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A Molecular Simulation of Natural Gas Dehydration by 3A Zeolite Nanostructure

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Abstract

The adsorption and separation properties of 3A zeolite are investigated by using Grand Canonical Monte Carlo (GCMC) simulation. To obtain the adsorption isotherms of water, methyl mercaptan, and methane on 3A zeolite, COMPASS Force Filed is used. The adsorption isotherms of the pure components and the ternary mixtures of water, methyl mercaptan, and methane on 3A zeolites are calculated. The Sips Model is taken into account for the description of water adsorption on 3A zeolite. In addition, the effects of pressure and temperature on the adsorption of components are examined. The results demonstrate that the water has high adsorption selectivity on 3A zeolite, and this kind of adsorbent is a good candidate for the dehydration of natural gas.

Keywords: Molecular Simulation, Dehydration, 3A Zeolite, Mercaptan, Adsorption.

1. Introduction

One of the main energy resources is natural gas (Chong et al., 2016), but it consists of different impurities such as water and sulfur (Rashidi et al., 2015). Among impurities that can be found in the natural gas, water is the most common undesirable impurity, which is associated with natural gases in the vapor form. The presence of water may cause corrosion, hydrate formation, and freezing in the pipeline, so the dehydration of natural gas is more crucial (Amran et al., 2011; Chang et al., 2015; Gandhidasan et al., 2001; Kohl, 1974; Mohebbi and Mosayebi Behbahani, 2015; Shirazian and Ashrafizadeh, 2015b). Two techniques of absorption by liquid desiccants and adsorption by solid desiccants are employed for the dehydration of natural gas (Najibi et al., 2012; S. Ranjani, 2005).

In the second dehydration method, the water is adsorbed by solid desiccants, most often with molecular sieve, silica gel, or alumina. Due to a high polar surface within zeolite pores, water vapor and other polar components are adsorbed on zeolites even at very low concentrations. This exclusive feature distinguishes zeolites from other commercially available adsorbents (Farag et al., 2011).

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Zeolites belong to the tectosilicate family of minerals and crystalline nanoporous materials with interconnected channels, which are accessible to molecules of suitable size (Karimi et al., 2012). Zeolites are widely used in separation processes as an adsorbent due to their mesoporous and microporous structures.

The significant selectivity of zeolite materials are attributed to the large internal surface area and highly distributed active sites which are accessible with a uniform pores size, high thermal resistance, chemical inertness, and a high mechanical strength (Bayati et al., 2008; Chen and Deem, 2002; Xu et al., 2001).

Pressure swing adsorption (PSA) is a well-established gas separation technique in the dehydration of natural gas (Grande, 2012). 3A zeolite is utilized in drying natural gas by the PSA process which preferentially adsorbs water molecules, while other molecules are excluded. Zeolite A is normally synthesized in the sodium form, commonly known as zeolite 4A. when approximately 75% of sodium ions are replaced by larger potassium cations, the resulting material is known as zeolite 3A (N. Y. Chen, 1994). The framework of zeolite 4A upon full ion exchange of sodium by potassium is not changed more.

Over last decades, a few works have been developed and tested for the adsorption of water on 3A zeolites. Len et al. studied the adsorption isotherm of water on 3A zeolite, and they discussed the effect of cations on adsorption isotherm (Lin et al., 2015). Simo et al. investigated water and ethanol adsorption/desorption kinetics on 3A zeolite for the design purposes of a fuel ethanol dehydration by pressure swing adsorption process (Simo et al., 2009). The thermodynamic and kinetic study of ethanol-water adsorption on 3A zeolites was studied by Carmo et al. Their results showed that in the experimental temperatures and concentrations the Langmuir isotherm sufficiently correlated to the experimental data. The kinetic studies have shown that by an increase in the temperature, the diffusivity of 3A zeolite will increase (Carmo et al., 1997). Farag et al. studied the dehydration of natural gas by using 3A molecular sieve. Their purpose was to build a pilot scale unit for the dehydration of natural gas by using 3A molecular sieve (Farag et al., 2011). Shirazian et al. evaluated the performance of 3A zeolite membrane for the separation of water vapor and methane as a model of natural gas (Shirazian and Ashrafizadeh, 2015a).

