Full Length Article

Accumulation behaviors of methane in the aqueous environment with organic matters

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GRAPHICAL ABSTRACT
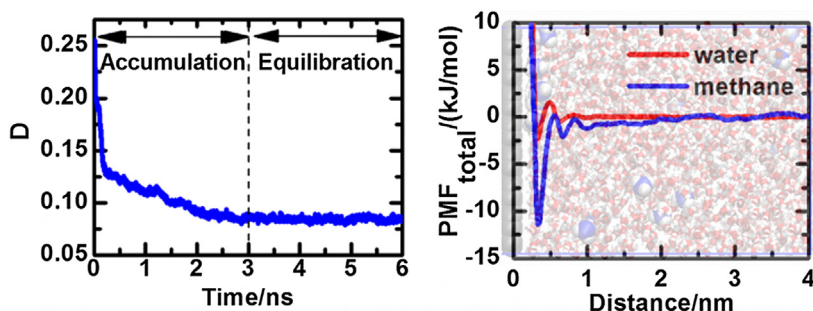
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ABSTRACT

Shale gas has received extensive attention and is becoming an important supplement to worldwide energy. Water is inevitable when developing shale gas with hydraulic fracturing. Thus it is necessary to understand the dynamic behavior of methane in water environments. Here, molecular dynamics simulations were performed to study the dynamic behavior of methane in the aqueous solutions with organic matters (OM). It is found that methane will accumulate at the OM-water interface and form a dense gas region spontaneously. The accumulation process is found to be little dependent on the gas saturation and the pressure within the simulating range, while it is closely related to the temperature and surface wettability. To explain the accumulation phenomenon of methane, the potential of mean force was calculated. We found that both the organic wall-gas interaction and the water-gas interaction are beneficial to the accumulation of methane and the former takes the leading role, while the gas-gas interaction impedes the accumulation. Our results imply the potentials of thermal exploitation and altering the surface wettability to enhance shale gas recovery. The dynamic behaviors of methane in aqueous solutions concerned in the present study are of great importance to estimate shale gas reserves, understand shale gas flow mechanisms and develop shale gas more efficiently.

1. Introduction

With the growing demanding of energy and gradual dwindling of conventional energy, the energy extracting focus is shifted to unconventional energy like shale gas. Unconventional energy was underappreciated previously due to the poor understanding of reservoir accumulation mechanisms and technical limitations of exploitation. Until recently, the successful implement of hydraulic fracturing [1,2] makes it possible to develop unconventional energy on a large scale. Especially, shale gas, a kind of unconventional energy mainly composed of methane, is reported to have a broad distribution, abundant reserve and lower pollution [3]. Thus shale gas has received extensive attention and is becoming an important supplement to energy worldwide. Nevertheless, the existence of abundant nanopores always invalidates the conventional Darcy's law in shale formations [4–6]. Especially, the multi-scale pore structure which can span from nanometer to meter makes shale gas flow mechanisms even more complicated [7]. Numerous studies suggest that tight shale formations exhibit fractal characteristics with scale-invariance [8,9]. Thus many mathematical methods based on fractal theory have been proposed recently to study mechanisms of gas flow in tight porous media [10–14]. Most of these mathematical models are derived on the basis of gas flow in a single nanopore. So it is necessary to have a comprehensive understanding of the occurrence behaviors and transport mechanisms of shale gas molecules in nanopores.

When methane molecules are confined in nanopores, the adsorption can no longer be neglected [15]. The adsorption capacity of shale was evaluated by experiments [16,17] and computer simulations [18–20], and the effects of temperature, pressure and particle and pore size were investigated. Besides, adsorption layers of hydrocarbons near the solid surface have been observed [21–23], and methane could form one to multi-adsorbed layers with increasing the width of slit pores from 0.7 nm to 2.0 nm [24].

For shale gas, water is ubiquitous in the entire process of generation, storage and exploitation. On one hand, experiments have found the existence of connate water in organic matters (OM) in the shale [25]. On the other hand, in the process of hydraulic fracturing, high-pressure water is injected into the shale formation to induce fissures and interconnected cracks [1,2]. Consequently the existence of water increases the complexity of methane occurrence behaviors and flow mechanisms. Confined water in nanochannels usually displays many fascinating and unconventional phenomena, such as the unusual phase transition, the extra fast motion and the excellent on-off gating behavior [26–30], which are completely different from those in bulk systems. In addition, anomalous water structures near the surface can affect the hydrophobic interactions of polar objects in solutions and the slip of water transport in hydrophobic nanochannels.

