Supercritical CO\textsubscript{2} and CH\textsubscript{4} uptake by

illite-smectite clay minerals

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Abstract

Clay minerals abound in sedimentary formations and the interaction of reservoir

gases with their sub-micron features has direct relevance to many geo-energy appli-
cations. The quantification of gas uptake over a broad range of pressures is key towards

assessing the significance of these physical interactions on enhancing storage capacity

and gas recovery. We report a systematic investigation of the sorption properties of

three source clay minerals – Na-rich montmorillonite (SWy-2), illite-smectite mixed

layer (ISCz-1), and illite (IMt-2) – using CO\textsubscript{2} and CH\textsubscript{4} up to 30 MPa at 25 to 115 °C.

The textural characterization of the clays by gas physisorption indicates that micro-
pores are only partly accessible to N\textsubscript{2} (77 K) and Ar (87 K), while larger uptakes are

measured with CO\textsubscript{2} (273 K) in the presence of illite. The supercritical excess sorption

experiments confirm these findings, while revealing differences in uptake capacities that

originate from the clay-specific pore size distribution. The Lattice Density Functional

Theory (LDFT) model describes accurately the measured sorption isotherms by using

a distribution of properly weighted slit pores and clay-specific solid-fluid interaction

energies, which agree with isosteric heats of adsorption obtained experimentally. The

model indicates that the maximum degree of pore occupancy is universal to the three
clays and the two gases, and it depends solely on temperature, reaching values near
unity at the critical temperature. These observations greatly support the model’s pre-
dictive capability for estimating gas adsorption on clay-bearing rocks and sediments.

Introduction

The physical interactions between clay minerals and supercritical gases, particularly CO$_2$
and CH$_4$, have received increasing attention in the context of geological carbon storage
and unconventional hydrocarbon recovery. Clay minerals are very common in geological
formations (≈30 wt% of all sedimentary rocks), and are present in large fractions in shales
(≈30 to 90 wt%) and oil sands (up to ≈80 wt%). The presence of clays contributes
largely to sub-micron properties of these rocks, including the presence of nanoscale pores with
width less than 100 nm. One significant physical interaction within clay nanopores is gas
adsorption, which creates a dense adsorbed phase that increases gas storage capacity and
affects the gas transport through the pore space. In a typical sandstone reservoir (20 %
porosity with 10 to 18 wt% clay content), sorption of CO$_2$ by clay minerals can increase
CO$_2$ storage capacity by up to 20 to 30 % relative to the capacity associated with residual
trapping. Sorption of CO$_2$ on the mudstones that form the majority of caprocks has
shown to enhance the sealing efficiency and retention potential from retarded diffusion of
the gas. The excess uptake by adsorption in hydrocarbon shale reservoirs contributes to
20 to 80 % of the total Gas-In-Place (GIP). This level of uptake indicates the potential
not only for increased CO$_2$ capacity, but also for enhanced release of hydrocarbon gases
induced by the preferential adsorption of CO$_2$.

The abundance of clay minerals in shale and mudstones determines their petrophysical
properties, such as porosity, permeability, or wettability, to a great extent, often allowing
their approximation as quartz-clay systems. The adsorption properties of these rocks are
also attributed to their clay mineralogy, which tends to be dominated by smectite, illite, and illite-smectite mixed layers (I-S clay minerals). Notably, new experimental
evidence indicates that CO\textsubscript{2} can access both the internal (i.e. the interlayer space between basal surfaces) and external surface area of clay minerals irrespective of whether a swelling (e.g. smectite\textsuperscript{26,32–35}) or a non-swelling (e.g. illite) clay\textsuperscript{16} is considered. These observations have prompted research on quantifying the adsorption properties of clay minerals at subsurface conditions, where most gases are in their supercritical state. These experimental data are key towards evaluating the sealing stability and capacity of potential storage sites upon introduction of supercritical CO\textsubscript{2}\textsuperscript{36} or to devise injection policies that increase hydrocarbon production from unconventional reservoirs.\textsuperscript{25}

The available data sets for supercritical adsorption on I-S clay minerals and rocks dominated by them remain quite scattered, with only a limited number of studies reporting measurements at multiple temperatures and with different gases. The lack of systematic investigations has resulted in conflicting observations in terms of uptake capacity of source clays\textsuperscript{37} and its relation with the textural properties, such as micropore volume and surface area.\textsuperscript{28,38,39} Moreover, there is a lack of validation of experimental data at reservoir pressure and temperature against suitable adsorption models that account for the complex pore structure of clay minerals, and the specific fluid-fluid and solid-fluid interactions.\textsuperscript{40–42} In this context, the use of a simplistic modeling approach based on the Langmuir equation is problematic as the basic assumptions of the model,\textsuperscript{43} such as monolayer adsorption or no adsorbate-adsorbate interactions, are not fulfilled in clay nanopores.

