Methane and CO₂ Adsorption Capacities of Kerogen in the Eagle Ford Shale from Molecular Simulation

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CONSPECTUS: Over the past decade, the United States has become a world leader in natural gas production, thanks in part to a large-fold increase in recovery from unconventional resources, i.e., shale rock and tight oil reservoirs. In an attempt to help mitigate climate change, these depleted formations are being considered for their long-term CO₂ storage potential. Because of the variability in mineral and structural composition from one formation to the next (even within the same region), it is imperative to understand the adsorption behavior of CH₄ and CO₂ in the context of specific conditions and pore surface chemistry, i.e., relative total organic content (TOC), clay, and surface functionality. This study examines two Eagle Ford shale samples, both recovered from shale that was extracted at depths of approximately 3800 m and having low clay content (i.e., less than 5%) and similar mineral compositions but distinct TOCs (i.e., 2% and 5%, respectively). Experimentally validated models of kerogen were used to estimate CH₄ and CO₂ adsorption capacities. The pore size distributions modeled were derived from low-pressure adsorption isotherm data using CO₂ and N₂ as probe gases for micropores and mesopores, respectively. Given the presence of water in these natural systems, the role of surface chemistry on modeled kerogen pore surfaces was investigated. Several functional groups associated with surface-dissociated water were considered. Pressure conditions from 10 to 50 bar were investigated using grand canonical Monte Carlo simulations along with typical outgassing temperatures used in many shale characterization and adsorption studies (i.e., 60 and 250 °C). Both CO₂ and N₂ were used as probe gases to determine the total pore volume available for gas adsorption spanning pore diameters ranging from 0.3 to 30 nm. The impacts of surface chemistry, outgassing temperature, and the inclusion of nanopores with diameters of less than 1.5 nm were determined for applications of CH₄ and CO₂ storage from samples of the gas-producing region of the Eagle Ford Shale. At 50 bar and temperatures of 60 and 250 °C, CH₄ adsorption increased across all surface chemistries considered by 60% and 2-fold, respectively. In the case of CO₂, the surface chemistry played a role at both 10 and 50 bar. For instance, at temperatures of 60 and 250 °C, CO₂ adsorption increased across all surface chemistries by 6-fold and just over 2-fold, respectively. It was also found that at both 10 and 50 bar, if too low an outgassing temperature is used, this may lead to a 2-fold underestimation of gas in place. Finally, neglecting to include pores with diameters of less than 1.5 nm has the potential to underestimate pore volume by up to 28%. Taking into consideration these aspects of kerogen and shale characterization in general will lead to improvements in estimating the CH₄ and CO₂ storage potential of gas shales.

INTRODUCTION

The production of natural gas from shale gas and tight oil plays comprises approximately half of the natural gas production in the U.S. today. According to the U.S. Energy Information Administration (EIA), production from these opportunities is expected to rise from approximately 14 trillion cubic feet (Tcf) in 2015 to up to 30 Tcf in 2040, which will represent nearly 70% of total gas production in 2040. Most natural gas today is produced through hydraulic fracturing, often in combination with horizontal drilling. This process involves forcing water-based fracturing fluids under high pressure from a wellbore against the rock formation until fracturing occurs. The water contains micrometer-sized particles known as proppant that fill the expanding fracture, thereby “propping open” the fracture network. This allows the transport of hydrocarbons from the formation back to the wellbore and ultimately to the surface for recovery. According to the U.S. EIA, in 2000, 26 000 hydraulically fractured wells producing 3.6 billion cubic feet per day (Bcf/d) constituted less than 7% of U.S. production.

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while by 2015 the number of these wells had increased to 300,000 at a production rate of more than 53 Bcf/d, representing nearly 70% of U.S. production. As more is learned about these complex systems, the techniques for recovering unconventional natural gas are becoming more refined and ultimately cost-effective even in a climate of low gas prices.

