BUTANE CONDENSATION IN KEROGEN PORES AND IN SMECTITE CLAY: NMR RELAXATION AND COMPARISON IN LAB STUDY

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ABSTRACT

Previous studies have shown that highly pressurized methane gas can be measured by NMR, with a rather short T_2 relaxation. We propose a new model in which hydrocarbon gases condense inside the hydrocarbon-philic pores because of capillary condensation if the reservoir temperature is lower than the critical point of the gas component. This is due to the favorable conditions for capillary condensation for nano-scale pores inside the kerogen and between clay mineral crystals.

We used butane vapor to saturate unconventional shale samples containing a known amount of total organic carbon (TOC) and a pure smectite sample purchased from the Clay Minerals Society. Butane condenses inside the unconventional shale samples and in the pure smectite sample at room temperature under low pressure. Moreover, the amount of condensed butane can be measured by weight and correlated to its nuclear magnetic resonance (NMR) response.

The T_2 relaxation of butane in the unconventional shale samples and in clay minerals is less than 10 ms. We conclude that bulk volume irreducible (BVI) in unconventional gas plays may include gas condensed inside nanopores. Our model provides an improved understanding of the gas storage and a basis for an improved analysis of NMR logs in these reservoirs.

INTRODUCTION

Unconventional shale gas and shale oil reservoirs have attracted much attention in recent years. Because of the complexity of unconventional shales (mineralogy and presence of kerogen), they are poorly understood and applications of conventional logs are challenging. NMR logging tools are often used in unconventional shales plays and the interpretation of these logs requires a better understanding of the hydrocarbon storage modes in unconventional shales.

Laboratory research activities are ongoing to understand the storage modes of light hydrocarbons within shale samples for both detection and quantification. Methane adsorption on clay minerals and in shale core samples have been studied in lab experiments, normally at high pressure. Lu et al. (1995) showed that methane can be adsorbed by illitic clay. Sigal and Odusina (2011) showed that methane stored in Barnett shale samples under high pressure at ambient temperatures can be measured by NMR measurements with T_2 relaxation times of 8 to 9 ms where the rapid relaxation of methane gas in a relatively homogeneous gradient is attributed to surface

relaxation.

Our previous laboratory studies show that hexane vapor can condense into Woodford shale samples and smectite clays likely due to capillary condensation (Chen et al., 2012; Zhang et al., 2012). We concluded that hexane vapor condenses in nanopores inside kerogen and in the minuscule pores between smectite clay flakes where the resultant hexane in liquid form shows a T_2 relaxation below 10 ms. This is due to the fact that any undersaturated vapor will condense in pores of sufficiently small dimensions according to Kelvin equation, such as water vapor condensing in a silica wedge (e.g. Fisher et al, 1981). In this study we used butane gas below saturation pressure and found that butane also condenses inside the kerogen pores and minuscule pores inside and between smectite clay flakes due to capillary pressure. The same set of Woodford shale core samples and a smectite sample from the Clay Mineral Society is used for the current experiments. Our NMR instrument has similar specifications to downhole tools leading to the expectation that hydrocarbon signals detectable in the laboratory will be detected downhole as well.

SAMPLE AND METHOD
Twenty five (25) Woodford shale samples have various amounts of TOC, ranging from 1 to 6 wt% (Chen et al., 2012). The smectite sample (SWY2), is a Na smectite. Mineralogy and previous water vapor saturation experiments references can be found in Zhang et al (2012).

The shale samples were dried at 110° C for 24 hours and cooled in vacuum. Butane gas saturation was performed using two different methods (Figure 1). In Method 1, a sample was put into a glass flask connected to an empty flask and vacuum was applied. When vacuum is reached, butane is released through a valve to the empty glass flask. The maximum of butane gas that can be released into the glass system is 1 atm. In Method 2, a sample is placed in a stainless steel cell and pumped down to a full vacuum; then butane gas is released into the system until pressure in the system reaches a desired pressure (Figure 1). Weights before and after vapor saturation were recorded and compared. As the systems are both well sealed, differences were attributed to adsorbed/condensed hydrocarbon by the shale and smectite clay samples. After vapor saturation, the samples are scanned continuously with an NMR instrument to understand the desorption process of the butane.

All NMR measurements were made using an Oxford Maran II NMR relaxometer, using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with an echo time (TE) of 300 μs, relaxation delay time (RD) of 0.5 sec, and number of scans at 4000. The rather short RD was chosen to minimize the signal from the gaseous phase, as the longitudinal relaxation of gas is long. The acquired echoes were inverted to T_2 distributions using in-house software that is essentially the same as the one used in the Baker Hughes log interpretation suite. The total amounts of butane from NMR experiments are presented in volumetric percentages of the rock samples, using the Hydrogen Index (HI) of liquid butane.

