



Methane adsorption measurements and modeling for organic-rich marine shale samples



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ABSTRACT

Understanding methane sorption behavior in the gas–shale system is of great importance for evaluating reservoir production potential and reducing exploration risk. In this study, methane sorption capacities of total 12 organic-rich marine shale samples from the southwest of China were measured by volumetric method. The absolute sorption results were modeled using Langmuir, Brunauer–Emmett–Teller (BET), Dubinin–Radushkevich (D–R) and Dubinin–Astakhov (D–A) models. The accuracy of each model for quantifying shale gas sorption capacity was analyzed and compared by using a residual error analysis technique. The impacts of organic and inorganic constituents on the methane sorption capacity were also analyzed. The experimental results indicate that the maximum absolute methane sorption capacity of the collected marine shale samples is between 0.50 cm³/g and 3.41 cm³/g, which positively correlates with the total organic carbon (TOC) content. The TOC-normalized methane sorption capacity shows a positive correlation with the total clay mineral content and exhibits a significant increase with increasing illite–montmorillonite mixed layers content when it is greater than 9%. For the results of gas sorption modeling, the D–A model is superior to the Langmuir, D–R and BET models, because of the additional parameter describing the micro-heterogeneity of shale rocks. The most commonly used Langmuir model gives a reasonable fit for most of the shale samples, which is comparable to D–A modeling results when TOC content is greater than 5%. The BET model performs poorly and thus it is not recommended for methane–shale sorption modeling exercise. Therefore, both D–A and Langmuir models are recommended for describing methane adsorption on organic-rich shale samples.

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1. Introduction

Shale gas is the fastest growing natural gas resource and has enormous resource potential in the United States and Canada [1–5]. Following the shale gas revolution in the United States and the continuous improvement of drilling and hydraulic fracturing techniques, shale gas has attracted interest from many other countries, such as China, Canada, India and Australia [6,7]. Gas is stored in shale source rocks in two principal ways: (1) as free gas within pores and natural fractures, (2) as adsorbed molecules on the surface of organic matter and inorganic minerals [8]. With different petrophysical properties, the adsorbed gas amount varies from 20% to 85% of the total gas capacity in shales [9]. In order to evaluate the economic potential of gas shale reservoirs as well as to reduce the subsequent exploration risk [3,4,10–13], it is essential to obtain the reliable adsorption capacity in methane–shale system.

The sorption isotherm plays an important role in the reservoir evaluation and is routinely determined by direct experimental measurements. However, limited investigations were reported for the methane sorption isotherms of shale in literatures. The gained knowledge from methane–coal sorption system lays the foundation for the characterization of sorption behavior in methane–shale system [14,15]. In addition to the direct laboratory measurement, various adsorption models have been tested to define the essential sorption capacity for coals. These models include Langmuir model, extended Langmuir model, Brunauer–Emmett–Teller (BET) model, Dubinin–Polanyi theory, Freundlich model and others [14–17]. Among these models, the Langmuir model is the most commonly used one because of its simplicity.

Similar to coal, gas sorption isotherms in shale are conventionally modeled using Langmuir model [18–20]. However, the reported experimental data in the literature were not always well modeled by Langmuir model for methane–shale system [21,22]. Unfortunately, no effort has been made to test the validity of

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different sorption models for methane–shale adsorption behavior. Therefore, it is essential to evaluate the performance of different sorption models in the methane–shale system.

Three marine shale units of Early Cambrian, Early Lower Silurian and Late Permian age in upper Yangtze area (UYA) are the main shale gas resources in China [23]. Among these three, the Cambrian and Silurian shale units are currently considered as the major development targets because of their great thickness, high TOC content, widespread occurrence, as well as favorable mineral composition [7,23,24]. Nevertheless, the methane adsorption behavior of these two shale intervals is still poorly understood. In this study, both experimental investigation and modeling work were analyzed based on 12 organic-rich marine shale samples. The goals of this study are: (1) to assess the maximum methane sorption capacity of marine shale samples from UPA in the southwest of China, (2) to test the validity of different sorption models for methane–shale system, and (3) to discuss the effect of organic matter and mineral constituent on methane sorption capacity. This work may have broad applications for reservoir assessment and evaluation, including gas-in-place (GIP) estimation [13], gas transport dynamics during depletion [25], reservoir geomechanical responses [26], carbon sequestration [27] and others.

2. Experimental methods

2.1. Sample collection and preparation

Fresh shale blocks were collected from outcrops in the potential production regions located in UYA of southwest China (Fig. 1). The short-hole drillings were used to obtain the unweathered shale samples. In this study, 12 marine shale samples (7 samples from the Lower Silurian Longmaxi formation and 5 samples from the Lower Cambrian Niutitang formation) were prepared and investigated for gas sorption capacity estimation. Both formations were known to be organic-rich and the thickness of each formation is more than 80 meters as shown in Fig. 1 [28,29].