A question remains as to whether following the depletion of these unconventional shale gas and tight oil reservoirs, might they be used as reliable storage opportunities for CO2. Because of the lack of an economic incentive for companies to reliably store CO2 in subsurface formations, a first step may be to mimic the CO2 utilization path that has taken place with enhanced oil recovery (EOR) today. Investigation of the interaction and subsequent adsorption of CO2 within these complex natural systems will provide greater insight into the feasibility of using CO2 as an enhanced recovery fluid in addition to whether the depleted reservoirs may serve as a permanent sink for CO2. Gas shales are complex structural and mineralogical systems comprising a heterogeneous mixture of calcite, quartz, pyrite, clay, and kerogen. Their composition impacts the “fracability” of the rock and hence their ability to produce oil and gas. Lessons learned from enhanced coalbed methane (ECBM) recovery have shown that when CO2 is used to enhance the recovery of natural gas because of its preferred adsorption within the coal matrix, the CO2—coal carbon interaction changes the geomechanical attributes of the coal. For example, Hagin and Zoback found that CO2 injection into samples from the Powder River Basin induced a constitutive change in coal properties; specifically, these samples became more viscous, less elastic, and less brittle in response to CO2 adsorption. Studies carried out by Vishal et al. measuring the permeability of subcritical CO2 in naturally fractured Indian bituminous coal over a range of down-hole stress conditions were also consistent with these findings. Depending upon the mineralogical composition of the gas shale, there is a risk that the injection of CO2 may similarly lead to difficulty in fracturing. However, shales that are rich in carbonate and quartz lead to a formation that is more brittle and potentially more “fracable” than those that are higher in clays and kerogen, for instance. The brittleness index (BI), which attempts to quantify shale play brittleness as a function of mineral composition and diagenesis, is typically expressed as a ratio of quartz (or quartz and dolomite) to total soft (clay and kerogen) and hard (quartz, feldspar, carbonates) components. In particular, Eagle Ford Shale falls into this category with average carbonate and quartz contents of 60% and 18%, respectively. It is important to understand the nature of the interaction of CO2 with the kerogen components of shale to determine its impact on the geomechanical properties of the rock.

Named for the town of Eagle Ford, Texas, the Eagle Ford Shale is a late-Cretaceous formation that extends from the Mexican border in south Texas to the East Texas Basin and is approximately 50 miles wide and 400 miles long. With an average thickness of 250 feet, it is underlain by the Buda Limestone and Woodbine Formation and is succeeded by the Austin Chalk at a depth of approximately 4000 to 12,000 ft. Although historically the Eagle Ford Shale was viewed as a source rock for the Austin Chalk play, there has been significant activity recently. Depending on the location, the wells drilled in the reservoir tap into the dry-gas, gas-condensate, and oil windows. Oil production peaked in 2015 at approximately 1.7 million barrels per day and decreased to just over 0.9 millions barrels per day in 2016. Natural gas production also peaked in 2015 at approximately 7000 million cubic feet per day (Mcf/d) and steadily declined to just under 6000 Mcf/d at the end of 2016.

The unconventional nature of these complex systems is due to the fact that the hydrocarbons reside in a nanoporous matrix composed of heterogeneous distributions of clay, kerogen, calcite, quartz, and feldspar. This is different from conventional hydrocarbon systems, which are composed primarily of sand-sized grains, where the grain spacing gives rise to pores with sizes on the order of tens of micrometers that are largely connected. Simply put, it is significantly easier to recover hydrocarbons from well-connected micrometer-sized pore networks than from isolated nanopore networks. In addition, the added complexity associated with the high clay and kerogen composition can impact the rock rheological attributes and subsequent “fracability” of the rock, making recovery even more cumbersome. Coarse-grained models have been used in the past to assist in the prediction of recovery from conventional sources, but it has become widely accepted that these techniques fail at the nanoscale since they rely on Darcy flow, which is not the transport mechanism at the nanoscale, where fluid—fluid interactions compete with pore wall—fluid interactions. This leads to the application of molecular-level models or statistical mechanics to assist in elucidating the chemical physics that determines the adsorption and transport properties of hydrocarbons in gas shales. These results may be used to accurately determine the gas capacities of these reservoirs once they are depleted and to assist in defining the interplay of CO2 with subsurface fluids.

The composition of the Eagle Ford Shale varies throughout the formation depending on whether one is in the gas-producing or oil-producing regime. The oil-producing region corresponds to an average clay content of 11% with a breakdown of 25% illite + mica, 43% illite/smectite, and 32% kaolinite. The gas-producing region corresponds to an average total clay content of 20% with a breakdown of 36% illite + mica, 53% illite/smectite, 7% kaolinite, and 5% chlorite and a total organic content (TOC) between 2 and 6%. The two Eagle Ford samples under investigation in the current work are consistent with the composition from the gas-producing part of the formation. Their mineral composition will be discussed later in this Account in greater detail, but these samples contain less than 5% illite and have TOCs of 2 and 5%, respectively. Because of the low clay content of these samples in particular, the focus of the models in this work are on kerogen. This is a suitable first step since the kerogen is the hydrocarbon source and likely where CO2 would be stored if storage in these depleted formations becomes a viable option.

