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Molecular Simulation of Propane−Propylene Binary Adsorption Equilibrium in Zeolite 13X

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In the present work, a recently developed force field for molecular simulation of the adsorption properties of linear alkanes in the sodium form of faujasite (FAU), MFI, and MOR-type zeolites is applied to reproduce experimental results of propane adsorption properties in zeolite 13X. The Lennard−Jones (LJ) parameters for interactions between the sp^2-hybridized bond of propylene and the other atoms of this system are successfully determined by fitting against experimental isotherms. This new set of parameters allows the calculation of adsorption properties of propane−propylene mixtures, as well as the isosteric heat of single-component adsorption of propane and propylene in zeolite 13X. Good agreement between simulation results and experimental data for propane and propylene adsorption loadings at temperatures of 303, 323, 343, 373, 423, and 473 K and pressures in the range of 0.2−110 kPa confirms the applicability of the force field. In addition, molecular simulation will be used to guide the desorbent choice for propane/propylene separation by cyclic adsorptive processes.

1. Introduction

Separation of hydrocarbons by adsorption has great importance in the petrochemical industry. Olefin/paraffin separation requires cost-effective technologies to replace energy-consuming processes, such as cryogenic distillation. Separation based on adsorption offers a viable alternative, because of its less-extreme operational conditions.[1] Adsorptive separation in molecular sieve zeolites is an efficient way of removing unsaturated hydrocarbons from other hydrocarbon gas streams. Aluminosilicate zeolites have gained increased attention, because of their importance in the oil and gas industry. Faujasite (FAU) zeolites are among the most widely used zeolites in separation processes.[2] Sodium and calcium forms of zeolite X were studied via the gas chromatographic method to determine the potential of separation of ethylene from ethane and methane.[3] The use of Cd−exchanged wider-pore zeolite 13X as base material in the separation of isobutene from *n*-butane improves the isobutene selectivity.[4] Isotherms and heats of adsorption of propane and water vapor in zeolites X and Y with varying content of exchanged cations were measured, showing a reduction of the amount of adsorbed water and also a reduction in the amount of propane with decreasing exchange cation concentration.[5]

Molecular simulations represent a very efficient tool to predict the physical and chemical properties of a wide range of materials. However, experimental data still remain crucially important for validation of the simulations. Molecular dynamics (MD) and Monte Carlo (MC) simulation techniques have been widely used to study microscopic and macroscopic properties of guest molecules in all-silica zeolitic hosts.[6−10] It was shown that grand-canonical Monte Carlo simulations (GCMC) with a suitable force field may provide a reasonably accurate prediction of the adsorption data for single-component and binary mix-
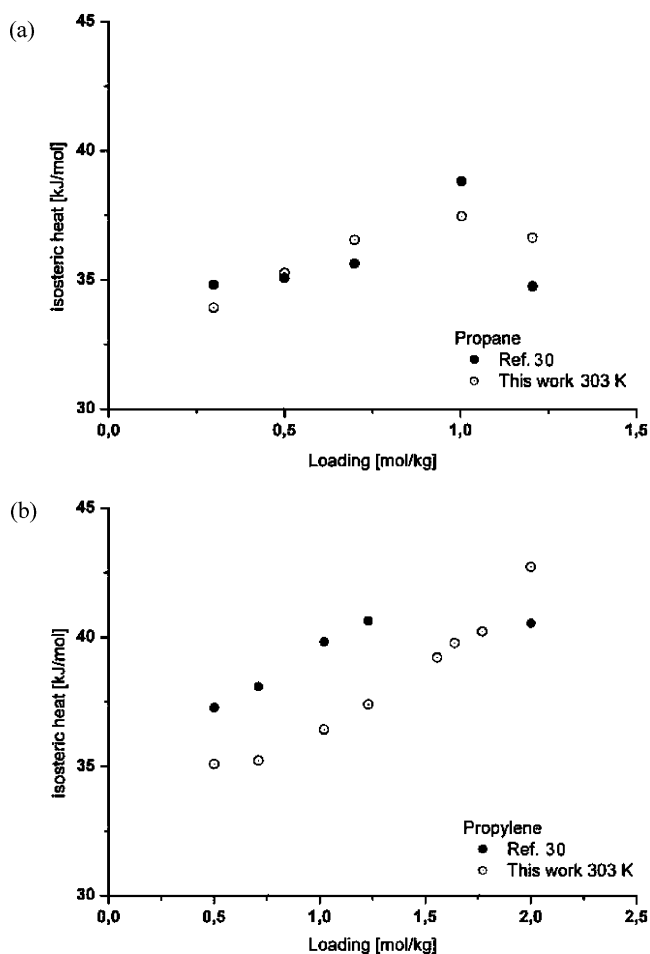

