<th>ϵ/k_B[K]</th>
<th>σ[A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>148</td>
<td>3.73</td>
</tr>
<tr>
<td>CH₃</td>
<td>98</td>
<td>3.75</td>
</tr>
<tr>
<td>CH₂</td>
<td>46</td>
<td>3.75</td>
</tr>
<tr>
<td>C (graphite)</td>
<td>28</td>
<td>3.40</td>
</tr>
</tbody>
</table>

However, for chain hydrocarbon molecules, the interaction sites are treated differently. For example, n-butane molecules contain two outer methyl groups (CH₃) and two inner methylene groups (CH₂). Each group is considered to be an interaction site with a set of LJ parameters. Therefore, n-butane molecules contain a total of four united-atom sites. Propane molecules contain two methyl groups (CH₃) and one methylene group (CH₂) whereas ethane molecules contain two methyl groups (CH₃). The LJ parameters for the alkane TraPPE force fields are summarized on Table 5.1. The carbon (graphite) LJ parameters were obtained from Cracknell et al. (1993).

The LJ parameters in Table 5.1 are suitable for “like” pseudoatoms. For “unlike” pseudoatoms, the LJ parameters were computed using the Lorentz-Berthelot mixing rules (Allen and Tildesley, 1987):

\[
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{5.6}
\]
5.3. MODEL VALIDATION

Prior to generating the pure and binary gas adsorption isotherms, the GCMC simulation technique was validated using the Music simulator. The validation process involved generating pure methane and pure ethane adsorption isotherms inside 100-Å slit pores considering only fluid-fluid interactions. The interaction energy between the carbon atoms comprising the pore walls and the hydrocarbon molecules were assumed to be zero. Therefore, the generated methane and ethane densities inside the simulation boxes were equivalent to the bulk densities. For comparison, methane and ethane bulk densities as functions of pressure were obtained from the National Institute of Standards and Technology (NIST) webbook (Lemmon et al., 2015). As shown in Figure 5.5, the GCMC molecular simulation technique was able to reproduce the known methane and ethane bulk densities with a good accuracy.

\[ \varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \]  

(5.7)

Figure 5.5: Methane (at 313K) and ethane (at 373K) densities as functions of pressure obtained from GCMC molecular simulator and NIST webbook.
5.4 Pure Methane Adsorption

The first part of this study investigated methane adsorption in shales. Methane adsorption isotherms were generated by the GCMC molecular simulator at various slit pore sizes and were compared with experimental measurements.

5.4.1 Methane adsorption isotherms from molecular simulations

The GCMC molecular simulation technique was applied to generate methane adsorption isotherms as a function of pressure at 40°C (313K) and at various slit pore sizes. The LJ potentials for methane and graphite shown in Table 5.1 were included in the simulation. The gas fugacity which was required as an input parameter, was calculated using the Peng-Robinson equation of state (Reid et al., 1987).

The methane adsorption isotherms generated by the GCMC molecular simulator are shown in Figure 5.6. The excess adsorption is plotted on the y-axis. As defined by Wilcox (2012), excess adsorption is “the additional amount of fluid particles present as a consequence of adsorption”. Therefore, excess adsorption is calculated by subtracting the bulk phase density from the total density inside the slit pore at a given pressure and temperature. Overall, the results indicate that as the slit pore size increases, the methane adsorption decreases.

5.4.2 Methane adsorption isotherms from experimental measurements

The gas adsorption experimental apparatus described in the previous chapter was used to measure methane adsorption on Utica sample U3 and Permian sample P5. The adsorption measurements were conducted at 40°C temperature. Methane adsorption measurements conducted by Heller and Zoback (2014) on a Marcellus shale sample were also included in the experimentally measured data set. Figure 5.7 plots the methane excess adsorption as a function of pressure for the three shale samples.
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Figure 5.6: Methane excess adsorption at 40° C from GCMC molecular simulator at various pore sizes.

5.4.3 Laboratory experiments vs. molecular simulations

The methane adsorption measurements obtained in the three shale samples were compared with the GCMC molecular simulation results. To do so, the simulated isotherms assuming different slit pore sizes were averaged based on the pore size distribution in order to generate a single adsorption isotherm by the GCMC molecular simulation technique and compare it with the experimentally measured isotherm. The pore size distribution for the shale samples was estimated by the low-pressure sorption technique using the Quantachrome autosorb iQ2 described in the previous chapter. Figure 5.8 shows the normalized cumulative pore volume generated from the PSD analysis for the three shale samples.

Each pore width was assigned a “weight” based on its contribution to the total pore volume. Hence, a single weighted average methane adsorption isotherm corresponding to each shale sample was generated by the GCMC molecular simulation technique. The following equation was used to calculate the weighted average isotherms:

\[
n^\text{sim}_{\text{ads}}(p) = \sum_{i=1}^{m} f_i n^\text{sim}_{\text{ads},i}(p)
\]  

(5.8)

where \(n^\text{sim}_{\text{ads}}(p)\) is the weighted average adsorbed gas as a function of pressure, \(f_i\) is the normalized volume fraction of pore size \(i\) (Figure 5.8) and \(n^\text{sim}_{\text{ads},i}(p)\) is the adsorbed
Figure 5.7: Methane excess adsorption isotherms measured on Utica sample U3 and Permian sample P5. The adsorption measurements of the Marcellus sample were obtained from Heller and Zoback (2014).

Table 5.2: Pore volumes obtained from PSD analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>PV, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marcellus</td>
<td>0.034</td>
</tr>
<tr>
<td>U3</td>
<td>0.030</td>
</tr>
<tr>
<td>P5</td>
<td>0.052</td>
</tr>
</tbody>
</table>

gas in mmol/cm$^3$ from GCMC molecular simulations corresponding to pore size $i$ (Figure 5.6).

Additionally, the units of the experimental measurements were converted from SCF of gas per ton of rock to mmol of gas per cm$^3$ of pore volume. The units of the experimental measurements were converted using the following equation:

$$n_{ads}^{exp}(p) = \frac{0.0312 \cdot n_{ads}^{measured}(p) \cdot \rho_{g}^{SC}}{PV}$$  \hspace{1cm} (5.9)$$

where $n_{ads}^{exp}(p)$ is the adsorbed gas in mmol/cm$^3$ as a function of pressure, 0.0312 is a unit conversion factor, $n_{ads}^{measured}(p)$ is the measured adsorbed gas in SCF/ton at different pressures (Figure 5.7), $\rho_{g}^{SC}$ is the gas density at standard conditions (0.0423 mol/l) and $PV$ is the sample pore volume in cm$^3$/g from the PSD analysis. The pore volumes for the studies shale samples are shown in Table 5.2.

Figure 5.9 shows the comparison between the experimental measurements and
5.4. PURE METHANE ADSORPTION

Figure 5.8: Normalized cumulative pore volume as a function of pore width generated from the PSD analysis for (a) U3 and P5 samples and for (b) Marcellus sample.

the GCMC molecular simulation. The results indicate that up to approximately 900 psi, the GCMC simulation was able to reproduce the experimental measurements. However, beyond 900 psi, the GCMC simulation deviated from the experimental measurements and underestimated the adsorption isotherms. Using experimental data of methane adsorption on high-volatile bituminous coal, Mosher et al. (2013) observed a similar discrepancy at pressures between 5 MPa (725 psi) and 15 MPa (2,175 psi).

There are several possible reasons that could cause the GCMC to underestimate the adsorption isotherms at high pressures. First, the pore size distribution analysis could not detect the mesopores between 4 nm and 2 nm and micropores below 2 nm. Therefore, these mesopores were not included in the weighted average calculation for the GCMC simulation. As observed by Alnoaimi (2016) using CT scan imaging of CO$_2$ injection in shale, adsorbing molecules start to penetrate through the micropores at relatively higher pressures compared to the macropores. This means that as the pressure was increasing during the adsorption measurements, micropores started gradually to influence the adsorption capacity. This phenomena was not captured by the simulated isotherms (GCMC) which considered only pore sizes estimated by PSD analysis at low pressures. Thus, the GCMC molecular simulator underestimated the methane adsorption isotherms at high pressures (>900 psi). In addition, the simplified, rigid and perfect graphite slit pore model may not reflect the complex and
Figure 5.9: A comparison of methane excess adsorption as a function of pressure between experimental measurements and GCMC molecular simulation technique for shale samples (a) Marcellus (b) U3 and (c) P5.
chemically heterogeneous pore structure that may enhance methane adsorption as argued by Liu and Wilcox (2012).