The objective of this study is to quantify the adsorption of supercritical gases on dry I-S clay minerals over a broad range of pressures and across various temperatures, thereby establishing a baseline for future studies on clays and clay-rich rocks with more complex features. To this aim, we measured a comprehensive set of unary adsorption and desorption isotherms of CO\textsubscript{2} and CH\textsubscript{4} on three source clay minerals, SWy-2 (Na-rich montmorillonite from Wyoming, USA), ISCz-1 (illite-smectite mixed layers from Slovakia), and IMt-2 (illite from Montana, USA) up to 30 MPa at 25, 50, 80 and 115°C. The structural characterization of the clays was performed via physisorption analysis using N\textsubscript{2}, Ar, and CO\textsubscript{2}, following the
most recent IUPAC guidelines. The supercritical adsorption data were described using the Lattice Density Functional Theory (LDFT) model, which uses the pore volumes and pore size distributions (PSD) obtained from the independent textural analysis of the clays as input parameters. The model provides insight into the uptake of supercritical CO\textsubscript{2} and CH\textsubscript{4} within clay nanopores, including pore size-dependent adsorption behaviors and filling capacities. These features are key towards describing supercritical adsorption on clay minerals and clay-bearing rocks that are characterized by a wide range of micro- and mesoporosity.

Materials and Experimental Methods

The clay samples, SWy-2, ISCz-1, and IMt-2, have been sourced from the Source Clay Repository of the Clay Minerals Society (Virginia, USA), and were ground to particles smaller than 50 \( \mu \text{m} \). The samples were degassed \textit{ex situ} at 200 \( ^\circ \text{C} \) for at least 12 h prior to the measurements. At this degassing temperature, strongly bound water molecules are moved from within the nano-structure of clay minerals\textsuperscript{44,46} resulting in reproducible measurements of surface areas\textsuperscript{45} The pure gases were obtained from BOC (Surrey, UK) at purities of 99.9992\% for N\textsubscript{2}, 99.999\% for Ar and He, 99.995\% for CO\textsubscript{2}, and 99.5\% for CH\textsubscript{4}. The critical properties of the adsorbates are reported in the Supporting Information (SI).

Gas Adsorption Experiments

The textural properties of the clay minerals were characterized by low-pressure adsorption and desorption experiments using N\textsubscript{2} (77 K) and Ar (87 K) for micro- and mesopore analysis, and CO\textsubscript{2} (273 K) for further micropore analysis as recommended by the most recent IUPAC guidelines.\textsuperscript{46} The experiments were performed in the pressure range of \( 3 \times 10^{-7} \) to \( 1 \times 10^{-1} \) MPa using Autosorb iQ (Quantachrome Instruments, Florida, USA) equipped with the CryoSync module, which enables achieving cryogenic temperatures above the standard boiling point temperature of N\textsubscript{2} (77 K). For experiments with CO\textsubscript{2}, a liquid circulating ther-
mostat (Julabo CORIO CD-200F, Seelbach, Germany) was used to control the temperature of a bath containing a water-ethylene glycol (50 vol\%) mixture. The high-pressure adsorption measurements of CO$_2$ and CH$_4$ have been performed in the pressure range of 0.02 to 30 MPa at 25, 50, 80 and 115°C using a gravimetric sorption analyzer with a magnetic suspension balance (IsoSORP HPII) from Rubotherm (Bochum, Germany). The measured quantity in these experiments is the excess amount adsorbed, which represents the amount of adsorbate found in the pore space in addition to the amount that would be present as a bulk supercritical fluid in the same pore space at the given pressure and temperature. The details of the set-up, experimental protocols, and the working principles of the magnetic suspension balance have been described in our recent work and are again summarized in the SI.

