Abstract

Potential for sequestration of carbon dioxide in organic rich shale is investigated in this work. Adsorption isotherms and Onsager diffusion coefficients are determined using molecular dynamics simulations for atomistic kerogen models. The kerogen unit models prepared by (Ungerer et al., 2014) are used in this study. To build representative solid state models for kerogen, eight kerogen molecules are placed in a periodic cubic cell. Once the initial configuration of kerogen molecules is prepared, constant-temperature constant- volume simulations and then constant-temperature constant-pressure simulations are performed to obtain the final structures. For the final structure, computed density and adsorption isotherms are within the reported experimental values. Grand Canonical Monte Carlo (GCMC) simulations are performed for CH$_4$-CO$_2$ mixtures to investigate binary adsorption isotherms in kerogen models with different maturities. Equilibrium molecular dynamics (EMD) simulations are used to determine Onsager diffusion coefficients. As pressure for each species in the binary mixtures increases, its adsorbed amount increases and adsorbed amount of the other species decreases. Adsorbed amount of CO$_2$ is higher than that of CH$_4$ for all kerogen types at all pressures tested due to the strong permanent quadrapole moment of CO$_2$. Due to higher adsorption affinity of CO$_2$ to kerogen pore surfaces compared to CH$_4$, its Onsager diffusion coefficients are smaller than those for CH$_4$ for all kerogen types.

Introduction

Shale gas is expected to account for 30% of world natural gas production by 2040 (U.S. Energy Information Administration, 2014). Large scale production of gas from shale resources can lead to large capacities for storage of CO$_2$ in these resources. Furthermore, due to the higher affinity of the organic matter to CO$_2$ compared to CH$_4$, injection of CO$_2$ can replace the adsorbed CH$_4$ and therefore, enhances the recovery of natural gas (Kazemi and Takbiri-Borujeni, 2016c). Modeling transport and storage of CO$_2$ in organic pores of shale is complex due to small sizes of the pores and also differences in magnitude of intermolecular forces between fluid molecules and solid molecules at the pore walls (Kazemi and Takbiri-Borujeni, 2015; Kazemi...
and Takbiri-Borujeni, 2016a,b). In this study, CO$_2$ sequestration in kerogen is investigated by computing transport and storage coefficients for binary mixtures of CO$_2$-CH$_4$ mixtures in atomistic kerogen unit models.

To characterize the species transport and storage properties of kerogen based on its chemical compositions and burial history, it must be first extracted from the inorganic matrix, which is a challenging task. In addition, once kerogen is extracted, performing experimental characterization of storage and transport properties in reservoir conditions is extremely difficult (Colll et al., 2015). Molecular simulations are credible alternatives to physical experiments for characterization of the kerogen (Brochard et al., 2012). An appealing feature of this approach includes the ability to perform an endless set of numerical tests at different pressures and temperatures, and types and compositions of fluids, without degrading or altering the sample.

There have been several studies on CO$_2$ storage and enhanced gas recovery in shale. Cygan et al. (2012) carried out molecular simulations to study the molecular interactions in interlayer of montmorillonite and showed that these simulations can accuracy predict carbon storage mechanisms in complex natural materials. Liu and Wilcox (2012) performed GCMC simulations by including oxygen-containing functional groups to graphite and found that these groups can enhance the adsorption of CO$_2$. They also studied adsorption selectivity of CO$_2$ over CH$_4$ and showed that the selectivity of CO$_2$ over CH$_4$ decreases as pressure increases. Firouzi and Wilcox (2012) performed non-equilibrium molecular dynamics simulations of flow of CH$_4$ and CO$_2$ in a three-dimensional carbon-based pore network. They investigated the effect of porosity in pore network on the permeability.

Mass transport in organic pores of shale is of diffusive nature (Colll et al., 2015) and therefore, it is crucial to understand the species diffusion through these pores. Species diffusion manifests itself into different diffusion coefficients, namely self-, corrected (or Maxwell-Stefan), and Fickian diffusion coefficients. Diffusion of pure fluids in organic pores of coal and shale has been extensively studied using molecular simulations, however, there are only a few molecular studies on multicomponent diffusion phenomena in organic nanopores. Colll et al. (2015) studied transport of hydrocarbon mixtures through kerogen using molecular simulations. They found that Onsager’s autocorrelation coefficients scale linearly with the adsorption loading and inversely with the alkane chain length. They proposed a scaling law to predict transport coefficients for linear alkanes in a mixture. Zhao et al. (2016) computed diffusion coefficients of carbon dioxide-methane mixtures at different temperatures, pressures, and mixture compositions in a bituminous coal model. They showed that the dominating mechanism for the mixture diffusion in coal changes from surface diffusion to configurational diffusion at high pressure.