To match between the adsorption isotherms from molecular simulation (GCMC) and the adsorption isotherms from experiment at pressure step 900 psi and higher, the contribution from slit-pore sizes 1 nm, 1.5 nm, and 2 nm (10Å, 15Å, and 20Å) was increased gradually in the weighted average calculation of the GCMC adsorption isotherm (Equation 5.8). As discussed earlier, the contribution from these slit-pores was assumed to be zero based on the normalized pore volume from the PSD analysis (Figure 5.8). Yet, a good match between molecular simulation (GCMC) and experiment was observed below 900 psi (Figure 5.9). However, at 900 psi and higher, Figure 5.10 shows that a good match between molecular simulation (GCMC) and experiment was possible when adsorption densities inside slit-pore sizes 1 nm, 1.5 nm and 2 nm were added to the adsorption densities of the higher slit-pore sizes. The volumes assumed for the three slit-pore sizes at 900 psi, 1100 psi and 1300 psi were added to the PSD of the three samples (Figure 5.11). The results illustrate the contribution of micropores (1 - 2 nm) in enhancing methane adsorption (or any other adsorptive molecules such as CO$_2$) at high pressures during which the micropores can be accessed.

5.5 Pure Ethane Adsorption

Molecular simulation of pure ethane adsorption was conducted in order to test the LJ parameters for the methyl group (CH$_3$), two of which form the ethane molecule. The adsorption of ethane in the graphitic slit-pores were simulated at 65°C (338.15K) assuming different slit pore sizes. The simulated adsorption isotherms were compared with experimental data obtained from Gasparik et al. (2014). Ethane adsorption was measured on two shale samples (Namurian shale and Posidonia shale). The adsorption isotherm estimated for the Namurian shale was compared with the molecular simulation results. In addition to the adsorption measurements, Gasparik et al. (2014) provided the PSD for the shale sample. This made it possible to assign a weight for each slit-pore size and estimate a weighted average isotherm for the GCMC data as
Figure 5.10: A comparison of methane excess adsorption as a function of pressure between experimental measurements and GCMC molecular simulation technique for shale samples (a) Marcellus (b) U3 and (c) P5 after including mesopores (2 - 4 nm) and micropores (1 - 2 nm) in the simulated adsorption isotherm at 900 psi pressure and higher.
5.5. **PURE ETHANE ADSORPTION**

Figure 5.11: (a) Marcellus, (b) U3 and (c) P5 pore side distributions from low-pressure sorption in a Quantachrome Autosorb iQ (Quantachrome, 2014) with the addition of micropores from methane adsorption analysis.
described in the previous section.

Figure 5.12 plots ethane excess adsorption as a function of pressure. The experimental data were obtained from Gasparik et al. (2014) and compared with GCMC molecular simulation results. The figure indicates that the GCMC molecular simulator was able to reproduce the experimental measurements especially between 600 and 1,000 psi. Below 600 psi, the molecular simulation underestimated the adsorption isotherms but both measured and simulated data were within the same order of magnitude.

![Figure 5.12: A comparison of ethane excess adsorption as a function of pressure between experimental measurements conducted on a shale sample by Gasparik et al. (2014) and the GCMC molecular simulation technique.](image)

**5.6 Pure n-Butane Adsorption**

Molecular simulation of pure n-butane adsorption was conducted in order to test the LJ parameters for the methyl group (CH$_3$) and methylene group (CH$_2$) which form the n-butane chain molecule. In the case of simulating n-Butane adsorption, it was found that the LB mixing rule (Equations 5.7) did not accurately estimate the solid-fluid interaction energy. According to Duh et al. (1997), Delhommelle and Millié (2001), Song et al. (2003) and Do and Do (2005), the LB mixing rule normally overestimates the well depth parameter ($\epsilon$). Yet, it remains the most widely used rule due to its simplicity (Do and Do, 2005). As observed in the pure methane
and pure ethane cases, the GCMC molecular simulator was capable of reproducing experimental measurements with a fair accuracy without introducing a “correction” factor to the LB mixing rule. However, in the pure n-butane case, a solid-fluid binary interaction parameter, $k_{sf}$, was introduced to Equation 5.7 for the solid-fluid interaction energy as follows (Do and Do, 2005):

$$
\epsilon_{sf} = (1 - k_{sf}) \sqrt{\epsilon_{ss} \epsilon_{ff}}
$$

(5.10)

To determine the solid-fluid binary interaction parameter $k_{sf}$, the n-butane adsorption isotherms by the GCMC molecular simulation technique were compared with experimental measurements conducted by Olivier et al. (1994) on carbon materials at 30°C at low pressures (up to 35 psi). Figure 5.13 plots the n-butane adsorption isotherms measured experimentally and simulated by the GCMC. The figure indicates that the molecular simulation results were close to the experimental measurements and within the same order of magnitude especially at pressures higher than 4 psi. The GCMC molecular simulations were conducted assuming a solid-fluid binary interaction parameter ($k_{sf}$) of 0.20. All subsequent molecular simulations involving n-butane molecules considered the solid-fluid binary interaction parameter in the mixing rule.

![Figure 5.13: A comparison of n-butane adsorption as a function of pressure between experimental measurements conducted on carbon materials by Olivier et al. (1994) and the GCMC molecular simulation technique.](image-url)
5.7 Binary Mixture Adsorption

The results of the pure methane, pure ethane and pure n-butane adsorption showed that the single-component adsorption can be modeled fairly well by the GCMC molecular simulator. It was also found that the LJ parameters for TraPPE force fields and the LB mixing rules were adequate in describing the interaction energy between the hydrocarbon molecules and the carbon walls except for n-butane molecule where a binary interaction parameter was introduced to the LB mixing rule.

Next, the same model was applied to simulate the adsorption isotherms of a methane/ethane binary mixture. The simulated adsorption isotherms for the binary mixture were compared with experimental measurements conducted by Wang et al. (2015). Then, the molecular simulations were extended to two additional binary hydrocarbon mixtures: methane/propane and methane/n-butane. The behavior of binary mixture adsorptions were explored by calculating selectivity. Selectivity is defined as the ratio of mole fractions of the two species in the pore (i.e. adsorbed) divided by the ratio of mole fractions in the bulk (Cracknell et al., 1993; Kurniawan et al., 2006). Selectivity occurs due to the difference in interaction energies between the two adsorbates. This leads to enhanced adsorption of one adsorbate relative to the other (Kurniawan et al., 2006). In this work, selectivity was generally determined for higher carbon number molecule (i.e. ethane, propane or n-butane) relative to the lower carbon number molecule (i.e. methane) at different pore pressures. For example, the selectivity of n-butane over methane was calculated as follows:

$$S_{nC_4/C_1} = \frac{x_{nC_4}/x_{C_1}}{y_{nC_4}/y_{C_1}}$$  \hspace{1cm} (5.11)

where $S$ represents the selectivity, $x$ is the mole fraction in the adsorbed phase and $y$ is the mole fraction in the bulk gas phase.

5.7.1 Methane/ethane mixture

Wang et al. (2015) conducted adsorption measurements for methane/ethane mixtures
on a Marcellus shale sample using a thermogravimetric method. The temperature range of the experiments were 40-60°C (313.15-333.15K). The mole fraction of ethane in the mixture ranged between 4% and 10% (typical for shale-gas compositions). The mixed-gas excess adsorption results were reported in mg/g of rock. To be able to compare with GCMC molecular simulations, the reported measurements were converted to g/cm³ pore volume using the following formula:

\[ m_{\text{excess}}^{\text{exp}} = \frac{m_{\text{excess}}^{\text{measured}}}{1000} \frac{1000}{PV} \]  

(5.12)

where \( m_{\text{excess}}^{\text{exp}} \) is the excess adsorbed mixed-gas in g/cm³, \( m_{\text{excess}}^{\text{measured}} \) is the measured excess adsorbed mixed-gas in mg/g and PV is the sample pore volume in cm³/g. The reported total pore volume of the Marcellus sample was 0.0346 cm³/g.

GCMC molecular simulator reports adsorbed densities in absolute terms. As explained earlier, to obtain excess adsorption, bulk densities of the methane/ethane mixture were subtracted from the absolute adsorption densities at each simulated pressure point. The following formula was applied to calculate the bulk density as a function of pressure:

\[ \rho_{\text{bulk}} = \frac{pM_{\text{mix}}}{Z_{\text{mix}}RT} \]  

(5.13)

where \( \rho_{\text{bulk}} \) is the bulk density in g/cm³, \( p \) is pressure in MPa, \( M_{\text{mix}} \) is the molecular weight of the mixture in g/mol, \( Z_{\text{mix}} \) is the compressibility factor of the mixture from Peng-Robinson equation of state, \( R \) is the gas constant (8.3144598 cm³ MPa K⁻¹ mol⁻¹) and \( T \) is temperature in K. The molecular weight of the mixture was calculated by:

\[ M_{\text{mix}} = \sum_{i=1}^{N} n_i M_i \]  

(5.14)

where \( n_i \) is the mole fraction of component \( i \) and \( M_i \) is the molecular weight of
component $i$.

Molecular simulations were performed at 60°C (333.15K) temperature for 90% methane and 10% ethane mixture (Figure 5.14a) and 96% methane and 4% ethane mixture (Figure 5.14b). At 40°C (313.15K), molecular simulations were performed for 90% methane and 10% ethane mixture (Figure 5.14c). Wang et al. (2015) did not report the PSD of the Marcellus sample used in their study. Therefore, a weighted average excess adsorption isotherm by GCMC molecular simulator could not be established. The authors indicated that micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm) were approximately 23%, 74% and 3%; respectively. All molecular simulations were performed at slit pore sizes 20Å, 50Å and 100Å. The results indicate that the methane/ethane excess adsorption isotherm fell within the generated excess adsorption isotherms by the GCMC molecular simulator for different slit pore sizes. The isotherm from experiment was slightly higher than the isotherm generated for slit pore size 50Å for all three simulation cases. These results illustrate clearly the capability of the GCMC molecular simulator in predicting the behavior of binary hydrocarbon mixture adsorption in carbon-based pores.

