Fuel 218 (2018) 67–77

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Determination of the absolute adsorption/desorption isotherms of CH_4 and n-C_4H_{10} on shale from a nano-scale perspective

Yueliang Liu[a], Huazhou Andy Li[a,b,*], Yuanyuan Tian[b,c], Zhehui Jin[a], Hucheng Deng[b,c]

[a] School of Mining and Petroleum Engineering, Faculty of Engineering, University of Alberta, Edmonton T6G1H9, Canada
[b] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (Chengdu University of Technology), Chengdu 610059, Sichuan, PR China
[c] College of Energy Resources, Chengdu University of Technology, Chengdu 610059, PR China

ARTICLE INFO

Keywords:
Density of the adsorption phase
Absolute adsorption/desorption isotherms
Hysteresis phenomenon
Grand Canonical Monte Carlo simulations
Thermogravimetric analysis

ABSTRACT

Accurate description of absolute adsorption/desorption behavior for hydrocarbons on shale is of critical importance to the understanding of the fundamental mechanisms governing the storage, transport, and recovery of shale gas or shale gas condensate in shale reservoirs. By applying a thermogravimetric method, we first measure the excess adsorption/desorption isotherms of pure CH_4 and n-C_4H_{10} on shale samples over the temperature range of 303.15–393.15 K. The maximum test pressures considered for CH_4 and n-C_4H_{10} are 50 bar and 2 bar, respectively. Grand Canonical Monte Carlo (GCMC) simulations are then applied to calculate the density of the adsorption phase by considering the fluid-pore surface interactions. We use such calculated density of the adsorption phase to calibrate the excess adsorption/desorption isotherms, which enables us to eventually obtain the absolute adsorption/desorption isotherms. Such approach for estimating the density of the adsorption phase is essentially different from the commonly used approaches in which the density of the adsorption phase is considered to be independent of temperature, pressure, and pore size.

The adsorption/desorption test results show that both CH_4 and n-C_4H_{10} exhibit more adsorption as temperature decreases or pressure increases. Their adsorption/desorption isotherms exhibit hysteresis phenomenon and this phenomenon weakens as temperature increases. Comparatively, the hysteresis behavior observed for n-C_4H_{10} is more obvious than that for CH_4. Compared with CH_4, n-C_4H_{10} has higher adsorption capacity under the same condition, indicating its higher affinity towards the shale with organic matters. As for the conventional approaches, the density calculated from the van der Waals constant b or the liquid hydrocarbon density can be used to reasonably well evaluate the absolute adsorption isotherms of n-C_4H_{10} on shale, but tends to underestimate the absolute adsorption of CH_4 on shale. GCMC simulations show that the density of the adsorption phase is strongly correlated with system pressure, temperature, and pore size. Compared to the conventional approaches, GCMC simulations can better capture the *in-situ* density of adsorption phase; on the basis of the *in-situ* density of adsorption phase, we can then achieve more accurate determination of the absolute adsorption isotherms of a given hydrocarbon on shale. This study raises the imperativeness of leveraging more sophisticated simulation tools (such as GCMC) for more accurate determination of absolute adsorption isotherms.

1. Introduction

Shale resources (such as shale gas or shale gas condensate) have emerged as a key energy resource in recent years. Shale rocks generally have higher total organic carbon (TOC) content than the conventional ones, resulting in hydrocarbons being more apt to adsorb on shale surface [1]. Thereof, a significant proportion of reserves in shale reservoirs can be in the adsorbed state. During the production of shale gas or shale gas condensate, desorption plays an important role. Adsorption/desorption of hydrocarbons usually exhibits an interesting phenomenon of hysteresis, and the knowledge about the adsorption/desorption behavior of hydrocarbons in shale is crucial for estimating the hydrocarbon storage capacity and understanding the mechanisms of the subsequent hydrocarbon recovery.