Figure 1. Heats of adsorption for (a) propane and (b) propylene, as a function of loading in zeolite 13X.

tures.[11] However, the transferability of potentials still requires more attention, because force field parameters may produce incorrect results when applied to molecular simulations of different zeolite frameworks.[12]

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Table 1. Intramolecular Force Field Parameters for Na^+ Faujasite[a]

parameter	O_{Al}	O_{Si}	Na	CH_4	CH_3	CH_2-sp^3	CH_2-sp^2	CH-sp^2
CH_4								
ϵ/k_B [K]	115.00	115.00	582.17	158.50	130.84	94.21	116.07	86.31
σ [Å]	3.47	3.47	2.72	3.72	3.74	3.84	3.70	3.73
CH_3								
ϵ/k_B [K]	93.00	93.00	443.73	130.84	108.00	77.70	95.81	71.25
σ [Å]	3.48	3.48	2.65	3.74	3.76	3.86	3.72	3.75
CH_2-sp^3								
ϵ/k_B [K]	60.50	60.50	310.00	94.21	77.70	56.00	68.99	51.30
σ [Å]	3.58	3.58	2.95	3.84	3.86	3.96	3.82	3.85
CH_2-sp^2								
ϵ/k_B [K]	77.30	77.30	398.40	116.07	95.81	68.99	85.00	63.21
σ [Å]	3.50	3.50	3.14	3.70	3.72	3.82	3.68	3.70
CH-sp^2								
ϵ/k_B [K]	62.50	62.50	289.02	86.31	71.25	51.30	63.21	47.00
σ [Å]	3.46	3.46	3.17	3.73	3.75	3.85	3.70	3.73
Na								
ϵ/k_B [K]	23.00	23.00	124.40	582.170	443.73	310.00	398.40	289.02
σ [Å]	3.40	3.40	2.16	2.72	2.65	2.95	3.14	3.17

charge	O_{Al}	O_{Si}	Na	Si	Al
q [e]	−1.20	−1.025	+1.00	+2.05	+1.75

[a] The partial charges (in units of e) of the framework and the Na^+ cations are given at the bottom of the table. Most parameters are taken from Calero et al.[14] The parameters of the sp^2-bonded atoms are taken from Jakobtorweihen et al.[17] The LJ parameters for the sp^2-carbon−cation interactions were obtained by adjusting the force field through fitting a full isotherm. The methodology is described in ref 14. O_{Al} are oxygens that are bridging one Si and one Al atom, and O_{Si} are oxygens that are bridging two Si atoms.

Table 2. Parameters for United Atom (UA) Force Field[a]

parameter	value
bond energy constant	k_1/k_B = 96 500 K/Å²
reference bond length	
CH_i—CH_j	r_0 = 1.54 Å
CH_i=CH_j	r_0 = 1.33 Å
bend energy constant	
propane	k_2/k_B = 62 500 K/rad²
propylene	k_2/k_B = 70 400 K/rad²
reference bend angle	
propane	θ_0 = 114°
propylene	θ_0 = 119.7°

[a] Data taken from refs 14 and 17.