Modeling

LDFT Model for Supercritical Adsorption

The LDFT model for single-component adsorption was used in this study to describe the excess adsorption of supercritical CO$_2$ and CH$_4$. Briefly, this model discretizes the internal space of adsorbents using a distribution of properly weighted model pores of simple geometries (slit pores in this study) so that fluid molecules form a regular lattice pattern (see Figure S6). The lattice theory was first introduced by Ono and Kondo and later formalized by Aranovich and Donohue, enabling its application to supercritical adsorption systems. The LDFT model has been adapted to estimate the adsorbent-adsorbate interaction energies and to examine the adsorbed layer densities. The capability of the model highlighted in this study is the incorporation of pore size distributions, making it suitable for understanding adsorption on clay minerals characterized by both micro- and mesoporosity. The LDFT model has also compared well with the grand canonical Monte Carlo (GCMC) simulations, showing its reliability and efficiency with less computation time.
The lattice occupancy of the \( j \)th layer inside a slit pore with \( J \) lattice layers can be calculated from solving the following set of nonlinear equations:

\[
0 = \epsilon_{sf} + \epsilon_{ff}(z_2\theta_{j+1} + z_1\theta_j - z_0\theta_b) + kT \ln \left( \frac{\theta_j(1 - \theta_b)}{\theta_b(1 - \theta_j)} \right) \quad \text{For} \quad j = 1 \quad (1)
\]

\[
0 = \epsilon_{ff}(z_2\theta_{j-1} + z_2\theta_{j+1} + z_1\theta_j - z_0\theta_b) + kT \ln \left( \frac{\theta_j(1 - \theta_b)}{\theta_b(1 - \theta_j)} \right) \quad \text{For} \quad 1 < j < J \quad (2)
\]

\[
0 = \epsilon_{sf} + \epsilon_{ff}(z_2\theta_{j-1} + z_1\theta_j - z_0\theta_b) + kT \ln \left( \frac{\theta_j(1 - \theta_b)}{\theta_b(1 - \theta_j)} \right) \quad \text{For} \quad j = J \quad (3)
\]

where \( \epsilon_{sf} \) and \( \epsilon_{ff} \) are surface-adsorbate and adsorbate-adsorbate interaction energies, respectively, between nearest neighbors; \( z_2, z_1, \) and \( z_0 \) (3, 6, and 12) are coordination numbers of the assumed hexagonal lattice configuration; \( \theta_j \) and \( \theta_b \) are degrees of lattice occupancy in the \( j \)th layer and bulk, respectively; \( k \) is the Boltzmann’s constant; and \( T \) is temperature.

The excess amount adsorbed is calculated as follows:

\[
n_{\text{LDFT}}^{\text{ex}} = c_{\text{sat}} \sum_{i=1}^{I} \frac{v_{\text{pore},i}}{J_i} \sum_{j=1}^{J} \left[ \rho_j(\rho_c, \rho_{\text{max}}, \theta_j) - \rho_b(\rho_c, \rho_{\text{max}}, \theta_b) \right] \quad (4)
\]

where \( v_{\text{pore},i} \) is the specific pore volume of lattice pores with \( J_i \) layers and \( I \) is the number of lattice pore classes used in the model. The latter are obtained from discretization of experimental PSDs (see Figure S5 and S7). To convert lattice occupancy into density, a mapping function is used that is parameterized in terms of the critical density, \( \rho_c \), and maximum packing density, \( \rho_{\text{max}} \). The calculated values of \( n_{\text{LDFT}}^{\text{ex}} \) are corrected by a saturation factor, \( c_{\text{sat}} \), to account for packing inefficiencies. For each clay mineral, values of \( c_{\text{sat}} \) (adsorbate- and temperature-dependent), \( \rho_{\text{max}} \) and \( \epsilon_{sf} \) (both adsorbate-dependent) are obtained by fitting Equation 4 to the experimental data (see SI for details on the numerical solution procedure and the minimization problem).
Isosteric Enthalpy of Adsorption

