



Phase behavior and flow in shale nanopores from molecular simulations



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ABSTRACT

Phase behavior and flow in shale nanopores, due to fluid heterogeneity, cannot be described by bulk and continuum-based formulations. The interactions between fluid and rock molecules are important in both phase behavior and flow. As a result, frameworks from bulk equations of state in phase behavior, and continuum mechanisms and Klinkenberg slippage in flow may become inapplicable. Recently, we have studied both phase behavior and flow in nanopores using density functional theory and various molecular simulations. This work addresses a number of issues related to the adsorption of mixtures of hydrocarbons, carbon dioxide and water as well as methane flow at different pressure conditions in nanopores. For flow, we use the dual control volume-grand canonical molecular dynamics (DCV-GCMD) simulation as in our previous work. We use a smaller pressure difference between high and low pressure reservoirs connected to the nanopores. We find that similar to our past work, the flux of methane in the slit pores can be two orders of magnitude higher than the results from the Hagen-Poiseuille equation.

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1. Introduction

Recovery and production from shale reservoirs depend on fluid-in-place and flow in porous media. Fluid phase behavior in shale gas and light oil reservoirs may be drastically different from conventional reservoirs. Unlike conventional rocks, shale is composed of organic (such as kerogen) and inorganic matters (such as clay and quartz). The pores in shale media may be in the nanometer range and both kerogen and clay minerals may contain large amount of fluids in the form of adsorbed molecules [1]. Fluids in shale nanopores may be inhomogeneous and cannot be described as bulk [2]. In addition to adsorption on the rock surface in nanopores, hydrocarbon dissolution in kerogen may also contribute to fluid content in shale permeable media [3]. Fluid flow in shale nanopores is also drastically different from flow in large pores where the Darcy law provides the description. In nanopores, because of fluid inhomogeneity, the Knudsen diffusion and the continuum-based models such as Klinkenberg modification of flow may not apply. In the following, we will discuss our line of attack in phase behavior and flow in shale nanopores.

1.1. Phase behaviors

In a recent work [1], we have divided fluids in shale media into three distinct categories: free molecules, adsorbed molecules, and molecules that move to the kerogen matrix. Free molecules which are present in fractures and large pores behave as bulk fluid. Adsorbed molecules are found near the surfaces of nanometer pores in kerogen and clay minerals. The substrate composition affects the properties of adsorbed molecules. Molecules that move into the kerogen may provide additional fluid-in-place. Kerogen may swell as much as 20% in normal decane and may be more in aromatics [4,5]. For phase behavior description in shale media, we may divide the pores into pores larger than 10 nm, in pores less than 10 nm, and dissolution in kerogen [1].

In pores larger than 10 nm, the contribution from surface adsorption to total fluid in the pores is small. Fluid can be considered homogeneous and critical properties are close to bulk. Mainly the interface curvature affects phase behavior and saturation pressures (bubblepoint or dewpoint). Due to curvature, the dewpoint pressure of rich gas condensates and the amount of liquid dropout often increases. Consequently, less liquid will be produced [1]. On the other hand, the bubblepoint pressure can be suppressed significantly [1,6–9].

In pores less than 10 nm, surface adsorption becomes significant

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and confined fluids are heterogeneous. The inhomogeneity arises from confinement and fluid-surface interactions. Phase behavior can be greatly different from the bulk. In small pores, there is no two-phase. At this scale, because the sizes of molecules and nanopores become comparable, fluid-fluid and fluid-surface interactions from molecular perspective should be taken into account. Grand canonical Monte Carlo simulations (GCMC) take into account the inhomogeneity in density distributions and fluid-surface interactions; they are the most common tools to study adsorption and phase behavior of fluids in small nanopores [1,2]. Based on GCMC, we discuss three aspects of phase behavior in small nanopores:

a) Phase Behavior of Confined Hydrocarbon Mixtures from GCMC

Shale gas is generally composed of hydrocarbon mixtures, such as methane, ethane, propane and butane. The phase behaviors of gas mixtures under nano-confinement are very different from bulk. Under confinement, the packaging effect and strong fluid-surface interaction may result in multi-layer adsorption. Recently, a number of experimental and computer simulation studies on phase behavior of confined hydrocarbon mixtures appeared in the literature. Luo et al. [10] measured the confinement effects on the adsorption of binary mixture of octane and decane and observed a clear separation between bubble points of bulk and confined fluids. Pitakbunkate et al. [11] used GCMC simulations to study adsorption of pure and binary mixture of methane and ethane in shale nanopores. They observed shift of critical properties of confined hydrocarbons. Jin and Nasrabadi [12] used Gauge-GCMC simulations to study phase diagram of hydrocarbon binary and ternary mixtures in nanopores and observed that confined effect is stronger for the heavier components than the lighter components. Although computer simulations have been used to study phase diagram of confined hydrocarbon mixtures, the effect of pressure on adsorption of hydrocarbon mixtures has received limited attentions.