### 5.7.2 Selectivity analysis

The GCMC molecular simulator was applied to estimate the adsorbed gas density for binary hydrocarbon mixtures. The binary mixtures were 90%CH$_4$-10%C$_2$H$_6$, 90%CH$_4$-10%C$_3$H$_8$ and 90%CH$_4$-10%nC$_4$H$_{10}$. The molecular simulations were conducted at 60°C (333.15K). Figure 5.15 shows the p-T diagram obtained from a Peng-Robinson equation of state simulator for the three binary hydrocarbon mixtures. As shown in the p-T diagram, 333.15K is above the cricondentherm point of the three mixtures. Therefore, liquid formation due to isothermal processes is excluded and any condensation should only be due to adsorption effects.

Figure 5.16 shows selectivity of ethane relative to methane as a function of pressure for the 90%CH$_4$-10%C$_2$H$_6$ mixture assuming different slit pore sizes. The selectivity curves indicate that ethane preferentially adsorbed ($S_{C2/C1} > 1$). Ethane preferential adsorption is attributed to the higher potential forces (deeper well depth in the LJ
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Figure 5.14: A comparison of excess adsorption for methane/ethane mixture as a function of pressure between experimental measurements (Wang et al., 2015) and GCMC molecular simulation technique for (a) 90%CH$_4$-10%C$_2$H$_6$ at 60°C (b) 96%CH$_4$-4%C$_2$H$_6$ at 60°C and (c) 90%CH$_4$-10%C$_2$H$_6$ at 40°C.
Figure 5.15: The p-T diagram of 90%CH$_4$-10%C$_2$H$_6$, 90%CH$_4$-10%C$_3$H$_8$ and 90%CH$_4$-10%nC$_4$H$_{10}$. The black line indicates the pressure range for generating the adsorption isotherms at 333.15K.

Graph) of ethane molecules compared to methane molecules. As introduced earlier, ethane molecules were modeled as chain molecules with two bonded methyl groups. The potential force of a single ethane molecule therefore involved the two methyl groups leading to higher potential force than a single methane molecule. A similar ethane selectivity behavior relative to methane was observed by Tan and Gubbins (1992). However, the authors assumed the ethane molecule to be single sphere with LJ parameter: $\sigma = 3.95\text{Å}$ and $\epsilon/k_B = 243.0\text{K}$.

Propane molecules contain two methyl groups and a methylene group. Therefore, the potential forces for propane molecules are even higher than ethane and methane molecules. Therefore, the selectivity of propane relative to methane observed for the 90%CH$_4$-10%C$_3$H$_8$ mixture (Figure 5.17) was significantly higher than the selectivity of ethane relative to methane. At 100 psi and 10Å slit-pore size, propane selectivity was around 70 and the ethane selectivity was less than 10. In addition to potential forces, heat of adsorption plays a role in the preferential adsorption of propane and ethane relative to methane. Propane and ethane (longer chain molecules) have higher heat of adsorption than methane (Du et al., 1998; Li et al., 2007). The higher heat of adsorption causes the energy barrier that the adsorbed molecules need to overcome in
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order to evaporate back to the gas phase to be higher (Do, 1998). In both mixtures (methane-ethane and methane-propane), the selectivity was decreasing as pressure was increasing. The reduction in selectivity with increasing pressure can be attributed to two factors: size entropy effects and variations in critical temperatures.

![Graph showing ethane selectivity as a function of pressure for 90%CH₄-10%C₂H₆ mixture at 60°C (333.15K).](image)

Size entropy effects appear as pressure increases in the slit pores. Basically, the component with the smaller number of carbon atoms becomes favorable to adsorb because it is easier for the smaller molecule (i.e. methane) to fill in the vacant sites within the adsorption layer (Krishna et al., 2002). Propane molecules are longer/bulkier than ethane molecules. Therefore, size entropy effects is more pronounced for propane-methane mixture than for ethane-methane mixture. Figures 5.16 and 5.17 indicate that the magnitude of selectivity reduction over methane with increasing pressure was higher for propane in the methane-propane mixture than for ethane in the methane-ethane mixture.

Variation in critical temperatures of the mixture constituents could also cause the selectivity of propane or ethane relative to methane to decrease with increasing pressure. The critical temperatures of propane and ethane (370K and 305K) are higher than the critical temperature of methane (191K). Thus, as pressure increases, methane becomes increasing compressed more compared with propane in methane-propane mixture and with ethane in methane-ethane mixture (Kurniawan et al., 2006). Consequently, the density of methane in the pore increases, causing the
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Figure 5.17: Propane selectivity as a function of pressure for 90%CH\textsubscript{4}-10%C\textsubscript{3}H\textsubscript{8} mixture at 60\textdegree C (333.15K).

Selectivity to go down.

From Figures 5.16 and 5.17, one can observe that for smaller pore sizes, selectivity is larger. As pore size increases, the average distance between a molecule and another molecule increases (going to the right on the x-axis of Figure 5.4) which in turn not only causes the magnitude of the potential force of each mixture constituent to decrease but also causes the magnitude of the potential force difference between methane and ethane or methane and propane to decrease. Hence, the selectivity decreases with increasing pore size.

Figure 5.18 plots the selectivity of n-butane relative to methane as a function of pressure for the 90%CH\textsubscript{4}-10%n-C\textsubscript{4}H\textsubscript{10} mixture. Given the size of n-butane molecule, its potential force is even higher than propane, ethane and methane. Therefore, the selectivity of n-butane relative to methane is expected to be higher than for example, propane selectivity. Figure 5.18a indicates that n-butane selectivity was rather smaller than propane selectivity. For slit-pore size 100A, n-butane selectivity relative to methane was less than unity (Figure 5.18b) indicating preferential adsorption of methane over n-butane at the considered temperature and mole fraction conditions. This suggests that strong size entropy effects may have prevented the selective adsorption of n-butane relative to methane to appear in the 100A slit pore. For pore sizes 10A, 20A and 50A, n-butane selectivity was initially above one but decreased as pressure was increasing. Ultimately, the strong size entropy effects caused n-butane...
5.7. BINARY MIXTURE ADSORPTION

selectivity to go below one (selectivity reversal).

5.7.3 Molecular analysis

The selectivity behavior for the three mixtures (90%CH$_4$-10%C$_2$H$_6$, 90%CH$_4$-10%C$_3$H$_8$ and 90%CH$_4$-10%n-C$_4$H$_{10}$) can also be explained by plotting the number of molecules of both mixture components as a function of distance from the center of the slit-pore. Figure 5.19 shows the number of methane and ethane molecules inside 50A slit-pore for the 90%CH$_4$-10%C$_2$H$_6$ mixture. The figure indicates that as pressure increased from 100 psi (Figure 5.19a) to 500 psi (Figure 5.19b), the added methane molecules due to adsorption was just slightly greater than the added ethane molecules. Therefore, ethane selectivity decreased by a small fraction from 4.1 to 3.5 (Figure 5.16). However, when the pressure increased to 1500 psi, the additional methane molecules far exceeded ethane molecules due to the size entropy effects. As a result, ethane selectivity decreased to 2.3.

Figure 5.20 shows the number of methane and propane molecules inside 50A slit-pore for the 90%CH$_4$-10%C$_3$H$_8$ mixture. At 100 psi (Figure 5.20a), the number of adsorbed propane molecules was substantially higher than the number of adsorbed methane molecules. Therefore, propane selectivity over methane was 12.4. However, as pressure increased to 500 psi (Figure 5.20b), size entropy effects appeared to cause...
Figure 5.19: Number of methane and ethane molecules inside 50Å slit-pore for 90%CH₄-10%C₂H₆ mixture at (a) 100 psi, (b) 500 psi, (c) 1000 psi and (d) 1500 psi.
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Figure 5.20: Number of methane and propane molecules inside 50Å slit-pore for 90%CH$_4$-10%C$_3$H$_8$ mixture at (a) 100 psi, (b) 500 psi, (c) 1000 psi and (d) 1500 psi.

the added methane molecules in the adsorbed state (close to the pore wall) to be greater than the added propane molecules. Hence, propane selectivity decreased to 7.0. Ultimately, at 1500 psi, the molecular simulation results indicated that the slit-pore was only accepting methane molecules due to their smaller size compared to propane molecules causing propane selectivity to further decrease to 2.7.