Molecular simulations of CO2 adsorption in the organic matrix using pure and functionalized graphene surfaces as a proxy for kerogen show that the adsorption capacity is strongly correlated with the surface heterogeneity and pore size distribution. Surface functionalities can interact selectively with the quadrupole moment of CO2 an effect that has been shown to be enhanced in smaller pores (d < 2.0 nm), as overlapping wall potentials combine to further stabilize CO2 in the pore volume. Heller and Zoback examined the role of adsorption in the production from gas shales sourced from the Barnett, Marcellus, Montney, and Eagle Ford plays as well as for pure carbon, used as a proxy for kerogen. The Barnett sample displayed the largest adsorption capacity as well as the highest TOC (5.3%) among all of the samples, while the Eagle Ford sample was least adsorptive but not lowest in TOC (1.8%).
This discrepancy was attributed to the difference in clay composition (4.9% for Eagle Ford vs 51.4% for Marcellus) indicating that clay may play an important role in adsorption. Furthermore, the CO₂ adsorption capacity was 2−3 times greater than the CH₄ adsorption capacity on all of the samples. This observation is consistent with many reported values of the exchange ratio, i.e., the molar ratio of CO₂ that is anticipated to displace CH₄.¹¹ This parameter largely dictates the CO₂ storage potential in a material. For example, the CO₂ storage potential in coal has been estimated to lie in the range of 260 to 1480 gigatons (Gt), where the low and high estimates reflect conservative and optimistic ratios for CO₂/CH₄ exchange. This exchange ratio typically ranges from 2:1 to 3:1 but can reach as high as 5:1 for supercritical CO₂ (scCO₂) and varies with depth and shale composition.

Several studies have argued that the potential for CO₂ storage in ECBM may become self-limiting as a result of a loss of permeability caused by CO₂-injection-induced coal matrix swelling.¹²,¹³ However, it has been determined that the magnitude of swelling varies roughly linearly with the magnitude of absorption of CO₂ within the organic matter. Thus, as the adsorption on gas shales is approximately an order of magnitude less than that observed on coals, the observed swelling strain should be at least an order of magnitude smaller.¹⁰

Since the exchange ratio is instrumental in predicting CO₂ storage potential in shales, it is important to describe a reliable method for estimating the gas in place (GIP). Reservoirs that produce both gas and condensate are typically difficult to describe, as condensate can drop out as the reservoir pressure falls below the dew point. However, the shale samples examined in this study fall within the "dry-gas window," and GIP estimates can be approached via simple gas equations of state. Procedures for GIP estimates have been outlined by the United States Geological Survey (USGS);¹⁴ however, discrepancies in GIP estimates can be linked to several factors. Historically, overestimates have been attributed to a failure to account for the volume consumed by the sorbed gas. Correction for this “double counting” can be done by subtracting out the free gas volume taken up by the adsorbed gas (termed the Gibbs correction, or excess adsorption).¹⁵ The excess adsorption (nₑ) can be calculated from the absolute loading (nₐ), the bulk-phase gas density (ρₐ), and the volume occupied by the bulk gas (Vₐ):¹⁶

\[ nₑ = nₐ - \frac{Vₐ}{ρₐ} \]

More difficult to treat are underestimations, as these are likely caused by inadequate characterization of the porosity of the material, leading to an undermeasurement of the volume due to the nanopores.

GAS ADSORPTION AS AN IMAGING TOOL FOR DETERMINING PORE SIZE DISTRIBUTION

Low-pressure gas adsorption (LPGA) has been established as an effective technique to measure International Union of Pure and Applied Chemistry (IUPAC) micropores (<2 nm), mesopores (2−50 nm), and some macropores (>50 nm).¹⁷ The strength of LPGA methods lies in using the resulting isotherm data to calculate pore capacities, surface areas, and pore size distributions (PSDs) with mathematical models such as nonlocal density functional theory (NLDFT) or quenched solid density functional theory (QSDFT). These models account for adsorbent pore-filling mechanisms that significantly improve material characterization because they account for the interactions between adsorbent surfaces and adsorbate gases. Material characterization based on techniques such as the Barrett−Joyner−Halenda (BJH) method can underestimate pore characteristics by as much as 20−30% as they do not account for these interactions in micropores and mesopores with sizes of less than approximately 10 nm.¹⁶ A surface adsorbent must be selected to approximate kerogen when using DFT methods. As organic matter such as kerogen has been established as the primary source of shale porosity⁸,¹⁹ by studies such as that by Kuila et al.,¹⁰ who used LPGA results in conjunction with X-ray diffraction (XRD) and field-emission

