



## Full Length Article

# Ono-Kondo lattice model for propane multilayer adsorption in organic nanopores in relation to shale gas

Wanying Pang, Zhehui Jin\*

School of Mining and Petroleum Engineering, Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB T6G 1H9, Canada



## ARTICLE INFO

## Keywords:

Excess adsorption  
 Absolute adsorption  
 Propane  
 Multilayer adsorption  
 Organic nanopores  
 Molecular simulations

## ABSTRACT

Accurate characterization of shale gas adsorption capacity is of great importance to the gas-in-place estimation and prediction of well productivity. Propane is one of major constituents in shale gases which can have multilayer adsorption behavior on pore surfaces. While experiments can measure excess adsorption, the absolute adsorption, which describes adsorbed gas capacity, has to be converted from the excess adsorption. In previous works, absolute adsorption is usually calculated from excess adsorption with adsorbed phase volume or density based on the single-layer adsorption model. However, for heavier alkanes, such as ethane and propane, which can have multilayer adsorption behavior, single-layer adsorption model becomes invalid. While molecular simulation can characterize the multilayer adsorption behavior, it comes with expensive computational costs. Currently, there is no viable model to characterize the absolute adsorption of hydrocarbons which can have multilayer adsorption behavior. In this work, we conduct grand canonical Monte Carlo (GCMC) simulation to study propane adsorption in shale nanopores over a wide range of pressures at temperature higher than the critical temperature. We find that propane can form multiple adsorption layers, thus, using single-layer adsorption model to obtain the absolute adsorption becomes unjustifiable. Based on the propane density distribution characteristics, we propose a multilayer adsorption model and use Ono-Kondo (OK) lattice model with multilayer structures to regress propane excess adsorption and subsequently obtain the absolute adsorption in each layer. For propane, we take into account the correlation effect arising from strong adsorbate–adsorbate interactions beyond mean field theory (MFT) and the only predetermined parameters are number of layers and adsorption layer width. The proposed OK model shows an excellent agreement with GCMC simulations on the excess adsorption and absolute adsorption in each layer, with discrepancies less than 6% above 50 bar. The proposed OK model can readily take into account the propane multilayer adsorption behavior, while significantly reducing calculation time. Our method presents a reliable and highly-efficient approach for accurate characterization of adsorption of hydrocarbons with multilayer structures and provide important insights into the gas-in-place estimation in shale.

## 1. Introduction

Shale gas has become a very important unconventional fossil fuel thanks to advancement of fracturing technologies and greatly increased global energy supply [1–4]. Unlike conventional reservoirs, where hydrocarbons are stored in porous media with pore sizes in the range of hundreds of nanometers or a few micrometers, there are extensive amount of nanosized pores as small as a few nanometers in shale [5–9]. In nanopores, where pore size is comparable to the hydrocarbon molecular size, the fluid distribution is inhomogeneous and surface adsorption becomes significant [10]. The adsorbed gas behaves differently from free gas and may contribute 20%–85% of the total gas content [11]. Therefore, characterization of adsorbed gas in shale is key to the

accurate estimation of gas-in-place and prediction of well productivity.

There have been a large number of experimental measurements on methane excess adsorption in shale, based on both gravimetric and volumetric methods. Gasparik et al. [12] measured high-pressure methane excess adsorption isotherm in shale and found that excess adsorption has a maximum within the pressure range of 0–25 MPa at 65 °C and the shape of excess adsorption is mainly controlled by thermal maturity and clay mineralogy. Rexer et al. [1] measured maximum methane excess adsorption uptake within the temperature range of 300–473 K and found that it decreases with increasing pressure at high pressures. Zhou et al. [13] found that methane excess adsorption firstly reaches maximum and then decreases with increasing pressures. Although these experimental works provided important understandings

\* Corresponding author.

E-mail address: [zhehui2@ualberta.ca](mailto:zhehui2@ualberta.ca) (Z. Jin).<https://doi.org/10.1016/j.fuel.2018.07.086>

Received 5 June 2018; Accepted 19 July 2018

0016-2361/© 2018 Elsevier Ltd. All rights reserved.

about methane adsorption behavior, the mainly reported values are excess adsorption and the absolute adsorption, which represents actual gas adsorption capacity, still needs to be converted from the excess adsorption.

While methane is the major constituent of shale gas, heavier hydrocarbon such as ethane, propane and butane still can exhibit a large quantity in shale reservoirs [14]. However, there has been only limited number of experimental works for heavier hydrocarbon adsorption in shale. Zhao et al. [5,15] studied adsorption behavior of methane, ethane, propane, n-butane and *iso*-butane in isolated kerogen. They found that ethane, propane, n-butane and *iso*-butane present a significant hysteresis in adsorption/desorption isotherms in entire pressure range [5]. Gasparik et al. [16] measured ethane excess adsorption and found that excess adsorption amount firstly increases with pressure and then decreases. Liu et al. [14] measured excess adsorption/desorption isotherms of methane and n-butane on shale and reported higher adsorption capacity of n-butane than methane.