Table 3. Single Component Isosteric Heats of Adsorption

	Q_i [kJ/mol]		
component	ref 19	ref 15	this work[a]
C_3H_8	35.8	32.4	35.0
C_3H_6	42.5	46.1[b]	39.6

[a] Temperature = 303 K. Nonframework cations = 88 Na per unit cell. [b] From refs 15 and 32. Calculated using the Clausius−Clapeyron relationship from single isotherm data taken from the literature.

FAU-type zeolites have a structure that is based on the linking of sodalite cages through hexagonal prisms to form a three-dimensional framework of interconnected supercages ∼12.5 Å in diameter. These supercages are linked through 12-membered-ring windows ∼7.4 Å in diameter. The cations located around the crystallographic sites counterbalance the negative charges that are induced by the presence of Al atoms in the framework.[13] The composition of the synthetic form is $Na_xAl_xSi_{192−x}O_{384}$, where $0 \leq x \leq 96$. Zeolite X contains 77−96 Al atoms per unit cell and zeolite Y has an aluminum density of <77 Al atoms per unit cell.[14]

Equilibrium adsorption isotherms of propane in zeolite 13X were calculated by molecular simulation, using force field parameters that were based on the force field according to Calero et al.,[14] for a pressure range of 0.2−110 kPa and temperatures of 303, 323, 343, 373, 423, and 473 K. Simulation boxes with 76, 86, and 88 Na^+ cations were used in this work. We used different cation densities, because, in the literature, three different number of cations are reported for zeolite 13X. In 1979, Dzhigit et al. reported the use of zeolite NaX with 76 Na per unit cell.[5] In 1995, Tarek et al. described a zeolite sample that contained 86 cations per unit cell.[15] The number of 88 Na cations per unit cell for zeolite 13X is mentioned in the work of Ungerer et al.[16]

For the adsorption equilibrium isotherms of propylene, the Lennard-Jones (LJ) interaction parameters for the sp^2-bonded carbons were taken from the work of Jakobtorweihen et al., which originally was developed for application in all-silica zeolites.[17] Although ab initio calculations of adsorption energies

of butene isomers in NaY zeolites have been published,[18] to the best of our knowledge, there is no published data of MC simulations of alkenes in Na faujasites; therefore, the interaction parameters between the Na atom and the sp^2-carbons must be established and validated through determination of the properties, such as heats of adsorption and adsorption properties of binary mixtures of propane and propylene.

The objectives of this work are to use molecular simulations to describe the isosteric heats of adsorption and equilibrium adsorption isotherms of propane and propylene on zeolite 13X, as well as the x−y diagram of the corresponding mixtures and to compare the results with experimental data.[19,20] The novelty of this work is the establishment of a new set of parameters for cation interactions with alkene double-bond carbons.