Figure 5.21 shows the number of methane and propane molecules inside 50Å slit-pore for the 90%CH$_4$-10%n-C$_4$H$_{10}$ mixture. Even though n-butane is highly adsorptive, only a small number of n-butane molecules were observed close to the pore wall at 100 psi (Figure 5.21a) causing its selectivity over methane to be only 1.2 (Figure 5.18). With increasing pressure, the size of n-butane molecules which contain two outer methyl groups and two inner methylene groups prevented additional molecules to adsorb with whereas methane molecules were continually adsorbing. Consequently,
at 1500 psi (Figure 5.21d), n-butane selectivity over methane decreased by an order of magnitude to 0.2 (selectivity reversal).

5.8 Discussion

As observed in the previous section, the selectivity of ethane, propane and n-butane over methane decreased as pressure increased due to size entropy effects which resulted in preferential adsorption of methane at higher pressure. In real gas and gas-condensate cases, the opposite will occur. That is, preferential desorption of methane compared to heavier hydrocarbon species is expected with depletion (pressure decline).
Production data from shale gas wells in North America were reported by Freeman et al. (2012). In addition to the rate and pressure data, compositional analyses of fluid samples collected from surface separators at semi-regular intervals were provided. Figure 5.22 plots the compositional deviation of methane, ethane, propane, n-butane and n-pentane as a function of time of one of the wells. The first fluid sample which was collected after approximately nine days of production was used as the base sample. In the subsequent samples, the compositional deviation was estimated using the following equation:

\[
CD = \frac{X_i}{X_1}
\]  

(5.15)

where \( CD \) is the compositional deviation, \( X_i \) is the concentration of the hydrocarbon component and \( X_1 \) is the concentration of the hydrocarbon component in the first fluid sample. The results indicate that the composition of the fluid samples deviated with time. Compositional deviation due to liquid dropout below dew point pressure is ruled out because the well was drilled in the dry gas region.

As observed in Figure 5.22, the relative composition of methane increased with time, whereas the relative composition of the other hydrocarbon constituents (i.e. ethane, propane, n-butane and n-pentane) decreased. The increase in the relative composition of methane was due to methane preferential desorption which caused methane concentration in the well stream to increase. The decrease in the relative composition of the other hydrocarbon constituents was due to their higher affinity to the shale pore walls during flow to the wellbore which caused chromatographic separation. Chromatographic separation was observed at the core-level during gas-condensate core-flooding experiments in Chapter 2.

Figure 5.22 also indicates that the magnitude of the reduction in the relative composition was dependent on the molecular size. The decline of relative composition of heavier components was greater than that of lighter components. Overall, the produced gas became leaner with depletion.
Figure 5.22: Compositional deviation as a function of time. Except for methane, the concentration of hydrocarbon species decreased with depletion (i.e. the produced well stream became leaner). The compositional deviation data were reproduced from Freeman et al. (2012).

5.9 Summary

This chapter described the successful application of molecular simulation by the grand canonical Monte Carlo (GCMC) technique to generate adsorption isotherms for pure and binary hydrocarbon mixtures. The pure component adsorption isotherms for methane, ethane and n-butane and the binary hydrocarbon adsorption of methane-ethane mixture show that the GCMC molecular simulation technique is capable of reproducing experimental results. Methane adsorption isotherms were generated for various slit pore sizes and the results show that as the pore size decreases, the amount of adsorption increases.

The binary hydrocarbon adsorption isotherms were presented using selectivity calculations for 90\%CH\(_4\)-10\%C\(_2\)H\(_6\), 90\%CH\(_4\)-10\%C\(_3\)H\(_8\) and 90\%CH\(_4\)-10\%n-C\(_4\)H\(_{10}\) mixtures. At low pressures, results indicate that the higher carbon number molecule preferentially adsorbed ($S > 1$). However, as pressure increased, the selectivity started to decrease. In the 90\%CH\(_4\)-10\%n-C\(_4\)H\(_{10}\) mixture, the selectivity declined to less than unity (selectivity reversal).

The decline in selectivity with increasing pressure is an indication of size entropy
effects where the partially-filled pores can more easily fit methane molecules compared with longer chain molecules. In terms of multicomponent gas production, this phenomenon basically means that initial production contains both light and heavy components from the free gas phase. However, as reservoir pressure depletes, methane from the adsorbed phase starts to desorb preferentially and the adsorption sites where methane molecule used to reside start to accept more longer chain (heavy) components. As a result, the produced gas becomes leaner as pressure decreases in the reservoir. In gas-condensate systems of liquid-rich shales, this means that significant volumes of condensates, which contain predominantly heavy components, are left behind in the reservoir in the adsorbed phase.
Chapter 6

Vapor-Liquid Equilibrium by Molecular Simulation Techniques

6.1 Introduction

In the previous chapters, the effect of the nanometer-sized pores on permeability, adsorption and compositional behavior of hydrocarbon mixtures were studied using experimental and molecular simulation techniques. In this chapter, the molecular simulation techniques were extended to investigate the effect of the nanometer-sized pores on the critical properties of confined hydrocarbons.

As noted the literature review section of Chapter 1, researchers have indicated that the critical properties of confined fluids in nanometer-sized pores shift due to the increased pore-fluid interaction (Evans et al., 1986a,b; Ball and Evans, 1989; Morishige et al., 1997; Morishige and Shikimi, 1998; Vishnyakov et al., 2001; Zarragoicoechea and Kuz, 2004; Singh et al., 2009; Singh and Singh, 2011). To the best of my knowledge, the application of molecular simulation techniques to study the critical properties of pure and mixed hydrocarbons in unconventional resources is still limited. Didar and Akkutlu (2013) applied the Gibbs ensemble Mone Carlo (GEMC) molecular simulation technique to study the shift of pure methane critical properties under confinement. Pitakbunkate et al. (2015) applied the grand canonical Monte Carlo (GCMC) molecular simulation technique to study the shift of the critical properties
of confined pure methane, pure ethane and methane-ethane mixture.

In this work, the critical temperature ($T_c$), critical pressure ($p_c$) and critical density ($\rho_c$) of pure methane, pure ethane, pure propane and pure n-butane confined in graphitic slit-pores were investigated. Initially, the Gibbs ensemble was selected as the molecular simulation method and was validated with the known phase coexistence properties of hydrocarbons in the bulk. However, applying this method to study the vapor-liquid equilibrium of hydrocarbon components in the pore was not successful. Therefore, the GCMC molecular simulation technique, presented in the previous chapter, was selected as an alternative method.

6.2 Methodology

6.2.1 Gibbs ensemble Monte Carlo (GEMC)

The Gibbs ensemble Monte Carlo (GEMC) molecular simulation technique was developed by Panagiotopoulos (1987a,b) to estimate phase coexistence properties of single and multicomponent systems from a single computer simulation. Calculations of phase coexistence by simulation have been proposed by Rowlinson and Widom (1982), Chapela et al. (1987) and Heffelfinger et al. (1987). Their proposed methodology involves simulating a two-phase system in a small box. However, the presence of a real surface between the two phases makes the simulations slow to equilibrate and the densities of the two phases close to the interface difficult to estimate especially when simulating a system with small total number of molecules.

The Gibbs methodology provides a significant enhancement over those techniques. Instead of a single box, the Gibbs methodology involves two boxes; a box from a region deep inside the liquid phase (phase I) and the other box from a region deep inside the gas phase (phase II). Thus, the two-phase system has no physical contact between the two phases but they are thermodynamically connected (Panagiotopoulos et al., 1988; Wilding, 1995). The Gibbs ensemble is carried out at constant number of molecules ($N$), volume ($V$) and temperature ($T$). The number of molecules ($N$) is the total number of molecules in the two boxes, $N = N^I + N^{II}$, and the volume
(V) is the total volume of both boxes, \( V = V^I + V^{II} \). The two boxes represent a canonical ensemble at constant NVT. As outlined by (Panagiotopoulos et al., 1988), the simulation contains three trial moves:

1. **Particle displacement:** a randomly selected particle is displaced within the box a predetermined distance. Each box is treated independently. For box I, the move is accepted with a probability:

\[
P = \min[1, \exp\{-\beta[U^I_{\text{new}} - U^I_{\text{old}}]\}] \tag{6.1}
\]

where \( U^I_{\text{new}} \) and \( U^I_{\text{old}} \) are the potential energy functions of the new and old configurations; respectively. \( \beta \) is calculated using Equation 5.2 shown in the previous chapter. For box II, an identical procedure is applied.

2. **Volume change:** the volume of a randomly chosen box is changed by \( \Delta V \). Simultaneously, the volume of the other box is changed by \(-\Delta V\) in order to conserve the total volume of the system. For example, if the volume of box I is changed by \( \Delta V \), then the ratio of the probabilities of the new and old configurations is:

\[
P^I_{\text{vol}} = \frac{\exp[-\beta p(V^I + \Delta V) - \beta U^I_{\text{new}} + N^I \ln(V^I + \Delta V)]}{\exp[-\beta pV^I - \beta U^I_{\text{old}} + N^I \ln(V^I)]} \tag{6.2}
\]

where \( V^I \) is the volume of the box I prior to the volume change attempt, \( \Delta V \) is the magnitude of volume change and \( N^I \) is the number of particles in box I. The pressure \( p \) appears in the above equation because the volume change in this case is considered part of an isothermal-isobaric ensemble which has constant-\( N^I pT \).