In addition to these experimental studies, there have been a variety of molecular simulations studies which were performed on water adsorption on zeolites. Our understanding of the relationship between the microscopic properties of the confined molecular fluids in zeolites is enhanced by molecular simulation (Beerdsen et al., 2003; Quirke, 2005). Lella et al. simulated the water adsorption in NaY and NaX faujasite, as well as in silicalite-1using Grand Canonical Monte Carlo simulation (Di Lella et al., 2006). Beauvais et al. studied the water adsorption in the model of NaY and NaX faujasite by molecular simulation. They found that the adsorption of water depends on the Si/Al ratio of the aluminosilicate faujasite (Beauvais et al., 2005). Grand Canonical Monte Carlo simulation was used by Joos et al. for the molecular simulation of water and CO_2 adsorption on 13X zeolite. They postulated that their model is able to reproduce the trends in experimental isotherm for water and carbon dioxide (Joos et al., 2013). The molecular simulations of pure and mixed-gases of ethanol/water adsorption in micropores of an NaA zeolite crystal have been studied by Furukava et al. (Furukawa et al., 2004). Csanyl et al. studied the adsorption of H_2O, CO_2, H_2, and CH_4 as two-, three-, and four-component mixtures on NaA zeolite in atomic details (Csányi et al., 2012). To the best of our knowledge, there is no relevant literature about molecular simulation and experimental data toward the adsorption of mercaptans on 3A zeolite.

With the above in mind, in this work, Grand Ensemble Monte Carlo (GCMC) simulation have been employed to investigate the adsorption of pure H_2O, methyl mercaptan, as well as H_2O/methyl mercaptan/CH_4 ternary mixtures on 3A zeolite. To this end, the adsorption isotherms from low pressure to 1000 kPa are simulated. In addition, the adsorptions of ternary mixture based on industrial concentrations are simulated.

2. Simulation details

In this study, the Accelrys Material Studio (MS) simulation packages are used. The topology and structure of water, methane, and methyl mercaptan were generated by the Minimizer sub module of the package. Zeolite A, framework type code LTA, is a three-dimensional, cage-type microporous aluminosilicate with an Al-to-Si ratio of 1 resulting in a comparatively high cation content acting to neutralize the framework (Mace et al., 2013). Two interconnecting channels exist in LTA zeolite, namely α cages and β cages, which are also called supercages and sodalite cages. Each supercage is surrounded by six supercages that are connected through eight-membered rings, referred to as 8R. Apertures of 4.2 Å of the 8R are the chief effective channels of LTA zeolite (Čejka et al., 2007). In each zeolite 3A unit cell, there are 12 K^+ cations distributed in the α-cage (supercage) in three different positions: site I (8 K^+), site II (3 K^+), and site III (1 K^+). The crystal structure of the 3A zeolite adopted in this work is represented by a super cell consisting of 2×2×2 unit cells. In the fully hydrated form of zeolite 3A, the framework unit cell has the chemical formula $8(K_{12}[(AlO_2)12(SiO_2)_{12}]\cdot 24H_2O)$. The primary building units (PBUs) of zeolite 3A are alternating SiO_4 and AlO_4 tetrahedra with silicon or aluminum atoms at their centers and oxygen atoms at the vertices. The space group of the super cell is fm3c with a lattice parameter of 24.555 Å(Bandyopadhyay, 1998). According to the number of K ions required, K ions were located in the LTA framework by using the “cation locator” available in MS Sorption. The CVFF Force Field is used to locate cations in the framework, which contains only ionic atom- type and non-bonded parameters.