**Creating 3D Kerogen structures**

Kerogen unit molecules with different types and maturities (IIA, IIB, IIC, IID, and IIIA), prepared by Ungerer et al. (2014) are used to investigate the storage and transport of binary gas mixtures. Unit structures for IIA and IID kerogen are shown in Fig. 1. Molecular formula for each kerogen type and maturity are listed in Table. 1.
To build representative solid state models, eight kerogen molecules are placed in a $10 \times 10 \times 10$ nm periodic cubic cell using Moltem-plate software (Jewett et al., 2013). Fluid molecules are not included in the initial configurations. Instead, two spherical dummy particles are used to generate pore spaces in 3D structures. Lennard-Jones diameter of dummy particles is selected to be 15 Å. The dummy particles are deleted after 3D structure is developed. COMPASS (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) class2 force field is used to describe the interactions between atoms, bonds, and angles (Sun, 1998). Once the initial configurations of kerogen molecules are prepared, constant-temperature constant-volume (NVT) simulations are performed at $900 \text{ K}$ for $3 \text{ ns}$. Density of the structures are 0.052, 0.046, 0.046, 0.033, 0.046 g/cm$^3$ during NVT simulation time for kerogen types IIA, IIB, IIC, IID, and IIIA, respectively. Three conformations are sampled from NVT simulations. Each sampled conformation goes under successive constant-temperature constant-pressure (NPT) simulations for a temperature range of 900 to 338 K at 20 MPa pressure. Each NPT simulation is performed for 500 ps. All simulations are performed with 1 fs timestep using LAMMPS molecular simulator (Plimpton, 1995).

Final 3D structures for IIA and IIB kerogen are shown in Fig. 2. Porosity of kerogen structures are computed using the method described in Liang et al. (1998). Domain sizes of the structures and their porosity and density values are presented in Table 2.
Figure 2—3D structures for IIA and IIB kerogen.

Table 2—Size, porosity, and density of kerogen structures.

<table>
<thead>
<tr>
<th>Kerogen type</th>
<th>Box Sizes(Å³)</th>
<th>Porosity (%)</th>
<th>Structure Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>36.91 × 36.91 × 36.91</td>
<td>13</td>
<td>1.03</td>
</tr>
<tr>
<td>IIB</td>
<td>35.85 × 35.85 × 35.85</td>
<td>15</td>
<td>1.01</td>
</tr>
<tr>
<td>IIC</td>
<td>35.35 × 35.35 × 35.35</td>
<td>16</td>
<td>1.02</td>
</tr>
<tr>
<td>IID</td>
<td>31.43 × 31.43 × 31.43</td>
<td>17</td>
<td>1.05</td>
</tr>
<tr>
<td>IIIA</td>
<td>35.27 × 35.27 × 35.27</td>
<td>16</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Results and Discussions

In this section, CH₄ adsorption isotherms are calculated and compared against the published experimental measurements. Furthermore, transport and adsorption isotherms of binary mixtures of CO₂-CH₄ inside kerogen structures are investigated.

Adsorption Isotherms

GCMC simulations are performed to determine adsorption capacity of kerogen with different maturities. For each structure, GCMC moves are used to place CH₄ molecules in the domain, minimizing energy for a pressure range of 20 to 140 atm. Adsorption isotherms are determined for each kerogen type and maturity and demonstrated along with the published experimental adsorption results of Rexer et al. (2014) and Zhang et al. (2012) in Fig. 3. Molecular simulation and experimental results are shown with hollow and solid markers, respectively.
Rexer et al. (2014) experimentally measured adsorption isotherms of bulk shale and isolated kerogens for immature, oil window, and gas window samples of Lower Toarcian Posidonia shale with TOC ranging from 5.8 to 10.9 wt% and density ranging from 1.024 to 1.368 gr/cm³. Geochemical investigations have shown that Posidonia kerogen is of type II. Adsorption isotherms of CH₄ for type IIA and IID Posidonia samples at 65°C (or 338 K) are shown in Fig. 3. Zhang et al. (2012) used samples from Devonian-Mississippian Woodford Shale to study CH₄ adsorption at a temperature range of 35 to 65°C.