![Probe gas isotherms for two Eagle Ford samples, EF1 (squares) and EF6 (circles). The adsorption and desorption branches are represented by solid and open symbols, respectively.](image-url)
scanning electron microscopy to validate the significance of organic matter for pore capacities, graphitic carbon has been established as an effective approximation to represent the surface adsorbent for DFT methods. Using CO₂ as an adsorbate at 273 K with a Quantachrome Autosorb IQ2 instrument results in access to pores with sizes of 0.3 to 1.5 nm, while using N₂ and Ar at 77 and 87 K, respectively, results in access to pores ranging from at least 1.5 nm to approximately 33 nm for N₂ and 27 nm for Ar on a carbon sorbent. Detailed information regarding surface area measurements on nanoporous materials can be found in the thorough review by Thommes and Cychosz.21

Two Eagle Ford samples were chosen for the current investigation and are termed EF1 and EF6 throughout this Account. The TOCs of the shale samples were measured by removing all of the inorganic carbon by acid digestion. Inorganic carbonates were removed by repeatedly adding 40 mL of HCl (1 N) to the samples until no effervescence was observed under a microscope. The samples were placed in an oven at 60 °C for approximately 4 h between successive HCl treatments. Once no effervescence was detected, the samples were dried at 40 °C for at least 96 h. The dried samples were processed on a Carlo Erba NA 1500 Series 2 elemental analyzer that combusts the samples at approximately 1020 °C with pure oxygen. The sample compositions were determined by collecting X-ray diffractiongrams on a Rigaku model CM2029 powder X-ray diffractometer. Diffractograms were collected over the 2θ range from 5° to 70° using a Cu Kα X-ray source. Distinct diffraction peaks were used to match given mineral phases with peak identifications from the National Institute of Standards and Technology (NIST) database. The EF1 sample was obtained from a core that was extracted from a depth of 3864 m. The XRD analysis showed a mineral breakdown of approximately 12% quartz, 86% calcite, and less than 5% illite and a TOC of approximately 2%. The EF6 sample was extracted from a depth of 3890 m and has a mineral breakdown of approximately 24% quartz, 70% calcite, and less than 5% illite and a TOC of just over 5%.

Figure 1 shows nitrogen isotherms (adsorption and desorption branches) and CO₂ adsorption isotherms for samples EF1 and EF6, while Figure 2 shows the combined PSD using both CO₂ and N₂ as probe gases. CO₂ allows access to pores with diameters of less than 1.5 nm, while N₂ allows access to pores with diameters between 1.5 and 30 nm. Close examination of the pore volume data obtained from CO₂ adsorption indicates that EF1 with a TOC of 2% has a cumulative pore volume of 0.008 cm³/g and cumulative surface area of 21 m²/g in the range of pore sizes from 0.3 to 1.5 nm, while EF6 with a TOC of 5% has a cumulative pore volume of 0.006 cm³/g and cumulative surface area of 16 m²/g in the same pore size region. The N₂ adsorption experiments revealed a cumulative pore volume of 0.02 cm³/g and surface area of 10 m²/g for EF1 and a cumulative pore volume of 0.03 cm³/g and surface area of 15 m²/g for EF6 in the range of pore sizes from 3 to 30 nm. In the case of EF1, if CO₂ had not not been used to complete the PSD analysis, nearly 28% of the nanopore volume and just over 50% of the active surface area would have been neglected. In the case of EF6, approximately 15% of the nanopore volume and 70% of the active surface area would have been neglected. Clearly, relying solely on N₂ for determination of the nanopore volume would lead to a significant underestimation of the total pore volume, which may significantly impact the estimates for GIP in addition to the CO₂ storage potential.