To remove bad interactions within the systems and obtain the low energy for the systems, energy minimization using Forcite Plus is used for all the structures in a way which constrains unit cell parameters from changing, and only extra framework cations are allowed to move during energy minimization. The K^+ sites of zeolite 3A play a very important role in molecule sorption and transport. The partial atomic charges associated with each atomic species were set as -0.74 for O, +0.80 for Si, +1.42 for Al, and +0.74 for the extra framework cation K^+ (Guo et al., 2011; Mace et al., 2013).Cutoff distance of 12 Å for the calculation of non-bounded and Van der Waals interactions are used and atom based summation method is selected for potential. Because Grand Canonical Monte Carlo (GCMC) is commonly used for the simulation of equilibrium level of the gas adsorption in nanoporous materials, and it is based purely on the descriptors of statistical thermodynamics (García-Martínez, 213), the adsorption isotherms are computed using GCMC algorithm via the Sorption module in the Materials Studio. Also, the COMPASS-Force Field is used for adsorption simulations (Sun, 1998). All simulations are performed for 10^6 steps.

Data are fitted by using Langmuir and Sips theoretical models and Data fit V. 9.0 software.

The Langmuir adsorption model explains adsorption by assuming that an adsorbate behaves as an ideal gas in isothermal conditions.

$$\frac{C}{C_s}=\frac{bP}{1+bP} \tag{1}$$

The Sips isotherm equation is sometimes called the Langmuir-Freundlich equation in the literature because it has the combined form of Langmuir and Freundlich equations.

$$\frac{C}{C_s}=\frac{(bP)^{1/n}}{1+(bP)^{1/n}} \tag{2}$$

where b, n, and C_s are adjustable parameters.

3. Results and discussion

3.1 Adsorption isotherm

The obtained adsorption isotherm of water on 3A zeolite is compared with the experimental data presented by Lin and co-workers (Lin et al., 2015) in Figure 1. The results are in good agreement with the experimental data, and it demonstrates that the simulation model can well describe the adsorption behaviors of water on 3A zeolite.

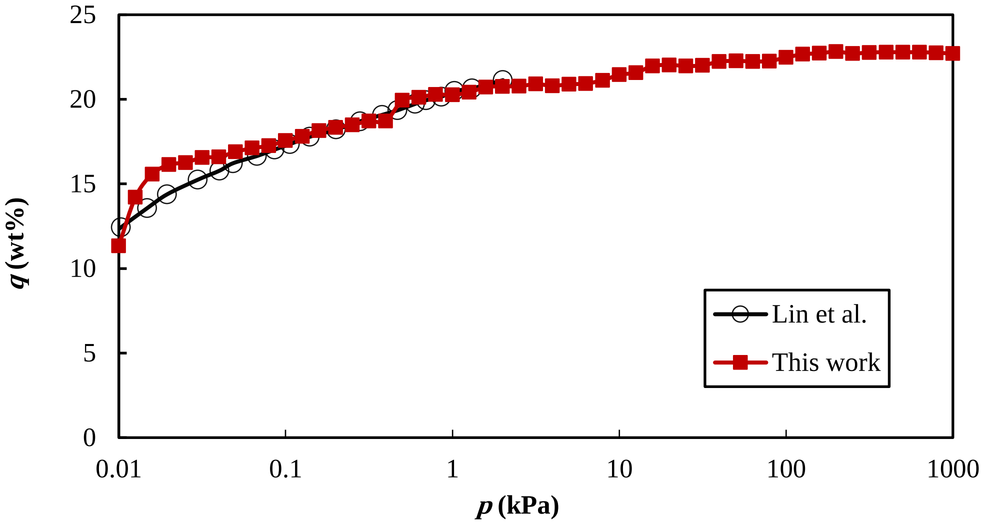

Figure 1
Adsorption isotherms of water on 3A zeolite by the experiment and simulation at 313 K.

