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An improved Langmuir model for evaluating methane adsorption capacity in shale under various pressures and temperatures

Zhihui Ye [a], Dong Chen [a, *], Zhejun Pan [b], Guangqing Zhang [a], Yang Xia [a], Xiang Ding [a]

[a] College of Petroleum Engineering, China University of Petroleum (Beijing), Beijing 102200, China
[b] CSIRO Energy Flagship, Private Bag 10, Clayton South VIC 3169, Australia

A B S T R A C T

A large amount of experimental data for methane adsorption capacity in shale are available and the Langmuir model is capable to describe most of these adsorption isotherms. Two parameters used in the Langmuir model are the Langmuir pressure constant P_L and the Langmuir volume constant V_L. However, experimental data also demonstrate that the gas adsorption capacity of shale is greatly affected by temperature and the classic Langmuir model, with temperature independent V_L and temperature dependent P_L, could not well interpret the experimental data. This is partly attributed to the isosteric heat of adsorption, which makes V_L vary with temperature. The change of V_L with temperature for gas adsorption in shale and its dependency on shale properties are still not well understood. In this study, the variation characteristics of V_L with temperature for gas shale are investigated through a modeling analysis on the published gas sorption data on the shales from the US, China, Canada, and etc. The classic Langmuir model is improved by considering the temperature dependent V_L. The results show that the improved Langmuir model can reasonably describe the shale gas sorption data with less fitting parameters required and it allows a better understanding of gas sorption capacity under the combined effect of temperature and pressure. In addition, the model parameter analysis indicates that the adsorption capacity of shale samples with lower TOC is more likely to be affected by temperature change on the basis of the limited data available. More experiments are required to investigate how the shale properties affect the thermal impact on the gas adsorption capacity on gas shale.

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1. Introduction

Shale gas sorption capacity is one of the most important parameters to estimate the shale gas reserve and understand the gas production behavior from shale reservoirs (e.g., Pan and Connell, 2015). A number of work have been performed to understand the characteristics of shale gas sorption for shales from different basins (Lancaster and Hill, 1993; Lu et al., 1995; Ross and Bustin, 2007, 2008; Chalmers and Bustin, 2008; Strapoc et al., 2010; Zhang et al., 2012; Wang et al., 2013; Hu, 2014). The Langmuir isotherm equation is usually applied to describe the gas adsorption by fitting two parameters: Langmuir volume constant V_L, which represents the maximum gas adsorption capacity at infinite pressure and Langmuir pressure constant P_L, which governs the curvature shape of gas adsorption corresponding to the pressure at which

adsorption volume is half of the V_L.

Since many shale reservoirs are thick, they usually have a significant temperature difference along the vertical direction, affecting the shale gas storage behavior. The temperature dependence of methane sorption capacity on shales has been reported in a few publications (Lu et al., 1995; Ross and Bustin, 2007; Strapoc et al., 2010; Zhang et al., 2012; Ji et al., 2014; Hu et al., 2015). Lu et al. (1995) measured gas adsorption in two Devonian shale samples at various temperatures and reported a general reduction of adsorption with increasing temperature. Similar results of reduction in adsorption capacity for Woodford and Tarrant shales were reported by Zhang et al. (2012). Hu et al. (2015) measured the methane adsorption isotherm for Woodford shale samples at 35–65 °C and presented that lower adsorbed amount is obtained at higher temperature. Ji et al. (2014) measured the sorption capacity of two Triassic lacustrine shale samples from Ordos Basin at various temperatures, and observed the reduction of gas adsorbed amount with increasing temperature as well. However, few efforts have been made to investigate the relationship between sorption

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* Corresponding author.
  E-mail address: dong.chen@cup.edu.cn (D. Chen).

reduction and shale properties.

In the classic Langmuir equation under different pressure and temperature conditions, P_L is temperature dependent while V_L is temperature independent. However, in many experiments, the classic Langmuir equation failed to reasonably describe the gas adsorption capacity under varying pressure and temperature conditions for shales. Different from the classic Langmuir model, most experimental results indicate that V_L is temperature dependent. Some researchers (Lu et al., 1995; Zhang et al., 2012; Rexer et al., 2013) attributed the temperature dependence to the isosteric heat of adsorption, because gas adsorption is an exothermal process and increasing temperature would restrain this process. Therefore V_L decreases with increasing temperature in many experiments.