RESULTS AND DISCUSSION
Butane Vapor Condensation in Shale Samples
The amount of butane condensed is measured by weight difference before and after butane saturation and by the amount of liquid butane from NMR measurements. The results are consistent. Because we are looking into capillary condensation, we used pressures lower than or near the saturation pressure of butane (~2.6 atm.). Table 1 shows the experimental conditions using sample 206 as an example.
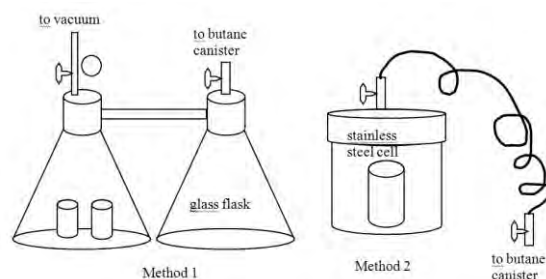

Figure 1. Experimental methods for butane vapor saturation: in Method 1, butane gas is injected to the empty glass flask after vacuum is reached. The pressure in the glass system can reach 1 atm; In Method 2, higher butane pressure can be maintained in the stainless steel sample cell after vacuum is reached.

Table 1. Experimental parameters for butane condensations using sample 206 as an example

Sample	Sample form	Butane pressure	Time Duration	Volume of sample (cc)	Weight of liquid butane by weight gain (g)	Volume % from weight diff.	Volume % from NMR
206	plug	1 atm	20 days	17.228	0.184	1.78%	2.0%
206	crushed	1 atm	14 days	7.087	0.101	2.36%	2.5%
206	plug	2.5 atm	2 days	9.743	0.126	2.86%	2.9%

Various amounts of butane condensed in the shale samples using Method 1. Three sandstone samples with no TOC and little clay are also used as control. Figure 2 shows the butane condensed in volumetric percentage of these samples at 1 atm vs. TOC. There is a general positive correlation between the amount of butane condensed and TOC, suggesting butane condensation is likely closely related to the oil-wet kerogen surface and nanopores inside kerogen. However, there are points that deviate from the linear feature, especially the samples below the line, i.e. sample with rather high TOC values but small amounts of condensed butane. There are several possible reasons for this. Firstly, this is likely due to the type and maturity level of kerogen, as kerogen in different samples may have different amounts and types of pores. Preliminary results of a focused ion beam scanning electron microscopy (FIBSEM) study on three samples show that the kerogen in sample 202 and 206 at TOC 7.3% and 8.4%, respectively, has well developed nanopores. Secondly, other mixed wet minerals may also play a role in capillary condensation; we used a pure smectite sample as an example for this.

The Method 1 butane vapor saturation experiments of shale plug samples show an essentially unimodal T_2 distribution with the main peak around 0.5-2 ms (Figure 3, red lines). To evaluate whether butane vapor goes into all possible pores in which butane can condense into liquid, we crushed 6 samples into small chips, and repeated the experiments. The T_2 distributions are of similar shapes but the main peaks move to the right (Figure 3, blue lines) and the amounts of butane condensed in the crushed samples are higher than in the plugs (Table 2). It is possible that the pores exist

within pockets where they are well connected and the communication between pockets is not well established. The crushed sample increases the number of pockets to the air and opens more nanospaces previously not connected to the outside. Another possibility is that condensation occurs in some of the newly created micro-/nano-fractures due to crushing, and this explains that the shift of T_2 to the right side.

Four samples are used for Method 2, in which the pressure of butane vapor is kept around 2.5 atm. The volume of butane condensed in Method 2 was always greater than the condensed volume in Method 1 (Table 3). This is consistent with the notion
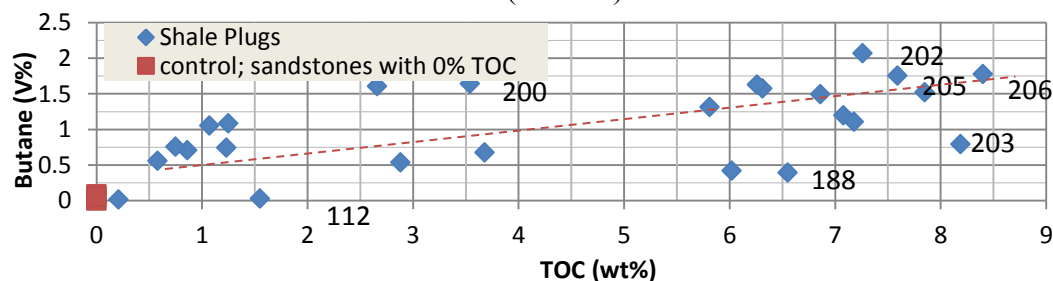