The simulations of the adsorption of pure water on 3A zeolite have been performed at 300, 350, 400, and 450 K over a pressure range of 0.01 to 1000 kPa. The calculated adsorption isotherms of pure water on 3A zeolite at different temperatures are shown in Figures 2 and 3. It can be seen that with an increase in the temperature, the absorption of water on zeolite decreases, while by an increase in the pressure, the absorption of water on zeolite rises. The simulation results are compared with the Langmuir and Sips models in Figures 2 and 3. It can be observed that the Sips model is in good agreement with the simulation data, but the Langmuir model could not explain the behavior of the water adsorbed on 3A zeolite. Therefore, the Sips model was taken into account for the description of water adsorption on 3A zeolite.

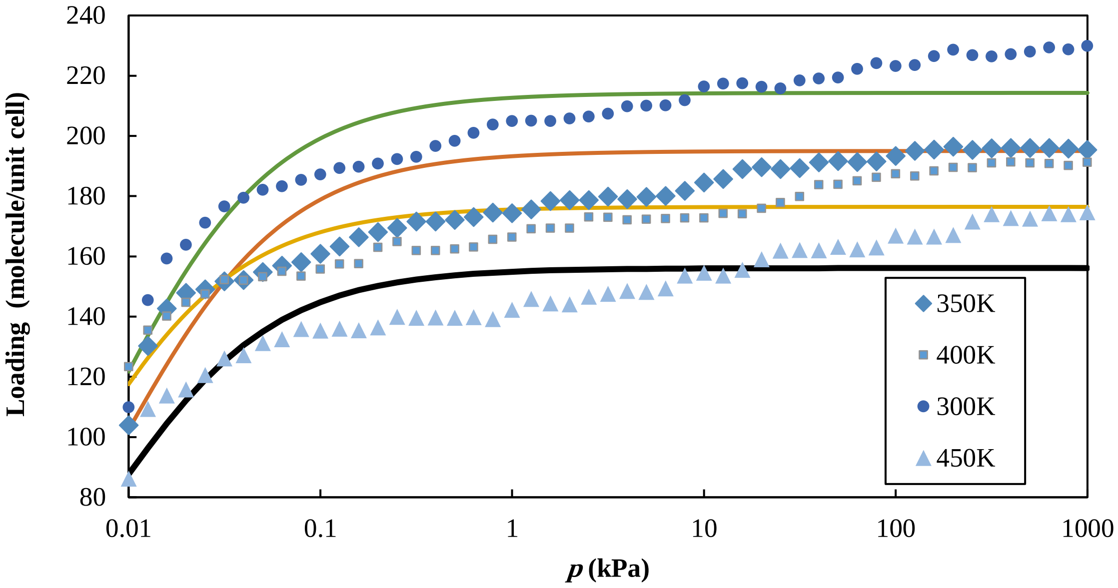

Figure 2
Adsorption isotherms of water on 3A zeolite and single-site Langmuir model regressions at different temperatures.

