Full Length Article

Experimental study of supercritical methane adsorption in Longmaxi shale: Insights into the density of adsorbed methane

Shangwen Zhou [a,b,*], Huaqing Xue [a,b], Yang Ning [c], Wei Guo [a,b], Qin Zhang [a,b]

[a] PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, PR China
[b] National Energy Shale Gas R & D (Experiment) Center, Langfang 065007, PR China
[c] Department of Chemical & Biomolecular Engineering, University of Houston, Houston, TX 77004, USA

A R T I C L E   I N F O

A B S T R A C T

To investigate the methane adsorption capacity and the characteristics of gas shales under high pressures, we conducted total organic carbon (TOC), low-pressure nitrogen adsorption (LPNA), and high-pressure methane adsorption experiments (up to 30.0 MPa) on eight Lower Silurian Longmaxi shale samples collected from northeastern Chongqing, China. The experimental results show that the excess adsorption capacity increases to its maximum value and then decreases with further increasing pressures. TOC and the specific surface area of micro-pores are positively correlated with the maximum methane adsorption capacity. The density of adsorbed phase is the key parameter for converting excess adsorption isotherms into absolute adsorption isotherms and has been determined based on three methods for comparison. The DR-based excess adsorption model in the third method has shown to be more reliable than other methods, in which the density of supercritical methane is considered to be lower than the liquid methane density at the boiling point (0.423 g/cm^3). The absolute adsorption isotherms were obtained after determining the density of adsorbed phase. The actual adsorption capacity would be underestimated when only low-pressure experiments (0–10 MPa) were performed. The analysis of the adsorbed-phase volume demonstrates that the adsorbed methane is stored not only in micropores (< 2 nm) but also in meso-macropores (2–200 nm) as $V_{micro} < V_a < V_{BJH}$. The findings in this work lay the foundations for the further investigation of the shale gas adsorption mechanisms.

1. Introduction

Shale gas has received increasing attentions in recent years due to its remarkable success of commercial production in North America [1–3], which has inspired significant exploration in many other countries. The proven reserve of shale gas in China is about 5440×10^8 m^3, and the production is about 78×10^8 m^3 in 2016 [4]. The exploration and development of shale gas reservoirs in China, particularly in southern Sichuan Basin, has made significant progress in the past few years [5]. Shale gas consists of free gas and adsorbed gas, and mainly exists in nanopores of organic matter and clay minerals [6–9]. Gas-in-place (GIP), the sum of free gas and adsorbed gas, is a key parameter for economic evaluation of a shale gas reservoir. Therefore, accurately determining the adsorbed gas content is critical for the assessment of shale gas reserves and the design of effective production strategies [10].

Methane adsorption in gas shales has been extensively studied by volumetric and gravimetric isothermal adsorption experiments [11–14]. However, the maximum pressure in most of the previous experiments was lower than 15 MPa, which is far below the actual

formation pressure [15–20]. The *in-situ* pressure of Longmaxi formation in the southern Sichuan Basin is about 26 MPa at a depth of 2000 m, with a pressure gradient of 13 MPa/km [4,5]. In this regard, experiments with a high-pressure range (> 25 MPa) are essential for accurate estimation of the actual adsorption capacity in shale formations, but these studies are currently lacking [21–23].

Another important issue is that methane in shale formation is typically at the supercritical state as the formation temperature and pressure is much higher than its critical temperature and pressure (-82.5 °C and 4.64 MPa) [24,25]. As supercritical adsorption, the Gibbs excess adsorption observed in experiments is different from the absolute adsorption (the actual adsorption) [24–28]. Hence, the excess adsorption should be converted into the absolute adsorption in the calculation of true shale GIP and the amount of adsorbed gas at *in-situ* temperatures and pressures [23]. In addition, this conversion is also necessary for the thermodynamic and kinetic analysis of shale gas adsorption [23,29]. Nevertheless, the conversion can be only applied after the density or the volume of adsorbed phase is determined. In the fact of the adsorbed-phase volume varying significantly among samples,

Nomenclature	n_L	maximum adsorption capacity fitted by Langmuir equation, mmol/g rock under STP conditions
D	pore-structure parameter (dimensionless)	P	equilibrium experimental pressure, MPa
m_{abs}	mass of absolute methane adsorption, g	P_L	Langmuir pressure, MPa
m_{ex}	mass of excess methane adsorption, g	V_{sc}	volume of the sample container, cm^3
m_s	mass of the sample, g	V_s	volume of the sample, cm^3
m_{sc}	mass of the sample container, g	V_a	volume of adsorbed phase of methane, cm^3
n_0	maximum adsorption capacity fitted by D-R equation, mmol/g rock under STP conditions	ρ_a	density of adsorbed phase of methane, g/cm^3
		ρ_g	density of free gas phase of methane, g/cm^3
n_{ex}	excess methane adsorption capacity, mmol/g rock under STP conditions	Δm	magnetic suspension balance readings, g

researchers usually determine the adsorbed-phase density as that is a property of a supercritical fluid [30,31]. Since the adsorbed-phase density cannot be measured readily by any experimental method, it was presumed as the liquid-phase methane density (0.423 g/cm^3) or the van der Waals density (0.373 g/cm^3) in many publications [23,30–32], either of which is independent of temperature, pressure, and adsorbents. Alternatively, the adsorbed-phase density can be determined by fitting adsorption isotherms with models such as the extended Langmuir model, Dubinin-Radushkevich (D-R) model, Dubinin-Astakhov (D-A) model and so on [30–34]. However, comparative studies of those methods for the determination of adsorbed phase density have rarely been executed.

