



Study of the confined behavior of hydrocarbons in organic nanopores by the potential theory



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ABSTRACT

To accurately describe the confined behavior of hydrocarbons in nanopores has become a top priority for the effective development of unconventional resources. In this paper, the multicomponent potential theory of adsorption (MPTA) is coupled with the cubic Peng–Robinson (PR) equation of state (EOS) to investigate and represent the confined behavior of pure hydrocarbons and their mixtures in organic nanopores. In this theory, the fluid–fluid interactions are modeled by the PR EOS. For the fluid–solid interactions, the 10–4–3 Steele potential is used for slit-like nanopores, and a modified Lennard–Jones (LJ) 10–6 potential is used for cylindrical nanopores. Then a prediction process for the behavior of methane, ethane, propane and their mixtures (binary and ternary mixtures) is performed. The results are compared against experimental data on the adsorbents of activated carbons (slit-like nanopores) and MCM-41 silica (cylindrical nanopores) to validate the accuracy of the theory and process. Results indicate that for the sets of experimental data considered in this work, the theory is capable of predicting the confined behavior of pure components in wide ranges of pressure and temperature. For pure components, because of the different interaction energy between fluids and solid walls, the density of confined fluids in the slit-like nanopores (activated carbon type) is much higher than that in the cylindrical nanopores (MCM-41 silica type). As a position (z) approaches the pore surface, the effect of fluid–solid interactions is enhanced, and the density of confined fluids is increased. For binary mixtures, the mole fraction of the heavier component (C_2H_6/C_3H_8) around the pore surface is extremely higher than that of the lighter component (CH_4). The higher the difference between the two components, the higher the difference of the mole fractions and fluid densities of the two components in nanopores. For a ternary mixture, the confined behavior of the three components within nanopores is significantly different. As a position approaches the pore center, the mole fraction of the lightest component is increased gradually, and the mole fraction of the heaviest component is reduced gradually. The medium component shows a tendency of increasing first and reducing then. This investigation makes it possible to get some new insights on the confined behavior of hydrocarbons in nanopores with different geometries.

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1. Introduction

The presence of nanopores in unconventional reservoirs has been confirmed by numerous studies. To accurately describe the behavior of confined hydrocarbons in such nanopores has become a top priority for the effective development of unconventional

resources. For the behavior of fluids in confined nanopores, because of the interplay of fluid–fluid interactions and fluid–solid interactions, the fluids usually present two different phases, a bulk phase and an adsorbed phase. The behavior differs significantly from that observed in a conventional PVT cell. Meanwhile, as the dimensions of a confining space decrease, it becomes more pronounced. The current commonly-used powerful approaches to describe the behavior of confined fluids in nanopores include density function theory (DFT), lattice gas model, molecular simulation (MS) and experimental investigation. Compared with these theoretically complicated methods, a potential theory is a less

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sophisticated and highly accurate approach to study the thermodynamic properties of nanoconfined fluids [38,6,29,39,48]. It is originally proposed by Polanyi for the pure component in 1914. Then, combined with Raoult's law, several attempts have extended the original Polanyi's theory to multicomponent mixtures.

For the behavior of multicomponent fluids, the prediction models based on pure fluids are often directly extended to the multicomponent fluids. There include thermodynamically consistent models and thermodynamically inconsistent empirical models. By comparison, the thermodynamically consistent approach is a more accurate approach, such as ideal adsorption solution theory (IAST), real adsorption solution theory (RAST), vacancy solution theory and superlattice model [9,38,49,50]. Considering simplicity, a well-established macroscopic model by IAST is the commonly-used approach among them. It is originally developed based on the assumption that the adsorbed phase is treated as an ideal solution of the adsorbed components [30]. This theory has no restriction on the type of an isotherm equation. In addition, it can also be used to describe the adsorption equilibria on heterogeneous adsorbents, the so-called heterogeneous-IAST [18,36]. But for high pressure/supercritical fluids, the IAST cannot be used to describe the adsorption equilibria [7,24,29]. Considering the effect of non-ideality of an adsorbed phase, the RAST is developed [9]. Strictly speaking, the success of these models in predicting multicomponent adsorption equilibria highly depends on a correct choice of single-component isotherm equations that best describe experimental data. In addition, from the numerical fitting of adsorption isotherms, some simpler thermodynamically inconsistent models have also been applied to multicomponent fluids, such as an extended Langmuir model, an extended Freundlich model and a FH-VSM model [1,34,51]. The advantage of these models is that the expression for equilibria is analytical and explicit, and it leads to the computation of phase equilibria much faster. But for these models, when the maximum adsorption capacity differs significantly for different species, their prediction accuracy is decreased [18,38,51]. Ahmed et al. (2011) [52] experimentally investigated the breakthrough curves of a three-component mixture (C_3H_8 - nC_4H_{10} - iC_4H_{10}) on 5A molecular sieve zeolite and correlated the experimental equilibrium isotherm data by using an extended Langmuir model and an extended Freundlich model. They found the extended Freundlich model can give a better correlation. Hartman et al. [16,50] combined the extended Langmuir model and IAST to investigate the influence of adsorption behavior of hydrocarbons on the gas storage capacity and original gas-in-place (OGIP). Compared with these approaches, a multicomponent potential theory of adsorption (MPTA) describes the potential energy of fluid-fluid and solid-fluid interactions in detail. It was developed by Shapiro and Stenby [38]. In their model, these two types of interaction energies (fluid-fluid and solid-fluid) are treated separately. Then, through a combination with an interaction model, MPTA can be used to deal with the phase behavior of high pressure and critical fluids of pure component fluids and mixtures [4,29,38,39].

