Competitive adsorption of methane and ethane in montmorillonite nanopores of shale at supercritical conditions: A grand canonical Monte Carlo simulation study

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HIGHLIGHTS

- The first study of competitive adsorption of CH_4/C_2H_6 in clay nanopores of shale.
- We study the sorption behavior using GCMC simulations at supercritical conditions.
- Effects of pressure, temperature, mole fraction, and water content are analyzed.
- The preferential adsorption of C_2H_6 over CH_4 fails at elevated pressures.
- Enlarging the pore or increasing the water content impedes C_2H_6/CH_4 selectivity.

GRAPHICAL ABSTRACT
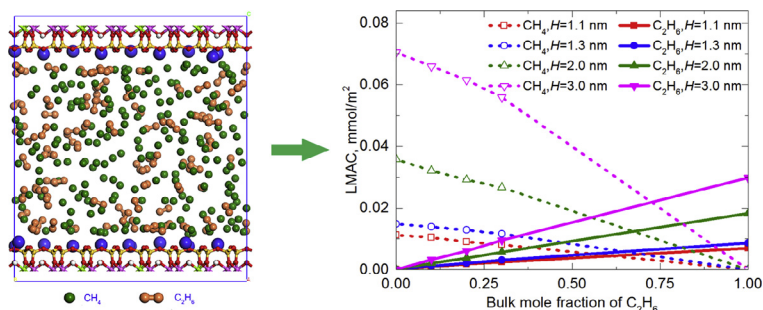
ABSTRACT

Because ethane acts apart from methane as a significant component in shale gas, knowledge of the competitive adsorption behavior of methane and ethane in shales, primarily under supercritical conditions, is crucial to understanding the fundamental mechanisms governing fluid storage, transport, and hydrocarbon production. Using grand canonical Monte Carlo simulations, we studied the adsorption behavior of single and binary mixtures of methane and ethane in montmorillonite slits having apertures ranging from 1.1 to 3.0 nm, for pressures up to 40 MPa over a temperature range of 333–393 K. The dependences of adsorption isotherms and selectivity on pore size, pressure, temperature, fluid composition, and water content were examined. With increasing pressure, the selectivity of ethane relative to methane decreases and tends to approach a constant smaller than unity, indicating that the adsorption propensity of ethane fails at higher pressures. The weaker interactions among adsorbate molecules, posterior adsorption saturation, and smaller molecular size of methane lead to its higher adsorption affinity at elevated pressures. Enlarging the pore or increasing the water content suppresses the selectivity of ethane over methane; selectivity decreases more steeply with pressure at lower temperatures. While there is only negligible selectivity variation with fluid composition at low pressures, the preferential adsorption of ethane at high pressures is facilitated by decreasing its mole fraction in the bulk fluid. We also discussed the implications of our work on shale gas exploitation. This study provides better insight into the storage mechanisms of shale gas and sheds light on the reliable estimation of gas-in-place and, more generally, competitive adsorption of mixtures in nanoporous materials.

1. Introduction

In recent years, hydrocarbon production from shale systems has emerged as a pivotal energy resource, owing to huge reserves and profitable yields after hydraulic fracturing, along with the promising potential for CO_2 storage [1–4]. According to the Energy Information Administration (EIA), total production of shale gas in the United States has surged from 3.6 billion cubic feet per day (Bcf/d) in 2000 to ~46.2 Bcf/d in 2017, constituting ~60% of the country's natural gas production [5,6]. Gas storage in shale primarily exists in three patterns: free gas within pore networks and natural fractures, adsorbed gas onto the surface of shale matrix, and dissolved gas in shale kerogen and formation fluid [7,8]. Among these mechanisms, gas adsorption plays a dominant role because recent studies suggest that the adsorbed gas can account for > 50% of the total gas content in shale [9], and adsorption/desorption behavior is responsible for the long-term sustainability of gas production [10]. Therefore, the fundamental nature of gas adsorption on shales is essential to shedding light on the principles governing gas storage and promoting the effective evaluation and reliable production of shale resources.

Much attention has been paid to CH_4 adsorption and its competitive adsorption with CO_2/N_2 on shales/coals, which is beneficial for enhanced gas recovery and CO_2 sequestration [11–16]. For example, Zhang et al. [11] measured CH_4 adsorption isotherms on bulk shales and isolated kerogens to study the effects of organic matter type and thermal maturity. The sorption and desorption capacities of CH_4 and CO_2, as well as their mixtures, on dry coals were experimentally determined by Busch et al. [12], from which the preferential adsorption behavior of CO_2 was observed. The investigations have also been extended to high-pressure conditions and wet coals [13,14]. Gensterblum et al. [14,15] explored the influences of coal maturity and moisture on CO_2 and CH_4 adsorption isotherms, and proposed a conceptual model to elucidate the inner mechanism.

Owing to the heterogeneous molecular structure of shales/coals and the extremely complex adsorption behavior, especially at sedimentary conditions, accurate estimation of adsorption isotherms is challenging, because it requires not only sophisticated equipment but also strict measurements and data-interpretation procedures [17]. Therefore, molecular simulation has been employed as a useful tool to complement the experiments [18–24]. On the basis of grand canonical Monte Carlo (GCMC) simulations, Liu and Wilcox [19] analyzed the effect of several oxygen-containing chemical groups on CO_2/CH_4 adsorption capacities in functionalized graphitic slits. A similar technique was also utilized to examine the impact of water on the adsorption capacities of CH_4, CO_2, and their binary mixtures in clay nanopores, from which a negative contribution of water content was reported [20–22]. Using an extended poromechanical model, Zhang et al. [23] related the GCMC simulation results to coal swelling and suggested that the volumetric strain increases with the mole fraction of CO_2. Most recently, the influences of kerogen maturity and moisture content on the adsorption behavior of CH_4 and CO_2 in the realistic kerogen models have also been probed [24].

