Phenomenological Study of Confined Criticality: Insights from the Capillary Condensation of Propane, n-Butane, and n-Pentane in Nanopores

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ABSTRACT: We use the comparison of experimentally measured isotherms for propane, n-bu tane, and n-pentane in 2.90, 4.19, and 8.08 nm MCM-41 to show that the current model for the progression of capillary condensation may not hold true for chain molecules, such as normal alkanes. Until now, the capillary condensation of gases in unconnected, uniformly sized and shaped nanopores has been shown to progress in two distinct stages before ending in supercriticality of the confined fluid. First, at relatively low temperatures in isothermal measurements, the phase change is accompanied by hysteresis of adsorption and desorption. Second, as temperature increases, the hysteresis critical temperature is surpassed, and the phase change occurs reversibly. Although propane followed this progression, we observed a new progression for n-bu tane and n-pentane, in which hysteresis continues into the supercritical region of the confined fluid. We attribute this behavior to the molecular chain lengths of the adsorbates. Through further comparison of observations, adsorption, and critical properties of the adsorbates, we discovered new pressure phenomena of the confined supercritical fluids.

1. INTRODUCTION

Confinement in nanopores is widely known to affect the phase behavior of fluids.1 For example, confinement has been shown to suppress the gas-to-liquid phase transition. Studies of this confinement-induced phase change, called capillary condensation, have led to subsequent investigations into the criticality of the confined fluid and the dependency of capillary condensation on pore size. Regarding the former and assuming isothermal measurements, two critical temperatures have been attributed to nanoconfined fluids: the hysteresis critical temperature, T \text{ch}, and the pore critical temperature, T \text{cp}.

In relatively well-characterized adsorbents with unconnected and uniformly sized nanopores, such as MCM-41, isotherms measured at low temperatures commonly display hysteresis over the capillary condensation phase transition (i.e., the phase change occurs at a lower pressure during desorption than adsorption). Until now, for simple gases, the width of the hysteresis loop was always found to decrease with increasing temperature until coincidence of adsorption and desorption at T \text{ch}. Thus, T \text{ch} is the temperature above which no hysteresis is observed.1,4 Hysteresis has been attributed to different pore filling and emptying mechanisms due to pore wall roughness and physical processes in metastable states (e.g., cavitation) over different temperature ranges.5

Previous studies have indicated that further increases in temperature above T \text{ch} lead to observations of the pore critical temperature, T \text{cp}, which is analogous to the bulk critical temperature, T \text{cp} although it has been experimentally shown to occur below T \text{c} \text{p}.2,6 Whereas two phases, i.e., a vapor-like and a liquid-like phase, may exist below T \text{cp}, only a supercritical-like phase resides within the nanopores above T \text{cp} where observed increases in the density of the confined fluid with pressure are termed continuous pore filling.1,3

Experimentally, Thommes and Findenegg derived the pore critical temperatures of sulfur hexafluoride in controlled pore glass from isochors by initially estimating the critical temperatures from the experimentally measured densities of the confined fluids and then from coexistence curves of the confined fluid. The results from both methods were in agreement.6 More recently, using experimental isotherms for argon,2,7,8 carbon dioxide,5,7,8 nitrogen,7,8 ethylene,7,8 and oxygen2,7,8 in MCM-41, Morishige et al. defined T \text{cp} as the discontinuity in a plot of the slopes of the capillary condensation phase transitions versus the temperatures at which the isotherms were measured.2,7,8 Both of the studies2,5,7,8 show the pore critical temperature to decrease with decreasing pore size; however, the rate with which T \text{cp} decreases with decreases in pore size was observed to depend on the adsorbate—adsorbent pairings. For example, Morishige et al. experimentally found nitrogen, oxygen, ethylene, carbon dioxide, xenon, and argon to follow a linear trend that passed through the origin in a plot of (T \text{c} − T \text{cp})/T \text{c} versus \sigma/\sigma \text{p}, which can be written as the proportionality:9