Figure 2. The amounts of butane condensed in shale plug samples are plotted against the TOC values. The condensation experiments for all samples in this plot are done with Method 1.
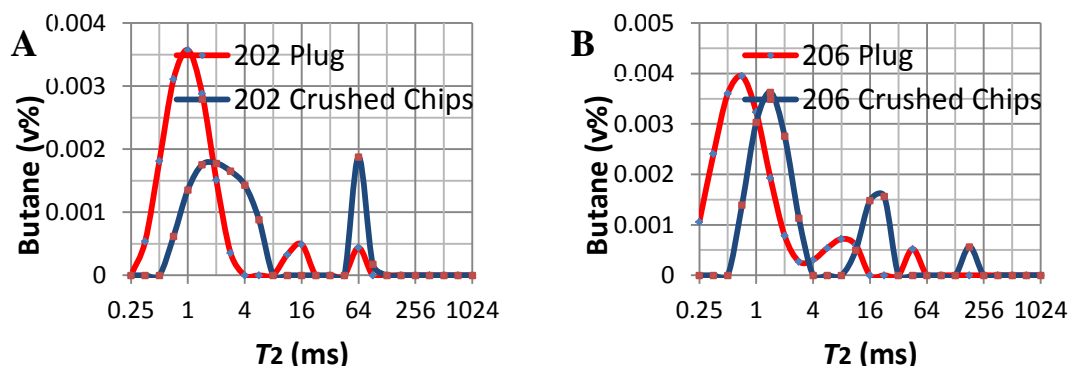

Figure 3. T_2 distribution of butane liquid in shales samples in plug form and crushed form. Experiments in these plots are done with method 1.

Table 2. Comparison of the amounts of butane condensed in six shale samples in plug and crushed form; All experiments were carried out in Method 1. The amounts of butane are from weight difference.

Plug # of sample	Plug sample Butane v%	Crushed Sample Butane v%
054	1.61	1.94
093	0.02	0.20
112	0.03	0.38
188	0.39	1.83
202	2.07	2.51

Table 3. Comparison of butane condensation of plug samples using Method 1 and Method 2; the amounts of butane are from weight difference.

Plug # of Sample	Method 1 Butane v%	Method 2 Butane v%
112	0.03	0.07
188	0.39	1.55
202	2.07	2.19
206	1.78	2.87

that the higher the butane pressure, the more butane condensed. However, the T_2 distributions of the two methods are not uniform; sample 206 has a different T_2 distribution for each method, whereas the T_2 distributions for sample 202 are consistent between the two methods. The Method 1 shows two modes, one below 1 ms and the second mode is around 6 ms (Figure 4B). Comparison of the same samples for both methods shows a positive correlation between the amount of butane

condensed and the pressure of the butane vapor.

Desorption of Butane Gas from Shale Samples

The desorption experiments reversed the process of saturation. After each shale sample was saturated with butane vapor, it was transferred to a closed vial initially at zero butane partial pressure. The NMR experiments are performed without interruption. The results show a noticeable decrease of measureable butane inside the sample (Figure 5). This is caused by butane diffusing out of the sample and into the vial. Desorption or evaporation will continue until equilibrium between the partial pressure and vapor pressure of the butane remaining in the sample is reached.
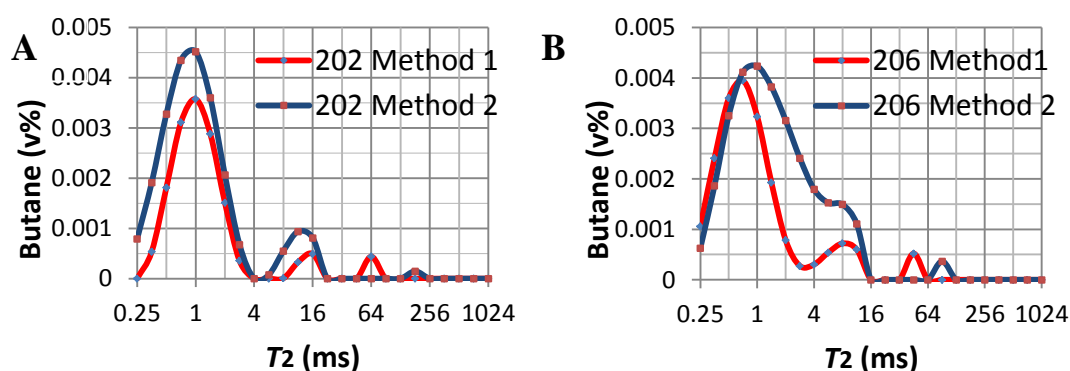

Figure 4. A. Comparison of T_2 distribution of sample 202 with method 1 and method 2 with different methane pressure; B sample 206 shows a big difference of T_2 distribution between methods.

