Molecular simulations of competitive adsorption of carbon dioxide — methane mixture on illitic clay surfaces

Leebyn Chong [a, b], Evgeniy M. Myshakin [a, c, *]

[a] National Energy Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh, PA, 15236, USA
[b] Oak Ridge Institute for Science and Education, 100 ORAU Way, Oak Ridge, TN, 37830, USA
[c] AECOM, 626 Cochran's Mill Road, P.O. Box 10940, Pittsburgh, PA, 15236, USA

A B S T R A C T

Molecular dynamics and Monte Carlo simulation studies were carried out to investigate adsorption behavior of carbon dioxide and methane mixtures on illitic clay surfaces under dry conditions. Various compositions of the mixtures and distributions of isomorphic substitutions in clay layers were chosen to explore competitive adsorption depending on component concentration and charge localization. The simulations show that carbon dioxide is preferentially sorbed on the illitic surface and is capable to promote methane desorption. Density distributions of the molecular species in pore space reveal formation of multilayers on the clay surfaces at elevated pressures. Mixed adsorption isotherms were compared with adsorption isotherms of pure compounds and thermodynamic quantities were reported to characterize the interaction of the carbon dioxide and methane with the clay surface.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In practical applications like enhanced hydrocarbon recovery and CO_2 storage in depleted natural gas reservoirs, there is a complex interaction between water (brine), CO_2 and CH_4 molecules [1,2]. A stimulated shale reservoir is typically characterized with hydraulic and natural fractures and pore networks in rock matrix. The behavior of fluids in those pores and fractures, and their interactions with minerals and organic matter control gas storage and release in shale matrix, influence mass transport in the fractures, and ultimately determine production from unconventional reservoirs. CO_2 may preferentially adsorb in pores, particularly in (organic) kerogen and on (inorganic) external clay surfaces, and displace CH_4 in shale [1]. Characterization of carbon dioxide and methane interaction with clay minerals is mandatory to reliably determine gas storage and release in shales and predict reservoir performance. The clay minerals like montmorillonite, kaolinite, and illite constitute a substantial portion of shale with illite or inter-stratified illite-smecite often as dominant components [2].

Grand canonical Monte Carlo (GCMC) simulations of pure methane and carbon dioxide adsorption on montmorillonite surfaces and the effect of water on adsorption behavior of CH_4 and CO_2 have been investigated by Jin and Firoozabadi [3,4]. Using nanopore sizes from 1 to 4 nm at T = 298 K and pressures up to 10 MPa, they found the adsorption of CH_4 is dominated by dispersive force interactions with clay surfaces while adsorption of CO_2 is strongly affected by electrostatic interactions with clay surface and inter-layer cation charges. The presence of water suppresses adsorption of CO_2 and CH_4 at the clay surfaces. Water forms the first layer closest to the surface, and CO_2 and CH_4 form the second layer.

Using GCMC simulations Yang et al. [5] studied the adsorption isotherms for the binary CO_2/CH_4 mixtures intercalated in Na-montmorillonite as a function of molar fraction of CO_2 in bulk phase composition at the pressures of 0.1 and 1.0 MPa and T = 318 K. The authors have calculated the strength of clay surface interaction with CO_2 (as the isosteric heat of adsorption at nearly zero adsorption loading of a single component) to be 55.4 and 40.5 kJ/mol at 1.40 and 2.06 nm of basal d_{001}-spacings, respectively. For methane, the corresponding values are computed to be 18.9 and 12.5 kJ/mol at 1.40 and 2.06 nm, respectively, in close agreement with the experimental value (16.0 kJ/mol) for CH_4 adsorption in the pillared clays [6]. It was shown that as the bulk phase CO_2 molar

fraction approaches 0.5, the intercalated methane level converges nearly to zero. The selectivity parameter expressed as $(x_{CO2}/x_{CH4})/(y_{CO2}/y_{CH4})$, where x and y are mole fractions of two species in adsorbed and bulk phases, respectively. At 1.40 *nm* of pore size, the selectivity parameter can be above 90, while at 2.06 *nm*, the value changes from 25 to 70 depending on pressure and bulk composition [5]. The greater selectively at the smaller interlayer spacing is attributed to stronger CO_2 interaction with clay surfaces in a more confined environment compared to methane molecules as inferred from the strengths of clay surface interactions given above.

The clay minerals demonstrate a substantially higher CO_2 selectivity over methane adsorption indicating that CO_2 molecules may competitively replace CH_4 molecules in the interlayer space. This suggests that geological storage of CO_2 in shales [7] where clay minerals constitute a significant portion of inorganic matter can induce production of an additional methane volume. Recently, CH_4 adsorption isotherms were measured in clay-dominated rocks to show that the clay mineral composition and the pore sizes significantly affect gas adsorption [8]. Swelling clay samples, exhibiting internal surfaces for adsorption, display the highest CH_4 adsorption capacity [8]. The additional volume of methane for enhanced gas production can also be promoted by the competitive adsorption of CO_2 on external surfaces of pores in rock matrix and natural fracture walls. Those competitive adsorption/desorption processes can be accounted for by means of mixed-gas adsorption isotherms [9,10]. For a perspective of reservoir simulators, use of mixed-gas isotherms allows more realistic predictions of gas mixture behavior in shales, which is extremely complex in nature. The shale samples demonstrate the great variety of pore sizes from nano- (<2 *nm*), meso- (2–50 *nm*), and macro-pore (>50 *nm*) size distributions with majority of pore sizes falling within tens of *nm* [11]. Previous simulation works limited to pore-size <4 *nm* show a strong effect of the confining environment represented by the adjacent clay surfaces on the adsorption capability [3,5,12–14]. Moreover, the scopes of the works were focused on studies of pure systems and/or narrow ranges of pressure regimes [3,5,12–14].

