The Ono–Kondo model and an experimental study on supercritical adsorption of shale gas: A case study of on Longmaxi shale in southeastern Chongqing, China

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ARTICLE INFO

ABSTRACT

Adsorbed gas, the presence of which is a significant difference between the shale gas and conventional gases, has attracted considerable attention, particularly in China. A series of shale gas adsorption isotherms were measured at 30 °C and at pressures up to 10.94 MPa for the lower Silurian marine shale of the Longmaxi Formation collected in southeastern Chongqing, China. The maximum adsorbed gas content was 0.72–3.89 m^3/t. Using measurements of the total organic carbon (TOC), thermal maturity, X-ray diffraction and low-pressure nitrogen adsorption, the basic characteristics of the shale reservoir were analyzed. The Ono–Kondo model was used to fit the measured methane adsorption isotherms with correlation coefficients as high as 0.9896–0.9976. The model characterized the filling adsorption features of nanopores under supercritical conditions. Monolayer saturated adsorption is generally less than the maximum adsorption, suggesting that as pressure increases, methane adsorption tends to become a multilayer adsorption. Among the geological parameters, TOC displayed a strong positive correlation with shale gas adsorption capacity. No obvious relation between the shale gas adsorption capacity and the clay was observed, indicating that organic matter has more significant contribution to shale gas adsorption than clay. The adsorption capacity significantly increased linearly with increasing total surface area, suggesting significant effects of pore structure on the shale gas storage. On the basis of the pressure sensitivity of adsorption rate, the adsorption process was divided into three stages: (1) an initial low-pressure stage, (2) an intermediate-pressure stage, and (3) a high-pressure stage. The third stage displayed methane desorption at high pressure. The similarities and differences of the Langmuir model and the Ono–Kondo model were assessed. An evaluation of which model is more accurate is difficult because both models can show good fits to experimental data. However, considering the methane adsorption mechanism, the Ono–Kondo model appears to be more reliable in describing the process of methane adsorption in shale because it predicts a more reasonable supercritical adsorption and can reflect the adsorption transformation from monolayer to multiple layers.

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1. Introduction

As the majority of oil and gas have been discovered and are getting exhausted, unconventional resources are gradually becoming as exploration targets, particularly the shale gas. The natural gas within shale has been suggested to be a potential resource, and is available in the form of free gas, adsorbed gas, and dissolved gas (Curtis, 2002). Adsorbed gas, the presence of which is a significant difference between the shale gas and conventional gases, has attracted considerable attention. Adsorbed gas constitutes approximately 20%–85% of the total shale gas content (Curtis, 2002; Montgomery et al., 2005; Ross and Bustin, 2007). China is still in the early stage of the shale gas exploration and development. Research on adsorbed gas is significant for

understanding the mechanism of the shale gas accumulation. Quantitative analysis of the adsorbed gas content is also significant in resource assessment and the selection of favorable areas for shale gas.

The adsorption of shale gas is a complex process controlled by the properties of organic matter, composition of matrix minerals, pore structure characteristics, amount of water, and reservoir pressure and temperature. Previous studies indicated that organic matter provides the main sites for adsorbed shale gas storage; strong positive correlations between the abundance of organic matter and the shale gas adsorption capacity have been documented (Bi et al., 2014; Chalmers and Bustin, 2007, 2008; Ji et al., 2014; Jarvie et al., 2007; Loucks et al., 2009; Rexer et al., 2013; Zhang et al., 2012). In several studies, clay was considered as important contributors to the shale gas adsorption capacity, particularly montmorillonite and illite/smectite mixed-layer, which possess larger surface areas for shale gas adsorption (Gasparik et al., 2012; Ji et al., 2012).

