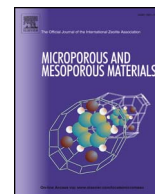




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## Low-field NMR laboratory measurements of hydrocarbons confined in organic nanoporous media at various pressures

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## ABSTRACT

Low-field NMR laboratory measurement are conducted to characterize the adsorption-desorption process of hydrocarbon gases at various pressures in nanoporous media. The investigated media are oil-wet polymer-based spherical activated carbon (AC) beads and a crushed core sample from a gas-producing shale formation containing nanoporous kerogen structures. NMR relaxation times are used to observe the occurrence of sorption phenomena for propane and methane at room temperature under controlled pressure conditions. Results from a PVT simulation software, incorporating a novel phase equilibrium model, show very good agreement between acquired NMR data and simulation results.  $T_1$ - $T_2$  inversion recovery data confirm  $T_2$  and  $T_1$ - $T_2$  ratio cutoff approaches to separate hydrocarbon in nano-scale pores from hydrocarbon in interparticle pores.

### 1. Introduction

The commercial production of hydrocarbon from unconventional shale reservoirs emerged since approximately 5 years. The potential of NMR measurements for probing core samples in the laboratory and subsurface formations by logging tools was identified early on. NMR is sensitive to rock and fluid properties, both being critical for understanding the storage and production behavior of shale reservoirs. Despite a large number of research works and publications (e.g., [1–4]) there are still questions and uncertainties on how to best acquire, process, and interpret NMR data in shale reservoirs.

In previous work we showed that NMR relaxation time measurements are suitable to investigate methane adsorption at elevated gas pressures in a polymer-based spherical activated carbon (AC) as well as in various microporous metal-organic frameworks [5–7]. To further the conceptual understanding of NMR data in organic nano-scale pores, it was decided to conduct measurements on well-defined activated carbon beads and a more complex shale core sample using propane as model hydrocarbon, as well as methane and propane to study the NMR fingerprint of the adsorption behavior of a binary mixture.

### 2. Laboratory measurements

The laboratory device used for low-field NMR measurements at

elevated gas pressures was developed and built at University of Leipzig, Germany [5]. A sketch of the setup is shown in Fig. 1. It consists of a pressure cell accommodating the sample, a gas loading station, and shimmed permanent magnets to generate the static  $B_0$  field for acquiring NMR data at 5.06 MHz. The NMR coil is not shown. CPMG echo trains and inversion recovery (IR) data were acquired at 20 °C and pressures up to 70 bar. The  $\pi/2$  pulse duration was 25  $\mu$ s and the minimum interecho spacing  $TE = 0.2$  ms. The delay time for the IR measurements was varied in 32 steps from 0.1 ms to 2 s, achieving full polarization of the adsorbed hydrocarbon phase for long delay times.

The selected activated carbon (AC) beads have a particle diameter of approximately 0.4 mm. The average intraparticle pore diameter is around 3 nm covering a wide range from below 1 nm to above 50 nm [8]. The intraparticle porosity is 1.2 cm<sup>3</sup>/g, and the BET surface area is 1503 m<sup>2</sup>/g. The ratio of intra-versus interparticle porosity is approximately 40:60 with an estimated ratio of 40:55:5 for micro-, meso-, and macropores for the intraparticle pore volume.

The shale core sample originates from the Fayetteville formation in Arkansas, USA, a predominantly methane-bearing hydrocarbon reservoir. For performing adsorption measurements, the shale core was crushed to particles with a diameter smaller than 0.35 mm and a median diameter of 0.25 mm. The total porosity is 3.6 pu and the total organic content (TOC) is 5–6%. Other contributing minerals are quartz (47%) and clay (34%), as well as plagioclase, calcite, apatite and pyrite

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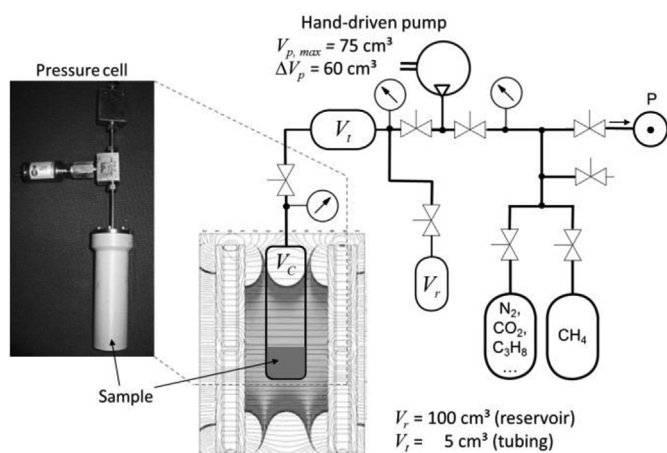


Fig. 1. Laboratory setup at University of Leipzig.

(several percent each). More information on the laboratory setup, AC beads, and some results are found in recent publications [5–9].

### 3. Simulation versus measurements

The effect of adsorption has been widely introduced in the oil and gas industry for gas-in-place calculations in unconventional shale reservoirs. Most approaches employ a Langmuir-type isotherm model to take into account a mono-layer of adsorbed gas, but recent work suggests that this model is not adequate in all cases [10].