Received: January 14, 2018
Revised: February 28, 2018
Published: April 3, 2018
propane and only investigated one temperature for each adsorbate and adsorbent.\(^\text{19}\) We conclude with measurements of isotherms for \(n\)-pentane in 2.90 nm MCM-41 at 24.8 °C and two temperatures (48.6 and 72.1 °C) previously not reported in the literature.\(^\text{11}\)

2. MATERIALS AND METHODS

2.1. MCM-41. Three different samples of MCM-41 were obtained from Glantreo, Ltd. MCM-41 is a nanoporous silica characterized by unconnected cylindrical pores with an easily tuned, uniform pore size distribution.\(^\text{20–22}\) The simplicity of the MCM-41 pore geometry precludes pore networking and blocking effects, making it an ideal adsorbent for fundamental studies.\(^\text{23}\) Using a TriStar II 3020 sorption analyzer (V1.01, Micromeritics Instrument Corporation) and Micro-Active software (Micromeritics Instrument Corporation), the three samples were characterized with nitrogen isotherms measured at 77.3 K. Although MCM-41-S and MCM-41-M did not exhibit hysteresis, the H1 hysteresis loop exhibited by MCM-41-L confirmed that the pores in the sample were of uniform size and unconnected.\(^\text{24}\) Ioneva et al. performed a study in which they measured isotherms for propane and \(n\)-butane at temperatures from 5 to 50 °C in three different pore sizes of MCM-41. Although two decades ago, Ioneva et al. performed a study in which they measured isotherms for propane and \(n\)-butane at 283 K in various nanoporous materials that had been templated with different surfactants,\(^\text{19}\) our work provides the first comprehensive data set for both adsorbates, for Ioneva et al. did not display any isotherms for propane and only investigated one temperature for each adsorbate and adsorbent.\(^\text{19}\)

surface

Table 1. Properties of the Adsorbents Determined from Nitrogen Adsorption Isotherms at 77 K

<table>
<thead>
<tr>
<th>sample</th>
<th>BET(^\text{24}) surface area [m(^2)/g]</th>
<th>BJH(^\text{2}H) adsorption pore diameter [nm]</th>
<th>BJH(^\text{2}H) desorption pore diameter [nm]</th>
<th>D-H(^\text{2}H) adsorption pore diameter [nm]</th>
<th>D-H(^\text{2}H) desorption pore diameter [nm]</th>
<th>NLDF(^\text{2}H) pore diameter [nm]</th>
<th>t-plot micropore volume [cm(^3)/g]</th>
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<tr>
<td>MCM-41-S</td>
<td>1043.01</td>
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<td>2.78</td>
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<td>5.47</td>
<td>6.32</td>
<td>5.89</td>
<td>8.08</td>
<td>0.021102</td>
</tr>
</tbody>
</table>

Brunauer–Emmett–Teller\(^\text{25}\) Barrett–Joyner–Halenda\(^\text{26}\) with the Halsey thickness curve and Faas correction. Dollimore–Heal\(^\text{27}\) Non-Local Density Functional Theory\(^\text{8,29}\) for nitrogen at 77.3 K in cylindrical pores with oxide surfaces.

\[(T_c - T_\text{aq})/T_c \sim \sigma/r_p \quad (1)\]

where \(\sigma\) is the Lennard-Jones size parameter and \(r_p\) is the radius of the pore.\(^\text{9–11}\)

In the measurements of adsorption isotherms, there are two degrees of freedom associated with the phase transition of confined pure fluid—temperature and pore size—which means that if both are fixed, then the capillary condensation pressure is well determined. At the critical point, the degrees of freedom reduce to one (cf. the bulk critical point has no degree of freedom; it is fixed for an individual substance). Thus, if in the previous discussion of criticality, temperature, rather than pore size, is held constant, there will also be a critical pore size, \(d_c\) below which supercriticality of fluid also occurs.\(^\text{10,12}\) Therefore, supercriticality in confined pure fluids can occur either below the critical pore size at a fixed temperature or above the critical temperature at a fixed pore size.