However, fluid composition in shale systems is very complex and its state varies from dry gas to liquid [25–27]. As shown in Fig. 1, in shale gas reservoirs such as Marcellus and Barnett, fluid contains ~80% methane; in Eagle Ford gas condensate and Bakken tight oil, the molar fractions of methane are 56.9% and 36.7%, respectively. Nevertheless, as the second primary component, ethane accounts for up to 16% of the fluid concentration in shale (Fig. 1). Given that C_2H_6 may show adsorption capacity on shale superior to that of CH_4, understanding the adsorption characteristics of CH_4/C_2H_6 mixtures in shale is crucial for the accurate estimation of gas-in-place and may provide better insight into shale gas production [28–30].

Some experimental and numerical studies on the adsorption behavior of CH_4 and C_2H_6 in shales have been conducted. Using thermogravimetric analysis (TGA), Wang et al. [28] measured the single-component and binary mixture sorption isotherms of CH_4 and C_2H_6 on the Marcellus shale and used the multicomponent potential theory of adsorption (MPTA) model to describe the data. Then, they adopted this technique to study the sorption kinetics of CH_4/C_2H_6 mixtures in gas shales and observed a production lag in C_2H_6 relative to CH_4, indicating the stronger affinity of C_2H_6 [29]. Sharma et al. [30] probed the adsorption capacity and diffusivity of pure CH_4 and C_2H_6 in neutral montmorillonite pores (without interlayer ions) by means of GCMC and molecular dynamics (MD) simulations. Collell et al. [31] simulated the adsorption data of CH_4/C_2H_6 mixtures on a mature kerogen model and examined the suitability of the ideal adsorbed solution theory (IAST) and an improved Extended Langmuir model. They suggested that these theoretical models provide good estimates of adsorption isotherms at low pressures ($P < 1$ MPa); however, this agreement is worsened at high pressures (up to 20 MPa), especially in confined structures. In our previous work, we also conducted MD simulations to study the adsorption behavior and density profiles of hydrocarbon mixtures in shale organic pores and developed a model to quantify recoverable oil-in-place in shale systems [32].

Even though some advances have been made to discern the competitive adsorption behavior of CH_4 and C_2H_6 on shales, three unresolved problems exist in the literature. The first is inadequate adsorbent material. Typically, shale matrix is composed of both organic matter (kerogen) and inorganic substances, e.g., quartz, calcite, and clays. Although carbonaceous materials play an important role in shale gas adsorption and storage, experimental studies have confirmed that the clay minerals also contribute tremendously to the adsorption capacity of shale gas, owing to the large amounts of nanopores and ultra-high specific surface area [33–35]. Recent low-temperature nitrogen adsorption tests yielded Brunauer-Emmett-Teller (BET) surface areas of 76.4 m^2/g for montmorillonite [34,36], indicating that the large surface area inside the interlayers of clay minerals provides appreciable sites for gas adsorption. Therefore, the adsorption capacities of clay-rich shales and pure minerals can be comparable or even higher than organic-rich shales, as observed by Gasparik et al. [37] and Ji et al. [34]. However, very limited research involving CH_4 and C_2H_6 adsorption in clay minerals has been reported. Sharma et al. [30] conducted a tentative study of pure component adsorption; nevertheless, the isotherms and selectivity of binary mixtures were predicted using IAST, which has not been validated with realistic adsorption curves. The second problem lies in insufficient adsorption data. Wang et al. [28] performed the first systematic measurement of CH_4/C_2H_6 competitive adsorption on shales; however, they reported only total excess adsorption data for the mixtures instead of the adsorption capacity of each adsorbate. In addition, their experimental samples are shale rocks instead of isolated clay minerals; thus the adsorption properties of CH_4/C_2H_6 in clay are
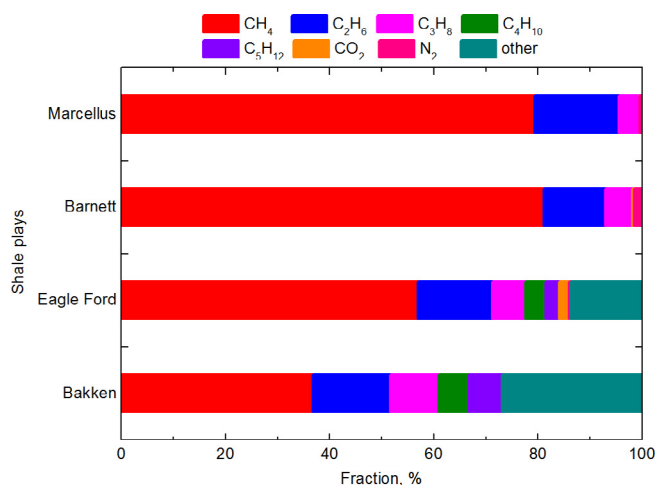

Fig. 1. Fluid composition of a few currently active shale plays [25–27].