The isosteric enthalpy of adsorption, $\Delta h$, is commonly used to quantify the strength of adsorbate-adsorbent bonding, thereby revealing useful insight on the nature of the adsorbent and adsorbed phase. To this aim, the experimental sorption isotherms are described using the following form of the virial equation:

$$\ln(P/n) = \frac{1}{T} \sum_{i=0}^{m_a} a_i n^i + \sum_{i=0}^{m_b} b_i n^i$$  \hspace{1cm} (5)

where $P$ is pressure, and $a_i$ and $b_i$ are temperature-independent virial coefficients. Equation 5 can be applied to excess quantities directly, but only up to moderate densities. In this study, we have used the density range, $\rho_b \leq 0.1 \times \rho_{\text{liq}}$, corresponding to about 5 MPa for CO$_2$ and 8 MPa for CH$_4$. Under these conditions, GCMC simulation results on shale rocks confirm that there is no significant deviation between excess and absolute quantities. The Henry’s constant is estimated from the zeroth order coefficients, $K_H = \exp[-(a_0/T + b_0)]$, while the isosteric heat of adsorption at zero coverage is obtained from the temperature dependence of $K_H$:

$$|\Delta h_0| = R \left[ \frac{d \ln(K_H)}{d(1/T)} \right]$$  \hspace{1cm} (6)

where $R$ is the ideal gas constant. Accordingly, the isosteric heat of adsorption as a function of loading can be estimated from the adsorption isosteres:

$$|\Delta h(n)| = -R \left[ \frac{d \ln(P)}{d(1/T)} \right]_n = -R \sum_{i=0}^{m} a_i n^i$$  \hspace{1cm} (7)
Results and Discussion

Textural Properties of I-S Clay Minerals

Clays contain nanopores of varied size, including micro- (< 2 nm), meso- (2 to 50 nm) and macropores (> 50 nm). With reference to Bergaya and Lagaly\(^6\), these are largely associated with the so-called interlayer regions, as well as voids created through the assembly of clay mineral particles and their aggregates. The physisorption isotherms of \(\text{N}_2\) (77 K), \(\text{Ar}\) (87 K), and \(\text{CO}_2\) (273 K) for SWy-2, ISCz-1, and IMt-2 are shown in Figure 1. The shapes of both

![Adsorption (closed symbols) and desorption (open symbols) isotherms of (a) \(\text{N}_2\) at 77 K and (b) \(\text{Ar}\) at 87 K on the clay minerals. The inset plots show the filling of the micropores for \(P/P^o < 0.01\). (c) Adsorption isotherms of \(\text{CO}_2\) at 273 K up to 760 Torr \((P/P^o \approx 0.03)\). The lines are to guide the eye. The values of \(P^o\) for \(\text{N}_2\) (at 77 K), \(\text{Ar}\) (at 87 K), and \(\text{CO}_2\) (at 273 K) are approximately 760, 760 and 26141 mmHg, respectively.

\(\text{N}_2\) and \(\text{Ar}\) isotherms for all three clay minerals indicate the presence of a cavitation-induced H3 hysteresis loop that closes around \(P/P^o \approx 0.4\); this type of isotherms implies that these materials consist of a fair amount of small mesopores\(^6\) and is characteristic of slit-shaped pores,\(^6\) which in clays are formed by the stacking of platy mineral particles. The steeper increase of the isotherms measured on ISCz-1 for \(P/P^o > 0.01\) suggests a broader mesopore distribution as compared to SWy-2 and IMt-2. The inset plots of Figure 1a and b reveal
appreciable adsorbed amounts in micropores ($P/P^o < 0.01$) with SWy-2 showing the largest amount adsorbed compared to the other two clays. This trend is better identified through the measurements with CO$_2$ (Figure 1c), for which the strength of adsorption increases in the order of ISCz-1 < IMt-2 < SWy-2.

These experimental observations are verified by the pore volumes of the clay minerals computed using the non-local density functional theory (NLDFT, for N$_2$ and Ar) and summarized in Table 1. The corresponding PSDs are reported in the SI (Figure S5). The total pore volume of the clay minerals increases in the order IMt-2 < ISCz-1 < SWy-2 with values estimated using Ar as the probing gas being systematically larger (20 to 40% for the total pore volume) than those obtained from N$_2$ measurements across the entire PSD (micro-, meso-, and macropores). Notably, ISCz-1 shows the largest mesopore volume and a broader distribution of mesoporosity, while SWy-2 and IMt-2 show larger micropore volumes (contributing to 8% and 16% of the total pore volume, respectively). These observations highlight that the textural properties of mixed layer clay particles (ISCz-1) are not the result of the simple combination of the properties of the constituent layers.