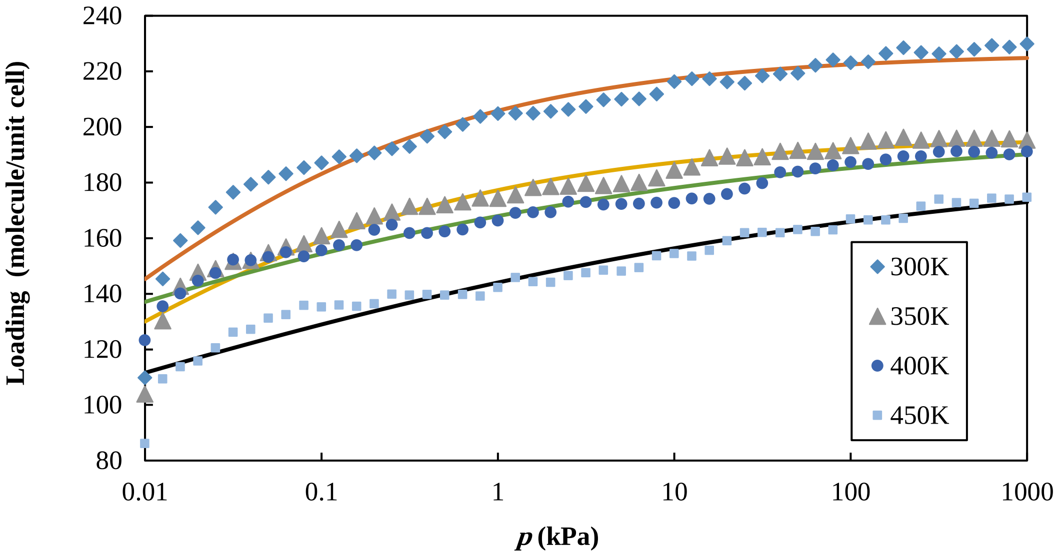

Figure 3
Adsorption isotherms of water on 3A zeolite and Sips model regressions at different temperatures.

In Figures 4 and 5, the absorption isotherms of pure methyl mercaptan on 3A zeolite at different temperatures as a function of pressure are shown. Mercaptan has a far less adsorption than water on 3A zeolite. This is due to their molecular structure and the structure of zeolite. 3A zeolite has a greater tendency to bond with water molecules. It is clear from Figure 5 that the Sips model provides a better fitting to the absorbed mercaptan.

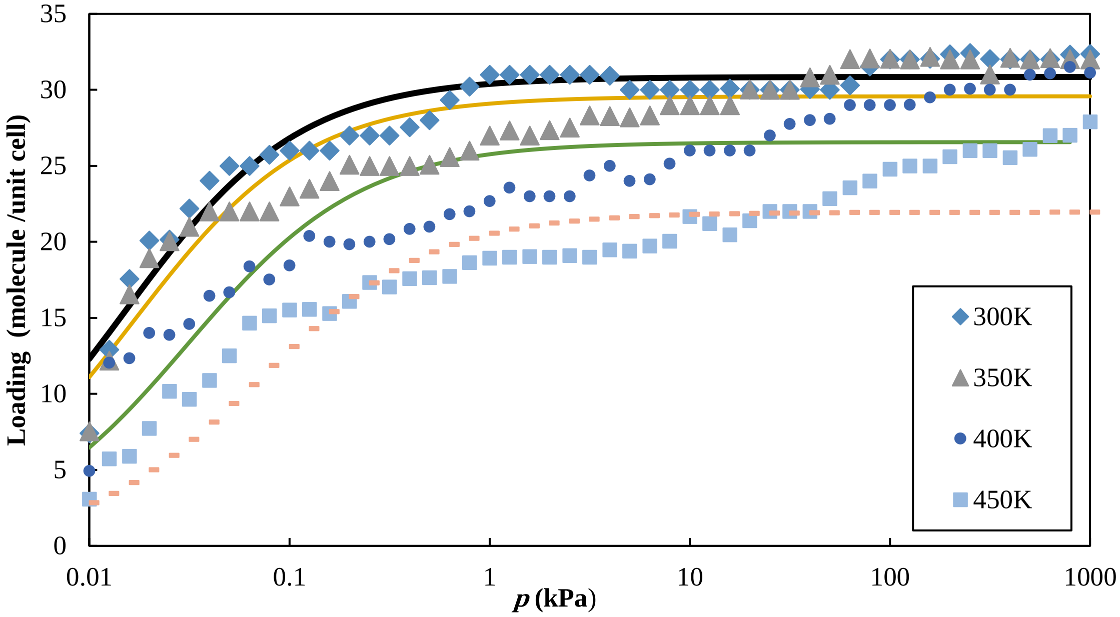

Figure 4
Adsorption isotherms of methyl mercaptan on 3A zeolite and single-site Langmuir model regressions at different temperatures.