In spite of the burgeoning importance of nanopores to fields including biology, medicine, electrical engineering, fuel storage, and petroleum engineering,\(^\text{13–18}\) little beyond the information gathered from the few studies mentioned previously is known about the interplay of temperature, pore size, and criticality.\(^\text{1}\) In the course of our research on the confined-phase behavior of \(n\)-alkanes, which are the main components of natural gas and oil, we present here a study on the confined phase behavior of propane, \(n\)-butane, and \(n\)-pentane to elucidate the relationships among capillary condensation, adsorption, desorption, and the critical properties of the confined fluids. First, we measure isotherms for propane and \(n\)-butane at temperatures from 5 to 50 °C in three different pore sizes of MCM-41. Although two decades ago, Ioneva et al. performed a study in which they measured isotherms for propane and \(n\)-butane at 283 K in various nanoporous materials that had been templated with different surfactants,\(^\text{19}\) our work provides the first comprehensive data set for both adsorbates, for Ioneva et al. did not display any isotherms for propane and only investigated one temperature for each adsorbate and adsorbent.\(^\text{19}\) We conclude with measurements of isotherms for \(n\)-pentane in 2.90 nm MCM-41 at 24.8 °C and two temperatures (48.6 and 72.1 °C) previously not reported in the literature.\(^\text{11}\)
2.2. Adsorbate Dosing. Propane (99%, AirGas, Inc.), n-butane (99%, AirGas, Inc.), and n-pentane (99.8% Alfa Aesar) were used as adsorbates. The adsorbates were introduced to the system using a 6000 series dual cylinder Quizix pump (Chandler Engineering). Housing the fluids in the pump prevented contamination of the fluids with air and allowed for pressurization of the fluids for experiments carried out above 21 °C. Using the pump, propane and n-butane could be pressurized up to 15 and 2.2 bar, respectively.

Isotherms were measured from 5 to 73 °C with temperature control accuracy of ±0.1 °C using a novel gravimetric apparatus.24 Both adsorption and desorption were measured using the static method (without flow). For adsorption, the amount of fluid in the system was increased in stepwise fashion using a series of two-way valves and variable lengths of eighth inch Hastelloy tubing connecting the Quizix pump to the core holder. For desorption, controlled volumes of fluid were vacuumed out of the system using a Welch Duo-Seal Vacuum Pump (Sargent-Welch Scientific Co.). For adsorption and desorption, the system was closed between pressure increase and decrease steps, respectively. Likewise, all doses were allowed to equilibrate for approximately 2 h until the system pressure became constant.24 Detailed descriptions of both the experimental apparatus and procedure, including extensive error analysis, can be found in Barsotti et al.24

3. RESULTS AND DISCUSSION

3.1. Determination of Capillary-Condensation Pressure. The isotherms for propane and n-butane in all three adsorbents are presented in Figure 2. The abrupt changes in adsorption at the high-pressure ends of the isotherms, if shown, are the bulk condensation. The changes at intermediate pressures can be the confined-phase transition (condensation or evaporation) or continuous filling or emptying without phase transition. Continuous filling and emptying only occur above \( T_{cp} \).
As shown in Figure 2, these changes were not always sharp but occurred continuously over a range of pressures. In the literature, the absence of an exact phase-change pressure for subcritical confined fluid is most commonly attributed to imperfections of the adsorbent, such as pore wall roughness and pore-size distribution. This necessitates the determination of a pressure over the phase transition to represent the capillary-condensation ($P_{cd}$) or evaporation pressure ($P_{de}$) at temperatures below $T_{cp}$.

At temperatures above $T_{cp}$ we may assign a pressure to represent the continuous filling, namely the maximum-pore-filling ($P_{ma}$) or emptying ($P_{md}$), pressure. Of course, prior to determining $T_{cp}$, one cannot tell with confidence whether capillary condensation, capillary evaporation, continuous pore filling, or continuous pore emptying occurs, particularly at relatively high temperatures. While $T_{cp}$ is discussed in the next section, we show here that the same method may be used to determine $P_{cd}$, $P_{de}$, $P_{ma}$ and $P_{md}$. Until Section 3.2, we use $P_m$ as an umbrella term to represent these four pressures and include the subscripts “a” and “d” to represent adsorption and desorption, respectively.