Instead of relying on an adsorption-desorption model, we developed a multi-component gas model to compute density and film thickness of adsorbed gas [11]. The calculations are based on a new thermal equilibrium model for nano-scale pores, where the adsorption potential of fluids confined in a slit pore of a given material is computed. Fig. 2 shows calculated density profiles of propane in a carbon slit pore of 1 nm width at five pressures (0.1, 1, 2, 4, and 8 bar).

As expected, the density at the pore surface is close to the liquid density (0.5 g/cc for propane at 8.4 bar and 20 °C). In the middle of the pore, the density can be lower by more than 2 decades at low pressures (free propane gas has a density of 0.0018 g/cc at ambient conditions), while it is close to the liquid density at high pressures.

### 4. Activated carbon – $T_2$ distributions

NMR CPMG  $T_2$  measurements were performed for propane in activated carbon (AC) pores with  $TE = 0.2$  ms at varying pressures. The

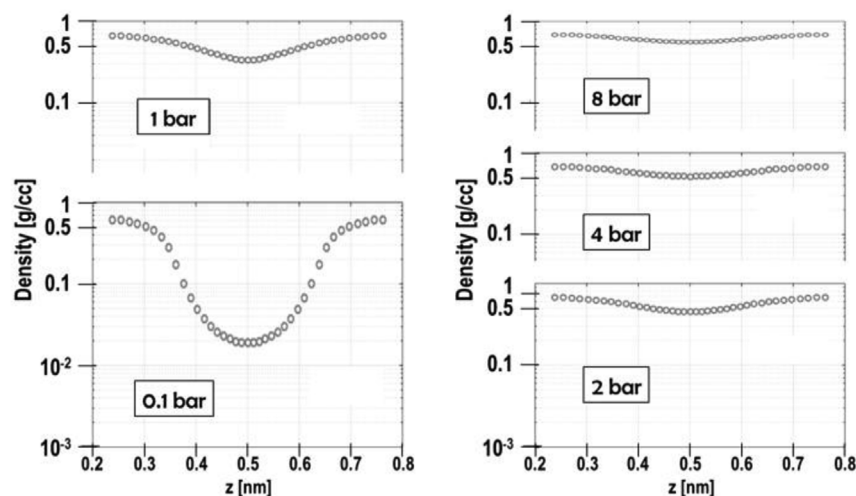


Fig. 2. Simulated density profile of propane in a carbon pore of 1 nm width at 0.1, 1, 2, 4 and 8 bar.

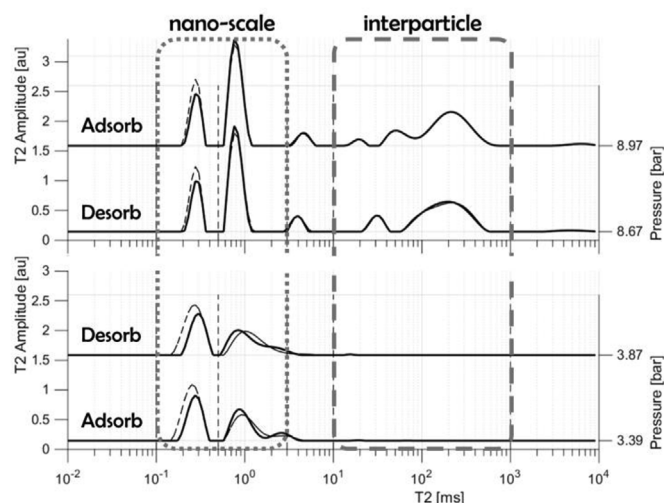


Fig. 3.  $T_2$  distributions for propane at two pressures in activated carbon during adsorption and desorption. Dashed line: original data; solid line: after background signal removal.

aim was to generate isotherm adsorption and desorption curves showing the sorption behavior in the nano-scale pores at low pressures as well as the liquefaction of propane in the interparticle pores above the dew point, i.e., above 8.4 bar at 20 °C. A background signal with  $T_2 = 140$   $\mu$ s was determined from measurements without a sample and subtracted from the data. Fig. 3 shows the  $T_2$  distribution for propane adsorbed in the AC sample at pressures above and below the dew point, before and after removing the background signal.

The bulk  $T_2$  relaxation time of propane gas at 8 bar (i.e., below the dew point pressure) is approximately 3.5 s with a linear pressure dependency. Above the dew point,  $T_2$  is approximately 10 s and virtually independent of pressure. The measured  $T_2$  response of propane in AC beads (Fig. 3) is reduced by four to five decades to roughly 0.1 ms–1 ms in the nano-scale pores and by approximately two decades to around 100 ms in the interparticle pores. The large  $T_2$  reductions indicate a high affinity between fluid and pore surface for hydrocarbon in AC pores and a strong surface relaxation effect driven by the large surface area. No distinct difference is observed between the  $T_2$  distributions of adsorption and desorption measurements in either peak positions or signal amplitudes.

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