Langmuir isotherm is defined as

\[
q = q_{\text{sat}} \frac{Kp}{1 + Kp},
\]

where \( q \) is absolute adsorption amount in mmol/gr, \( q_{\text{sat}} \) is maximum adsorption amount, \( K \) is the equilibrium constant, and \( p \) is pressure. Computed adsorption results are fitted to Langmuir-type isotherms and plotted as solid lines in Fig. 3. Langmuir constants are calculated using Equation 1 and are listed in Table 3. Equilibrium constants are similar for all the kerogen types. However, maximum adsorption amounts increase as kerogen becomes more mature. Amount of adsorbed CH₄ increases as pressure increases for all kerogen maturities. At a specific pressure, as maturity of kerogen increases, adsorbed CH₄ quantities increase. Kerogen structures for type IID and IIIA have similar adsorbed quantities and the highest among all kerogen types. Adsorbed CH₄ quantities are 1.25 and 1.28 mmol/gr TOC at 140 atm for IID and IIIA kerogen. The lowest adsorbed amount belongs to IIA kerogen, where it reaches to 0.99 mmol/gr TOC at 140 atm.

<table>
<thead>
<tr>
<th>Kerogen type</th>
<th>( q_{\text{sat}}, ) mmol/kg</th>
<th>( K, 1/\text{atm} )</th>
<th>Goodness of fit, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIA</td>
<td>1.729</td>
<td>0.0078</td>
<td>99.96</td>
</tr>
<tr>
<td>IIB</td>
<td>2.247</td>
<td>0.0075</td>
<td>99.96</td>
</tr>
<tr>
<td>IIC</td>
<td>2.236</td>
<td>0.0071</td>
<td>99.87</td>
</tr>
<tr>
<td>IID</td>
<td>2.404</td>
<td>0.0079</td>
<td>99.04</td>
</tr>
<tr>
<td>IIIA</td>
<td>2.269</td>
<td>0.0091</td>
<td>99.89</td>
</tr>
</tbody>
</table>

Experimental results of Zhang et al. (2012) and Rexer et al. (2014) demonstrate the same trend for adsorption isotherms as molecular simulation results do. For instance, type IID kerogen in Rexer et al.
(2014) has highest adsorbed amount while type IIA kerogen has the lowest, where it reaches to 0.83 mmol /gr TOC. Results in Zhang et al. (2012) for type II kerogen is within the range of the molecular simulation results and slightly higher than results in Rexer et al. (2014).

**Binary Adsorption Isotherms**

GCMC simulations are performed to investigate the binary adsorption of CH$_4$ and CO$_2$ mixtures in kerogen. Pressure range studied for each species is from 20 to 170 atm for each kerogen type. All the simulations are performed at 350 K. CH$_4$ and CO$_2$ molecules are modeled using OPLS-AA and COMPASS class2 force fields, respectively.

Adsorbed amounts for CO$_2$ is higher than those for CH$_4$ for all kerogen types at all pressures. This is because of the strong permanent quadrapole moment of CO$_2$ (Liu and Wilcox, 2012). As pressure of each species increases, its adsorbed amount increases and at the same time, the adsorbed amount of other species decreases. For instance, for type IIA kerogen, amount of the adsorbed CH$_4$ increases from 0.16 to 0.66 mmol/gr as CH$_4$ pressure increases from 20 to 170 atm for a CO$_2$ pressure of 20 atm (red hollow circles) (Fig. 4a). Amount of adsorbed CO$_2$ increases from 0.39 to 1.14 mmol/gr when the CO$_2$ pressure increases from 20 to 170 atm at a CH$_4$ pressure of 20 atm (Fig. 4b). At a CH$_4$ pressure of 170 atm, amount of adsorbed CO$_2$ increases from 0.23 to 1 mmol/gr. Amount of adsorbed CO$_2$ decreased by 41% and 14% when CH$_4$ pressures are 20 and 170 atm, respectively. Similar trends are observed for all the kerogen types and maturities.