Nearly all available experimental studies identify capillary condensation and capillary evaporation as the midpoint of the confined phase transition. However, the midpoint is a nonphysical observation, the determination of which requires highly subjective user-defined limits for the slope of capillary condensation. Therefore, we instead determine $P_m$ as the inflection point of the abrupt increase in the isotherms. Unlike the midpoint, the inflection point is a physical phenomenon representing the maximum condensation or evaporation rate. It was determined by fitting the Lorentzian function to the first derivative of the amount adsorbed with respect to pressure ($dm/dP$) across the abrupt increase. The derivative $dm/dP$ was determined from the experimental data using the central difference:

$$\frac{dm}{dP} = \frac{m_{i+1} - m_{i-1}}{P_{i+1} - P_{i-1}}$$  \hspace{1cm} (2)

where $m$ and $P$ indicate the data for amount adsorbed (grams) and pressure (bars), respectively.

The pressure-dependent first derivative from eq 1 was then fitted to a Lorentzian function:

$$\Lambda(P) = \frac{\omega \gamma^2}{(P - P_m)^2 + \gamma^2} + C$$  \hspace{1cm} (3)

where $\omega$ is the peak height, $\gamma$ is the half width of the peak at its half-maximum height, $C$ is a constant that controls the baseline of the function, and $P_m$ is the inflection-point pressure. Note that the maximum value of the Lorentzian, $\max[\Lambda(P)]$, is the sum of $\omega$ and $C$. An example of the Lorentzian fit is given in Figure 3, where the Lorentzian was fit to desorption data for n-butane in MCM-41-S at 49.5 °C and adsorption data for propane in MCM-41-M at 5.3 °C. $P_m$ values for the isotherms are shown in Table 2.

To analyze the relationships between $P_m$ and the pore sizes of the adsorbents, $P_m$ is plotted versus pore size for both adsorbates in Figure 4. For propane and n-butane, $P_m$ was found to increase both with increasing temperature and pore size, as has been commonly shown in the literature; however, the pressures for n-butane show greater linearity across the range of pores than propane. Comparison of the data points at 20.8 °C shows the trend for propane to be concave up, while that for n-butane is nearly linear.

3.2. Pore Critical Temperature. First, the pore critical temperatures of propane were determined. Based on the relationship between the slope of a given isotherm to the super- or subcriticality of the adsorbate, we determined $T_{cp}$ using the method introduced by Morishige et al. \(^2\) in which the reciprocal of the average slope of the whole pore condensation or continuous filling step is plotted against temperature. $T_{cp}$ was then determined as the discontinuity in the slopes of lines fit to the data points at lower and higher temperatures, as shown in Figure 5. However, instead of using the reciprocal of the average slope, for better accuracy, we use the reciprocal of the maximum.
of the Lorentzian. Although it is a different input, $\max[\Lambda(P)]$ is consistent with the average slope used by Morishige et al., as both account for the phase transition or continuous filling and the background adsorption or desorption, which in the case of $\max[\Lambda(P)]$ are included in $\omega$ and $C$, respectively. The reciprocal is employed simply to provide better resolution in Figure 5.

The discontinuity temperatures, broadly termed $T_{\text{co}}$, obtained for propane are presented in Table 3. These are the pore critical temperatures only if the pore size is above its critical value $d_c$. As shown in Table 3, the discontinuity temperatures increased with pore size, reflecting the well-known behavior of pore critical temperatures.7,11 Therefore, all three pore sizes are above $d_c$ and the temperatures represent $T_{\text{cp}}$. Note that the propane discontinuity temperatures were obtained from the adsorption data because the hysteresis loop was found to disappear below $T_{\text{co}}$ as shown in Figure 2.

