Influence of Framework Flexibility on the Adsorption Properties of Hydrocarbons in the Zeolite Silicalite

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Computer simulations of the adsorption of hydrocarbons in zeolites are usually performed using rigid zeolite frameworks. This allows for the use of grid interpolation techniques to compute the hydrocarbon−zeolite interaction very efficiently. In this paper, we investigate the influence of the framework flexibility on the adsorption properties of hydrocarbons adsorbed in the zeolite silicalite. We find that at low loading, the influence of the framework flexibility on the heat of adsorption and the Henry coefficient is quite small. However, for molecules such as isobutane and heptane with inflection behavior, the influence at high loading seems to be much larger.

Introduction

Zeolites are microporous crystalline materials based on covalently bonded TO_4 tetrahedrons in which the tetrahedral atom T is usually Si or Al. Because of their special structure and properties, there are several applications of zeolites in industrial processes such as (selective) adsorption, ion exchange, and, maybe most important, catalysis. Knowledge of the adsorption behavior of long-chain hydrocarbons in the pores of zeolites is of considerable importance for our understanding of this catalytic activity of zeolites.[1−4] This adsorption behavior is usually quantified by means of the adsorption isotherm, which is the quantity of hydrocarbons adsorbed at a given temperature and pressure. Experimentally, the determination of adsorption isotherms can be quite time consuming because of the slow diffusion of long-chain hydrocarbons in the pores of a zeolite.[5] It is therefore important to determine whether molecular simulations provide an attractive alternative for studying the adsorption behavior of hydrocarbons in zeolites.

In the past few years, the adsorption and diffusion of hydrocarbons in zeolites have been studied extensively using computer simulations.[2−4,6−22] In many of these studies, it was assumed that the zeolite framework taken from crystallographic data is rigid.[23] This allows for the use of grid interpolation techniques to compute hydrocarbon−zeolite interactions very efficiently. For a typical simulation, this saves more than an order of magnitude of CPU time.[6,24] In ref 20, an overview of these grid interpolation techniques is presented.

Because of the increasing amount of available computer power in the past few years, it is now possible to investigate whether the rigid framework approximation is really valid. For molecular dynamics simulations, it is generally believed that the influence of the flexibility is rather small for molecules that are small compared to the pore diameter of the zeolite[25,26] but much larger for hydrocarbons that fit tightly into the channels of the zeolite. For example, the diffusivity of aromatics in silicalite changes by an order of magnitude if the framework flexibility is taken into account.[27] Similar effects have been found for butane and isobutane in silicalite.[28] Auerbach and co-workers found that the framework flexibility has only a small influence on the site-to-site jump constant for benzene in zeolite NaY. Instead, a much larger influence on the energy dissipation of a single benzene molecule was found.[29] Framework flexibility effects might also be present for molecules in cation-containing zeolites where vibrations of the framework, cation, and adsorbate are strongly coupled.[30] For a review of recent molecular dynamics simulations in zeolites, we refer the reader to refs 31−34.

Also, for the adsorption of hydrocarbons, it is generally believed that flexibility is important only if the adsorbate fits tightly into the zeolite pore, for example, for light hydrocarbons in the zeolite DD3R[35] or for aromatics in silicalite.[36] For different alkane−zeolite potentials, the Henry coefficient of linear alkanes in the zeolite silicalite as a function of the number of carbon atoms is always a linear function, whereas experiments show a systematic decrease for longer chains.[14] Previously, this effect has been attributed to the flexibility of the framework. Despite numerous studies on adsorption behavior, a systematic study of the influence of the flexibility on thermodynamic properties of linear and branched hydrocarbons is still somewhat lacking.

In this paper, we investigated the influence of framework flexibility on the adsorption properties of linear and mono-branched (2-methyl) hydrocarbons in the well-studied zeolite silicalite. This zeolite consists of two channel types, the zigzag and straight channels that cross at the intersections; see Figure 1. The adsorption of hydrocarbons in this zeolite is of special interest because it has been suggested that silicalite membranes are capable of separating linear and branched hydrocarbons.[10,37−43]

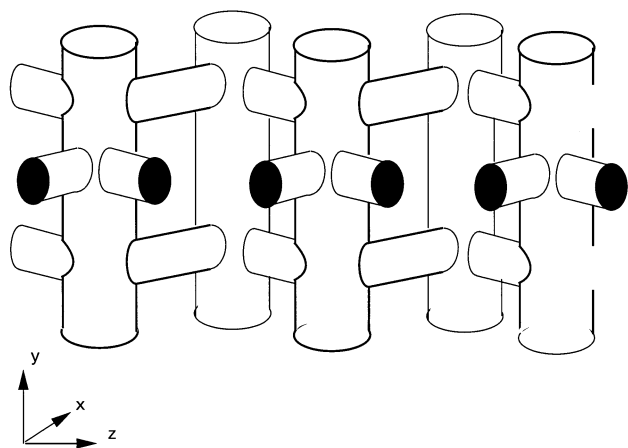* E-mail: vlugt@ilorentz.org and merijn@science.uva.nl.

Figure 1. Schematic representation of the zeolite silicalite (framework type: MFI). Straight channels (*y* direction) and zigzag channels (in the *x*−*z* plane) cross each other at the intersections.