![Figure 4—Binary adsorption isotherms for CH4-CO2 mixtures in type IIA kerogen.](image)

The adsorption isotherms are fitted to Langmuir multicomponent adsorption isotherms using

$$
\frac{c_1}{c_{1,sat}} = \frac{A_1 P_1}{1 + A_1 P_1 + A_2 P_2},
$$

$$
\frac{c_2}{c_{2,sat}} = \frac{B_1 P_2}{1 + B_1 P_1 + B_2 P_2}.
$$

(2)

Here and throughout the remainder of this paper, subscripts 1 and 2 for concentrations, partial pressures, etc. refer to CH$_4$ and CO$_2$, respectively. Coefficients obtained for the best fit are listed in Table 4.
Table 4—Calculated parameters for the binary adsorption isotherms (Equation 2)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>IIA</th>
<th>IIB</th>
<th>IIC</th>
<th>IID</th>
<th>IIIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>0.01538</td>
<td>0.00775</td>
<td>0.02488</td>
<td>0.02174</td>
<td>0.01617</td>
</tr>
<tr>
<td>$A_2$</td>
<td>0.02884</td>
<td>0.02721</td>
<td>0.02607</td>
<td>0.02491</td>
<td>0.02492</td>
</tr>
<tr>
<td>$c_{1,\text{sat}}$</td>
<td>0.79194</td>
<td>1.59680</td>
<td>0.75161</td>
<td>0.75345</td>
<td>0.97402</td>
</tr>
<tr>
<td>$B_1$</td>
<td>0.01904</td>
<td>0.01865</td>
<td>0.01961</td>
<td>0.02931</td>
<td>0.02111</td>
</tr>
<tr>
<td>$B_2$</td>
<td>0.00271</td>
<td>0.00281</td>
<td>0.00318</td>
<td>0.003582</td>
<td>0.00294</td>
</tr>
<tr>
<td>$c_{2,\text{sat}}$</td>
<td>1.49632</td>
<td>1.82895</td>
<td>1.75217</td>
<td>1.92903</td>
<td>2.03316</td>
</tr>
</tbody>
</table>

Fitted Langmuir adsorption coefficients are compared with the computed ones in Fig. 5. The straight line in Fig. 5 shows 100% match between the fitted isotherm and molecular simulation results. CO$_2$ adsorption results are fitted to Langmuir multicomponent adsorption isotherm with high accuracy ($R^2 > 98\%$ for all kerogen types).

![Figure 5](image_url)

Figure 5—Comparison of the fitted Langmuir adsorption coefficients with the computed ones for the binary mixture adsorption for CH$_4$ (red hollow circles) and CO$_2$ (filled circles). The straight line denotes the exact agreement.

Total adsorption quantity can be determined by adding the concentration of each component in Equation 2

$$c_t = c_1 + c_2.$$  (3)

Species mole fractions are determined as

$$y_1 = \frac{P_1}{P_t}, \quad y_2 = 1 - y_1,$$  (4)

where $P_t$ is the total mixture pressure. Mole fraction of each species in the adsorbed phase can be calculated as

$$x_1 = \frac{c_1}{c_t}, \quad x_2 = 1 - x_1.$$  (5)

Equilibrium relationship between free gas phase and adsorbed phase can be expressed as

$$\frac{x_1}{x_2} = \frac{c_{1,\text{sat}}}{c_{2,\text{sat}}} \frac{A_1y_1}{A_2y_2} \frac{1 + B_1P_1 + B_2P_2}{1 + A_1P_1 + A_2P_2}.$$  (6)

To distinguish between the free and adsorbed molecules for each species, adsorption selectivity is defined...
where $\alpha_1$ is adsorption selectivity of CH$_4$ over CO$_2$. Adsorption selectivity changes temperature, pressure, and composition of the gas mixture and type of adsorbent (Myers, 2004). Adsorption selectivity values near one indicate that the mixture is not separable by an adsorption process.