For box II which goes through \(-\Delta V\) volume change, the ratio of the probabilities of the new and old configurations is:

\[
P^{II}_{\text{vol}} = \exp[\beta p\Delta V - \beta \Delta U^{II} + N^{II} \ln(V^{II} - \Delta V) - N^{II} \ln(V^{II})] \tag{6.3}
\]
The probability of the combined moves is:

\[ P_{\text{vol}} = P_{\text{vol}}^{I} \times P_{\text{vol}}^{II} \quad (6.4) \]

As with other trial moves, the volume change is accepted with a probability given by the \( \min(1, P_{\text{vol}}) \):

\[ P = \min[1, \exp(-\beta[\Delta U^{I} + \Delta U^{II} - N^{I}k_{B}T \ln \frac{V^{I} + \Delta V}{V^{I}} - N^{II}k_{B}T \ln \frac{V^{II} - \Delta V}{V^{II}}])] \quad (6.5) \]

where \( k_{B} \) is the Boltzmann’s constant and \( T \) is temperature.

3. **Particle interchange:** a randomly selected particle from one of the two boxes is moved to the other box at a randomly selected location. The box that is losing a particle is represented by particle removal in the grand canonical ensemble (constant-\( \mu VT \)). Therefore, with the corresponding superscripts for \( U, N \) and \( V \), Equation 5.4 of the GCMC particle removal trial move is used to compute the particle removal probability. Simultaneously, the other box is accepting a new particle. This step represents a particle insertion trial move of the grand canonical ensemble. Equation 5.3 is therefore used to compute the probability of particle insertion with the corresponding superscripts. The probability of the combined moves is:

\[ P_{\text{int}} = P_{\text{int}}^{I} \times P_{\text{int}}^{II} \quad (6.6) \]

Assuming box I is losing a particle and box II is gaining a particle, the particle interchange is accepted with a probability as follows:

\[ P = \min[1, \exp(-\beta[\Delta U^{I} + \Delta U^{II} + k_{B}T \ln \frac{V^{II}(N^{I} + 1)}{V^{I}N^{II}}])] \quad (6.7) \]

In this work, the GEMC molecular simulation was applied using Towhee molecular simulation code. The code was developed by Martin (2013) and it is available as an open-source tool.
6.2.2 Potential model

Similar to the GCMC molecular simulation, the pairwise-additive Lennard-Jones (LJ) potential was used to model the interaction energy between the molecules of the system (Equation 5.5). The TraPPE force field presented in the previous chapter (Table 5.1) was also considered.

6.2.3 Simulation details

Each simulation in GEMC is conducted at constant temperature $T$. At the end of the simulation, the equilibrium density of one of the boxes would correspond to liquid density (higher) and the equilibrium density of the other box would correspond to vapor density (lower). Figure 6.1 shows how the density of methane in the two boxes evolved during the simulation steps. Each step consisted of $N$ trial moves where $N$ is the total number of particles in the system.

![Figure 6.1: An example of bulk methane liquid and vapor density convergence at 170K temperature. Red corresponds to liquid density and blue corresponds to vapor density.](image)

A phase envelope of temperature vs. density can be generated by conducting
the GEMC molecular simulations at different temperatures. Figure 6.2 plots the $\rho$-$T$ diagram for bulk methane. Each temperature corresponds to a single molecular simulation from which two density estimates were obtained. In the neighborhood of the critical point, the Gibbs ensemble becomes unstable and cannot provide accurate estimates of the coexistence curves (Mon and Binder, 1992; Wilding and Bruce, 1992; Wilding, 1995; Panagiotopoulos, 2000). In this case, the critical points from GEMC molecular simulations can be obtained by fitting the subcritical coexistence data to universal scaling laws (Panagiotopoulos, 2000).

![Figure 6.2: Methane $\rho$-$T$ diagram generated by performing GEMC molecular simulations at different temperatures.](image)

### 6.2.4 Critical points

The vapor-liquid critical parameters were estimated by fitting the coexistence densities to the law of of the rectilinear diameter (Rowlinson and Swinton, 1982) and the scaling law for the density (Rowlinson and Widom, 1982). First, the critical temperature ($T_c$) was obtained by least-square optimization applied to fit the following equation (Singh et al., 2009):

$$\rho_l - \rho_v = B \left( 1 - \frac{T}{T_c} \right)^\beta$$

(6.8)
where $\rho_l$ is the liquid density and $\rho_v$ is the vapor density. $\beta$ is the critical exponent and for three dimensional systems, it is 0.32 (Rowlinson and Widom, 1982). $B$ is a fitting parameter. The critical temperature ($T_c$) was then used to obtain the critical density ($\rho_c$) by least-squares fit of the following equation:

$$\frac{\rho_l + \rho_v}{2} = \rho_c + A \left(1 - \frac{T}{T_c}\right)$$

(6.9)

where $A$ is a fitting parameter. The critical pressure ($p_c$) was estimated from the Clausius-Clapeyron relation:

$$\ln p = -\frac{L}{R} \left(\frac{1}{T}\right) + c$$

(6.10)

where $p$ is the saturation pressure estimated by the GEMC molecular simulation, $L$ is the specific latent heat of vaporization, $R$ is the specific gas constant and $c$ is a constant.

## 6.3 Results and Discussions

### 6.3.1 Vapor-liquid equilibrium of the bulk phase

Figure 6.3 shows the bulk phase vapor-liquid coexistence envelope for methane, ethane, propane and n-butane. The coexistence envelopes were generated by the GEMC molecular simulation technique. The GEMC results were compared with experimental data obtained from Smith and Srivastava (1986). The results indicate that the agreement in the phase coexistence data between the GEMC molecular simulation technique and the experimental measurements were satisfactory. In addition, the critical temperature ($T_c$) and critical density ($\rho_c$) obtained by applying least-square optimization on the GEMC data were very close to the known critical points of the simulated hydrocarbon molecules.
Figure 6.4 shows the saturation pressure of methane, ethane, propane and n-butane estimated by the GEMC molecular simulation technique as a function of \(1/T\). The best-fit straight line equation in the form \(y = ax + b\) is equivalent to Equation 6.10. Therefore, the slope of the line \(a\) and y-intercept \(b\) are:

\[
a = -\frac{L}{R} \quad \text{(6.11)}
\]

\[
b = c \quad \text{(6.12)}
\]

By specifying the critical temperature \(T_c\) in Equation 6.10, the critical pressure \(p_c\) was estimated. Figure 6.4 indicates that the critical pressures were in good agreement with the known critical pressures for the four hydrocarbon molecules. Those observations indicate that the GEMC molecular simulation technique is capable to model the vapor-liquid equilibrium of hydrocarbon molecules in the bulk phase.

### 6.3.2 Vapor-liquid equilibrium in the nanopores by the GEMC molecular simulation technique

To study the vapor-liquid equilibrium in the nanopores by the GEMC molecular simulation technique, two approaches were proposed. In the first approach, a slit-pore was added to one of the simulation boxes and the other box was in the bulk phase. In the other approach, slit-pores were added to both simulation boxes. The first approach is called the pore-bulk GEMC and the second approach is called the pore-pore GEMC (Panagiotopoulos, 1987a). Given the shape and structure of the slit-pore model used in this study, both approaches could not be employed to generate vapor-liquid coexistence envelopes below the critical temperatures for pure component systems.

The phase rule dictates that for pure component systems, only one intensive variable can be specified independently. In this case, it was the temperature. Therefore, the molecular simulations in the Gibbs ensemble had to be carried out in the NVT
6.3. RESULTS AND DISCUSSIONS

Figure 6.3: Vapor-liquid coexistence envelopes for (a) methane, (b) ethane, (c) propane and (d) n-butane estimated by the GEMC molecular simulation technique (red circles) and how they compare with experimental data from Smith and Srivastava (1986) (blue triangles). The critical points estimated by least-square optimization (Equations 6.8 and 6.9) applied on the GEMC data are plotted as black circles. Black triangles are the known critical points for the hydrocarbon molecules.
Figure 6.4: Saturation pressure as a function of reciprocal temperature for (a) methane, (b) ethane, (c) propane and (d) n-butane from GEMC molecular simulation (red circles). The black circles are the estimated critical pressures by Equation 6.10 and the gray triangles are the known critical pressures for the hydrocarbon molecules.
scheme (constant number of molecules $N$, constant volume $V$ and constant temperature $T$) similar to the study of the bulk fluids discussed earlier. However, the volume of the slit-pores had to be maintained constant. This meant that in both approaches, the volumes of the two boxes (pore box and bulk box in the first approach and two pore boxes in the second approach) had to be maintained constant and were not allowed to change. Consequently, the density estimates for both boxes (or phases) were highly dependent on the input number of particles ($N$) at the start of the molecular simulation. For this technique to be useful, it should not be biased by $N$. In the study of bulk vapor-liquid coexistence, this bias was avoided by allowing the volumes of the two boxes ($V^I$ and $V^{II}$) to change while maintaining the total volume ($V = V^I + V^{II}$) to be constant. Ultimately, the GEMC molecular simulation technique was abandoned and the GCMC molecular simulation technique was applied instead to study the VLE of pure components.