Subsequently, the reciprocal of the maximum of the Lorentzian for $n$-butane in MCM-41-S and MCM-41-M was plotted in Figure 6. Because closure of the hysteresis loop was not observed for either adsorbent, both adsorption and desorption data are plotted in Figure 6. As shown, MCM-41-S exhibited two different temperatures for adsorption and desorption: $T_{\text{co}}$ was 25.4 °C and $T_{\text{co}}$ was 28.3 °C. Conversely, $T_{\text{co}}$ was not observed for MCM-41-M, while $T_{\text{co}}$ was found to be 41.3 °C. Although, a plot is also shown for MCM-41-L, not enough data points were available to accurately determine the discontinuity point for MCM-41-L, due to the maximum pressure of 2.2 bar for the experiments with $n$-butane, as discussed in Section 2. Therefore, we exclude $T_{\text{co}}$ for MCM-41-L from further analyses. Throughout this work, the reliability of this method of determining $T_{\text{co}}$ from discontinuities in the maximum of the Lorentzian was found to depend on the amount of available experimental data.

### 3.3. Hysteresis Critical Temperature

$T_{\text{ch}}$ was directly observed from Figure 2 to be the temperature above which hysteresis disappeared. For propane, $T_{\text{ch}}$ was approximately 20.8 °C in MCM-41-L and 5.3 °C in MCM-41-M and MCM-41-S. Considering the pore critical temperatures determined in Section 3.2, this verifies that propane follows the expected progression of confined phase behavior from hysteretic capillary condensation to reversible capillary condensation and then to supercriticality.

For $n$-butane, $T_{\text{ch}}$ was not observed in any of the pore sizes. Comparison of the hysteresis of propane to $n$-butane is shown in Figure 7, in which $P_{\text{ch}}$ is plotted versus temperature. As shown in Figure 7a, the adsorption and desorption pressures for propane coincided before $T_{\text{ch}}$. Conversely, in Figure 7b, no coincidence was observed for $n$-butane even above $T_{\text{ch}}$. Therefore, we term the observation of hysteresis above $T_{\text{ch}}$ or below $d_c$ supercritical hysteresis, which has continuous pore emptying along the desorption branch in addition to continuous pore filling along the adsorption branch.

Our observation of supercritical hysteresis is, to the best of our knowledge, the first in MCM-41 and should not be confused with the prolonged hysteresis that has been documented for natural adsorbents, such as shale rock,34 and microporous adsorbents, such as aerogels35 and metal organic frameworks,36 which are characterized by highly complex, and in many cases irregular, pore networks. For example, in shale rock, supercritical, or otherwise unexpected hysteresis, is attributed to pore blocking effects.34 In microporous materials, hysteresis is attributed to pore blocking,35 diffusion,36 and structural instabilities of the adsorbent, which commonly result in flexibility36 and permanent deformation38 of the pore network. In our study, the adsorbent is less complex with uniformly sized and shaped nanopores that are not interconnected, while it is also considerably more rigid than typical microporous adsorbents, such as aerogels.38 Thus, the observed phenomenon may not be attributed to pore blocking effects or to significant structural instabilities.

The exact same adsorbent packs were used for all experiments herein; thus, we infer one major cause of supercritical hysteresis to be the molecular chain length of the adsorbate. The longer carbon chain length of $n$-butane may be more prone to greater deformation in confinement, such as bond angle bending. To test the presence of supercritical hysteresis as a consequence of molecular chain length, we subsequently measured isotherms of

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**Table 2.** $P_{\text{m}}$ Values for All Isotherms Shown in Figure 2<sup>a</sup>

<table>
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<tr>
<th>adsorbate</th>
<th>adsorbent</th>
<th>temperature [°C]</th>
<th>$P_{\text{m}}$ [bar]</th>
<th>$P_{\text{m}}$ [bar]</th>
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<td>49.5</td>
<td>1.90</td>
<td>1.75</td>
</tr>
<tr>
<td>n-butane</td>
<td>MCM-41-L</td>
<td>8.7</td>
<td>0.99</td>
<td>0.90</td>
</tr>
<tr>
<td>n-butane</td>
<td>MCM-41-L</td>
<td>13.4</td>
<td>1.24</td>
<td>-</td>
</tr>
<tr>
<td>n-butane</td>
<td>MCM-41-L</td>
<td>20.8</td>
<td>1.47</td>
<td>1.35</td>
</tr>
<tr>
<td>n-butane</td>
<td>MCM-41-L</td>
<td>28.2</td>
<td>1.77</td>
<td>1.72</td>
</tr>
</tbody>
</table>

The values were determined by fitting the Lorentzian to the experimental data for each isotherm. The subscripts “a” and “d” designate adsorption and desorption, respectively.