The goal of this paper is study competitive adsorption process of the binary CH_4/CO_2 mixture of various compositions at illite surfaces in meso-pore space at pressures up to 60 MPa and temperatures corresponding to deep shale plays. The mixed isotherms are intended to be used in reservoir-scale simulators to predict CO_2 storage resources in shales with known clay mineral content and pore size distributions. The adsorption processes studied in this paper are applicable to dry gas shales and are not suitable for application to tight oil or condensate-rich shales. The presence of oil and/or condensate in shale systems has significant effects on the mobility and distribution of CO_2 and CH_4 saturation as compared to a system saturated with only gas.

2. Methodology

Monte Carlo simulations are a natural choice to simulate gas adsorption on clay surfaces at molecular level [3,4,12,15–18]. Typically, grand canonical (GCMC) or Gibbs ensemble (GEMC) Monte Carlo simulations are carried out to study adsorption at surfaces. The former approach requires estimations of chemical potentials for the species of interest, the latter one uses separate boxes for each phase to calculate the phase equilibrium for a target pressure and temperature condition and does not need chemical potentials of interacting species as input parameters. For multi-component adsorption process, GCMC simulations are sensitive to precise estimation of chemical potentials since even small variations in those values could lead to large deviations in compositions and densities of the mixture [19]. In this regard, GEMC simulations can be more convenient to reach equilibrium of a mixture, although

typically require more computation time compared to the GCMC counter-part. GEMC simulations are broadly used to study multi-component systems [20–25]. Lopes and Tildesley [20] employed GEMC approach to calculate multi-phase equilibria. Kristof et al. [23] using GEMC simulations reported good agreement between theoretical and experimental results for the CO_2–water–methanol system at high pressure conditions. The present work employs GEMC simulations to study the adsorption of carbon dioxide and methane on illite [001] surfaces. The Gibbs ensemble used in this study follows a similar procedure used by Makaremi et al. [18]. For the multiphase clay system, the configuration involves three boxes initially containing bulk carbon dioxide, bulk methane, and illite layers with potassium ions. Per the Monte Carlo method, a series of moves are applied to reach a target fraction of acceptances and rejections at a given equilibrium temperature and pressure. The allowed moves include volume changes, molecular exchanges, molecular translations, and molecular rotations. Carbon dioxide and methane molecules are allowed to exchange between boxes. The counter-balancing cations are allowed to have translational moves within the clay box. The clay box does not undergo volume changes, and displacement moves are not applied to illite particles. Once equilibrium is achieved, the two boxes containing the bulk phases have reached equal compositions and densities while the remaining clay box possesses illite, potassium, and sorbed CO_2 and CH_4.

In nature, the isomorphic substitutions are distributed between octahedral and tetrahedral layers in illite clays depending of source, rock maturity, and other factors [26]. In this work, the unit cell of the illite structures follow the stoichiometric chemical formulas $KAl_4(OH)_4(Al_{0.5}Si_{3.5}O_{10})_2$ and $KMgAl_3(OH)_4(Si_4O_{10})_2$ to represent two limiting structures; one with all substitutions located in tetrahedral layers, therefore, exposing unbalanced charge to sorbed species, and another with substitution localizations in octahedral one making charge shielded by overall neutral tetrahedral layers. The tetrahedral substitutions of the silicon atoms with aluminum and the octahedral substitution of the aluminum atoms with magnesium generate -1e charge for each unit cell and necessitate one potassium ion to counter-balance the charge. The isomorphic substitutions in the tetrahedral-octahedral-tetrahedral (2:1 TOT) clay sheets were placed in such a way that they show a repeated pattern in the directions of a and b lattice vectors. Al–O–Al linkages in the tetrahedral sheets were avoided according to Loewenstein's rule [27]. Using the unit cell with the parameters from Sainz-Diaz et al. [28], a $4 \times 2 \times 1$ supercell was constructed to generate a nano-pore clay system of 328 atoms (including 8 potassium ions as counter-ions) with an area of 2.08 b y 1.84 *nm* under periodic boundary conditions. For simplicity all angles in the supercell were taken orthogonal. K^+ counter-ions were randomly distributed and were able to move in the interlayer space. Five compositions of carbon dioxide/methane were explored (in molar fractions): 1:0, 0.8:0.2, 0.5:0.5, 0.2:0.8, and 0:1, respectively. For each composition, the combined number of carbon dioxide and methane molecules was set to 800 and initially segregated by molecule type into the two bulk phase boxes. After the size-effect analysis was conducted using the 0.5:0.5 mixture, the basal d_{001}-spacing of the clay lattice equal to 9 nm was taken for further simulations. At that distance, the equilibrated average density and composition of the carbon dioxide and methane in the middle of the pore space were converged to the equilibrated densities and compositions in bulk boxes. That confirms diminished interference between adsorption processes at the opposite clay surfaces and ensures applicability of the results to larger meso- and macro-pore spacings. Fig. 1 shows the clay layers used in the simulations together with counter-balancing ions and molecules adsorbed at clay surfaces and residing in pore space. Pore spacing or the interlayer distance (the