The excess adsorption amount measured in those works adopt gravimetric method, which uses the high-resolution balance to directly measure adsorption isotherms. In order to convert excess adsorption  $m_{ex}$  to absolute adsorption  $m_{abs}$ , the adsorbed phase density  $\rho_a$  is generally used as [15],

$$m_{abs} = \frac{m_{ex}}{1 - \frac{\rho_b}{\rho_a}} \quad (1)$$

Since it is well known that the adsorbed phase density depends on pressure and temperature conditions [17], Liu et al. [14] and Zhao et al. [15] calculated absolute adsorption by applying varying adsorbed phase density from GCMC simulation. In Liu et al.'s work [14], the adsorption layer is defined by the effective pore width and the saddle point from GCMC density distribution, and the adsorbed phase density of n-butane is the average density within such layer. They found that the adsorbed phase density obtained from GCMC can be higher than n-butane liquid density (502 kg/m<sup>3</sup>). On the other hand, Zhao et al. [15] calculated the adsorbed phase density as the average density within the region between the first and second peak in the density distributions from GCMC simulation. These conversions are conducted based on the single-layer adsorption model, which has been widely used for methane adsorption. However, unlike methane, heavier hydrocarbons can form multilayer adsorption [18,19]. As a result, simply using single adsorbed phase density to convert excess adsorption to absolute adsorption as depicted in Eq. (1) becomes invalid for heavier hydrocarbons. Currently, there is no work on the characterization of hydrocarbon absolute adsorption considering the multilayer adsorption structures.

While molecular simulation can characterize the multilayer adsorption behavior, it comes with expensive computational costs. Ono-Kondo lattice model [20–24] based on lattice theory has been used to study methane absolute adsorption in shale [25]. This model assumes that adsorbate molecules can occupy the lattice spaces in pores and readily calculate the excess and absolute adsorption. Very recently, we applied OK lattice model with multilayer structures to take into account the transition zone in methane adsorption and greatly improved the accuracy of absolute adsorption calculation [26]. It only requires pre-determined adsorption layer width to fit with experimentally or computationally obtained excess adsorption. Because OK lattice model can explicitly consider multilayer structures, it can potentially characterize adsorption behavior with multilayer adsorption structures and absolute adsorption in each layer.

In this work, we conduct grand canonical Monte Carlo (GCMC) simulation to study propane adsorption in shale nanopores over a wide range of pressures at temperature higher than the critical temperature. Carbon materials have been used to study hydrocarbon adsorption in organic matter, which is a main constituent of shale [10]. We use united atom model to simulate propane molecules. Propane excess adsorption is obtained following the same approach as in the volumetric method,

in which helium adsorption is used to calculate the effective pore volume. Based on the propane density distributions, we propose a modified OK model considering correlation effect due to strong adsorbate–adsorbate interactions beyond mean field theory (MFT) to regress excess adsorption. The number and width of adsorption layer are determined by density distributions from GCMC simulation. Based on multilayer structures, OK model can calculate the absolute adsorption in each layer.

The remainder of this work is organized as follows. In Section 2, we introduce the proposed OK model. In Section 3, we describe the molecular simulation methods and models used in this work. In Section 4, we study the propane adsorption behavior in carbon nanopores, including the density distributions and excess adsorption. We then characterize propane adsorption model based on GCMC results and then use the proposed OK model to regress propane excess adsorption. Afterwards, we compare the absolute adsorption in each layer between OK model and GCMC simulation. In Section 5, we present the key conclusions.

## 2. Ono-Kondo lattice model

In classical OK model with three-dimensional cubic lattice structure for single-component adsorbate,  $i$  represents the  $i$ -th layer of the adsorbate and  $i = 1$  describes the molecule in contact with the surface wall [23,24]. Each lattice layer is parallel to the planar surface and each site can be either occupied by adsorbate molecule or at vacancy. In this work, we assume that each propane molecule can only occupy one lattice site in OK model.

Consider taking an adsorbate molecule at site  $k$  and moving it to an empty site infinitely distant, the exchange of the molecules in the lattice with a vacancy can be given as [21,22]

$$M_k + V_\infty \rightarrow V_k + M_\infty \quad (2)$$

where  $k$  is the lattice site,  $\infty$  represents the site at infinite distance which can be seen as bulk,  $M$  and  $V$  represent the lattice site occupied by an adsorbate molecule and at vacancy, respectively. If such exchange reaches equilibrium at isothermal and isobaric condition, the change of Gibbs free energy  $\Delta G_i$  in layer  $i$  can be described as [21],

$$\Delta G_i = \Delta H_i - T\Delta S_i = 0 \quad (3)$$

in which  $\Delta H_i$  and  $\Delta S_i$  are the enthalpy and entropy changes in  $i$ -th layer due to molecule exchange and  $T$  is the absolute temperature. The change of entropy is given as [21]

$$\Delta S_i = k_B \ln W_{1,i} - k_B \ln W_{2,i} \quad (4)$$

with

$$\frac{W_{1,i}}{W_0} = x_i(1-x_b) \quad (5)$$

$$\frac{W_{2,i}}{W_0} = x_b(1-x_i) \quad (6)$$

where  $k_B$  is Boltzmann's constant,  $W_{1,i}$  denotes the number of configurations where fluid molecules occupy lattice sites and bulk phase is vacant at layer  $i$ ,  $W_{2,i}$  refers to the number of configurations where fluid molecules occupy bulk phase and lattice sites are empty at layer  $i$ ,  $W_0$  refers to the overall number of system configurations,  $x_i$  is the fraction of adsorbate molecules occupying the layer  $i$  and  $x_b$  is the fraction of adsorbate molecules occupying the bulk phase. In this work, the occupation fractions are given as [26],

$$x_i = \frac{\rho_{a,i}}{\rho_{am}} \quad (7)$$

and

$$x_b = \frac{\rho_b}{\rho_{am}} \quad (8)$$

Download English Version:

<https://daneshyari.com/en/article/6629894>

Download Persian Version:

<https://daneshyari.com/article/6629894>

[Daneshyari.com](https://daneshyari.com)