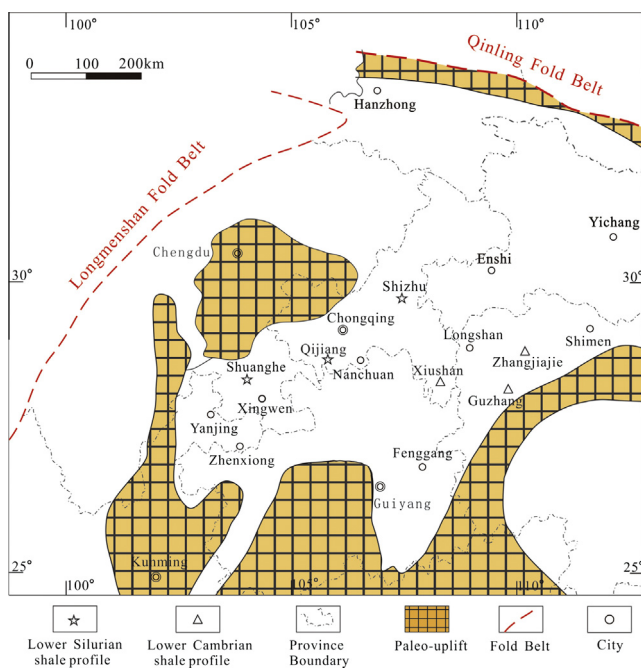


Fig. 1. Geographical map of UYA and sampling location.

2.2. Petrophysical experiment

Before the sorption experiments, the TOC content and mineral composition were characterized for all the collected samples listed in Tables 1 and 2. TOC was measured by LECO CS-230 carbon and sulfur analyzer. X-ray diffraction (XRD) instrument (RIGAKU D/Max-3B diffractometer) was employed to characterize the mineral composition for each sample. During the XRD measurements, the intensity data were collected in the 2θ range of 5–80° at steps of 0.02° (Cu K α). Si was used as the internal standard. Both analyses were performed at the Experimental Research Center of East China Branch, SINOPEC.

2.3. High-pressure sorption experiment

High pressure (up to ~8.5 MPa) methane sorption isotherms at 30 °C were measured using a volumetric apparatus (IS-300 isothermal adsorption/desorption analyzer) manufactured by Terra Tek, USA. The pulverized samples (>60 mesh) were prepared and used for the sorption capacity measurement. For each test, 100–150 g powder sample was used. In order to check the repeatability of the adsorption data, two of the shale samples were selected to carry out the repeatability tests and each sample was measured twice. The error for repeated measurements of sorption capacity is 1.2–2.5%.

2.4. Sorption isotherm models

2.4.1. Absolute adsorption estimation

The sorbed gas volume, as directly measured in the laboratory, is known as excess (or Gibbs) adsorption capacity. In fact, a certain volume in the pore space occupied by the adsorbed phase is no longer available to the free gas. The excess adsorption capacity, however, ignores this adsorbed phase volume, which will underestimate the total sorption capacity. Therefore, the absolute adsorption capacity was estimated by considering the adsorbed phase density. Mathematically, the absolute adsorption capacity can be calculated as follows:

$$V_{abs} = \frac{V_{Gibbs}}{1 - \rho_{gas}/\rho_{ads}} \quad (1)$$

where V_{abs} and V_{Gibbs} are the absolute and Gibbs adsorption capacity; ρ_{gas} is the bulk gas density calculated by equation of state (EOS); ρ_{ads} is the adsorbed gas density and it was assumed to be liquid density of 0.421 g/ml [14].

2.4.2. Adsorption model

2.4.2.1. Langmuir model. The Langmuir model is based on the assumption of adsorption homogeneity, such as equally available

Table 1
TOC content of the shale samples.

Formation	Sample ID	Location	TOC (wt%)	Mean (wt%)
Longmaxi (S_1)	LQ-1	Chongqing	7.68	3.91
	LQ-6	Chongqing	4.24	
	LQ-9	Chongqing	2.18	
	LQ-13	Chongqing	1.46	
	GS-6	Sichuan	5.23	
	GS-7	Sichuan	4.82	
	GS-15	Sichuan	1.76	
Niutitang (C_1)	CX-8	Chongqing	8.54	5.81
	CX-10	Chongqing	10.02	
	CX-18	Chongqing	2.17	
	HW-5	Hunan	4.40	
	HW-9	Hunan	3.90	

Note: geological age: S_1 – Lower Silurian; C_1 – Lower Cambrian.

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