A Sorption Study on the Effect of Partial Liquid Saturation of Supercritical CO2 on Clay and Organic-Rich Shales
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I. ABSTRACT
Rocks, specially shales have heterogeneous mineralogy. We anticipate sorption to be dependent on the association of the pores with the various shale constituents. Furthermore, since shales are expected to have varying levels of water or brine, the water-imbibed shales are better representatives of their natural conditions. However, to date, almost all sorption studies have been performed in the dry state. The purpose of this study is to (1) determine the relative affinity of water and hexane vapors in shales and siltstones during sub-critical adsorption; (2) the sorption capacity of illite clay and organic-rich shale samples in dry and in water-imbibed states during supercritical CO2. We find that vapor sorption can be related directly with clay content while hexane vapor is sorbed more in the organic pores. Organic matter pores also play a crucial role in retaining the supercritical CO2 sorption capacity even in the water-imbibed shales. The rate of sorption is reduced substantially in the presence of water due to the much lower diffusion coefficient of CO2 in liquid water than that of its gas state. Our findings can improve the current understanding of fluid storage mechanism in partially water-saturated shales for hydrocarbon production and CO2 sequestration applications.

II. INTRODUCTION
Porous rocks are classified as water- or oil-wet when the surface of their pores is mainly hydrophilic or hydrophobic. In order to differentiate between the water- and oil-wetting pores in shale rocks and to quantify their corresponding total surface, subcritical isotherms of water, hexane and nitrogen vapors in various OM-rich shales were measured. The BET method is used to calculate specific surface area. In its linear form, the BET isotherm equation is:

\[ p/p_0 = 1/(c_\times n \times m + c) \]

\[ \times \frac{1}{c \times n \times m} \times \frac{p}{p_0} \]

C=BET constant;

\[ p_0 \] =saturation pressure

Our results show that water vapor water vapor can act as a selective adsorptive for shales by preferentially probing hydrophilic pores (illite pores), whereas hexane adsorbs in both hydrophilic and hydrophobic pores (OM pores).

In the first part of this study, the presence of other fluid, such as liquid water is ignored in the experimental assessment of sorption in shales. Since OM pores are potentially hydrophobic as found earlier, those unoccupied OM pores in water-imbibed shales may facilitate sorption of supercritical gases. Supercritical CO2 sorption isotherms were determined experimentally for the organic-rich shale and illite clay samples in dry and water-imbibed conditions. The kinetics of the sorption was also studied by performing a PTA based study on the time profile of pressure associated with the progression of sorption in the samples.

III. METHODOLOGY & SAMPLES

• Samples
For subcritical nitrogen, water vapor and hexane analysis, we used 8 upper and lower Bakken shale samples and 4 middle Bakken siltstone samples with mineral compositions as listed below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay</th>
<th>Total Organic Carbon</th>
<th>Pyrolysis</th>
<th>Thermal Maturity</th>
<th>BET SSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK1</td>
<td>26%</td>
<td>1.3</td>
<td>8</td>
<td>3.6</td>
<td>29</td>
</tr>
<tr>
<td>BK2</td>
<td>25%</td>
<td>1.2</td>
<td>7</td>
<td>3.4</td>
<td>31</td>
</tr>
<tr>
<td>BK3</td>
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<td>1.1</td>
<td>6</td>
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<tr>
<td>BK4</td>
<td>23%</td>
<td>1.0</td>
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<tr>
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<tr>
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<td>1</td>
<td>2.2</td>
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We used three samples for supercritical CO2 sorption analysis: Illite clay from the Clay Mineral Society and two organic-rich shales from the Bakken formation belonging to the oil (BK1) and gas (EPU119) thermal maturity windows.

• Methodology
For subcritical nitrogen, water vapor and hexane analysis, adsorption and desorption isotherms were measured with a Micromeritics ASAP2020 analyzer. Nitrogen isotherms were recorded at liquid nitrogen boiling temperature (-197.5°C), whereas water and hexane vapor isotherms were recorded at ambient lab temperature (21°C to 23°C).

We designed a manometric apparatus for the supercritical sorption experiment as shown below. A tube with a plunger valve is also designed to allow for forced imbibition of water in samples. The material balance and CO2 equation of state proposed by Span and Wagner (1996) were used for the evaluation of isotherms.

• Correlation between sample clay content and nitrogen(a), hexane(b) and water(c) SSA results.

IV. RESULTS

• Water, Hexane and Nitrogen Isotherm Derived BET SSA

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• Nitrogen(77K), hexane(298k) and water (298k) isotherms for siltstone sample MB44 and shale sample U16.

V. CONCLUSIONS

• We quantify hydrophilic and hydrophobic pores in shales using select adsorptives.

• Water-imbibed shales do have sorption capacity for supercritical CO2.

• Presence of water inhibits CO2 sorption in the clay constituents but not in OM pores.

• Supercritical CO2 sorption in water-imbibed organic-rich shales suggested the possibility of CO2 sorption from its dissolved state in water.

Acknowledgement
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References

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