2. Models and Methods

2.1. The Configurational-Bias Monte Carlo Method. Equilibrium adsorption isotherms are calculated by MC simulations in the grand-canonical (μVT) ensemble, in which the temperature T and volume V of the system are fixed, as well as the chemical potential of each component (μ). This requires exchanges of molecules with a particle reservoir at a fixed chemical potential.[21,22] The alkane/alkene molecules are described with the united atom (UA) model, in which each CH_n group is treated as a single interaction center. In the configurational-bias Monte Carlo (CBMC) algorithm, the chain grows, starting from the first (united) atom, which is placed at a random position in the zeolite. The next atom is bonded to this atom by a harmonic potential. Several trial directions for this atom are chosen, and one of them is selected with a probability that is
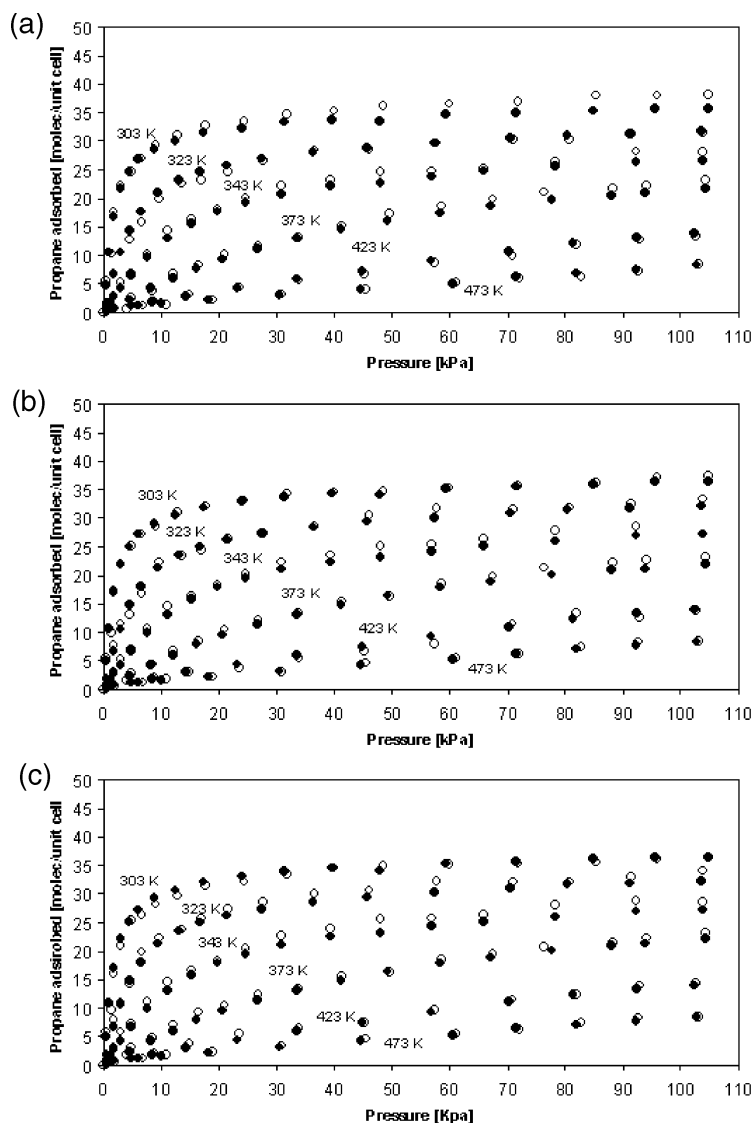
Figure 2. Propane adsorption isotherms for zeolite 13X: 76 Na atoms per unit cell, (b) 86 Na atoms per unit cell, and (c) 88 Na atoms per unit cell. Open symbols represent simulations, and closed symbols represent experimental data.[19]
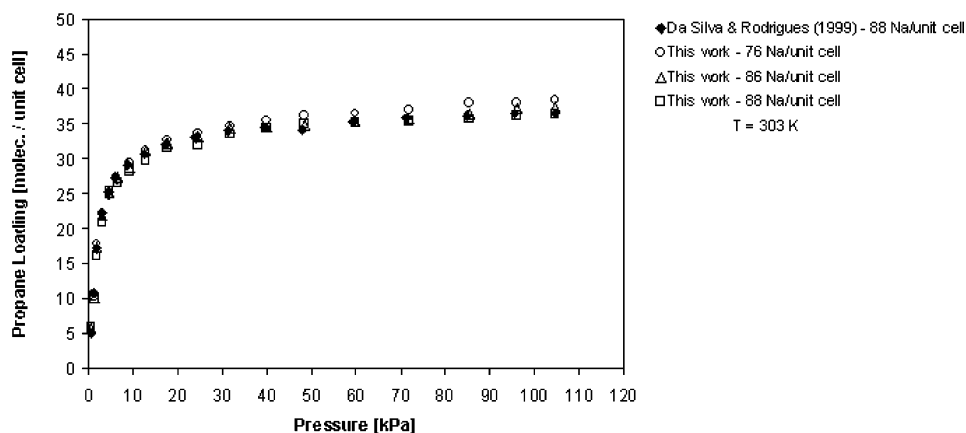
Figure 3. Propane in zeolite 13X: Comparison between simulations (open symbols) performed with different framework cation densities and experimental data (closed symbols).[19]

