Microporous and Mesoporous Materials 225 (2016) 331–341

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Adsorption of carbon dioxide, methane, and their mixture by montmorillonite in the presence of water

Ahmad Kadoura, Arun Kumar Narayanan Nair*, Shuyu Sun

Computational Transport Phenomena Laboratory, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

ARTICLE INFO

Article history:
Received 5 November 2015
Received in revised form
11 December 2015
Accepted 6 January 2016
Available online 16 January 2016

Keywords:
Montmorillonite
Adsorption
Monte Carlo simulations
IAST

ABSTRACT

Using grand canonical Monte Carlo (GCMC) simulations, we study the adsorption behavior of CH_4, CO_2, and their mixture at 298.15 K and pressures up to 50 bar in Na-, Cs-, and Ca-montmorillonite clays in the presence of water. Montmorillonite clays in the presence of preadsorbed water, preferentially adsorb CO_2 over CH_4 during both pure component and mixture adsorption. The atomistic model we have used, gives good agreement with available single-component experimental adsorption isotherms, for CH_4 and CO_2 molecules adsorbed onto montmorillonite clays in the presence of water. We observe the general trend that the presence of increasing preadsorbed water content in the clay interlayers, reduced adsorption amounts of pure CH_4 and CO_2 molecules. With a relatively large basal spacing (d = 30 Å), the favorability of adsorption of CO_2 by montmorillonite at relatively low pressures and intermediate water contents has been demonstrated using simulations. GCMC simulation is also used to assess the effect of water on the adsorption of N_2/CH_4, H_2S/CH_4, CO_2/N_2, and CO_2/H_2S binary mixtures in Na-montmorillonite clay. The ideal adsorbed solution theory is shown to agree well with the observed adsorption capacities and selectivities of mixtures in Na-montmorillonite clay.

1. Introduction

Naturally occurring clay minerals determine the key physical traits such as permeability and certain chemical properties such as gas adsorption of shales [1–4] and provide a distinctive material for carbon dioxide sequestration [5–8] and selective sorption [9–12]. Shale mineralogy varies widely such that some shales are silt-rich or carbonate-rich whereas others are dominated by clay minerals, for example, illite, chlorite, smectite, and kaolinite [4,13,14]. Processes such as Knudsen diffusion, slip flow (Klinkenberg effect) and adsorption at the solid matrix can affect permeabilities and Darcy-type flow would be disturbed in case of deviation from the laminar flow [15]. However, none of the above models predict the correct behavior of shale gas production data. Thus in spite of the recent improved success in shale gas production [16], the underlying adsorption and flow mechanisms in shale media are not well understood [17,18]. In nature, smectite such as montmorillonite is one of the most common type of swelling clay minerals [19–25]. To date, there have been numerous simulation studies on water adsorption and swelling in montmorillonites [23–35]. The stable basal *d*-spacing is around 10 Å for dry clays and increases upon interaction with water to the range 11.5–12.5 Å forming a fully saturated monolayer (1W) water arrangement [24,27,29,30–32,36]. Due to intake of more water, the *d*-spacing can increase to the next stable state (14.5–15.5 Å) where water forms a bilayer (2W) structure. Likewise, measured basal *d*-spacings for three layers of water (3W) are in the range 18.0–19.1 Å. In recent years, molecular modeling of the structure and dynamics of the water-methane mixture in the interlayer region of smectites has attracted interest [18,37–41]. These simulations demonstrated that montmorillonite surfaces facilitate methane hydrate crystallization from aqueous solution in agreement with experiments [42].

Geologic sequestration of carbon dioxide has recently emerged as an alternative for reducing greenhouse emissions [5–8,20,39,43–47]. According to experimental investigations [5,8], carbon dioxide adsorption capacity of clay minerals is comparable to that of coal. The swelling of organoclays in the supercritical CO_2 medium is also important in nanocomposite preparations and applications [48,49]. Preferential adsorption of ions and molecules on clay minerals such as montmorillonite can be used for ion exchange [9] and gas selectivity [10–12,18,50]. The main component of shale

* Corresponding author.
E-mail address: arun.narayanannair@kaust.edu.sa (A.K. Narayanan Nair).