Adsorbed hydrocarbons can account for 20–85 vol% of the total reserves in shale reservoirs [2]. Many previous researches focused on investigating the adsorption capacity of hydrocarbons on shale rocks [3–5]. CH_4, known to be the most abundant component in shale gas reservoirs, was mostly studied. Some heavier hydrocarbons, e.g., C_2H_6, C_3H_8, and n-C_4H_{10}, can be also present with a large quantity in shale

---

[*] Corresponding author at: School of Mining and Petroleum Engineering, Faculty of Engineering, University of Alberta, Edmonton T6G1H9, Canada.
E-mail address: huazhou@ualberta.ca (H.A. Li).

https://doi.org/10.1016/j.fuel.2018.01.012
Received 28 September 2017; Received in revised form 28 December 2017; Accepted 3 January 2018

reservoirs, up to 20 vol% [6]. But adsorptions of these heavier components in shale rocks are scarcely measured in the literature. Pedram et al. (1984) [7] measured the adsorption isotherms of C_2H_6, C_3H_8, and n-C_4H_{10} in two oil-shale samples and found that n-C_4H_{10} has the highest adsorption capacity, followed by C_3H_8 and C_2H_6. But it is noted that the oil-shale they used still have residual oil left in the samples, which can affect the gas adsorption on shale due to the large solubility of various hydrocarbons in shale oil. Therefore, such measured adsorption isotherms could not represent the actual adsorption capacity of gases on shale. Recently, Wang et al. (2015) [6] measured the excess adsorption isotherms of pure CH_4 and C_2H_6 on shale samples. C_2H_6 is shown to have a higher adsorption capacity than CH_4, and Wang et al. (2015) [6] attributed this finding to that C_2H_6 is more apt to get adsorbed on shale samples than CH_4. But this conclusion is made based on the measured excess adsorption isotherms, rather than the absolute adsorption isotherms; excess adsorption isotherms are generally not accurate enough as it neglects the adsorbed-phase volume occupied by the adsorbed gas.

By knowing the pore volume from the helium adsorption, volumetric method is commonly used to measure the adsorption isotherms of hydrocarbons on shale samples [8,9]. Recently, some scholars used the thermogravimetric analysis (TGA) technique to measure the adsorption isotherms [6]. Compared with the volumetric method, TGA loads a smaller sample amount into the setup; the magnetic suspension balance mounted in the TGA setup is capable of measuring the weight change down to 1 μg, rendering the TGA technique more accurate than the volumetric method. However, the adsorption isotherms directly measured by TGA technique are excess adsorption isotherms, which neglects the adsorbed-phase volume and thereby underestimates the total adsorption amount. The density of the adsorption phase is commonly used to correct the excess adsorption isotherms, yielding the absolute adsorption isotherms. In the adsorption phase, gas molecules are in an adsorbed state; to our knowledge, few efforts are dedicated to quantifying the density of the adsorption phase. Previously, constant density values are normally used to pragmatically represent the density of the adsorption phase. Dubinin (1960) [10] suggested that the density of the adsorption phase is a constant value which correlates with the van der Waals constant b. Later, the density of adsorption phase is argued to be equal to the liquid adsorbate density [5,11,12]. Li et al. (2002) [13] compared the aforementioned methods and claimed that the density of the adsorption phase is a function of the system temperature, but its value approaches that proposed by Dubinin (1960) [10]. Recently, with molecular simulations, Ambrose et al. (2012) [14] suggested that the density of the adsorption phase correlates with the system temperature, pressure, and pore size. Actually, fluids in confined space are strongly affected by fluid/pore-surface interactions, especially in shale samples which are usually abundant in nanoscale pores. It is, thereby, of critical importance to precisely capture the density of the adsorption phase in order to more accurately determine the absolute adsorption isotherms.