proportional to its Boltzmann weight. This process is continued until the complete chain is grown. The bias introduced by the growth of the chain is removed in the acceptance/rejection rules. Trial moves to insert and delete molecules must be added. The non-framework cations are also described as single interaction centers. However, the cations contain a partial charge, unlike the united carbon atoms. As the influence of zeolite framework flexibility is small for adsorption,[23] the zeolite structure is considered to be rigid and the cations are allowed to move freely in the zeolite. Details on the force field and the CBMC method can be found in refs 24–26.

2.2. Force Field Parameters. In the present work, the LJ interaction parameters for the sp³ carbons, the nonframework cations, and the zeolite atoms are taken from a recently
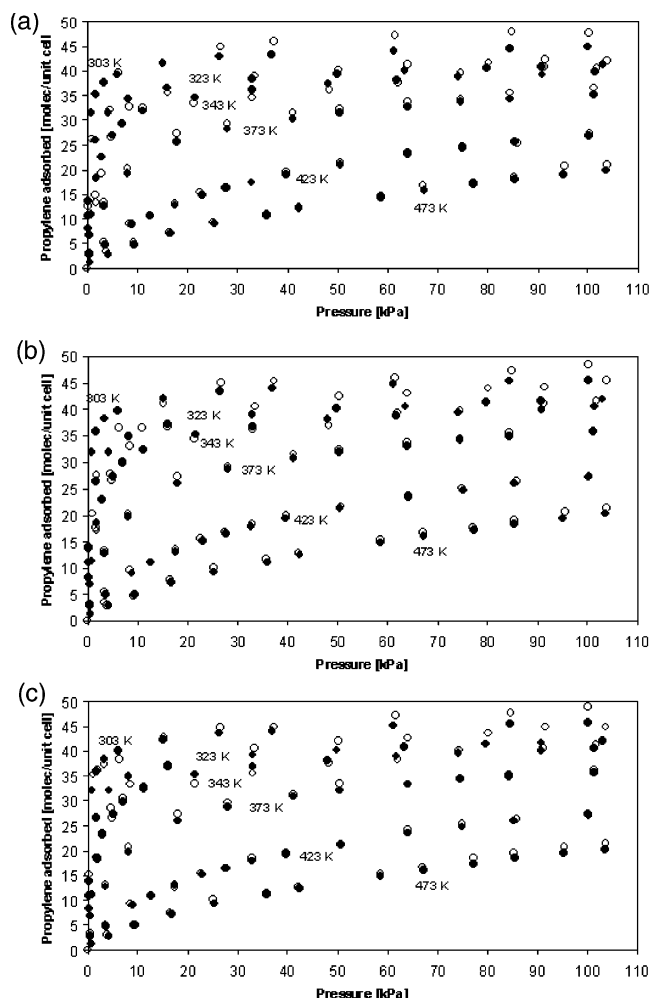
(a)

(b)

(c)

Figure 4. Propylene adsorption isotherms over zeolite 13X: 76 Na atoms per unit cell, (b) 86 Na atoms per unit cell, and (c) 88 Na atoms per unit cell. Open symbols represent simulations, and closed symbols represent experimental data.[19]

developed force field by Calero et al.[14] for alkane adsorption. As mentioned previously, for propylene adsorption, the interaction parameters between the sp^2 carbons, the nonframework cations, and the zeolite atoms were fitted against experimental isotherms.

As a first stage, we used the original set of parameters of Calero et al. and increased the number of parameters with the CH-sp^2 and CH$_2$-sp^2 pseudo-atoms, to explicitly fit a full isotherm over different pressures and temperatures. Furthermore, we calibrated the extended set of parameters against experimental data to obtain a best fit. Finally, we used the new set of parameters to compute the $x-y$ diagram of propane−propylene mixtures. The agreement with experimental results is very good.