The specific surface areas (SSA) obtained by the application of the BET equation are also summarized in Table 1. A good agreement is observed between estimates from N$_2$ and Ar measurements (6 to 9% relative difference), which also show a positive correlation with the measured total pore volume. The estimated SSA values are consistent with those reported in the literature, but significantly smaller than those obtained by liquid adsorption ($\sim100$ m$^2$/g for illite and $\sim500$ m$^2$/g for montmorillonite). While it is known that micropores in clays are only partly accessible to N$_2$, we show here for the first time that the same is true for Ar, thereby confirming that kinetics restrictions in very narrow micropores are present at cryogenic temperatures (77 and 87 K). Interestingly, an excellent agreement is found for IMt-2 between crystallographic skeleton density values ($\rho_{\text{cryst}} = 2.780$ g/cm$^3$) and values measured by He gravimetry ($\rho_{\text{sk}} = 2.784$ g/cm$^3$). However, a significant discrepancy is observed for SWy-2 ($\rho_{\text{sk}} = 2.709$ g/cm$^3 < \rho_{\text{cryst}} = 2.798$ g/cm$^3$), indicating micropore
Table 1: Summary of the textural properties of SWy-2, ISCz-1, and IMt-2. The methods applied to estimate these properties are described in the SI.

<table>
<thead>
<tr>
<th>Property</th>
<th>Probe gas</th>
<th>Unit</th>
<th>SWy-2</th>
<th>ISCz-1</th>
<th>IMt-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume†</td>
<td>N₂</td>
<td>cm³/g</td>
<td>0.080</td>
<td>0.078</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>cm³/g</td>
<td>0.110</td>
<td>0.101</td>
<td>0.044</td>
</tr>
<tr>
<td>Micro pore</td>
<td>N₂</td>
<td>cm³/g</td>
<td>0.007</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>cm³/g</td>
<td>0.008</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>CO₂†</td>
<td>cm³/g</td>
<td>0.009</td>
<td>0.006</td>
<td>0.007</td>
</tr>
<tr>
<td>Mesopore</td>
<td>N₂</td>
<td>cm³/g</td>
<td>0.055</td>
<td>0.062</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>cm³/g</td>
<td>0.059</td>
<td>0.064</td>
<td>0.026</td>
</tr>
<tr>
<td>Macropore</td>
<td>N₂</td>
<td>cm³/g</td>
<td>0.018</td>
<td>0.015</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>cm³/g</td>
<td>0.043</td>
<td>0.034</td>
<td>0.014</td>
</tr>
<tr>
<td>Specific surface area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET</td>
<td>N₂</td>
<td>m²/g</td>
<td>36.59 ± 0.06</td>
<td>32.38 ± 0.10</td>
<td>21.66 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>m²/g</td>
<td>33.38 ± 0.14</td>
<td>30.38 ± 0.16</td>
<td>19.80 ± 0.06</td>
</tr>
<tr>
<td>Skeletal density</td>
<td>He</td>
<td>g/cm³</td>
<td>2.709 ± 0.006</td>
<td>2.689 ± 0.009</td>
<td>2.784 ± 0.004</td>
</tr>
</tbody>
</table>

† NLDFT on zeolite cylindrical pore model
‡ GCMC on carbon slit pore model

inaccessibility to He. This peculiar pore accessibility in clays is also reflected in the micropore volumes obtained from CO₂ isotherms (using GCMC), which are 10% (SWy-2), 80% (IMt-2), and 100% (ISCz-1) larger than the values obtained using Ar. These observations highlight the importance of conducting physisorption analyses with multiple probing gases to correctly represent the pore volumes of each pore class – micropores by CO₂ and mesopores by N₂ and Ar – in developing adsorption models that use such textural information.

Supercritical Adsorption Isotherms of CO₂ and CH₄

The excess adsorption and desorption isotherms of supercritical CO₂ and CH₄ on SWy-2, ISCz-1, and IMt-2 at four temperatures (25 to 115 °C) up to 30 MPa are presented in Figure 2 as a function of the bulk fluid density. The full set of experimental data (excess amount adsorbed, measured density, and pressure) are also reported in the SI (Figure S9 and Table S2 – 5). For the three clays and for both gases, the excess isotherms are positive indi-
Figure 2: Supercritical adsorption (closed symbols) and desorption (open symbols) of CO$_2$ (squares) and CH$_4$ (circles) on (a) SWy-2, (b) ISCz-1, and (c) IMt-2 up to 30 MPa at 25, 50, 80 and 115°C. The inset plot of (c) shows the desorption points of IMt-2 under 1 mol/L. The solid lines are the LDFT model fits. The following fitted model parameters were obtained for SWy-2, ISCz-1, and IMt-2, respectively: $\epsilon_{st}/k = -1131.3, -898.3$ and $-1277.2$ K for CO$_2$ and $-859.5, -771.1$ and 969.7 K for CH$_4$, and $\rho_{\text{max}} = 26.95, 24.78$ and 25.43 mol/L for CO$_2$ and 26.45, 28.78 and 24.13 mol/L for CH$_4$.