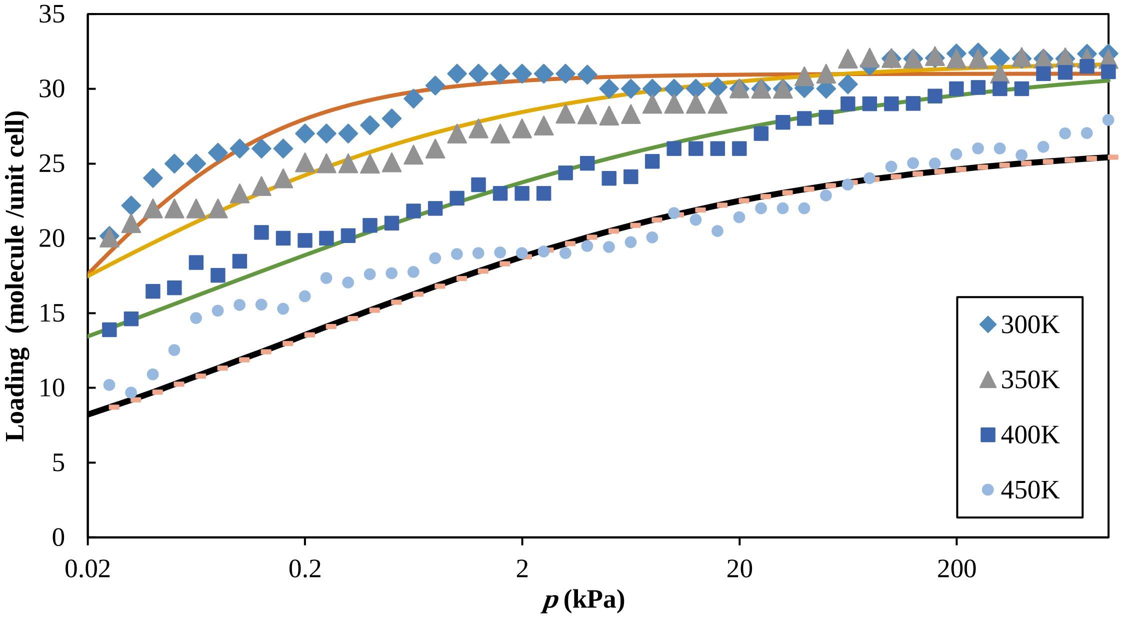

Figure 5
Adsorption isotherms of methyl mercaptan on 3A zeolite and Sips model regressions at different temperatures.

In Figure 6, water/methyl mercaptan ideal selectivity is presented as a function of pressure at different temperatures. Ideal selectivities were almost identical at all the temperatures and pressures. This behavior could be caused by high strength water absorption on zeolite. Zeolite structure has a tendency to absorb water, while zeolite pore size prevents the absorption of mercaptan.

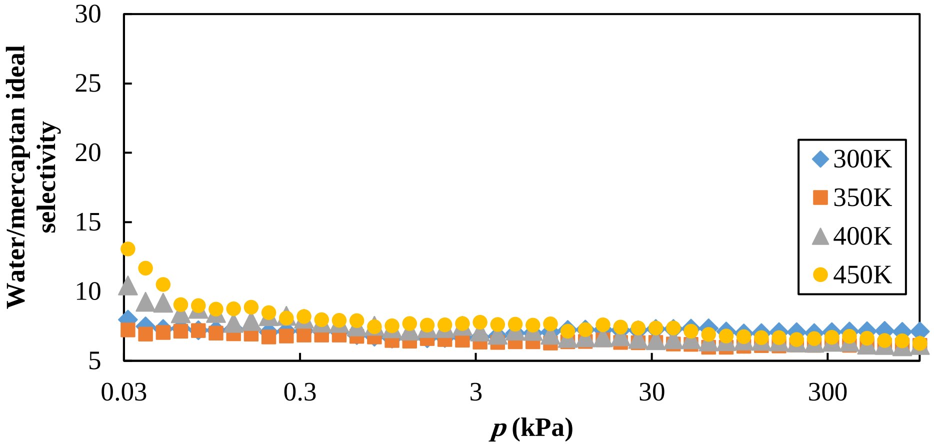

Figure 6
Water/methyl mercaptan ideal adsorption selectivity on 3A zeolite at different temperatures.