The attractive or repulsive interaction forces between molecules or atomic groups include short-ranged van der Waals forces (London dispersion force, dipole-dipole force and induction force), long-ranged coulombic forces and hydrogen bonds. These forces can occur between different polar and non-polar molecules, and even between atoms or groups within a fluid molecule. A fluid molecule in nanopores is affected not only by its surrounding molecules but also by pore surfaces, especially for the molecules close to the pore surfaces. They are called the fluid-fluid and solid-fluid (or wall-fluid) interactions. Because of the interplay of fluid-fluid and solid-fluid interactions, the behavior of bulk and adsorbed phases significantly differs [12,32]. The fluid-fluid interaction

can be represented by conventional equations of state (EOS) and some simplified potential models, such as the Lennard-Jones (LJ) potential model and the Square-Well (SW) potential model [41]. On the other hand, the solid-fluid interaction is the major cause for the presence of an adsorbed phase. A Steele 10-4-3 potential, the Tjatjopoulos potential model, the Dubinin-Radushkevich (DR) potential theory, the Dubinin-Radushkevich-Astakhov (DRA) potential model and the Frenkel-Halsey-Hill (FHH) model are the commonly-used potential energy models [5,29,31,42]. Singh et al. [40] investigated various thermos-physical properties of confined alkanes in bulk and slit pores of graphite and mica surfaces by the method of configurational-bias GC-TMMC (grand-canonical transition-matrix Monte Carlo) simulations, where the interaction potential between fluid molecules was described by a modified Buckingham exponential intermolecular potential model and the wall-fluid interaction was described by the Steele 9-3 potential. Vishnyakov et al. [43] and Li et al. [22] investigated the critical properties and VLE (vapor-liquid equilibrium) properties of confined fluids in slit-like nanopores using the Gibbs ensemble Monte Carlo (GEMC) simulation and a lattice gas model. In their model, the fluid-fluid interaction was represented by a truncated LJ 12-6 potential and the fluid-solid potential was simulated by the Steele 10-4-3 potential. Do et al. [11] discussed the influence of molecular shape on the adsorption of nitrogen, carbon dioxide and methane in confined nanospace. They also applied the Lennard-Jones 12-6 potential model for fluid-fluid interactions and the Steele 10-4-3 potential model for fluid-solid interactions. Monsalvo and Shapiro [29] extended the multicomponent potential theory of adsorption for subcritical fluids to the adsorption equilibria of supercritical fluids. The cubic Soave-Redlich-Kwong (SRK) EOS was used for the fluid-fluid interactions. For the fluid-solid interactions, both the Dubinin-Radushkevich-Astakhov (DRA) and the Steele 10-4-3 potential models were applied. Using the canonical Monte Carlo simulation, Reyes [37] calculated the vapor-liquid phase diagrams of a SW fluid confined in hard and weakly attractive cylindrical pores. It was shown that the liquid density increases as pore walls become more attractive in small pores. But for large pores, both the vapor and liquid densities increase for strong attractive walls. Real tight and shale rocks in unconventional reservoirs are usually composed of very complex pores, and it is not easy to simply model them in a single pore geometry [10,23,27,44]. The most common nanopore geometries in unconventional reservoirs include slit-like pores and cylindrical pores; see in Fig. 1. Therefore, in this work, in order to explore the effect of pore geometry, we will, respectively, utilize the Steele 10-4-3 potential and a modified LJ 12-6 potential to represent the solid-fluid potential in slit-like and cylindrical nanopores. For the slit-like nanopores, the commonly-used nanoporous material of activated carbons (AC) is applied. For cylindrical nanopores, the MCM-41 silica is applied. For the fluid-fluid interaction energy, the simple and easily-operating PR EOS is utilized. In addition, from Fig. 1, we can see that with the exception of the slit-like pores and the cylindrical pores, some nanopores within unconventional reservoirs also have irregular shapes, including bubble-like, elliptical and polygonal shapes. For the solid-fluid potential energy in such irregular pores, the MS calculations will be a good method.

In this paper, the multicomponent potential theory of adsorption (MPTA) is coupled with the cubic PR EOS to investigate and represent the confined behavior of pure hydrocarbons and their mixtures in organic nanopores. Both slit-like and cylindrical nanopores are studied. In this scheme, the fluid-fluid interactions are modeled by the PR EOS. For the fluid-solid interactions, the Steele 10-4-3 potential is used for slit-like nanopores, and a modified LJ 10-6 potential is used for cylindrical nanopores. Then a prediction process for the behavior of methane, ethane, propane

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