cating that sorption contributes to gas storage inside clay nanopores throughout the entire pressure range investigated. While all the measured isotherms possess the non-monotonic behavior that is characteristic of excess adsorption data, they also reveal subtle differences that originate from the clay-specific PSD discussed above. SWy-2 and ISCz-1 show similar uptake capacities and their isotherm shapes resemble that of a mesoporous material, such as silica gel, where the gradual increase in the adsorbed amount reaches a maximum at $\rho_b \geq 5$ mol/L. However, the larger fraction of mesopores in ISCz-1 is also responsible for the characteristic pore-filling mechanism that produces a stronger dependence of the adsorbed amount on temperature compared to SWy-2 (particularly evident for the CO$_2$ isotherms measured at 50 and 80°C). Smaller CO$_2$ and CH$_4$ uptakes are observed for IMt-2, reflecting its smaller total pore volume. However, the large fraction of micropores of IMt-2 results in a steep initial increase of the measured isotherms that is indeed typical of microporous materials. Interestingly, the isotherms of IMt-2 also show moderate, but not negligible,
hystereses for both CO$_2$ and CH$_4$ at all temperatures. Previous observations of hysteresis at supercritical conditions have been limited to swelling clay minerals, such as smectite, the microstructure of which is sensitive to water content. Because IMt-2 is non-swelling, we attribute this observation to strongly attached CO$_2$ and CH$_4$ that are only removed at sufficiently high temperatures. The supercritical desorption isotherms indeed show sorbed amounts of both gases that persist between 10 to 50 $\mu$mol/g at approximately 1.5 bar (inset of Figure 2c). Recent findings have revealed CO$_2$ interlayer trapping in muscovite (used as a proxy for illite) following incubation at 12 MPa and 90 $^\circ$C. While they are not sufficient to define the controlling mechanisms for this phenomenon, our sorption results support these observations and extend them to CH$_4$ while covering a broader range of temperature and pressure.

**Adsorption Model**

The LDFT model incorporates the materials’ PSDs and correctly describes the experimental isotherms as can be seen from the solid lines in Figure 2. Both adsorption and desorption data were used in fitting the isotherms of SWy-2 and ISCz-1, but only desorption data were used for IMt-2, because of the hysteresis loops and the limited amount of adsorption data. The values of the fitted parameters, $\epsilon_{sf}$ and $\rho_{\text{max}}$, are given in the caption of Figure 2. The attainment of $\rho_{\text{max}}$ corresponds to the complete filling of the lattice, at which the adsorbed density is equal to the bulk density. Comparable values were found for all three clay minerals for both CO$_2$ and CH$_4$, namely $\rho_{\text{max}} = 25.72 \pm 1.23$ mol/L for CO$_2$ and $\rho_{\text{max}} = 25.45 \pm 2.33$ mol/L, corresponding to $\rho_{\text{max}}/\rho_c \approx 2.5$. These values agree well with those previously reported from the application of the LDFT model for CO$_2$ and CH$_4$ on activated carbon, as well as with the liquid densities at triple point CO$_2$ and standard boiling point of CH$_4$ (Table 2). However, as indicated by GCMC simulations of supercritical adsorption in shale, adsorbed phase densities are not constant and may differ from the saturated liquid densities. The LDFT model shows a similar behavior as summarized in Ta-
Table 2: Comparison of the calculated adsorbed densities of CO$_2$ and CH$_4$ with their respective liquid densities.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$P$ (bar)</th>
<th>$T$ ($^\circ$C)</th>
<th>$\rho_{\text{liq}}$ (mol/L)</th>
<th>$P$ (bar)</th>
<th>$T$ ($^\circ$C)</th>
<th>$\rho_{\text{GCMC}}$ (mol/L)</th>
<th>$\rho_{\text{LDFT}}$ (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>5.187</td>
<td>-56.56</td>
<td>26.78</td>
<td>150</td>
<td>60</td>
<td>25.53</td>
<td>22.09</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.013</td>
<td>-161.48</td>
<td>26.33</td>
<td>150</td>
<td>60</td>
<td>17.42</td>
<td>15.26</td>
</tr>
</tbody>
</table>