Ji et al. (2014) applied an empirical linear relation to represent the decrease of Langmuir volume constant V_L with increasing temperature. Although this relation predicts the general trend of V_L decreasing with temperature increase, the accuracy is not satisfactory. A quantitative correlation with high accuracy is required.

The aim of the present work is to parameterize the reduction in sorption capacity as temperature increased, by considering the temperature dependent V_L based on the classic Langmuir model. The constant Langmuir volume constant V_L adopted in classical Langmuir equation is then modified to be a function of temperature. By analyzing the experimental data for gas sorption capacity on different shale samples, we proposed an exponential model to relate V_L to temperature. The model is applied to analyze the gas sorption data under a wide range of pressure and temperature conditions. Furthermore, a discussion part is added to propose potential reasons for the variation of V_L with temperature.

2. The improved Langmuir model

The present research proposes an improved Langmuir model by introducing an exponential relation expressing the temperature dependent V_L based on the Langmuir isotherm model.

The Langmuir isotherm model is expressed as (Langmuir, 1918)

$$V = \frac{V_L p}{p + P_L} \tag{1}$$

where V is the gas adsorption amount, p is the pressure, V_L is the Langmuir volume constant and P_L is the Langmuir pressure constant.

V_L is considered as a constant (temperature independent) in the classic Langmuir model. However, the experimental data (typically presented by Devonian shale, Antrim shale, Ordos Basin, Green River formation and Woodford shale) of the methane adsorption amount of different shale samples showed that V_L decreased with temperature increase. As shown in Fig. 1, a semi-logarithm plot between V_L and temperature T, the values of V_L for these shale samples are found to be exponentially related with temperature. Based on the exponential relationship between V_L and temperature T observed from the measured results of gas adsorption capacity, we proposed an exponential relation to describe the variation of V_L as a function of temperature T, expressed in Eq. (2). In this equation, the V_s is the theoretical maximum adsorption capacity for the adsorbent, and D_T is a reduction coefficient related with temperature increase.

$$V_L = V_s \cdot \exp(-D_T T) \tag{2}$$

In Eq. (1), P_L is the reciprocal of affinity constant b (Do, 1998):

$$P_L = \frac{1}{b} \tag{3}$$

The affinity constant b is a measure of the attachment of an adsorbate molecule that attracted onto a surface (Do, 1998) and it can be expressed as a function of temperature T, heat of adsorption Q, the universal gas constant R_g, and the b_s.

$$b = b_s \exp\left(\frac{Q}{R_g T}\right) \tag{4}$$

where b_s is defined as

$$b_s = \frac{\alpha}{k_{dn}\sqrt{2\pi M R_g T}} \tag{5}$$

where α is the sticking coefficient, k_{dn} is the rate constant for desorption at infinite temperature, M is the molecular weight, R_g is gas constant. Combine the coefficients in the Eqs. (4) and (5), the Langmuir pressure constant P_L can be expressed as

$$P_L = \frac{\sqrt{T}}{A \exp(B/T)} \tag{6}$$

where A and B are comprehensive coefficients that can be used in matching the adsorption data. The coefficient A is written as

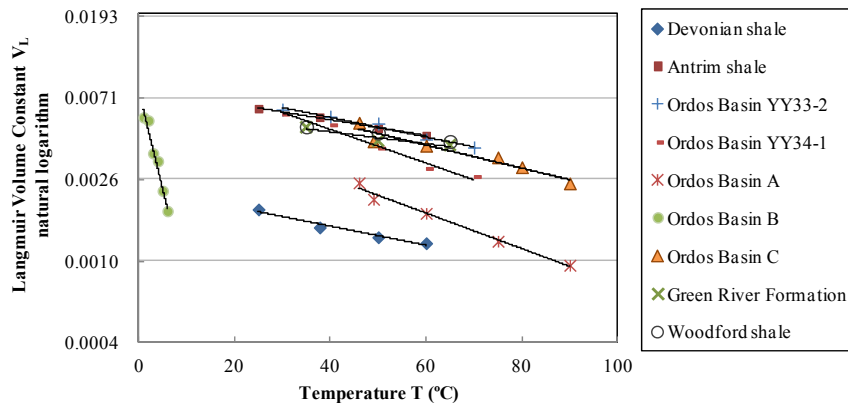$$A = \frac{\alpha}{k_{dn}\sqrt{2\pi M R_g}} \tag{7}$$

and B is written as

Fig. 1. The Langmuir volume constant V_L vs. temperature T for typical shale samples.