The pore size distribution data can be used in conjunction with grand canonical Monte Carlo (GCMC) simulation results to predict adsorption isotherms. Here the individual pore contributions are approximated by integration of the differential pore volume distribution curve over discrete regions, where the limits of integration straddle the targeted pore size. For example, the contribution for a 0.7 nm pore would be

\[ q_{0.7} = \int_{0.65 \text{ nm}}^{0.75 \text{ nm}} V(d) \, dx \]

The adsorption isotherm is predicted as a weighted sum of individual pore densities:

\[ q_{\text{simulated}} = \sum_i v_i \rho_i \]

where \( \rho_i \) represents the simulated pore density and the sum is taken over all pore sizes \( i \), where \( i \) spans 0.35, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.8, 2.2, 2.8, 3.4, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 12.0, 14.0, 16.0, 18.0, and 20.0 nm. The PSD was truncated at 20.0 nm, as it has been determined that excess...
adsorption for larger pore sizes is considered negligible and can instead be approximated by the bulk gas density under the conditions of interest.

**IMPACT OF SURFACE CHEMISTRY ON ADSORPTION CAPACITY**

Fundamentally, the adsorption capacity is a measure of the relative intermolecular forces (and their magnitudes) present in sorbate–sorbent and sorbate–sorbate interactions. These interactions can be roughly classified into two categories: dispersion–repulsion interactions and electrostatic interactions, which are connected to the surface chemistry through the following relationships. Dispersion–repulsion forces are described by the Lennard-Jones (LJ) potential:

\[ V(r) = 4\epsilon \left( \frac{\sigma_1}{r} \right)^{12} - \left( \frac{\sigma_1}{r} \right)^6 \]

where \( \epsilon \) denotes the depth of the potential well and \( \sigma \) represents the finite distance at which the interparticle potential reaches zero. For interactions between unlike particles, Lorentz–Berthelot mixing rules are employed, i.e., \( \epsilon_{12} \) is represented as the geometric mean of \( \epsilon_1 \) and \( \epsilon_2 \) and \( \sigma_{12} \) as the arithmetic mean of \( \sigma_1 \) and \( \sigma_2 \). The electrostatic interaction is a more complicated function of several contributions,

\[ \phi_{\text{elec}} = \phi_E + \phi_i + \phi_\text{M} \]

where the energy contributions on the right-hand side correspond to (from left to right) polarization, field-dipole, and field-gradient quadrupole. An additional contribution from sorbate–sorbate interactions on the surface may be included at high coverage.

The surface chemistries considered within this Account include the pure graphitic surface, a hydrated monovacancy, a hydroxyl group, and a carboxyl group (Figure 3). These functionalities were chosen to be representative of the actual chemical composition of the organic matrix of gas shale based on the known presence of water vapor within the organic matrix, knowledge of the water vapor–matrix chemical interaction, and support from experimental investigations in the literature. As per the physical descriptions previously discussed, CO₂ and CH₄ will interact via dispersion–repulsion forces according to the parameters outlined in Table 1. Furthermore, electrostatic interactions will occur between the surface and CO₂ as a result of the CO₂ quadrupole moment \((-13.71 \times 10^{-30} \text{ C m}^2)\) and to a lesser extent between the surface and CH₄ via the polarization contribution (the quadrupole moment is absent in CH₄). Additionally, since the polarizabilities of CO₂ and CH₄ are similar (ca. 2.64 \( \times 10^{-22} \) and 2.6 \( \times 10^{-24} \) cm³, respectively), differences in sorbate uptake can be attributed to the field-gradient quadrupole contribution, a condition that forms the basis for selective CO₂ uptake.