### 6.3.3 VLE in the nanopores by the GCMC molecular simulation technique

The GCMC molecular simulation technique was applied to study the vapor-liquid equilibrium in the nanopores by simply generating adsorption isotherms for pure hydrocarbon components at subcritical conditions. Figure 6.5 shows the adsorption isotherm for methane ($T_c = 190$K) at $T = 160$K and compares it with methane density measurements in the bulk obtained from the National Institute of Standards and Technology (NIST) (Lemmon et al., 2015). The plot shows a jump in methane density inside the 50Å slit-pore. A jump in methane density was also shown by NIST bulk estimates. The jump corresponded to methane undergoing a phase transition from vapor to liquid. The last density estimate before the phase transition and the first density estimate after the phase transition were acquired to construct the $\rho$-$p$ phase envelope for both the pore fluid and for the bulk fluid. The molecular simulations were repeated at varying temperatures and assuming different slit-pore sizes.

The phase transition inside the slit-pore is illustrated in Figure 6.6. The figure
indicates that phase transition occurred because when the pressure was increased slightly from 250 psi to 270 psi, the number of molecules inside the slit-pore increased substantially leading to methane density to be equivalent to the liquid density.

Figure 6.5: Methane bulk density from NIST (Lemmon et al., 2015) and methane density inside a 50-A slit-pore estimated by GCMC molecular simulation at 160K.

Figure 6.7 shows the $\rho$-$p$ vapor-liquid coexistence diagram for methane in the bulk (NIST) and inside 50-A and 100-A graphitic slit-pores (GCMC). The critical point is located at the tip of the phase envelope. The critical pressure ($p_c$) was obtained from the x-coordinate of the tip. The critical density ($\rho_c$) was determined by the calculating the arithmetic average of the liquid and vapor densities at the tip. The temperature at which the last vapor and liquid densities of the phase envelope were obtained was assumed to be the critical temperature ($T_c$). The critical properties in the bulk and inside the 50-A and 100-A slit-pores are tabulated in Table 6.1. The results indicate that there was a shift in the critical properties of methane due to pore confinement. Both the critical pressure ($p_c$) and critical temperature ($T_c$) decreased with decreasing pore size whereas the critical density ($\rho_c$) increased.

Figure 6.7 shows that the shift in the critical properties was due to shrinkage of the phase envelopes. The phase envelopes shrank because the density of the vapor phase before the phase transition in the slit-pore was higher than the vapor density in the bulk. The enhancement of the vapor density was attributed mainly to methane...
6.3. RESULTS AND DISCUSSIONS

Figure 6.6: Number of methane molecules inside a 50-A slit-pore estimated by GCMC molecular simulation at 160K for 250 psi and 270 psi pressure steps. The significant increase of the number of molecules in the center of the pore when the pressure increased from 250 psi to 270 psi led to phase transition from vapor to liquid.

Table 6.1: Methane critical properties in the bulk and inside 50-A and 100-A slit-pore sizes.

<table>
<thead>
<tr>
<th>Pore size</th>
<th>$\rho_c$, g/ml</th>
<th>$p_c$, psi</th>
<th>$T_c$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>0.1625</td>
<td>667</td>
<td>190</td>
</tr>
<tr>
<td>100A</td>
<td>0.2330</td>
<td>560</td>
<td>185</td>
</tr>
<tr>
<td>50A</td>
<td>0.2565</td>
<td>465</td>
<td>176</td>
</tr>
</tbody>
</table>

adsorption to the pore walls of the graphitic slit-pores as illustrated clearly in Figure 6.6 which indicates that methane molecules prior to phase transition ($p = 250$ psi) were mostly close to the pore walls (i.e. adsorbed).

The $\rho$-$p$ vapor-liquid coexistence diagram for ethane is shown in Figure 6.8. Similar to methane, the critical properties for ethane in the bulk and inside the graphitic slit-pores were obtained from the tip of the phase envelope and they are shown in Table 6.2. A shift in the critical properties upon pore confinement was also observed for ethane molecules. Ethane critical pressure ($p_c$) and critical temperature ($T_c$) decreased as the pore size decreased. The critical density ($\rho_c$) increased for the 100-A slit-pore but decreased slightly for the 50-A slit-pore.
Figure 6.7: Vapor-liquid coexistence envelopes of methane in the bulk and inside 50-A and 100-A slit-pores. The critical properties were estimated from the tip of the phase envelope.

Table 6.2: Ethane critical properties in the bulk and inside 50-A and 100-A slit-pore sizes.

<table>
<thead>
<tr>
<th>Pore size</th>
<th>$\rho_c$, g/ml</th>
<th>$p_c$, psi</th>
<th>$T_c$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>0.2070</td>
<td>705</td>
<td>305</td>
</tr>
<tr>
<td>100Å</td>
<td>0.2765</td>
<td>570</td>
<td>295</td>
</tr>
<tr>
<td>50Å</td>
<td>0.2750</td>
<td>510</td>
<td>290</td>
</tr>
</tbody>
</table>

Figure 6.9 shows the adsorption isotherms of propane and n-butane in 50-A slit-pores at 280K and 350K (propane) and 300K and 390K (n-butane). The plot also shows the density of both molecules in the bulk phase from NIST at similar pressure and temperature conditions. Unlike the bulk phase, no phase transition was observed when the molecular simulations were conducted for the slit-pore. Figures 6.10 and 6.11 show the number of molecules from the center of the 50-A slit pore at two pressure conditions for propane and n-butane, respectively. The figures indicate that the highly adsorptive behavior of the propane and n-butane hindered phase transition. When the pressure was increased, the added molecules became adsorbed and no molecules were observed in the center of the slit-pore.

The critical properties shift of pure components in nanopores translated to critical properties shift of their mixtures. Figure 6.12 shows the $p$-$T$ diagram of a 50%
methane and 50% ethane mixture in the bulk phase as well as in the 100-A and 50-A slit-pores. An equation-of-state based compositional simulator (PVTi) was used to construct the phase diagrams. For each case (bulk, 100-A slit pore or 50-A slit-pore), the corresponding critical temperatures ($T_c$) and critical pressures ($p_c$) of the mixture constituents (Tables 6.1 and 6.2) were considered. As observed in the $p-T$ diagrams, pore confinement caused the phase envelope of the methane-ethane mixture to shrink. Therefore, the area of the two-phase region decreased.

### 6.4 Summary

This chapter described the successful implementation of the Gibbs ensemble Monte Carlo (GEMC) molecular simulation technique to model the vapor-liquid equilibrium for methane, ethane, propane and n-butane pure components in the bulk phase. Least-square optimization was applied to estimate the critical properties of the modeled molecules and the results were in good agreement with experimental data available in the literature. However, the GEMC molecular simulation technique failed to model the vapor-liquid equilibrium of pure hydrocarbon molecules in nanopores.
Figure 6.9: (a) Adsorption isotherms of propane in 50-A slit-pore at $T = 280\text{K}$ and $T = 350\text{K}$ and how they compared with propane densities in the bulk at similar temperature and pressure conditions. (b) Adsorption isotherms of n-butane in 50-A slit-pore at $T = 300\text{K}$ and $T = 390\text{K}$ and how they compared with n-butane densities in the bulk at similar temperature and pressure conditions.

As an alternative, the grand canonical Monte Carlo (GCMC) molecular simulation technique was applied successfully to describe the vapor-liquid equilibrium of methane and ethane in the nanopores. The molecular simulation results showed that the critical properties of both molecules shifted due to pore confinement. The increased molecule-pore interactions (i.e. adsorption) in the nanopores caused the overall vapor density to be enhanced prior to transitioning to the liquid phase. Therefore, the phase envelope of the $\rho$-$p$ diagram shrank. Ultimately, this led to a decrease in the critical temperature ($T_c$) and the critical pressure ($p_c$) and an increase in the critical density ($\rho_c$) with decreasing slit-pore size. The shift in the critical properties of the pure components translated to shifts in the critical properties of their mixtures causing the shape of the phase envelope to change.
6.4. SUMMARY

Figure 6.10: Number of propane molecules inside a 50-A slit-pore estimated by GCMC molecular simulation at 280K. Propane molecules were only added to the adsorbed state when the pressure increased from 10 psi to 150 psi.

Figure 6.11: Number of n-butane molecules inside a 50-A slit-pore estimated by GCMC molecular simulation at 300K. n-Butane molecules were only added to the adsorbed state when the pressure increased from 5 psi to 75 psi.
Figure 6.12: The phase diagram of 50% methane and 50% ethane mixture in the bulk phase and in 100-A and 50-A slit pores. The shift in the critical properties of pure components translated to critical properties shift of their mixture.
Chapter 7

Conclusions and Future Work

7.1 Conclusions

In this work, the effect of nanopores on the transport mechanisms of gas and gas-condensate in gas shales and liquid-rich shales was investigated using laboratory experiments and molecular simulation techniques. Laboratory experiments were carried out to study compositional behavior of flowing gas-condensate mixture below the dew-point pressure across a Marcellus shale core sample, to investigate the effect rock mineralogy and pore structure on permeability and CO\textsubscript{2} adsorption, and to assess the impact of CO\textsubscript{2} adsorption in the nanoporous shale matrix on permeability. The grand canonical Monte Carlo (GCMC) molecular simulation technique was applied to investigate the competitive adsorption of binary hydrocarbon mixtures in carbons-based and nanometer-sized slit-pores and to explain the compositional behavior of the Marcellus gas-condensate core-flooding experiment. The GCMC molecular simulation technique was also applied to determine the effect of fluid confinement in the nanometer-sized slit-pore on the critical properties of methane, ethane, propane and n-butane which are the predominant constituents of gas-condensate mixtures.

