



An investigation into the thermodynamic characteristics of methane adsorption on different clay minerals



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ABSTRACT

In this work, we investigate the methane adsorption characteristics of common clay minerals using experimental and theoretical analyses. Models for the isosteric heat of adsorption and variation of the surface free energy were established using thermodynamic theory and an improved D-A model, respectively. The models were used to investigate changes of the isosteric heat of adsorption and variation of the surface free energy of the different clay minerals. Then, the adsorption thermodynamics and adsorption capacity characteristics of the different clay minerals were investigated. An improved D-A model was developed by combining the D-A equation and adsorption characteristic curve and was used to fit the methane adsorption isotherms of the clay minerals. The model fitting results replicated the experimental results. The variation of the surface free energy is a function of pressure and temperature, which increased rapidly with the pressure increase at low pressures, while the free energy increased more slowly at higher pressure and decreased with increasing temperature. The order of the variation of the surface free energy from largest to smallest is illite, chlorite, kaolinite and montmorillonite, which is in disagreement with the order of the methane adsorption capacity, indicating that the specific surface area is a major factor that affects the methane adsorption capacity of the clay minerals. The isosteric heat of adsorption decreased with increasing methane capacity. The initial isosteric heats of adsorption of the clay minerals were 26.088 kJ/mol, 25.543 kJ/mol, 20.503 kJ/mol and 24.229 kJ/mol for montmorillonite, kaolinite, illite and chlorite, respectively. This indicates that the intermolecular forces between the methane molecules and the clay minerals decreases in the following order: montmorillonite, kaolinite, chlorite and illite.

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1. Introduction

The study “Technically Recoverable Shale Oil and Shale Gas Resources: An Assessment of 137 Shale Formations in 41 Countries outside the United States” was conducted by the U.S. DOE’s Energy Information Administration (EIA) in 2013. This report, which contains an evaluation of the shale gas resources of 42 countries, notes that the global net technically recoverable shale gas resource is approximately $220.73 \times 10^{12} \text{ m}^3$ (EIA, 2013), indicating there is a significant developmental potential for shale gas resources throughout the world. There are three types of states of the gas in shale formation: free gas, adsorbed gas and dissolved gas (Curtis, 2002). Free gas mainly exists in micro-fractures or bigger pores in

organic matter or bigger pores among mineral grains in shale gas reservoirs, whereas adsorbed gas exists on the surface of the mineral grains and organic matter in the shale gas reservoirs (Zhang et al., 2004). Curtis (2002) drew a conclusion that adsorbed gas accounts for approximately 20–85% of the total gas content in five American shale gas reservoirs, suggesting that adsorbed gas plays an important role in shale gas resources. Therefore, it is important to investigate the methane adsorption capacity on the shales to explore shale gas resources more fully. In addition to environmental factors (e.g., pressure, temperature, moisture and the purity of methane), the physical and chemical properties of shales (e.g., organic matter and mineral compositions) can affect the methane adsorption capacity of shales. According to previous research (Liu et al., 2015; Liang et al., 2015; Xiong et al., 2015), it is suggested that the distribution of clay mineral contents of organic-rich shales was variable and frequently high, ranging from 11.1% to 65.94%, indicating that clay minerals have a distinct mineralogical

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composition of organic-rich shales. That is to say, the clay minerals have an important impact on the methane adsorption capacity of shales. Additionally, water has an important impact on the methane adsorption capacity of shales (Gasparik et al., 2014), but we do not consider the influence of the water in this paper. Therefore, different types of clay minerals are selected as the research object in the paper, which is an important element to evaluate the methane adsorption capacity of shales.

Recently, isothermal adsorption experiments were conducted, primarily to investigate the methane adsorption capacity of different types of clay minerals. Lu et al. (1995) studied the methane adsorption capacity of illite at a temperature of 310.8 K and below 8 MPa of pressure; Cheng and Huang (2004) reported the methane adsorption capacity of kaolinite and montmorillonite at low pressure (<0.3 MPa), and Ross and Bustin (2009) investigated the methane adsorption capacity of kaolinite and montmorillonite at pressures lower than 6 MPa; Ji et al. (2012a, 2012b, 2012c, 2013) investigated the methane adsorption capacity of montmorillonite, illite, an illite/smectite mixed layer, kaolinite and chlorite under different temperature and pressures; the influences of particle sizes on methane adsorption capacity were also discussed. Liu et al. (2013) examined the adsorption of methane on illite, kaolinite and montmorillonite below 18 MPa. Fan et al. (2014) investigated the methane adsorption capacity of montmorillonite, illite, kaolinite and chlorite under different temperatures and pressures. In addition, Chalmers and Bustin (2008a, 2008b), Song et al. (2013) and Zhang et al. (2013) investigated the influences of clay minerals on the methane adsorption capacity using a statistical method based on the adsorption isothermal experiments of shales. All research above contrasted and compared the methane adsorption capacity of different clay minerals using the Langmuir parameters under equilibrium conditions according to the results of the adsorption isothermal experiments. However, the adsorption amount reflects other factors as well, including the specific surface area of the clay minerals and the adsorption amount per unit surface area, rather than the specific differences in the methane adsorption capacity of the different types of clay minerals.