The adsorption of gas in microporous solids has been studied for several decades (Adamson, 1967; Cazorla-Amoros et al., 1998; Chen and Yang, 1994; Gregg and Sing, 1982; Talu and Myers, 1987; van der Plas, 1970). Some previous research was based on the Langmuir adsorption isotherm model. The Langmuir theory assumes that (1) the methane is a monolayer adsorbate, (2) the surface of the solid adsorbent is homogeneous at constant adsorption heat, (3) the molecules of the adsorbates do not undergo horizontal reactions, and (4) dynamic adsorption is equalized. In experimental and actual geologic conditions, shale gas acts as a supercritical fluid. Adsorption of shale gas is a multilayer adsorption with forces operating between the molecules. With increasing pressure, desorption occurs, which do not agree with the Langmuir assumptions. Several multilayer adsorption theories such as the Brunauer−Emmett−Teller (BET) theory, the Dubinin−Radushkevich (DR) theory, and the Dubinin−Astakhov theory are widely used models for microporous systems. These models are widely applied to adsorption of vapors on microporous adsorbents; however, several fundamental defects limit the utility and usefulness of the parameters obtained by fitting these models to experimental data. Taking the DR theory as an example, Aranovich and Donohue (2000) suggested that (1) the derivation of the DR equation follows an arbitrary assumption that there is a "Gaussian distribution of adsorption space" with respect to the adsorption potential (Do, 1998; Dubinin, 1965), (2) the energetic parameter is not clearly defined, (3) the equation does not reduce to Henry's law as relative pressure becomes zero, and (4) the equation can be used only at subcritical conditions, as it considers the saturation vapor pressure and hence is not applicable to many common gas systems at room temperature. In this study, the Ono−Kondo model [Eq. (1)] (Ono and Kondo, 1960) was used to discuss the supercritical adsorption isotherms of methane in microporous systems based on previous research (Aranovich and Donohue, 1995, 1996, 1997, 2000; Bradley et al., 1996). The Ono−Kondo lattice theory was initially used to describe the density alterations in a gas−liquid interface. Aranovich and Donohue (1995, 1996, 1997, 2000) subsequently applied the Ono−Kondo function to studies regarding gas adsorption on microporous solids, and their findings about the adsorption behavior of supercritical fluids were useful. This theory: (1) is simple but has a theoretical basis, (2) yields the correct limiting behavior, (3) can be used at supercritical conditions, (4) describes experimental data over an extended range of pressure and temperature, (5) predicts adsorption behavior over an extended range of conditions, and (6) calculates the data more accurately (Aranovich and Donohue, 2000). The Ono−Kondo model can be written as follows:

$$n = \frac{2n_0\rho_g\left[1 - \exp\left(\frac{\varepsilon_s}{k \cdot T}\right)\right]}{\frac{\rho_g\rho_{mc}}{\rho_{mc}-\rho_g} + \rho_{mc}\exp\left(\frac{\varepsilon_s}{k \cdot T}\right)} \tag{1}$$

where n is the adsorption density in mmol/g, n_0 is the saturated adsorption density of monolayer in mmol/g, ρ_g is the molar density of the free methane in mol/L, ρ_{mc} is the molar density of the maximum methane adsorption in mol/L, ε_s is the energy of the methane−micropore interaction, k is the Boltzmann's constant equal to 1.38×10^{-23} J/K, and T is the temperature in K.

The aim of this study is to investigate the characteristics and significance of supercritical adsorption, determine how the adsorption process proceeds with increasing pressure, and demonstrate the suitability of the Ono−Kondo model for prediction of supercritical adsorption. This study can provide significant guidance for characterization of the supercritical adsorption of shale over an extended range of pressure and temperature and it is also significant for improving the understanding of the mechanism of shale gas adsorption.

2. Sampling and methods

2.1. Samples and preparation

The southeastern Chongqing area in the Sichuan Basin, China, is part of the core area of the upper Yangtze region. In this area, organic-rich shale of the lower Silurian Longmaxi Formation occurs with a wide lateral distribution, great thickness, and shallow burial depth. Shale gas is abundant within the Longmaxi Formation, but the lack of bulk material from well drilling and logging from the initial stage of exploration has increased the difficulty of resource assessment of the shale gas. Therefore, the study of adsorbed gas, which is the main constituent of shale gas, is significant for the assessment of the Longmaxi organic-rich shale.

A total of nine shale core samples of the Longmaxi Formation were collected from one shale gas well in southeastern Chongqing, Sichuan Basin. Prior to measurement, 100 g of each core sample was ground into powder of 80−100 mesh size (sieve pore diameter 180−150 μm). These powdered samples were prepared for analysis of total organic carbon (TOC), thermal maturity, X-ray diffraction, and N2 adsorption, as well as methane isothermal adsorption experiments, which were conducted at the Chongqing Mineral Resources Supervision and Test Center.

2.2. TOC, thermal maturity and X-ray diffraction analysis

TOCs of the shale samples were measured using a Leco CS-230 carbon analyzer. Prior to measurement, the samples were treated with hydrochloric acid to remove carbonate. Because of the lack of vitrinite in the Longmaxi shale, the pyrobitumen reflectance was measured using a Zeiss microscope and an MPV−I microphotometer.

X-ray diffraction (XRD) analysis is primarily used to identify crystalline material and to provide information on unit cell dimensions (Ufer et al., 2008). The analyzed material was finely ground, homogenized, and the average bulk composition was determined. X-ray diffraction measurements of randomly oriented powder samples were conducted to determine the matrix mineral compositions using a ZJ207 Bruker D8 advance X-ray diffractometer at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5406 for CuKα1).

2.3. Low-pressure nitrogen gas adsorption

N2 adsorption analysis was carried out with a Micromeritics®