The Marcellus gas-condensate core-flooding experiment showed that gas composition of the flowing mixture changed not only due to condensate dropout as observed in conventional rocks but also due to preferential adsorption of the heavy components over the light components in the nanopores of the shale. GCMC molecular simulations
of binary hydrocarbon mixtures showed that as pressure decreased, the selectivity of
the longer chain molecule over methane increased. In other words, methane desorbed
preferentially as pressure decreased. In terms of multicomponent gas-condensate pro-
duction, this means that the produced gas becomes leaner as pressure goes down
in the reservoir and significant volumes of condensates, which contain predominantly
heavy components, are left behind in the reservoir in the adsorbed phase.

Additionally, the nanopores caused the permeability of the shale matrix to be ex-
tremely low. SEM images indicated that the nanopores resided mainly in the kerogen
and the clay minerals. A positive correlation was observed between TOC and perme-
ability in the Utica shale samples. The role of clay content on transport appeared in
the stress-dependent permeability. A positive correlation was observed between clay
content and pore throat compressibility. That is, as the clay content increased, the
shale permeability became more sensitive to effective stress. This caused permeabil-
ity reduction to be significant with increasing effective stress. Therefore, to achieve
more accurate reservoir simulations and production forecasting, stress-dependent per-
meability should be accounted for. Sensitivity analysis on a single-well model of a
clay-rich reservoirs showed that neglecting stress-dependent permeability caused the
cumulative gas production to be overestimated by a factor of two over ten years of
production.

Furthermore, the nanopores caused the permeability of shale to be very sensitive to
adsorption. Permeability measurements with CO$_2$ indicated that the adsorbed layer of
CO$_2$ reduced the size of pore throats leading to reductions in permeability by as high
as an order of magnitude. Sorption-induced swelling and molecular sieving effects
also caused the permeability of CO$_2$ to decrease compared to the permeability of
nonadsorbing gases. Adsorption measurements conducted on crushed samples showed
that the adsorbed volume was controlled mainly by the clay content because clay
minerals provided the surface area for adsorption.

The grand canonical Monte Carlo (GCMC) molecular simulation technique was
applied successfully to model the adsorption of single and binary hydrocarbons in
carbon-based nanometer-sized slit-pores. The results indicate that although heavy
hydrocarbon components have higher affinity to the pore walls, their selectivities over
methane decrease with increasing pressure mainly due to size entropy effects. This means methane adsorb preferentially at higher pressures. Therefore, preferential desorption of methane over heavier hydrocarbon species is expected with depletion. In terms of multicomponent gas production, this phenomenon means that initial production contains both light and heavy components from the free gas phase. However, as reservoir pressure depletes, methane from the adsorbed phase starts to desorb preferentially and the adsorption sites where methane molecule used to reside start to accept more longer chain (heavy) components. As a result, the produced gas becomes leaner as pressure decreases in the reservoir. In gas-condensate systems of liquid-rich shales, this means that significant volumes of condensates, which contain predominantly heavy components, are left behind in the reservoir in the adsorbed phase.

Finally, the nanopores impacted the critical properties of confined hydrocarbons. Molecular simulations showed that the critical temperature ($T_c$), critical pressure ($p_c$) and critical density ($\rho_c$) of confined methane and ethane molecules shifted. This caused the phase envelope of hydrocarbon mixtures to shrink, reducing the area of the two-phase region.

7.2 Future Work

For future investigations of gas and gas-condensate transport in nanopores, I have the following recommendations:

- Gas-condensate core-flooding experiments:
  
  In this research work, the gas-condensate core-flooding experiment was conducted on a Marcellus shale sample using a real gas-condensate fluid mixture. The limited supply of the fluid sample and the very low permeability of the shale sample caused the experiments to be conducted at transient flow conditions. For future work, it is recommended to perform the flow experiment on a shale sample that has permeability in the order of $\mu d$. In addition, if ample supply of real gas-condensate fluid sample could
not be made available, it is recommended to use synthetic gas-condensate mixtures.

- In this research work, pressure transducers were installed upstream and downstream of the core-holder only. For future work, it is recommended to install pressure transducers through the sampling ports in order to measure the pressure along the core during flow. Ideally, the pressure transducers should be installed at the sampling ports in order to avoid adding extra dead volume to the experimental apparatus.

- **Permeability measurements:**

  - The role of TOC and clay contents on the transport in shale rocks was investigated using Utica and Permian shale samples. Shale samples with varying mineral composition from additional shale plays could be tested to complement the current dataset.

  - The permeability measurements for the Utica and Permian samples were limited to low pore pressures (up to 1500 psi). It is recommended to measure the permeability at higher pore pressures by using a Quizix pump with a higher pressure rating. This will allow for analyzing the effective stress law (Heller et al., 2014) and how it is affected by clay content.

- **Adsorption measurements:**

  - The adsorption measurements highlighted the role of clay content in enhancing the adsorption capacity of shale samples. However, the role of TOC content and kerogen maturation could not be concluded in this study because it may have been masked by the role of clay content. It is therefore recommended to isolate the kerogen from the shale samples and then conduct the experiments on pure kerogen.

  - To isolate the kerogen, chemical methods can be used as outlined by Saxby (1970) and Goklen et al. (1984). After isolating the kerogen from shale samples, small amounts of kerogen will be provided. The sample cell of
7.2. **FUTURE WORK**

the current adsorption apparatus should then be replaced by a smaller sample cell in order to minimize the dead volume. Minimizing the dead volume will amplify the adsorption signature on the pressure signal and will allow for more accurate adsorption measurements.

- Competitive adsorption by the grand canonical Monte Carlo (GCMC) molecular simulation technique:

  - GCMC molecular simulation was applied to model the adsorption of single and binary hydrocarbon systems. Future research in this area should also focus on ternary and quaternary hydrocarbon systems.

  - CO$_2$ adsorption in the carbon-based slit-pores with the presence of other hydrocarbon components is worth investigating. CO$_2$ injection for enhanced coal-bed methane recovery has received considerable attention (Gunter et al., 1997; White et al., 2005; Jessen et al., 2008). Basically, the injected CO$_2$ displaces the sorbed methane. This technology has the potential to be applied as well for enhanced hydrocarbon recovery from shale formations where heavy molecules are trapped in the reservoir in the adsorbed state. Molecular simulations should be coupled with experimental measurements because as observed in Chapter 4, CO$_2$ adsorption caused the permeability of the shale samples to decrease significantly.

  - Molecular simulations have been conducted on slit-pore models with varying sizes. In the future, a pore network that captures the pore size distribution of a shale sample could be modeled.

  - Chapter 5 has focused primarily on carbon-based slit-pores (graphite). As concluded in Chapter 4, clay minerals played a significant role in controlling the adsorption capacity of the shale samples. Therefore, it is worth investigating the adsorption of methane and CO$_2$ in a clay model by molecular simulation techniques. To validate the molecular simulations, the results can be compared with methane and CO$_2$ adsorption measurements by Heller and Zoback (2014) conducted on pure clay minerals.
• Vapor-liquid equilibrium of hydrocarbons in nanopores:
  
  – The GEMC molecular simulation technique could not be applied to study the vapor-liquid equilibrium of pure hydrocarbons in nanopores. However, with some modifications to the molecular simulation algorithm, the method can be applied successfully.
  
  – To study the vapor-liquid equilibrium of pure hydrocarbons in nanopores, the NVT Gibbs ensemble Monte Carlo simulation technique can be applied with the known three trial moves (particle displacement, particle interchange and volume change). However, the volume change for the slit-pore should only be in one direction. That is, the length of the slit-pore can be increased or decreased to exchange volume with the other simulation box. In this case, the size of the slit-pore (i.e. the separation between the two slit walls) will be maintained constant. More details about this simulation scheme can be found in Panagiotopoulos (1987a).
  