**Comparison of CH₄ and CO₂ Adsorption at 60 and 250 °C**

The adsorption of CH₄ and CO₂ were investigated at temperatures of 60 and 250 °C, which are common outgassing temperatures used for shale characterization and testing. Outgassing a shale sample at 60 °C only partially removes some of the smaller hydrocarbons and free water within the pores, while outgassing at an intermediate temperature of 110 °C removes most of the free water and further outgassing at a temperature of 250 °C is sure to remove all of the free adsorbrates in the pores, including water and hydrocarbons. An example of this is shown in Figures S1 and S2 in the Supporting Information. Both Ar and CO₂ were used as probe gases to investigate the pore size distribution at 60, 110, 200, and 250 °C. There is a clear trend associated with increasing pore volume and outgassing temperature. The liquid-to-vapor transition for water at 60 °C is approximately 20 kPa (150 Torr); therefore, under a vacuum of 0.01 Torr, which is a typical outgas setting for the Autosorb iQ2 instrument, water will desorb from the shale. There has been concern in the shale community that outgassing at 250 °C may result in modification of the kerogen and possibly the clay minerals of the shale. Within the Eagle Ford samples investigated in this Account, illite was the primary clay mineral present. Illite is a clay composed of two tetrahedral layers, each of which is bonded to opposite sides of one inner octahedral layer, which classifies it as a 2:1 clay. In 1966 it was concluded that only adsorbed water was removed from montmorillonite at 400
Further studies have shown that no structural changes are expected in the clays at 250 °C, as structural water in 2:1 clays is not extracted until approximately 400 °C. More recently, dehydration of illite interlayers was shown to take place up to temperatures of 280–300 °C, and modeling attempts have corroborated experiments showing dehydration between 180 to 225 °C. Furthermore, an outgassing temperature of 250 °C is lower than the 500–550 °C temperature range at which normal illite clay minerals dehydroxylate, which involves the removal of structural hydroxyls. Examination of a standard RockEval pyrolysis curve (Figure 4 right) shows that a minimum exists between the S1 and S2 curves. The minimum, which is labeled here as the “pregeneration trough”, would ideally be calculated independently for each shale sample. Figure 4 shows the desorption of gas species within the pore matrix as a function of outgassing temperature, with the free water desorption taking place between 60 and 110 °C and the stored hydrocarbons residing in the smaller nanopores desorbing at temperatures between 110 and 250 °C. Hence, using 250 °C as an approximation for the maximum outgassing temperature is recommended across all shale samples, as it lies in the vicinity of the pregeneration trough for most samples.

Deciding what the appropriate outgassing temperature should be depends on the intention of the investigation. For instance, here the goal is to understand how much CH₄ the gas shales may contain in addition to determining how much CO₂ may be reliably stored within the pores once they are depleted. If one wishes to understand how CO₂ interacts with water and/or CH₄ and other smaller hydrocarbons through injection of enhanced gas recovery, then lower outgassing temperatures may be preferred since this scenario requires depiction of the natural system, not necessarily an empty pore matrix. This distinction is important to recognize in determining what the goals of one’s study may be.

Methane adsorption isotherms simulated at 60 °C over the pressure range from 0 to 50 bar are compared with experimental results in Figure 5. It is important to note that comparison of results from different samples—even from
within the same regime—is difficult because of sample heterogeneity and discrepancies in sample preparation, testing, and presentation. Also, the models presented in this Account neglect the clay composition for simplicity in addition to isolating the chemical effects of surface functionality on adsorption. Recent work by Ji et al. (2012)\(^4\) demonstrates that illite compared with other clays present in shale has the lowest methane capacity. Illite showed to have the lowest Langmuir adsorption constant and lowest BET surface area of the clay materials investigated, with the latter property showing a linear correlation to adsorption capacity. Methane adsorption results of Ji et al.\(^4\) at 50 \(^{\circ}\)C over a sample composed of 99% illite is included in Figure 5 for comparison. Rexer et al.\(^4\) tested an Alum Shale sample (44.4% quartz, 0.5% calcite, 5.9% illite, and 6.35% TOC) at 65 \(^{\circ}\)C, which exhibited greater CH\(_4\) capacity compared with the models presented here. Additional experimental data in Figure 5 from Rexer et al.\(^4\) on an Eagle Ford sample taken from the dry-gas window (8.2% quartz, 49.9% calcite, 19.5% illite, and 7.15% TOC) compare quite well to the simulation data of the current work. Although this sample has a greater illite content than the Eagle Ford samples on which the models are based, the CH\(_4\) capacity is similar, further supporting the small role that clay may play in adsorption. Al Ismail\(^4\) reported results for a Permian sample of similar composition and depth as the Eagle Ford samples examined in the current study. Furthermore, the cumulative pore volume of these Eagle Ford samples is smaller than that observed for the Permian sample (0.031 and 0.051 cm\(^3\)/g, respectively).

With the exception of the hydroxylated surface, which shows an increase in CH\(_4\) adsorption over the unmodified surface at high pressures (+16%), the functionalized surfaces generally

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Figure 6. Excess CO\(_2\) adsorption simulated at 60 \(^{\circ}\)C. The values are 1.9, 2.9, 1.8, and 2.2 times greater than the CH\(_4\) adsorption (Figure 5) for PG, CH, MH, and OH, respectively.