Tables 1 and 2 list all parameters used herein. We use a truncated and shifted potential ($r_{cut} = 12$ Å) and tail corrections are not used.[24] Coulombic interactions are calculated by Ewald summation, which is extensively described elsewhere.[21,25,28] In practice, the convergence of the Ewald sum is controlled by three variables: the real space cutoff radius (r_{cut}), the convergence parameter (α), and the largest reciprocal space vector used in the reciprocal space sum (k_{max}). In this work, the Ewald summation parameters $\alpha = 0.3$ and $k_{max} = 9$ are used.

UA beads are connected by harmonic bonding potentials,

$$u_{bond} = \frac{k_1}{2}(r - r_0)^2 \tag{1}$$

The bond bending between three neighboring beads is modeled by a harmonic cosine bending potential.

$$u_{bend} = \frac{k_2}{2}(\cos\theta - \cos\theta_0)^2 \tag{2}$$

Nonbonded interactions are described by LJ potentials, and Coulombic interactions between the cations and the zeolite are used:

$$u(r_{ij}) = \begin{cases} 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] & (\text{for } r_{ij} \leq r_{cut}) \\ 0 & (\text{for } r_{ij} > r_{cut}) \end{cases} \tag{3}$$

Most cross interactions between different (united) atoms are calculated using the Lorentz−Berthelot mixing rules, except for the interactions with the nonframework cations.[27]

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{4a}$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{4b}$$

2.3. Zeolite 13X Model. Three different compositions of the Na-FAU unit cell have been used in the simulations, to compare with experimental results: $Na_{76}Al_{76}Si_{116}O_{384}$, $Na_{86}Al_{86}Si_{106}O_{384}$, and $Na_{88}Al_{88}Si_{104}O_{384}$. These simulation boxes were obtained by random replacement of silicon by Al atoms, automatically following the Löwenstein rule. The zeolite samples used in the reference experimental work have cation densities of 76 and 88 Na atoms per unit cell, as determined by X-ray diffraction (XRD) analyses.[29]

3. Simulations Results

3.1. Isosteric Heats of Adsorption. Using the heats of adsorption is suitable to test force fields, via comparison of the molecular simulation results with the experimental data.[8,14,17,30] Isosteric heats of single component adsorption of propane and propylene have been obtained using the GCMC ensemble, from combined energy/particle fluctuations.[31] For the simulations, the total number of cycles was at least 2×10^6. The calculated heats of adsorption are shown in Table 3. Figure 1 shows a comparison between the simulations and experimental data for propane (Figure 1a) and propylene (Figure 1b), as a function of the loading in zeolite 13X. All calculations have been performed using a simulation box containing 88 cations per unit cell. The agreement between the results obtained by molecular simulation is excellent for propane and for propylene. The difference is ∼7%, which is as expected for predictions of isosteric heats by molecular simulations.[31]