In this study, eight core samples are collected from the Lower Silurian Longmaxi formation (LSLF) in northeast (NE) Chongqing area, NE Sichuan Basin, and methane adsorption experiments based on the gravimetric method are performed at pressures up to 30.0 MPa. The objectives of this study are to (1) investigate the methane adsorption capacity and characteristics under high pressure in Longmaxi shales, and (2) propose an improved method of calculating the adsorbed-phase density of supercritical methane in shale.

2. Experimental

2.1. Samples

Eight core samples were collected from the LSLF in northeast Chongqing area near Sichuan Basin (Table 1). The organic-rich shale of LSLF in this area is mainly composed of black shale, black mud-shale, carbonaceous mud-shale, and siliceous shale. The black shale presents the lack of benthos and the richness of lamellar beddings, pyrite crystal, and graptolites, but contains bacteria, algae, siliceous sponge spicules and radiolarian, which indicates low-energy and anoxic sedimentary environment of the deep-water continent shelf [35].

2.2. TOC and LPNA experiments

The total organic carbon (TOC) content was measured by LECO CS-

200 carbon and sulfur analyzer with an accuracy within 0.5%. Crushed samples were immersed in a 5% HCl solution for two days to eliminate all carbonate minerals. The samples were then dried in a stoving oven at 65 °C for two days.

The low-pressure nitrogen adsorption (LPNA) experiment was conducted on a Micromeritics ASAP 2420 apparatus at −196.15 °C. The shale samples were manually crushed and sieved into grains of less than the 200 mesh size (< 75 μm), dried in a vacuum oven at 110 °C overnight, and degassed in the apparatus under high vacuum (< 10 mmHg) for 12 h at 110 °C to further remove moisture and volatile matter. The relative pressure (p/p_0) for N$_2$ adsorption ranges from 0.0009 to 0.995. The Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), and t-plot equations were applied to N$_2$ adsorption isotherms to derive the total specific surface area, the meso-macropore surface area, and the micropore surface area and volume (Table 1) [36–38].

2.3. High-pressure methane adsorption

2.3.1. Gravimetric isothermal adsorption experiment

The high-pressure adsorption isotherm experiments are conducted on Rubotherm gravimetric adsorption instrument. Its core component is the magnetic suspension balance (MSB) with high precision of 10 μg [39,40]. The maximum test pressure and the temperature are 35 MPa and 150 °C, respectively. The long time fluctuation range of temperature can be controlled within 0.2 °C. The basic principle of this instrument is shown in Fig. 1.

The blank test (without shale samples) was first conducted in order to obtain the mass and volume of the adsorption cell. The whole system is pumped down to vacuum conditions, and then the measurement is conducted by dosing pure nitrogen into the adsorption cell up to 5 MPa. The apparent weight of the adsorption cell can be recorded from MSB, which is the interaction between the weight of the adsorption cell and the buoyancy induced by the dosing N$_2$. After the shale sample is put in the adsorption cell, the non-adsorbed pure Helium is dosed into the system after vacuumed. The apparent weight of the adsorption cell with shale also can be recorded from MSB. So the mass of the shale sample can be obtained by the above two steps. And then the adsorption cell is

Table 1
The TOC, pore surface area and pore volume of the shale samples.

Sample	Depth (m)	TOC (%)	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{BJH} (m^2/g)	V_{BET} (cm^3/g)	V_{micro} (cm^3/g)	V_{BJH} (cm^3/g)
X2-1	1955.67	4.1	23.43	7.81	13.85	0.0334	0.0041	0.0289
X2-2	1976.46	5.3	19.65	7.02	11.00	0.0284	0.0037	0.0242
X2-3	1981.00	5.8	22.60	8.31	12.40	0.0281	0.0044	0.0233
X2-4	1982.73	2.8	16.06	4.45	10.57	0.0269	0.0023	0.0244
X3-1	2364.54	3.1	9.83	2.22	7.64	0.0231	0.0012	0.0218
X3-1	2411.88	4.3	11.81	3.22	8.91	0.0231	0.0017	0.0217
X3-3	2437.57	3.7	12.17	3.64	8.81	0.0228	0.0019	0.0213
X3-4	2462.18	3.5	11.90	3.45	8.78	0.0242	0.0018	0.0227

S_{BET} and V_{BET}, the total surface area and volume by the BET equation [36]; S_{micro} and V_{micro}, the surface area and volume of micropores (< 2 nm) by the t-plot equation [37]; S_{BJH} and V_{BJH}, the surface area and volume of meso-macropores (2–200 nm) by the BJH equation [38].