x-y diagrams and adsorption selectivity of CO$_2$ over CH$_4$ for different kerogen types at various total pressures, $P_t$, are shown in Fig. 6. Red square markers demonstrate $x_{CH_4}$-$y_{CH_4}$ and green circle markers indicate $x_{CO_2}$-$y_{CO_2}$ values. Adsorption selectivity values of CO$_2$ over CH$_4$ are determined based on x-y values of each component using Equation 7. For all kerogen types, adsorption selectivity values are above one for all total pressures and species compositions demonstrating that CO$_2$ has higher adsorption tendencies compared to CH$_4$. Adsorption selectivity values plotted against CO$_2$ composition ($y_{CO_2}$) indicate a maximum value at a CO$_2$ composition less than 0.5 depending on kerogen type and total pressure. At some of selectivity graphs, the maximum point is not observable due to limited number of points. After the maximum point, adsorption selectivity decreases as CO$_2$ bulk composition increases. Comparing different kerogen types, adsorption selectivity values are within the same range of 2 to 7.

\[
\alpha_1 = \frac{x_1/y_1}{x_2/y_2} = \frac{c_{1,\text{sat}}}{c_{2,\text{sat}}} \frac{A_1}{A_2} \left( \frac{1 + B_1 P_t}{1 + A_1 P_t} \right) \frac{B_2 P_t}{A_2 P_t} \tag{7}
\]
For a certain composition, as the pressure increases, adsorption selectivity of CO2 over CH4 increases for the pressure range tested (Fig. 7). For instance, at 50-50% composition of CO2-CH4, adsorption selectivity increases from 2.45 to 3.94 as total pressure increases from 40 to 280 atm for type IIA kerogen. As kerogen becomes more mature, adsorption selectivity values subtly increase.

![Figure 7—Adsorption selectivity values for different kerogen types at 50-50% CH4-CO2 composition.](image)

**Binary Diffusion Coefficients**

Diffusion of each species in kerogen is affected by presence of other species. When CO2 is introduced into kerogen structures, competitive adsorption of CH4 and CO2 causes the diffusion coefficients to be different from a case where the other component is absent.

Equilibrium molecular dynamics (EMD) simulations are performed to calculate the diffusion coefficients based on the molecular trajectory of molecules

\[
L_{ij} = \frac{1}{6N} \lim_{t \to \infty} \frac{1}{t} \left\langle \sum_{i=1}^{N_i} (r_{i,i}(t) - r_{i,i}(0)) \cdot \left( \sum_{k=1}^{N_j} (r_{k,j}(t) - r_{k,j}(0)) \right) \right\rangle,
\]

where \(i\) and \(j\) refer to the different species in mixture and \(r_{l,i}(t)\) is the position of \(l^{th}\) molecule of component \(i\) at time \(t\).

Onsager coefficients for type IID kerogen are plotted in Fig. 8. As CH4 pressure increases, while CO2 pressure is kept constant, its Onsager diffusion coefficients increase. Due to higher adsorption capabilities of CO2 compared to CH4, its Onsager diffusion coefficients are smaller than those for CH4 for all kerogen types. Off-diagonal Onsager diffusion coefficients are almost one order of magnitude less than the diagonal terms (Fig. 8b).
Onsager diffusion coefficients are plotted at 185 atm in Fig. 9. Onsager diffusion coefficients for CH₄ are higher than those of CO₂ up to a certain CO₂ mole fraction (around 80%), after which Onsager coefficients for CO₂ become larger than those for CH₄. Increasing CO₂ concentration increases diffusion of CH₄ up to a certain point and further increase in CO₂ concentration may not cause more CH₄ diffusion.

**Conclusions**

In this work, adsorption and diffusion of binary mixtures of methane and carbon dioxide in atomistic kerogen models prepared by (Ungerer et al., 2014) are studied using molecular dynamics simulations. For all kerogen types, adsorption selectivity values of carbon dioxide over methane are above one for all pressures tested, which shows that carbon dioxide has higher adsorption affinities to the pore surfaces compared to methane. This is due to the strong permanent quadrapole moments of carbon dioxide. When carbon dioxide is introduced into methane-filled organic pores, their competitive adsorption causes carbon dioxide molecules to replace methane molecules at the adsorption sites. As concentration of each species in kerogen increases, its adsorbed amount increases and adsorbed amount of other species decreases. Due to higher
adsorption affinity of carbon dioxide compared to methane, its Onsager diffusion coefficients are smaller than those for methane for all kerogen types.

References