If the mercaptan, which should be adsorbed by the zeolite adsorbent, is not separated in the recovery process, it will cause a problem in the refinery system. Therefore, 3A zeolite shows high water absorption, and it is a suitable candidate for the dehydration of natural gas. For a closer look, the simulations of the adsorption of mixtures were performed. In separation processes, a criterion for the evaluation of good separation is the selectivity of a zeolite for different components of mixtures. Ideal adsorbed solution theory (IAST) was used for the prediction of the adsorption of gas mixture on 3A zeolite.

The adsorption of a ternary mixture of methane, water, and mercaptan was evaluated on zeolite. The composition of mixtures was selected based on the concentration of substrate composition of the incoming gas in a dehydration plant.

In Figure 7, the simulations results of the adsorption of water, methane, and mercaptan ternary mixtures on 3A zeolite are shown. It can be seen that despite a high concentration of methane in the mixture, its absorption is very low. Also, the simulation results show that the mercaptan is not absorbed on 3A zeolite in this situation. The simulation uptake results of mixture are different from the pure situation because the water molecules occupied the adsorption sites, and mercaptan molecules were not adsorbed on zeolite. Moreover, the same results are observed for the adsorption of the ternary mixture at different temperatures of 300, 400, and 450 K.

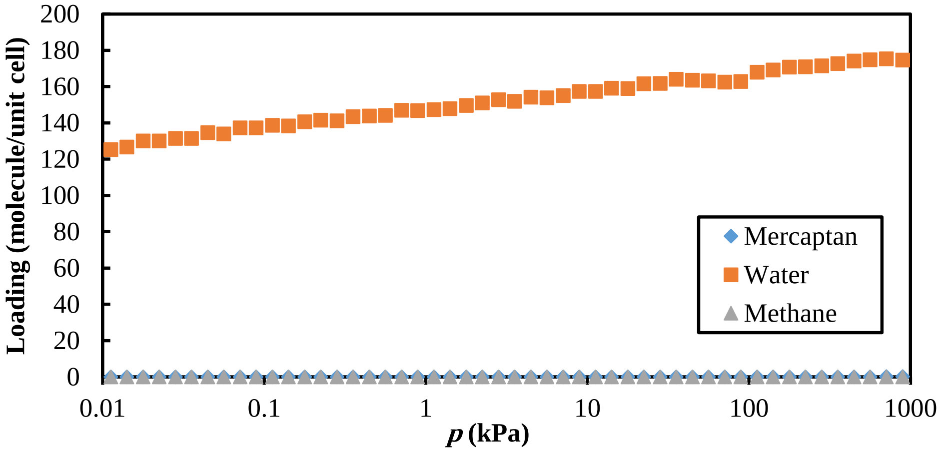

Figure 7
Adsorption isotherms of the ternary mixture of methane/water/methyl mercaptan (0.9962/0.0022/0.0016) on 3A zeolite at 350 K.

It has been concluded that the water has high adsorption selectivity on 3A zeolite, and the selective adsorption of water is important for the prevention of the blockage by methane and methyl mercaptan molecules at the entrance and inside of 3A zeolite. Therefore, 3A zeolite is a good adsorbent for the dehydration of natural gas.