† The area between the first two peaks of a density profile inside slit pores with structureless carbon surfaces simulated by GCMC
‡ The average density of the first two adsorbed layers

Table 2, where the average density values of the first two adsorbed layers in each clay mineral are reported for both CO$_2$ and CH$_4$. While for CO$_2$ the obtained values are about 20% below the saturated liquid density, the estimates for CH$_4$ are even lower (40%), reflecting the equilibration with a bulk phase that has a lower density under the same temperature and pressure conditions. For CH$_4$ on illite, adsorbed densities obtained by GCMC simulations (13.1 to 14.3 mol/L) reveal that this phenomenon persists even at a higher pressure (30 MPa at 90$^\circ$C).

**Adsorption Energetics**

The Henry’s constants, $K_H$, were obtained by describing the experimental data with Equation 5. The plots of ln($K_H$) against $1/T$ (Figure 3a) show good fits to linear regression ($R^2 = 0.967 - 0.996$) and the discernible linear regions of the virial plots (Figure S8a – c) validate the suitability of the approach to estimate the Henry’s constants. The data are summarized in Table 3 together with estimates of $\Delta h_0$ calculated from Equation 6 and the selectivity of CO$_2$ to CH$_4$ ($S = K_{H,CO_2}/K_{H,CH_4}$).

The values of $|\Delta h_0|$ decrease from SWy-2 to IMt-2, consistent with estimates by Ji et al. for CH$_4$ on rocks each dominated by clays in this study. While $|\Delta h_0|$ is expected to increase with decreasing pore diameter IMt-2 shows the lowest value of $|\Delta h_0|$ despite its larger fraction of micropores. This suggests that adsorption energetics in clays may be additionally
affected by other factors, such as the surface chemistry, as indicated by the observed decrease of \( |\Delta h_0| \) with increasing illite content\(^{53}\). These values are also on the lower end of the range indicated by the general approximation proposed for gas physisorption,\(^{80}\) i.e. \( |\Delta h_0| < 1.5 - 2|\Delta h_{\text{vap}}| \), where \( |\Delta h_{\text{vap}}| \) is the latent heat of condensation (10.3 kJ/mol for CO\(_2\) at 273.15 K and 8.2 kJ/mol for CH\(_4\) at 112 K\(^{81}\)). The estimates of \( \Delta h_0 \) obtained from the LDFT model in the Henry’s region (up to 0.3 bar) do not reveal any specific trend among the three clays (\( |\Delta h_{0,\text{LDFT}}^{\text{CO}_2}| \approx 16.3 \pm 0.8 \) kJ/mol and \( |\Delta h_{0,\text{LDFT}}^{\text{CH}_4}| \approx 13.1 \pm 0.5 \) kJ/mol). Most significantly, they compare well with their experimental counterparts and the observed discrepancy for IMt-2 is likely due to the model’s description of the large sorption amounts in the low-pressure regions that cause hystereses, as discussed earlier. Notably, the ratio of CO\(_2\) to CH\(_4\) is correctly described by the model, i.e. \( \Delta h_{0,\text{CO}_2}/\Delta h_{0,\text{CH}_4} \approx \Delta h_{0,\text{CO}_2}^{\text{LDFT}}/\Delta h_{0,\text{CH}_4}^{\text{LDFT}} \approx 1.2 \pm 0.1 \).

Figure 3b indicates that \( |\Delta h| \) increases as a function of loading by approximately 5 to 6 kJ/mol and 3 to 4 kJ/mol for CO\(_2\) and CH\(_4\), respectively. This behavior is the result of increasing lateral adsorbate interactions on relatively homogeneous surfaces\(^{73,82,83}\) of clay minerals as opposed to heterogeneous shales that show decreasing \( |\Delta h| \) for CO\(_2\) and CH\(_4\)\(^{53}\).
Figure 3: (a) ln($K_H$) plotted against the inverse temperature, $1/T$, for CO$_2$ (closed symbols) and CH$_4$ (open symbols). The dashed lines are linear fits to obtain the isosteric enthalpy of adsorption at zero coverage. (b) Isosteric enthalpy of adsorption of CO$_2$ (solid lines) and CH$_4$ (dotted lines) plotted against excess amount of adsorption.