3.2. Propane Adsorption in Na-FAU (Zeolite 13X). Propane adsorption equilibrium isotherms were simulated at temperatures of 303, 323, 343, 373, 423, and 473 K and pressure ranges of 1−100 kPa. Simulations for this system at 293 K and pressures from 10^{-2} kPa to 10^3 kPa have been reported by Calero et al.[14] The simulation methodology is identical to that given by Calero et al.,[14] and a detailed description of the Monte Carlo scheme can be found in ref 14. The number of MC cycles needed to calculate the isotherms was 2×10^6. The adsorption loadings calculated by molecular simulation have been corrected for a binder content of 20%, for comparison with the experimental loadings.[19] The agreement with the experiments is very good at all studied temperatures. Figures 2a, 2b, and 2c show equilibrium adsorption isotherms of propane over zeolite 13X, compared with the experimental results from Da Silva and
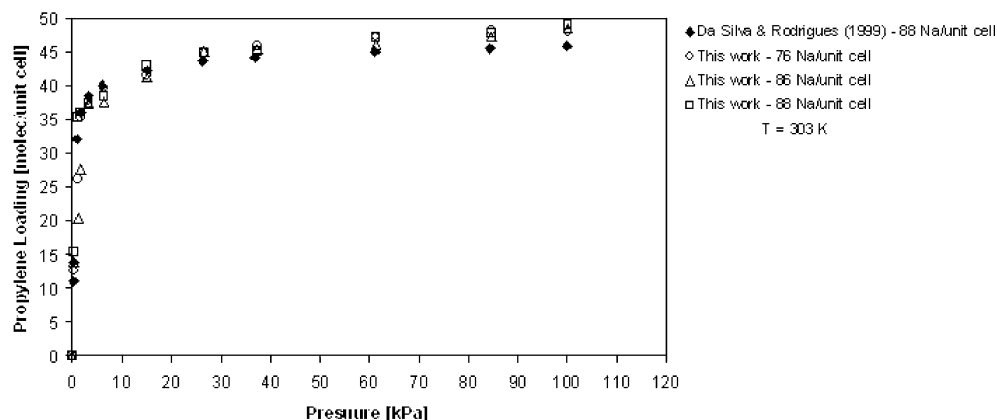
Figure 5. Propylene in zeolite 13X: Comparison between simulations (open symbols) performed with different framework cation densities and experimental data (closed symbols).[19]
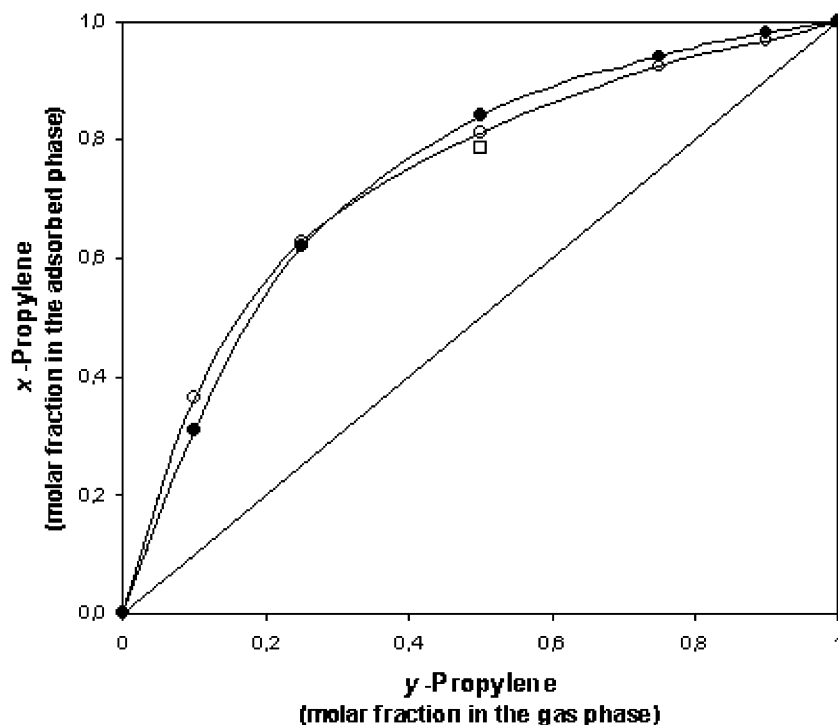

Figure 6. Propane/propylene in zeolite 13X: Equilibrium $x-y$ diagram at 303 K and a total pressure of 101 kPa. Closed circles are unpublished experimental data,[37] and open circles are simulations results; the open square is a point that was obtained from a 50:50 propane:propylene breakthrough curve.[20]

Rodrigues.[19] Figure 3 shows isotherms at 303 K in which the simulations performed with 76, 86, and 88 Na atoms per unit cell are compared with the experimental results for a zeolite 13X sample that contained 88 Na atoms per unit cell.[19,29] The differences between the simulations and experiments are smaller than the symbol size in this figure, and the shape of the isotherms is well-reproduced.