In this work, we use GCMC simulations to study adsorption of methane and n-butane binary mixtures in shale nanopores at different pressures. GCMC explicitly takes into account the molecular configurations and orientations which are important for heavier hydrocarbons. The effect of pressure on adsorption in hydrocarbon mixtures can provide important insights into hydrocarbon recovery from shale media.

b) Sorption of CO₂-H₂O mixtures in kerogen nanopores

Shale is composed of two different media: organic and inorganic materials. Organic matter in shale increases effective porosity [13] and can contribute as much as 50% to the total porosity [14]. In addition to organic matter, clay minerals may provide additional sorption capacity due to high internal surface area [15]. A few studies have reported that the clay mineral and its microporous structure may increase gas sorption capacity of organic-rich shales [16–18]. However, organic and inorganic materials have different surface compositions, which can affect adsorption.

Kerogen is generally considered hydrophobic with no charges on the surface, while clay minerals can be hydrophilic with various partially charged atoms on the surface. As a result, water may adsorb differently on the surfaces of these two media. Some shale gas reservoirs are water-saturated [19]. Preloaded water in clay-rich shales significantly reduces gas sorption [20] and even in the organic-rich shales, gas sorption capacity can be greatly reduced because of the moisture [21]. In a previous work, we have shown that even a small amount of water in an outside reservoir can greatly reduce gas sorption in clay nanopores [22]. The methane sorption capacity of other moisture-equilibrated organic materials

such as coals is substantially lower than the dry samples [23,24]. In general, water in shale reservoirs is often believed to be associated with clay minerals not kerogen [16]. However, there is no comparison on the effect of water in these two materials on gas adsorption. In this work, we will use the GCMC simulation to study sorption of CO₂-H₂O mixtures in kerogen nanopores and compare with clay minerals.

c) Adsorption selectivity of nC₄ and CO₂

Organic-rich shales may store significant amount of CO₂ via mineral reactions and sorption onto organic matter as well as mineral matter surfaces [25]. Kang et al. [26] predicted that the organic matter in shale can serve for CO₂ sequestration. Injected CO₂ not only could be sequestered in sorbed state but also enhance recovery of natural gas by in-situ molecular swapping mechanism that promotes release and desorption of sorbed gas [26,27]. Yuan et al. [28] used molecular dynamics simulations to study the enhanced recovery of confined methane with CO₂ and found that the injection of CO₂ into the carbon nanotubes can enhance methane recovery at least by 15% over that achieved from pressure drop. Wu et al. [29] also observed that CO₂ can rapidly and efficiently displace adsorbed methane. Kowalczyk et al. [30] observed two-stage process in narrow carbon micropores that the co-adsorbed CO₂ can enhance methane adsorption at low CO₂ partial pressure, but reduce methane adsorption due to stronger affinity of CO₂-surface and CO₂-CO₂ interactions as CO₂ partial pressure increases. Although displacement of methane due to the injection of CO₂ has been extensively studied, the effect of CO₂ on heavier hydrocarbon recovery has not been studied yet. The injected CO₂ can lower the viscosity of confined heavier hydrocarbon which can further facilitate the flow. In this work, we use the GCMC simulation to investigate sorption of pure nC₄ and nC₄-CO₂ mixture in kerogen. This study provides insight into heavier hydrocarbon recovery from CO₂ injection.

1.2. Flow in shale media

Shale wells have an early high production rate followed by a rapid decline. Understanding of flow in shale media can help planning and devising various enhancements. Flow in conventional reservoirs can be described by a continuum flow model such as Darcy's law [31–33] and the classical Navier-Stokes equation [34].

At high pressure, the flow may not be described by the Hagen-Poiseuille (HP) equation in nanopores [35]. The HP equation is considered to be valid when the mean free path of molecules is much smaller than the pore size. The HP equation basically describes convective flow and assumes that the velocity of molecules on the surface is zero and ignores surface adsorption. The HP equation for flux J_{HP} in flow direction x in slab geometry of pore size W is given as

$$J_{HP} = -\frac{W^3}{12\mu} \left(\frac{\partial P}{\partial x} \right), \quad (1)$$

where μ is the viscosity and P is pressure. Holt et al. [36] have measured gas and liquid flow in carbon nanotubes of pore sizes of around 2 nm. They show that the measured flux exceeds the prediction from the HP equation by three orders of magnitude. Shale nanopores are similar to carbon nanotubes with the surface being oil-wet; the hydrocarbon molecules tend to adsorb on the surface but not fixed permanently; the adsorbed density distribution is different from the bulk.

When there is slippage at the pore walls, Klinkenberg correction is often applied to the continuum based models. Klinkenberg

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