Furthermore, methane adsorption on different clay minerals is a type of supercritical adsorption, which also referred to as the adsorption of supercritical fluids, is the adsorption at above-critical temperatures. The Dubinin-Astakhov (D-A) model (Dubinin and Astakhov, 1971), deduced by the theory of adsorption potential, has wide application in aspects of solid-gas physical adsorption (Yang et al., 2013; Clarkson and Haghshenas, 2013; Sheng et al., 2014; Amankwah and Schwarz, 1995; Ozawa et al., 1976; Zhan et al., 2004; Hao et al., 2014), which is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption (Oura et al., 2003). The D-A model is suitable for modelling both supercritical adsorption and subcritical adsorption (where the temperature is below the critical temperature of the methane) (Do, 1998). Moreover, the adsorption characteristic energy is a function of temperature, as concluded by Yang et al. (2013), Clarkson and Haghshenas (2013) and Sheng et al. (2014) after applying the Dubinin-Radushkevich (D-R) or D-A equation when researching the methane adsorption mechanism of shales. This is inconsistent with adsorption potential theory. Therefore, the objectives of the paper are to investigate the mechanism of methane supercritical adsorption on clay minerals using an improved D-A model; this was conducted by combining the D-A equation with the adsorption characteristic curve. The calculation of the isosteric heat of adsorption and the variation of the surface free energy were established according to thermodynamic theories and the improved D-A model, which can be used to study changes in the isosteric heat of adsorption and the variation of the surface free energy of different types of clay minerals. The methane adsorption

capacity and adsorption thermodynamic characteristics of the different types of clay minerals are also discussed. It is anticipated that our research will provide a deeper understanding of the adsorption rule of methane on different types of clay minerals and reveal differences in the various aspects of the methane adsorption capacity on different types of clay minerals.

2. The adsorption isothermal experiments

The different types of clay minerals examined in this study were collected from the field, including montmorillonite, kaolinite, chlorite and illite. Detailed information on the sampling points and mineralogical compositions of the different types of clay minerals are listed in Ji et al. (2012b). The isothermal adsorption experiments of the different types of clay minerals were conducted by the volumetric method at different temperatures (308 K, 323 K, and 338 K), which were measured in the Gas Geochemistry Laboratory of the Bureau of Economic Geology. The isothermal adsorption experiments were performed on a HP5890 GC oven including reference volume, sample cell, pressure transducer and Valco valves. The experiments include the following steps: (1) Heat the samples with a sieve size of 500 μm at 105 $^{\circ}\text{C}$ in the oven for 24 h to ensure moisture evaporation; (2) Evacuate for the experimental setup; (3) Measure the void volume in the adsorption chamber; and (4) Measure the methane adsorption isothermally. The experimental dates of the methane adsorption on the different types of clay minerals are listed in Ji et al. (2012c). The temperature adsorption isotherms of the different types of clay mineral samples are shown in Fig. 1, and they are the data on which this study is based. From Fig. 1, we note that the slope of the curves reduces as the pressure increases and gradually levels out. The methane adsorption capacity decreases with increasing temperature. In addition, we can observe that the methane adsorption capacities of the different types of clay minerals decrease in the following order: montmorillonite, kaolinite, chlorite and illite, which is generally consistent with the order of the specific surface area of the different types of clay minerals (montmorillonite is 76.413 m^2/g , kaolinite is 15.281 m^2/g , chlorite is 7.118 m^2/g and illite is 11.738 m^2/g) (Ji et al., 2012c, 2013).

The methane adsorption amounts per unit surface area on the different types of clay minerals are shown in Fig. 2. As seen, we observe that the amounts of methane adsorption on the different clay minerals per unit area at different temperatures decreased in the following order: illite > chlorite > kaolinite > montmorillonite, which is in disagreement with the order of the methane adsorption capacity on the different types of clay minerals. These conclusions indicate that there are differences of the methane adsorption capacity on the different types of clay minerals. This may be related to the microstructure of the different types of clay minerals. The methane adsorption on the different types of clay minerals is a macroscopic behaviour. The thermodynamic theory may be used to explain the differences of the methane adsorption capacity on the different types of clay minerals. Therefore, a thermodynamic analysis model must be established, and the adsorption model would be adopted to calculate the amount of methane adsorption at a pressure under a certain temperature.

3. The improved D-A model

In general, some properties of the absorbent can be analysed by using the fitting parameters from the isothermal adsorption experiment data. Therefore, the adsorption models with physically significance parameters are adopted to fit these experiment data. The D-A model (Dubinin and Astakhov, 1971), which is suitable for both subcritical and supercritical adsorptions (Do, 1998), has been

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