  – To study the vapor-liquid equilibrium of binary mixtures in nanopores, the isobaric-isothermal NPT Gibbs ensemble Monte Carlo simulation technique can be applied. In this method, the number of particles $N$, pressure $p$ and temperature $T$ are kept constant. Based on the phase rule, for binary mixtures, two intensive can be specified in advance ($p$ and $T$). To allow for the pressure to maintain constant, one of the simulation boxes has to change its volume. In this case, the volume of the box containing the pore is fixed whereas the volume of the “bulk” box is allowed to fluctuate. More details about this simulation scheme can be found in McGrother and Gubbins (1999).
## Nomenclature

### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>bbl</td>
<td>Barrels</td>
</tr>
<tr>
<td>CCE</td>
<td>Constant composition expansion</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Constant volume depletion</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EOS</td>
<td>Equation of state</td>
</tr>
<tr>
<td>GCMC</td>
<td>Grand canonical Monte Carlo</td>
</tr>
<tr>
<td>GEMC</td>
<td>Gibbs ensemble Monte Carlo</td>
</tr>
<tr>
<td>LB</td>
<td>Lorentz-Berthelot</td>
</tr>
<tr>
<td>LJ</td>
<td>Lennard-Jones</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>MFP</td>
<td>Mean free path</td>
</tr>
<tr>
<td>MMSCF</td>
<td>Million surface cubic feet</td>
</tr>
<tr>
<td>NEMD</td>
<td>Nonequilibrium molecular dynamics</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
</tbody>
</table>
CHAPTER 7. CONCLUSIONS AND FUTURE WORK

PR          Peng-Robinson
PSD         Pore size distribution
PV          Pore volume
PVT         Pressure-volume-temperature
SCF         Surface cubic feet
SEM         Scanning electron microscopy
TC          Thermocouple
TCF         Trillion cubic feet
TOC         Total organic carbon
TraPPE      The transferable potentials for phase equilibria
TVD         True vertical depth
VLE         Vapor-liquid equilibrium
XRD         X-ray diffraction

Greek symbols

\( \alpha \)  Pressure pulse decay exponent
\( \beta \)  Gas compressibility
\( \Delta p \)  Pressure difference between upstream and downstream
\( \Delta p_0 \)  Pressure difference at time = 0
\( \delta \)  Collision diameter of gas molecules
\( \epsilon_{ij} \)  Lennard-Jones well depth
\( \epsilon_{sf} \)  Solid-fluid interaction energy
7.2. FUTURE WORK

$\Lambda$ Thermal de Broglie wavelength

$\lambda$ Mean free path

$\mu$ Viscosity

$\phi$ Porosity

$\rho_c$ Critical density

$\rho_g^{SC}$ Gas density at standard conditions

$\rho_l$ Liquid density

$\rho_v$ Vapor density

$\rho_{ads}$ Adsorbed phase density

$\rho_{bulk}$ Bulk density

$\rho_{gas}$ Gas phase density

$\sigma$ Lennard-Jones size parameter

$\sigma_{eff}$ Effective stress

$\sigma_{go}$ Interfacial tension between the liquid and gas phases

$\tau$ Tortuosity

$\theta$ Wetting angle

**Molecules**

Ar Argon

C$_2$H$_4$ Ethylene

C$_2$H$_6$ Ethane

C$_3$H$_8$ Propane
CH₂  Methylene
CH₃  Methyl
CH₄  Methane

i-C₄H₁₀  i-Butane
N₂  Nitrogen
n-C₄H₁₀  n-Butane
O₂  Oxygen

**Variables**

\( A \)  Cross-sectional area

\( a \)  Equation-of-state parameter

\( b \)  Equation-of-state parameter

\( b_{\text{slip}} \)  Klinkenberg slip factor

\( c \)  Proportionality factor

\( c_m \)  Pore throat compressibility

\( CD \)  Compositional deviation

\( d \)  Molecular diameter

\( d_p \)  Pore diameter

\( f_i \)  Normalized volume fraction of pore size \( i \)

\( h \)  Reservoir thickness

\( k \)  Rock permeability

\( k_\infty \)  Intrinsic permeability
7.2. FUTURE WORK

\( k_B \) Boltzmann constant

\( K_n \) Knudsen number

\( k_o \) Permeability at zero effective stress

\( k_{gas} \) Gas permeability

\( k_{sf} \) Solid-fluid binary interaction parameter

\( L \) Length

\( M \) Molecular weight

\( m_{\text{exp}}^{\text{excess}} \) Excess adsorbed mixed-gas from experiment

\( m_{\text{measured}}^{\text{excess}} \) Measured excess adsorbed mixed-gas

\( N \) Number of molecules

\( n_{\text{ads}}^{\text{absolute}} \) Moles of absolute adsorption

\( n_{\text{ads}}^{\text{excess}} \) Moles of excess adsorption

\( n_i \) Mole fraction of component \( i \)

\( n_{\text{ads},i}^{\text{sim}} \) Adsorbed gas from molecular simulation for pore size \( i \)

\( n_{\text{ads}}^{\exp} \) Adsorbed gas from experiment

\( n_{\text{ads}}^{\text{measured}} \) Measured adsorbed gas

\( n_{\text{ads}}^{\text{sim}} \) Weighted average adsorbed gas from molecular simulation

\( n_{\text{free}} \) Moles of free phase

\( n_{\text{total}} \) Moles of total adsorption

\( P \) Probability

\( p \) Pressure
\( p_c \) Critical pressure
\( p_g \) Pressure in gas phase
\( p_i \) Initial reservoir pressure
\( p_L \) Langmuir pressure
\( p_o \) Pressure in oil phase
\( p_p \) Pore pressure
\( p_{conf} \) Confining pressure
\( p_{cp} \) Pore critical pressure
\( p_{down} \) Downstream pressure
\( p_{eff} \) Effective pressure
\( p_{mean} \) Mean pore pressure
\( p_{up} \) Upstream pressure
\( q \) Gas flow rate
\( R \) Gas constant
\( r \) Radius of the contact curvature
\( r_p \) Pore radius
\( r_{ij} \) Distance between atoms \( i \) and \( j \)
\( S \) Selectivity
\( T \) Temperature
\( t \) Time
\( T_c \) Critical temperature
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\[ T_{cp} \] Pore critical temperature

\[ U(s'^N) \] Energy of new configuration

\[ U(s^N) \] Energy of old configuration

\[ V_L \] Langmuir volume

\[ V_p \] Adsorbed volume at pressure \( p \)

\[ V_R \] Volume of reference cell

\[ V_S \] Volume of sample cell

\[ V_{down} \] Downstream volume

\[ V_{up} \] Upstream volume

\[ X \] Concentration of hydrocarbon component

\[ x \] Mole fraction in the adsorbed phase

\[ y \] Mole fraction in the bulk gas phase

\[ Z \] Compressibility factor
Figure A.1 shows a schematic diagram of the gas-condensate core-flooding experimental apparatus. A data acquisition system and a temperature recorder are used to record the upstream pressure, downstream pressure and the temperature during the experiment. Initially, all the valves and pressure regulators are closed. The procedure to conduct a flow experiment is as follows:

1. Increase the confining pressure to 300 psi using the water pump (valve 16).

2. Vacuum the sample in the core-holder and the flow lines by connecting the apparatus to a vacuum pump through valve 13.

3. After vacuuming the sample, close valve 13 and disconnect the vacuum pump.

4. Increase the confining pressure to approximately 500 psi over the planned injection of the gas mixture.

5. Open valve 1 and valve 3 and use pressure regulator 2 to control the pressure of the piston cylinder containing the gas-condensate mixture.

6. Open valve 4 to monitor the pressure of the gas cylinder. The pressure inside the gas cylinder should be set higher than the intended injection pressure because
the pressure of the gas cylinder will be reduced using pressure regulator 5.

7. Use pressure regulator 5 to control the upstream (injection) pressure. The upstream pressure should be set at the dew point pressure of the gas-condensate mixture in order to insure liquid dropout along the core.

8. When the planned upstream pressure is reached, immediately open down stream valve 15 and use back pressure regulator 14 to control the downstream pressure.

9. If steady-state flow conditions is achieved, vapor sample can be collected during flow. Samples can be collected by simultaneously opening valves 7, 9 and 11 for a few seconds and then closing them. After that, valves 8, 10, and 12 are opened to collect the captured samples in Tedler sampling bags (Figure A.2). Figure A.3 shows a photo of the core-holder with the Tedler sampling bags.

10. Upstream and downstream samples can be collected through valves 6 and 13, respectively.

11. The above procedures are for collecting the samples in the “noncapture” mode. To collect samples in the “capture” mode, valves 4 and 15 are closed and after that samples are collected through the sampling ports as described in step 10.

12. After capturing the sample, disconnect the Tedler sampling bags.

13. The Tedler sampling bags are then connected to the gas chromatgraphy (Figure A.4) to analyze the characterized the captured samples.

14. The tubings that connect the sampling ports to the Tedler sampling bags should be vacuumed for the subsequent samples. To do so, connect the vacuum pump to valves 8. Then, open valve 8 to vacuum the tubing while valve 7 is closed. After that, close valve 8 and disconnect the vacuum pump. This vacuuming procedure is repeated for the other sampling ports.

15. If sampling bags are to be reused, they should always be vacuumed.
Figure A.1: Schematic diagram of the core-flooding experimental apparatus.

Figure A.2: Tedler sampling bag.
Figure A.3: Core-holder with sampling bags.
Figure A.4: Agilent 3000C gas chromatography.
APPENDIX A. GAS-CONDENSATE CORE-FLOODING PROCEDURES
Bibliography


BIBLIOGRAPHY