3.3. Propylene Adsorption in Na-FAU (Zeolite 13X). Numerous studies exist regarding the adsorption of alkanes in zeolites by molecular simulation.[6−11,21,22,24] However, the adsorption properties of alkenes in zeolites determined by molecular simulation found in the literature are scarce. A study in 2004 by Pascual et al. examined the adsorption of n-alkenes in silicalite-1, using the anisotropic united atom (AUA) force field model.[33] The work of Zhang et al. in 2003 reported molecular simulations of propane/propylene adsorption in zeolite 4A and seems to be the first study that has considered cation−sorbate interactions for alkenes, using the all-atom model.[34] In 2005, Jakobtorweihen et al. used a UA force field to calculate adsorption isotherms of several alkenes and their mixtures in

all-silica zeolites.[17] The present work is intended to determine reliable LJ parameters for the interaction between the non-framework cations and the sp²-hybridized groups of linear alkenes using the UA force field and to describe equilibrium adsorption properties of propylene in zeolite 13X, as well as their mixtures with propane.

Equilibrium adsorption isotherms were calculated using the CBMC simulations in the pressure range of 0.3−100 kPa at temperatures of 303, 323, 343, 373, 423, and 473 K. The simulated isotherms were compared with experimental data that was reported by Da Silva and Rodrigues.[19] Three different sodium densities have been studied, as shown in Figures 4a, 4b, and 4c. Figure 5 shows the isotherms of propylene in zeolite 13X at 303 K, as a comparison between the experimental results and simulation boxes of 76, 86, and 88 cations per unit cell. The simulated isotherms illustrate important aspects of propylene adsorption properties. First, at higher loadings (lower temperatures, high pressures), the simulations results are higher than the experimental data. This is explained by the use in experiments of pelletized zeolite with a binder content of 20%, which

can cause structural imperfections and inactivation of a large part of the zeolite, because of pore blocking.[14] On the other hand, the simulations reproduce a perfect zeolite crystal, and we feel that is the reason for the overestimation of the loading in simulations. At low loading, simulations and experiments show very good agreement. Note that the adsorption experiments are more accurate at low loading than at high loading, because the experimental data at high pressures are not accurate for a quantitative comparison with simulations.[35]

3.4. Propane/Propylene Binary Adsorption in Na-FAU (Zeolite 13X). Simulations of adsorption equilibria for binary mixtures of propane/propylene have been performed at a temperature of 303 K and several molar fractions of propylene. The $x-y$ diagram is shown in Figure 6. We calculated the adsorbed molar fraction of propylene in a 50:50 mixture of propane and propylene from the breakthrough curves of ref 20 (using the procedure outlined in ref 36). The adsorbed molar fraction of propylene agrees very well with the simulations and other experimental data.[37]

4. Conclusions

Adsorption isotherms of propane, propylene, and propane/propylene mixtures in zeolite 13X have been calculated using the configurational-bias technique in the grand-canonical Monte Carlo ensemble. The heats of adsorption were determined as a function of loading. The simulations have been performed for three different nonframework cation densities: 76, 86, and 88 Na atoms per unit cell. The determination of effective Lennard-Jones parameters for the interactions between hybridized sp^2 carbons and Na atoms in zeolite 13X is a new step in the understanding of adsorption properties of linear alkenes in Na-faujasites. These new sets of parameters successfully reproduce the equilibrium adsorption properties of propylene, as well as those of the propane/propylene binary mixtures. Thus, the force field is suitable for prediction of the equilibrium adsorption properties of linear alkanes, linear alkenes, and their mixtures when no experimental data are available.

Nomenclature

k_{max} = Ewald summation reciprocal space vector

k_1 = constant related to the bond stretching interaction

k_2 = constant related to the bond bending interaction

l = bond length [Å]

r_{cut} = cutoff radius

P = pressure

T = absolute temperature

V = volume

Greek Letters

α = Ewald summation convergence parameter [Å^{-1}]

ϵ = characteristic energy in pair potential

μ = chemical potential

θ = bending angle [rad]

σ = characteristic distance in pair potential

Acknowledgment

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