DOI: 10.1021/acs.langmuir.8b00125
Langmuir 2018, 34, 4473−4483
The supercriticality of \( n \)-pentane in MCM-41-S is inferred from Figure 9, where the adsorption branches for \( n \)-pentane in MCM-41-S and MCM-41-M at 24.8 °C are plotted. The proximity of the values of \( P_m \) is due to the similar pore sizes. The smaller slope in the smaller pore at \( P_m \) and the absence of sharp turning near the low-pressure end of the slope is the signature of continuous filling, and thus supercriticality. The corresponding plot for propane in Figure 9 confirms this inference. Therefore, \( n \)-pentane is supercritical in MCM-41-S at all temperatures in Figure 8, i.e., MCM-41-S is below \( d_c \) which strongly suggests the existence of supercritical hysteresis. Note that a third plot for \( n \)-butane is also shown in Figure 9, although its interpretation is less straightforward due to the ambiguities associated with the approximation of \( T_{cp} \) from \( T_{cLd} \) and \( T_{cAd} \) in Figure 6.

Even at 72.1 °C, which is more than 50 °C above the supercritical boundary of \( n \)-pentane, hysteresis occurred. Furthermore, the width of the hysteresis loop in the supercritical region is observed to increase with increasing temperature. These results confirmed the persistent occurrence of continuous filling in the adsorption branch and continuous emptying in the desorption branch at high temperatures.

**3.4. Comparison of the Phase Diagrams.** Comparison of the confined and bulk phase behavior of the three adsorbates is shown in Figure 10. Bulk saturation pressures from NIST\(^{39}\) were used to benchmark the accuracy of our work, while the bulk critical points were useful for comparison to the values of \( T_{cp} \) determined from the experimental data herein. NIST reports the critical pressures \( (P_c) \) and temperatures \( (T_c) \) for propane, \( n \)-butane, and \( n \)-pentane to be 96.75 °C and 42.5 bar, 151.85 °C and 38.0 bar, and 196.65 °C and 33.6 bar, respectively.\(^{39}\) Using curves fit to the bulk and confined critical temperatures, the critical boundaries of the fluids were estimated as shown in

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**Figure 4.** Comparison of the behavior of \( P_m \) for (a) propane and (b) \( n \)-butane. The circles, triangles, and squares indicate the measurements taken in MCM-41-S, MCM-41-M, and MCM-41-L, respectively. Filled symbols are adsorption, and empty symbols are desorption.
Figure 10 by fitting the experimental data to a quadratic polynomial. Because only the critical pore size was known for n-pentane, a full hypothetical critical boundary was not plotted for it.

Despite the need for more data in other pore sizes to achieve quantitative accuracy in the estimated critical boundaries, it can still be seen qualitatively that the subcritical region of the fluid (i.e., the area between the bulk saturation pressure and the critical boundary) shrinks as molecular chain length increases. Equation 1 confirms this trend, when written in terms of $T_{cp}/T_c$:

$$1 = \frac{T_{cp}}{T_c} \sim \frac{\sigma}{r_p}$$  

(4)

For two different adsorbates, indicated by the subscripts 1 and 2, in the same pore size,

Table 3. Discontinuity Temperatures Estimated from the Experimental Data Using the Lorentzian Function

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>adsorbent</th>
<th>$T_{cp}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>propane</td>
<td>MCM-41-S</td>
<td>30.0</td>
</tr>
<tr>
<td>propane</td>
<td>MCM-41-M</td>
<td>35.3</td>
</tr>
<tr>
<td>propane</td>
<td>MCM-41-L</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>
If $\sigma_1 > \sigma_2$, then
\[
\frac{1 - (T_{cp,1}/T_{c,1})}{1 - (T_{cp,2}/T_{c,2})} > 1
\]
which results in
\[
T_{cp,1}/T_{c,1} < T_{cp,2}/T_{c,2}
\]
This finding may indicate that hydrocarbons in real nanoporous systems, such as shale reservoirs, may also exist as supercritical fluids. In terms of oil and gas production, this could invalidate many of the equations of state currently used for predicting phase diagrams.