3.1. Adsorption thermodynamic

Adsorption is an impulsive process if it is characterized by a decrease in the total free energy of the system. The adsorption thermodynamics were studied to gain an insight into the adsorption behaviors. The isosteric heat, *Q*, of a component is defined as the partial molar enthalpy of the sorbate component in the reservoir minus its counterpart in the framework. The isosteric heat of adsorption is a key thermodynamic variable for designing practical gas separation processes such as pressure swing adsorption, vacuum swing adsorption, and temperature swing adsorption processes. The isosteric heats of adsorption were calculated from the temperature dependence of the equilibrium capacity by using the Clausius−Clapeyron equation. Since the framework is typically favored over the gaseous reservoir, the value of the isosteric heat is usually positive. At equilibrium, one may obtain:

$$Q^{sf} = h^s - h^f = T(s^s - s^f) \tag{3}$$

where, *s* is the partial molar entropy (Studio;, 2002.).

The variation of isosteric heat of adsorption versus water loading is presented in Figure 8. The isosteric heat decreases by raising the amount of the adsorbed. The isosteric heats of adsorption varied within a range of 100 to 120 kJ·mol^{-1}, and the results correspond to the range reported in the literature for zeolites (Breck, 1973; Lin et al., 2015).

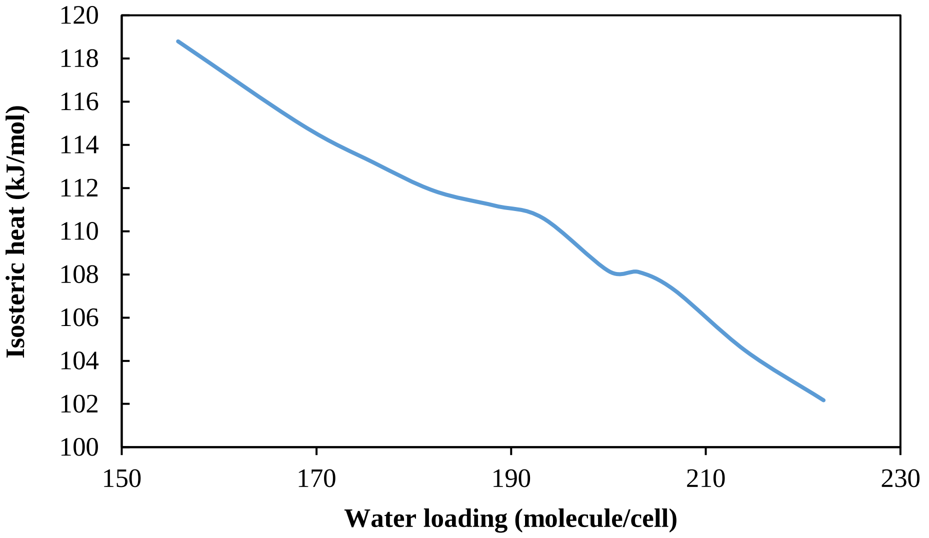

Figure 8
Isosteric heat of adsorption of water on 3A zeolite as a function of its loading at 300 K.

4. Conclusions

The adsorption of pure water, methyl mercaptan, and CH_4 as well as their ternary mixture on zeolite 3A were studied using the GCMC simulations. There was good agreement between the simulated isotherms and the experimental data in literature. The simulations provided some molecular understanding of the adsorption and selectivity of water, methane, and methyl mercaptan in 3A structures. 3A zeolite has a greater tendency to bond with water molecules. Sips model provided a better fitting to water and mercaptan absorbed on 3A zeolite. Our siting studies found the preferred binding sites for H_2O, mercaptan, and methane at high and low pressures.

We also propose that K/Na ion ratio on LTA zeolite can directly affect the molecules adsorption. Hence, water adsorption capacity on LTA can be increased by the increasing Na ion**.**

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Nomenclature

b	: Isotherm parameter (Sips or Langmuir constant)
C	: Loading of component
C_s	: Saturation loading of component
h	: Partial molar enthalpy
n	: Sips constant
p	: Pressure
Q	: Isosteric heat
s	: Partial molar entropy

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