Figure 7. Comparison of simulated CO\(_2\) and CH\(_4\) excess adsorption at 250 \(^{\circ}\)C. Carbon dioxide adsorption (solid circles) is shown to be 1.4, 4.3, 1.4, and 1.8 times greater than CH\(_4\) adsorption (open triangles) for PG, CH, MH, and OH, respectively.
exhibited lower CH₄ adsorption. This is intuitive from the presentation of the sorbate−sorbent interactions discussed previously together with a basic chemical understanding of polarity, as CH₄ is a nonpolar molecule. In particular, CH₄ adsorption at 10 bar is on average 0.03 mmol of CH₄/g of modeled kerogen, while at 50 bar the adsorption increases to a range of 0.05−0.08 mmol of CH₄/g of modeled kerogen across all of the carbon pore surfaces considered.

Conversely, polar CO₂ exhibits enhanced loading for surfaces modified with carboxyl (+4%) and hydroxyl (+33%) functionalities (Figure 6). More specifically, at 10 bar the CO₂ adsorption ranges from 0.06 to 0.13 mmol of CO₂/g of modeled kerogen and increases to a range of 0.11−0.18 mmol of CO₂/g of modeled kerogen at 50 bar for all of the carbon pore surfaces considered. In addition, the CO₂/CH₄ exchange ratio was calculated to be 1.9 for the unmodified surface, 2.9 for the carboxylated surface, 1.8 for the hydrated monovacancy, and 2.2 for the hydroxylated surface. These results fall within the range of exchange ratios typically reported for these materials.¹⁰,¹¹

Simulations were also performed at 250 °C, and the results are shown in Figure 7. To our knowledge, no experimental data were available for direct comparison with the simulation results at low or high temperature. With the exception of the carboxylated surface, CO₂ adsorption decreased to a larger extent than CH₄ adsorption relative to results obtained at 60 °C; hence, the CO₂/CH₄ exchange ratio is lower for these surfaces at 250 °C (1.4, 1.4, and 1.8 for PG, MH, and OH, respectively). Conversely, CH₄ adsorption decreased to a larger extent than CO₂ adsorption relative to the 60 °C adsorption results for the carboxylated surface, resulting in a larger CO₂/CH₄ exchange ratio of 4.3. More specifically, the CH₄ adsorption at 10 bar is approximately 0.005 mmol of CH₄/g of modeled kerogen and extends over a range of 0.01−0.02 mmol of CH₄/g of modeled kerogen across all of the surface functionalities considered. On the other hand, the CO₂ adsorption ranges from 0.005 to 0.03 mmol of CO₂/g of modeled kerogen at 10 bar and from 0.02 to 0.05 mmol of CO₂/g of modeled kerogen at 50 bar across all of the surface functionalities considered.

### IMPACT OF SURFACE CHEMISTRY ON GAS SELECTIVITY

The carbon dioxide to methane selectivity was measured as a function of pressure at 60 and 250 °C, and the results are presented in Figure 8. Generally, the hydrated vacancy and unmodified surface demonstrated CO₂/CH₄ selectivities that remained largely invariant to pressure. This behavior is typical of Langmuir adsorption observed on energetically homogeneous surfaces, which are capable of maintaining linear selectivity over a wide range. Alternatively, the hydroxylated and carboxylated surfaces show a strong preference for CO₂ at low and moderate pressures. This effect is minimized at higher pressures as pores within the microporous region become saturated, as it has been demonstrated that the extent of surface chemistry on enhanced CO₂ uptake and selectivity converges with the unmodified surface as the pore size enters the early mesoporous range (d > 2.0 nm).³⁵ In spite of reduced selectivity at high pressures, the carboxylated and hydroxylated surfaces demonstrate a strong preference for CO₂ over the entire pressure range, suggesting that kerogen with high carboxyl and/or hydroxyl content should have a greater storage capacity for CO₂.