Further comparison of the data measured for the fluids in confinement also indicates that for adsorbates where supercritical hysteresis is observed, two different phase diagrams may be
necessary to describe the phase behavior of the adsorbate: one for adsorption and one for desorption. For alkanes, specifically, this may revolutionize the way that shale gas and oil reservoirs are produced. Because long-chain hydrocarbons constitute a considerable fraction of both natural gas and oil, the supercritical hysteresis observed herein could carry over to the reservoir condition. At reservoir conditions, adsorption–desorption hysteresis implies differences in fluid injection and production pressures. This may necessitate the use of different phase diagrams to govern decision making regarding both. The phase diagram of the reservoir fluid is one of the main inputs for dynamic reservoir simulation. Because equations of state can only capture the equilibrium phase transition, metastability in either adsorption or desorption may complicate modeling efforts. We intend to focus our future work on studies of supercriticality and capillary condensation in both synthetic and natural nanopores in order to further investigate these implications.

4. CONCLUSIONS

We measured isotherms for propane and n-butane in three different pore sizes of MCM-41 and determined the corresponding phase-transition pressures. The pressures of both adsorbates in confinement showed proportionality to the pore size.

The pore critical temperatures of propane and n-butane were estimated by determinations of the discontinuity points of the maximum condensation (or evaporation) rates of the isotherms across the entire range of measured temperature. However, the discontinuity points for adsorption and desorption differed for n-butane in smaller pores and were termed \( T_{cx} \) and indicated new phenomena that have not been previously reported.

In comparing the hysteresis critical temperatures of both adsorbates as well as their values for \( T_{cx} \), propane was found to follow the commonly observed progression of capillary condensation from hysteresis to reversibility and then to supercriticality. However, n-butane displayed entirely new behavior in which no hysteresis critical temperature was observed, despite the supercriticality of the confined fluid. Thus, we hypothesize that long-chain n-alkanes may exhibit hysteresis above their pore critical temperature or below their critical pore size simply due to the length of these molecules. We tested this hypothesis through further isotherm measurements for n-pentane in the smallest pore size where it is known to be supercritical and found it, too, to exhibit hysteresis. We term the presence of hysteresis above the pore critical temperature or below their critical pore size supercritical hysteresis, which consists of the common continuous pore filling along the adsorption branch and the new continuous pore emptying along the desorption branch.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b00125.

Tables of all the isotherm data presented in Figures 2 and 8 (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of Saudi Aramco, Hess Corporation, and the School of Energy Resources and the College of Engineering and Applied Science at the University of Wyoming. We also thank Mr. Evan Lowry of the Piri Research Group at the Center of Innovation for Flow Through Porous Media at the University of Wyoming for his insightful discussions.

NOMENCLATURE

C constant that controls the baseline of the Lorentzian
dc critical pore size
m amount adsorbed
P pressure
Pc critical pressure of the bulk fluid
Pcap capillary condensation pressure
Pev capillary evaporation pressure
Pmp maximum pore filling or emptying pressure equal to the inflection point of the isotherm
Pmmax maximum pore filling pressure; it is the capillary condensation pressure if below the pore critical temperature or above the critical pore size
Pmd max maximum pore emptying pressure; it is the capillary evaporation pressure if below the pore critical temperature or above the critical pore size
Tc critical temperature of the bulk fluid
Tch hysteresis critical temperature
Tpc pore critical temperature
Tcx temperature representing a discontinuity in a plot of the inverse of the maximum of the Lorentzian versus temperature. It is the pore critical temperature when the pore size is larger than the critical pore size.
γ half width of the Lorentzian peak at its half-maximum height
Λ(P) Lorentzian
σ Lennard-Jones size of a molecule
ω peak height of the Lorentzian

REFERENCES