The objectives of this study are multifold: (1) to use GCMC simulations to capture the *in-situ* density distribution in carbon-slit pores under the effects of the system pressure, temperature, and pore size; (2) to determine the absolute adsorption/desorption isotherms of hydrocarbons on shale samples by knowing the *in-situ* density of the adsorption phase; and (3) to further analyze and compare the characteristics of the absolute adsorption/desorption isotherms of CH_4 and n-C_4H_{10}. As part of a comprehensive study on the adsorption/desorption behavior of hydrocarbons in shale reservoirs, we measure the adsorption/desorption isotherms of CH_4 and n-C_4H_{10} on two shale samples using the TGA technique, and then determine the absolute adsorption/desorption isotherms based on GCMC simulations. CH_4 is selected with the consideration that CH_4 is the most abundant component in shale gas or gas condensate, while n-C_4H_{10} adsorption/desorption isotherms are measured to represent the adsorption/desorption behavior of heavier hydrocarbons in shale reservoirs.

2. Experimental section

2.1. Materials and shale sample preparation

The purities of CH_4 and n-C_4H_{10} (Chongqing Tianke Gas Company, China) used in this study are 99.999 mol% and 99.998 wt%, respectively. The uncertainty of the adsorption/desorption measurements as a result of the gas purities can be negligible. Two shale samples, labeled with #1 and #2, are retrieved from the Longmaxi formation located at the depth of 3836 m and 1562 m, respectively, in the southeastern of Sichuan Basin (China). The temperature of the Longmaxi formation is in the range of 355.15–383.15 K and the pressure of this formation is in the range of 100–450 bar. The two shale samples are selected with different TOC contents to clarify the effect of TOC content on the adsorption capacity of hydrocarbons. In this experiment, the shale samples are crushed into small particles with diameters in the range of 1.00–1.18 mm (US Mesh 16-18). Then, to remove the moisture and *in-situ* gas, the shale particles are placed in an oven at 423.15 K, and being vacuumed for 48 h. Prior to their use in the adsorption/desorption measurements, the shale samples are stored in a zip-locked bag to avoid oxidation and water uptake.

2.2. Characterization of shale sample

This section presents the procedures used to characterize the shale samples as well as the characterization results. Various techniques, including the TOC measurement, the scanning election microscopy (SEM), and the N_2 adsorption/desorption test are adopted to characterize the shale samples.

The TOC content of two shale samples is measured by a combustion elemental analyzer. In this measurement, the organic carbon in shale samples are sparged with oxygen, forming carbon dioxide; then the TOC content is determined by detecting the amount of the carbon dioxide with the non-dispersive infrared detector. The TOC contents of the two shale samples are shown in Table 1. We observe shale sample #1 has a higher TOC content of 3.71 wt%, 3.78 times of that in shale sample #2. The measured TOC contents are in good agreement with the reported values for Longmaxi shale which range from 0.52 to 6.05 wt% [2].

The Hitachi TM-300 SEM setup is used to characterize the surface morphology at an accelerating voltage of 20.0 kV. Prior to scanning, shale surface is polished with argon ion. Subsequently, the polished shale surface is coated with a golden film with a thickness of 10 nm to improve the conductivity. Fig. 1 shows the FE-SEM images taken on the two shale samples. We then further conduct the energy-dispersive X-ray spectroscopy (EDX) analysis on the chosen points “a” and “b” in shale samples #1 and #2, respectively, as marked in Fig. 1. Fig. 2 shows the EDX test results. As seen from Fig. 2, a high concentration of carbon element is present at both sites, indicating that organic matter, i.e., kerogen, is residing in both sites. It can be also seen from Fig. 1 that the kerogen is surrounded by mesopores, which is a typical characteristic observed for kerogen in shale.

Pore size distribution and Brunauer-Emmett-Teller (BET) surface area [4] are characterized by the N_2 adsorption/desorption tests conducted with the Autosorb iQ-Chemiadsorption & Physi-adsorption Gas Adsorption Analyzer (Quantachrome Instruments, USA). Measured under a wide range of testing pressure, N_2 adsorption isotherms can characterize pore size distributions (PSD) in the micro-, meso- and

Table 1
TOC contents and BET surface areas of the two shale samples used in this study.

Shale sample No.	TOC content (wt%)	R_o (%)	BET surface area (m^2/g)
#1	3.71	2.35	2.98
#2	0.98	1.82	2.06