### CONCLUSIONS

This Account has examined two Eagle Ford shale samples, both recovered from shale that was extracted at a depth of approximately 3800 m and having similar mineral compositions but distinct TOCs (i.e., 2% and 5%). Given the complexity of the nanopore structure and chemistry of gas shales, which are composed primarily of interconnected clay and kerogen networks, water likely plays a role in the surface chemistry of the pores. The Eagle Ford samples considered in this work were low in clay and deliberately chosen so that the kerogen within these systems could be explicitly modeled. On the basis of the existence of adsorbed water and dissociated water on the kerogen surfaces of these natural systems, a series of surface
functionalities were considered to determine what role, if any, surface chemistry plays in terms of CH₄ and CO₂ adsorption. Adsorption was modeled up to 50 bar to be more representative of the subsurface conditions of shale. Temperature conditions of 60 and 250 °C were considered in order to show the dependence of the adsorption on the chosen outgassing temperature. Finally, to determine the nanopore volume and complete PSD, both CO₂ and N₂ were used as probe gases to cover the range of pore sizes from 0.3 to 30 nm. Following all of these considerations, one can then determine the impact each has on the methane and CO₂ storage capacity of the Eagle Ford Shale on the basis of these particular shale samples. The questions that may now be answered concern the impact of knowledge of the kerogen chemistry on gas capacity and the extent to which gas adsorption is underestimated when (1) the applied outgassing temperature is too low and (2) pore volumes less than 1.5 nm are neglected.

What Impact Does Knowledge of the Kerogen Chemistry Have on Gas Capacity?

At temperatures of 60 and 250 °C, the CH₄ adsorption at 10 bar was on average 0.03 and 0.005 mmol/g, respectively, for all of the surface functionalities considered. These were the only conditions under which the surface chemistry of the pores did not impact the extent of adsorption. At 50 bar, however, at temperatures of 60 and 250 °C the CH₄ adsorption ranged from 0.11 to 0.18 mmol/g and 0.01 to 0.02 mmol/g, representing increases of 60% and 100%, respectively.

In the case of CO₂, which tends to be more reactive with the pore surfaces, as expected, the surface chemistry played an even more dominant role. For instance, at 10 bar and temperatures of 60 and 250 °C, the CO₂ adsorption ranged from 0.06 to 0.13 mmol/g and 0.005 to 0.03 mmol/g, representing 6-fold and just over 2-fold increases, respectively. These conditions have the most pronounced effect on CO₂ adsorption in the simulated kerogen pores considered in this Account. At 50 bar, the surface chemistry continues to be an important consideration, i.e., at temperatures of 60 and 250 °C, the CO₂ adsorption ranges from 0.11 to 0.18 mmol/g and 0.02 to 0.05 mmol/g, representing 1.6-fold and 2.5-fold increases, respectively.

To What Extent Is Gas Adsorption Underestimated When the Applied Outgassing Temperature Is Too Low?

In the case of determining the true pore volume available to store either hydrocarbons or ultimately CO₂, one needs to carry out adsorption experiments on samples with “empty” pores. This includes those experiments such as low-pressure CO₂ and N₂ adsorption experiments that provide the PSD and pore volume data that are used for the model development to simulate adsorption capacities. Using an outgassing temperature that is too low will result in pores that contain residual gas and possibly water, which will lead to an underestimation of what the pores can hold assuming that the pores are depleted of hydrocarbons in the case of the reliable storage of CO₂. The methane adsorption simulation data from temperature conditions of 60 and 250 °C from this study can be used to estimate the residual gas that exists in the pores at the lower outgassing temperature. For instance, comparing the methane adsorptions at 60 and 250 °C, there remains an additional 0.025 mmol of CH₄/g of modeled kerogen at the outgassing temperature of 60 °C. Similarly, at 50 bar, depending upon the surface chemistry, there may remain an additional 0.04 to 0.06 mmol of CH₄/g of modeled kerogen left in the pores at 60 °C. This implies that at both pressures there may actually be 2 times more gas stored in the pores than is realized. Similarly, using an outgassing temperature that is too low in estimating the CO₂ capacity would lead to an underestimation of what the depleted shale reservoir may reliably store.

To What Extent Is Gas Adsorption Underestimated When Pore Volumes Less than 1.5 nm Are Neglected?

In the cases of the EF1 and EF6 samples with 2% and 5% TOC, respectively, the total pore volumes (i.e., for pores less than 30 nm in diameter) are 0.028 and 0.036 cm³/g, of which 28% and 15%, respectively, are represented by pores that are less than 1.5 nm in diameter. These are pores that go unmeasured without the use of CO₂ as a probe gas. Therefore, relying solely on N₂ for determining the pore volume for pores less than 30 nm in diameter would lead to a significant underestimation of the total pore volume, which may significantly impact the estimates of gas in place as well as CO₂ storage potential.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.accounts.7b00003.

Pore size distributions and corresponding cumulative pore volume increases as functions of outgassing temperature using argon and CO₂ as probe gases (PDF)

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