Only the liquid butane condensed inside the shale samples was detected because the wait time, RD, between adjacent scans was much smaller than the gas phase's longitudinal relaxation time, thus the gas signal was substantially reduced and the measured signal was mostly from the liquid.
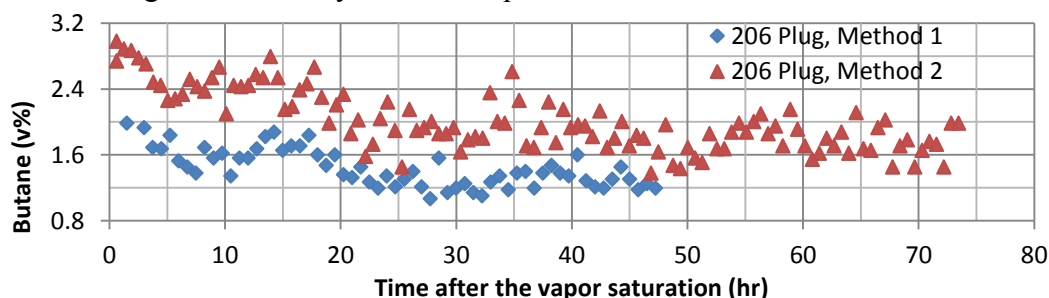

Figure 5. The amount of liquid butane inside the shale samples measured by NMR decreases with time after the vapor saturation experiments were over.

Butane condensation of Smectite Clay

Because shales can contain large amounts of clay minerals, a sample of smectite was purchased to demonstrate that butane vapor can also condense inside the minuscule pores within the clay. About seven grams of smectite sample was saturated with butane using both Method 1 and Method 2. In Method 2, the butane pressure was kept at 2.5 atm. The amounts of butane condensed in the sample are shown in Table 4. The resulting T_2 distribution of the smectite sample in Method 1 is noisy because the total of liquid is around 0.07 gram, and the signal is very close to the detection limit of the instrument. The T_2 distribution of the butane in the smectite sample using

Method 2 clearly shows a peak around 1 ms (Figure 6).

Table 4. Amount of butane condensed inside pure smectite; values calculated from weight difference

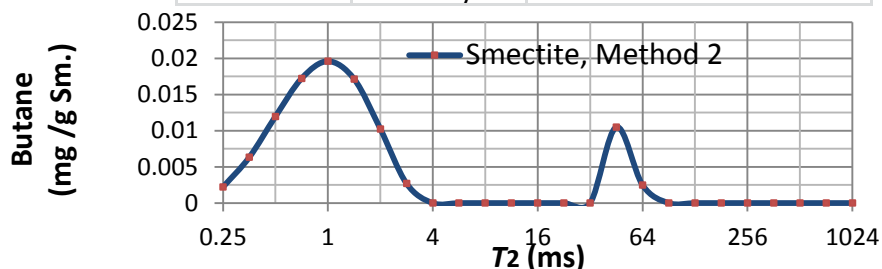|	Duration of experiments	Butane in smectite (mg/g dry smectite)
Method 1	7 days	10
Method 2	1 day	18

Figure 6. T_2 distribution of liquid butane of the pure smectite sample. A main peak around 1 ms is obvious.

CONCLUSIONS

Our experiments show that at the conditions close to atmospheric pressure, with vapor pressure less than or close to the saturation pressure, butane can condense inside shale samples with kerogen. The general positive correlation of condensed butane content with TOC support the premise that kerogen is an important storage mechanism for condensed gas. The deviation from a linear trend suggests that other factors, such as the quality of kerogen and clay minerals may also contribute to the condensation of butane inside the shale samples. Our experiments of smectite show that butane does condense into a liquid inside the nanopores between the clay crystals. Therefore, we conclude that when the pore size and pressure satisfy the Kelvin equation and the surface is hydrophobic, both nanopores in kerogen and nano/micropores between clay crystals can provide storage for hydrocarbons.

Our experiments show that the T_2 relaxation of a butane saturated samples can be range from 1 ms to 7 ms. The T_2 peak at higher vapor pressure can be equal to or larger than those saturated at low vapor pressure. When the hydrocarbon pressure is closer to reservoir conditions, the condensed hydrocarbon should occupy larger pores and the main T_2 peak should be larger than the values reported here.

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