http://dx.doi.org/10.1016/j.micromeso.2016.01.010
1387-1811/

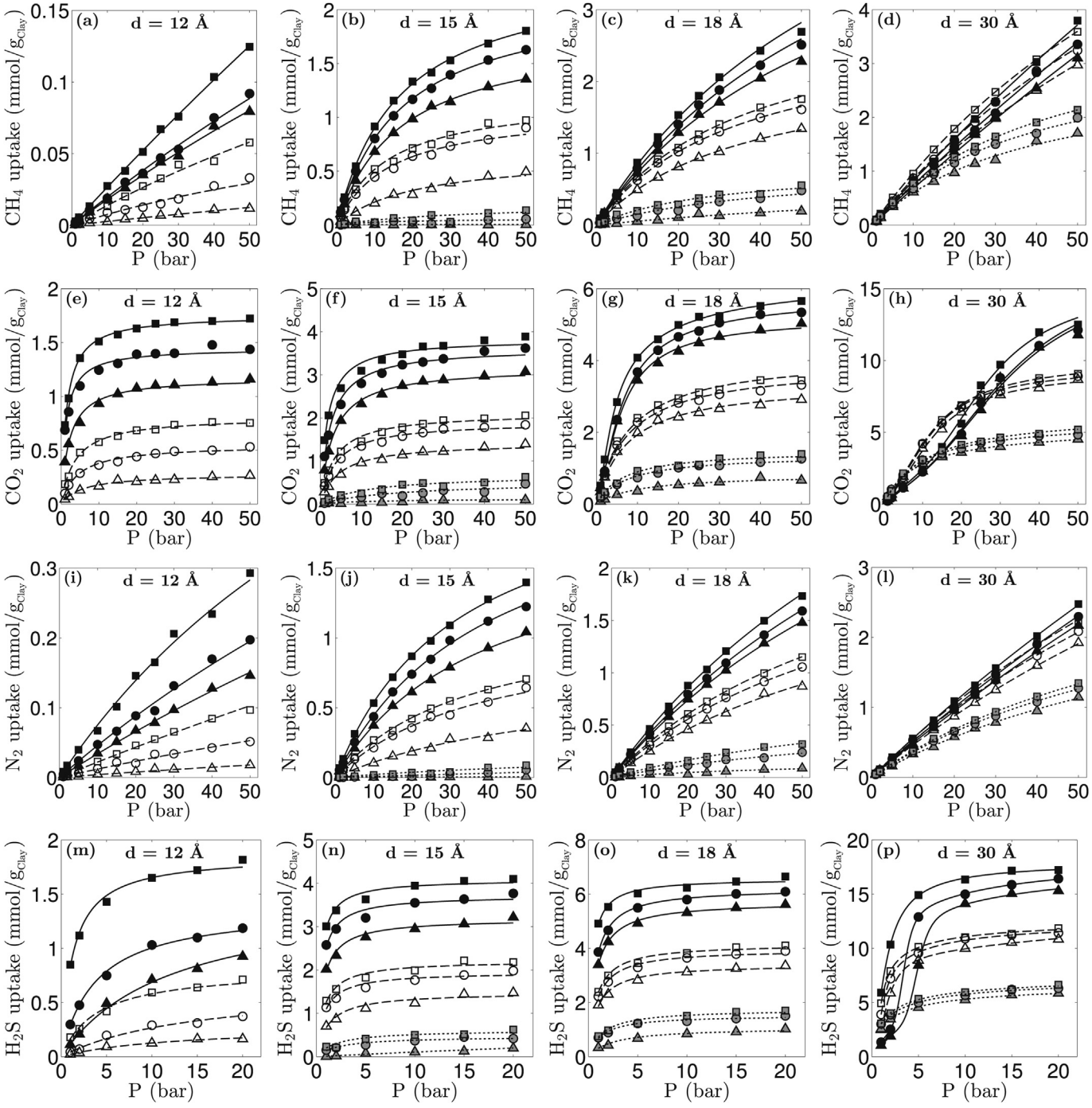

Fig. 1. Single-component adsorption isotherms for CH_4, CO_2, N_2, and H_2S molecules on Ca- (squares), Na- (circles), and Cs-montmorillonite (triangles) in the presence of 0.2 (black-filled symbols), 0.4 (open symbols), and 0.6 g/cm^3 (gray-filled symbols) of preadsorbed water at 298.15 K as computed from GCMC simulation. The lines are fitting results to the GCMC simulation data.

gas is methane, but the composition of the shale gas depends on multiple factors, most of which have geological and geochemical origins [51]. An important issue relevant to methane recovery [1,4] and CO_2 storage capacity [5,8] in clays involves the effect of the presence of preadsorbed water, which cannot be avoided owing to the hydrophilic nature of the samples. The presence of such adsorbed solvents leads to, for example, a striking increase of gas solubility in porous solids with pore size in the range of nanometers [52] and modified sorbate intake [53]. Experimental studies have considered adsorption on dry [1,3–6,10] as well as on moisture equilibrated [1,4,5,8,20,46,54] clays. The mixture adsorption data is typically predicted from pure component adsorption measurements using the capability of approximate methods such as the ideal adsorbed solution theory (IAST) [55,56]. In common practice, IAST can give fair predictions of gas mixture adsorption in many zeolites [57] and metal-organic frameworks [58].

Apart from experimental studies, the effect of moisture on gas sorption in montmorillonite clay minerals and the underlying sorption mechanisms have also been examined in computer simulations [7,11,18,38,39,44,46,50]. Up to now, there are not enough experimental adsorption isotherm data in this field, especially for adsorption on pure clay minerals. Sometimes the difference of