Actually, the practice of developing shale gas from the underground involves the interactions of methane, water and organic matters. Hence it is necessary to consider the dynamic behavior of methane-water mixtures near organic matters. A series of experiments [31–33] and molecular dynamics (MD) simulations [34–37] were conducted to study the influence of gas on the structure of liquid-solid interface. But the related results remain controversial [38,39]. Dammer and Lohse found dissolved gas in liquids could influence the structure of the liquid-wall interface significantly due to the wall hydrophobicity and gas concentration near the wall [34]. Nevertheless, Bratko and Luzar reported that gas concentration on the hydrophobic walls was not significant when more accurate molecular models for water and gas instead of Lennard-Jones (L-J) particles were used [39]. Recently Lee and Aluru investigated gas enrichment near extended surfaces for CO_2/H_2-water mixtures using MD simulations [35]. They showed that both the solvent-induced potential and the gas-wall potential played an important role in the gas enrichment. However, the physical origin and quantitative understanding of real gas dynamic behaviors near OM surface are not well-understood. Especially, occurrence behaviors of methane-

water mixtures near OM under reservoir conditions of high temperature and pressure haven't been investigated. And learning about the occurrence behaviors of methane-water mixtures is of great importance to estimate shale gas reserves, understand shale gas flow mechanisms and develop shale gas reservoirs more efficiently.

In this paper, equilibrium MD simulations were performed to study the dynamic behaviors of methane in water environments with OM under different temperature, pressure and wettability conditions. We observed that methane would accumulate at the OM-water interface spontaneously no matter what the gas saturation was. The underlying mechanisms driving methane to accumulate at the OM-water interface were revealed. Our results provide important basis for estimating shale gas reserves and understanding shale gas flow mechanisms, imply the potential of thermal exploitation and altering the rock wettability to enhance shale gas recovery as well.

2. Models and methods

2.1. Molecular models

Nanopores in organic matters are the main storage space for hydrocarbons in shale reservoirs [4,5,40]. Since the real molecular models of the organic matters in shale are quite complicated and unclear, carbon based models are extensively used to approximate the organic pores [15,41–43]. Actually, the cross-sectional shapes of the organic pores in shale vary a lot, including slit-, circular-, triangular- and square-type [5,44–46]. However, if we only focus on the region in the immediate vicinity of the organic pore surface, all the surface of organic pores with different shapes can be approximated as a plane. Thus in the present study, the model can be simplified as Fig. 1(a), where one layer of graphene was put in the middle of the system standing for the organic solid surface.

Methane molecules were used to represent shale gas [41,42]. Initially, methane molecules and water molecules were inserted randomly on both sides of the graphene [Fig. 1(a)]. In the process of equilibrium MD simulations, the size of the graphene layer remained constant, which was $3.4 \times 3.2\,nm^2$, same as the box lengths in x- and y-direction, while the length in z-direction of the system would change with the number of the molecules, the system temperature and pressure. And the periodic boundary conditions were employed in all directions.

In order to eliminate the influence of the graphene shaking on the results, the graphene was always freezed in the simulations, with the van der Walls interactions calculated only, employing the LJ parameters used by the previous researchers [47–49]. For water, the SPC/E model was used [35,36,38,50]. And the optimized potentials for liquid simulation all-atom (OPLS-AA) force field was applied to methane molecules [51,52]. More detailed force field parameters are summarized in Table 1. Lorentz-Berthelot mixing rules [53,54], $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$, were used to describe LJ parameters between different molecules.

2.2. Calculation methods

The molecular dynamics simulations were performed utilizing GROMACS 4.5.5 [55]. The van der Walls interactions were described using LJ 6-12 potential with a cutoff distance of 1.0 nm. And the electrostatic interactions were calculated using the particle mesh Ewald (PME) method with a fast Fourier transform (FFT) grid spacing of 0.16 nm and a cutoff distance of 1.0 nm. Firstly, energy minimization was conducted using steepest descent algorithm to relax the system. Then production molecular dynamics simulations were performed in the $NP_{zz}T$ ensemble for 60 ns with a time step of 2.0 fs, and the data of the last 40 ns were collected for analysis. $NP_{zz}T$ ensemble is the isothermal-isobaric ensemble maintaining constant temperature T and constant pressure p, where the number of particles N is also kept as a constant. The subscript zz means only the pressure in z-direction is