Notably, we do not observe the expected enhancement in the change of $|\Delta h|$ with loading due to molecular polarity, as CO$_2$ and CH$_4$ outline a similar behavior. This may partly be due to the limited range of densities used in the analysis.

The analysis of the adsorption energetics indicate that the three clay minerals are appropriate for enhanced CH$_4$ recovery through the injection of CO$_2$ as the released heat from CO$_2$ adsorption will lead to desorption of CH$_4$. The thermodynamic properties suggest that SWy-2 is most suited among the three clay minerals in this study for the application of CO$_2$ storage and enhanced recovery. The adsorption enthalpy indicates the strongest interaction with CO$_2$ and the highest average selectivity of CO$_2$ over CH$_4$. It should be highlighted that these conclusions apply to a thoroughly dried clay. While in actual geological formations clays are hydrated, the effect of water on the total extent of adsorption of reservoir gases (and, accordingly, energetics) remains uncertain. Experimental studies have shown that water may either decrease the adsorption capacity by competitively occupying sorption sites or increase it by providing more accessible micropore volume, as a result of clay swelling.
**CO$_2$ and CH$_4$ in Clay Nanopores**

The LDFT model provides insight into the uptake of supercritical CO$_2$ and CH$_4$ within clay nanopores including pore size-dependent adsorption behaviors and into the degree of pore occupancy of the supercritical adsorbed phase. Figure 4 shows the CO$_2$ excess adsorption isotherm on SWy-2 at 50$^\circ$C produced by the LDFT model with the individual contributions from each pore class, and Figure 4b – d show the lattice occupancy profiles for four selected pore classes. It can be seen that the adsorption process is controlled by pore filling (significant density enhancement above that of the bulk phase) up to small mesopores ($J = 6$, < 2.5 nm); for pores larger (upward and downward triangles), multiple layers are formed as the bulk density increases, while the center of the pore remains filled with bulk supercritical fluids. This observation of pore size-specific behavior compares well with the supercritical sorption mechanism shown by GCMC simulations$^{77,86,87}$ inside slit pores of clay minerals, in which the filling of adsorbates occurs for micropores while the adsorption layers on the surface dominate.

Figure 4: (a) CO$_2$ adsorption isotherm at 50$^\circ$C on SWy-2 (solid line) with isotherms of individual pores (dashed lines) in color. The pore sizes of the individual isotherms are indicated by the color scale. (b) – (d) Lattice occupancy profiles corresponding to three density values highlighted in (a) – maximum amount of adsorption, $n_{ex max}$, and points before and after $n_{ex max}$ with the same amount of excess adsorption – for the lattice pores with 3 (1.2 nm, square), 6 (2.4 nm, circle), 19 (7.6 nm, upward triangle), and 31 (12.4 nm, downward triangle) layers.
the adsorption behavior for larger mesopores. The observed difference in the extent of fluid densification inside pores suggests that supercritical adsorption on clay mineral surfaces should not be assessed using a single pore system.

Figure 5 shows the pore saturation factors, $c_{\text{sat}}$, plotted against the reciprocal of reduced temperature, $T_c/T$. It can be seen that $c_{\text{sat}}$ increases linearly with values approaching unity as the critical temperature of the fluid is reached. This reduction as $T$ increases beyond $T_c$ suggests that the adsorbed fluid does not occupy the entire space of the pore volume at these conditions, and $c_{\text{sat}}$ accounts for the temperature-dependent variability of the packing density in the LDFT model. Bénard and Chahine\textsuperscript{53} and Do\textsuperscript{58} similarly explained the phenomenon by attributing it to the compressibility and thermal expansion characteristics of the adsorbed phase that becomes greater above the critical temperature. It should be noted that the value of $c_{\text{sat}}$ for CO$_2$ on ISCz-1 at 50ºC is above 1 although it is considered to be physically implausible by the definition provided in this study. This again highlights the difficulty to accurately measure the PSD of clay minerals and may indicate the enhanced accessibility
of gases, such as CO$_2$, in clay nanopores. The most relevant observation is that the three clay minerals and the two gases outline a single characteristic line (Figure 5) suggesting that the degree of occupancy depends solely on temperature. This observation of temperature dependence drawn from multiple samples greatly extends the predictive capability of the model for supercritical adsorption on clay-bearing geosorbents.

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**Supporting Information Available**

This information is available free of charge via the Internet at http://pubs.acs.org.

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