To incorporate the flexibility of the zeolite framework, we need to have an additional force field describing the interactions between the zeolite atoms. The disadvantage of some zeolite force fields is that by changing the force field parameters, not only the flexibility but also the framework structure changes (i.e., the average positions of the zeolite atoms in a simulation using a flexible zeolite framework may or may not correspond to the zeolite crystal structure). To save computer time, we would like to use a force field that is as simple as possible, which means that we would like to avoid (if possible, of course) the use of electrostatic interactions that require an Ewald summation or similar method.[44] Therefore, one has to choose this force field carefully, which we will do in the next section. Using the model of Demontis[45] et al., we have constructed a model where the flexibility is taken into account explicitly without destroying the zeolite structure. An overview of our simulation technique is summarized in section 3. Results of adsorption isotherms, heats of adsorption, and Henry coefficients are presented in section 4, and we summarize our findings in section 5.

Models for Flexible Zeolite Frameworks

There are several force fields that can describe the flexibility of the zeolite framework; see ref 31 for an excellent review. The force field of Kramer and co-workers describes the O−O and Si−O interactions by a Buckingham potential with a Coulomb term and does not include any non-Coulombic Si−Si interactions.[46,47] This force field has the disadvantage that a computationally expensive Ewald summation is necessary to compute the interactions correctly. Furthermore, it is not trivial to tune the degree of flexibility of this model. Therefore, we have focused our attention on the conceptually simpler and more popular model of Demontis and co-workers.[45] In this force field, simple harmonic potentials are used between Si−O and O−(Si)−O bonds

$$V_{Si-O}(r) = k_{Si-O}(r - r_{0,Si-O})^2 \qquad (1)$$

$$V_{O-O}(r) = k_{O-O}(r - r_{0,O-O})^2 \qquad (2)$$

in which $r_{0,\ Si-O} = 1.605$ Å and $r_{0,\ O-O} = 2.61786$ Å are the equilibrium bond lengths and k_{Si-O} and k_{O-O} are the spring constants. Note that only nearest neighbors are considered. As no other pair contacts are involved, the initial topology of the framework bonds is conserved during a computer simulation.

The spring constants and equilibrium bond lengths of these potentials have been fitted to reproduce the IR spectrum of the zeolite silicalite. In the original model, the values of these parameters are $k_{O-O}/k_B = 2.6 \times 10^4$ KÅ^{-2} and $k_{Si-O}/k_B = 1.3 \times 10^5$ KÅ^{-2}. Also, in this model, there are no direct Si−Si interactions.

To reduce the number of parameters, we have chosen $k = k_{O-O} = 0.2 k_{Si-O}$ (which is approximately the case for the original model) and have varied only k_{O-O}. It is important to note that in this model, the parameters $r_{0,\ Si-O}$ and $r_{0,\ O-O}$ are constant for all bonded pairs. The key difference between the models is that the model of Kramer and co-workers does not use any topological information about the Si−O bonds of the zeolite, whereas this topology is explicitly present in the model of Demontis et al.

In principle, the flexibility of both models can be tuned by changing the parameters in the models. It is very important to note that this may also influence the structure of the zeolite. As we will show later, this makes the comparison between these models and a rigid framework based on the crystal structure quite unfair. It seems reasonable that framework flexibility can be taken into account by relatively simple potentials. However, it is not obvious at all that relatively simple harmonic potentials with fixed equilibrium bond lengths can correctly predict the equilibrium (crystal) structure of a zeolite (see, for example, ref 48). As we already know the crystal structure from experimental data, this is also not necessary. Therefore, we have also investigated a new model in which the equilibrium distances $r_{0,\ O-O}$ and $r_{0,\ Si-O}$ are no longer constants. Instead, these values have been taken directly from the crystal structure and therefore vary for different bonds. This reduces the spring constant k to some sort of potential-of-mean-force constant that describes the fluctuations around the crystal structure. The minimum-energy structure (which is the crystal structure) is reproduced exactly when $T \rightarrow 0$ or $k/k_B \rightarrow \infty$, and the harmonic potentials describe the fluctuations around this equilibrium structure. We will call this model the modified Demontis model. Note that we did not consider the even simpler Einstein crystal,[44] as we expect a correlation effect between neighboring oxygen atoms in the zeolite.

Simulation Technique

Details about the simulation technique and the force fields for alkane−alkane and alkane−zeolite interactions have been published previously; see refs 11, 14, 24, and 49−51. Therefore, we will give only a short summary below and focus on the differences between our earlier studies.

The linear and branched alkanes are described with a united-atom model (i.e., CH_3, CH_2, and CH groups are considered to be single interaction centers). The bonded interactions include bond-bending and torsion potentials, and the nonbonded interactions are described with Lennard-Jones potentials taken from ref 52. It is assumed that hydrocarbon−zeolite interactions are dominated by dispersive interactions with the oxygen atoms;[23] these interactions are described with a Lennard-Jones potential as well. This potential has been optimized to reproduce adsorption data correctly at low loadings for hydrocarbons in the zeolite silicalite using a rigid framework. However, it was found that this parameter set also correctly describes the adsorption properties in other zeolites.[2,53,54]

To compute Henry coefficients (the initial slope of the adsorption isotherm) and heats of adsorption, we have to simulate a single molecule in a zeolite (using a so-called *NVT* ensemble simulation) as well as a single isolated molecule
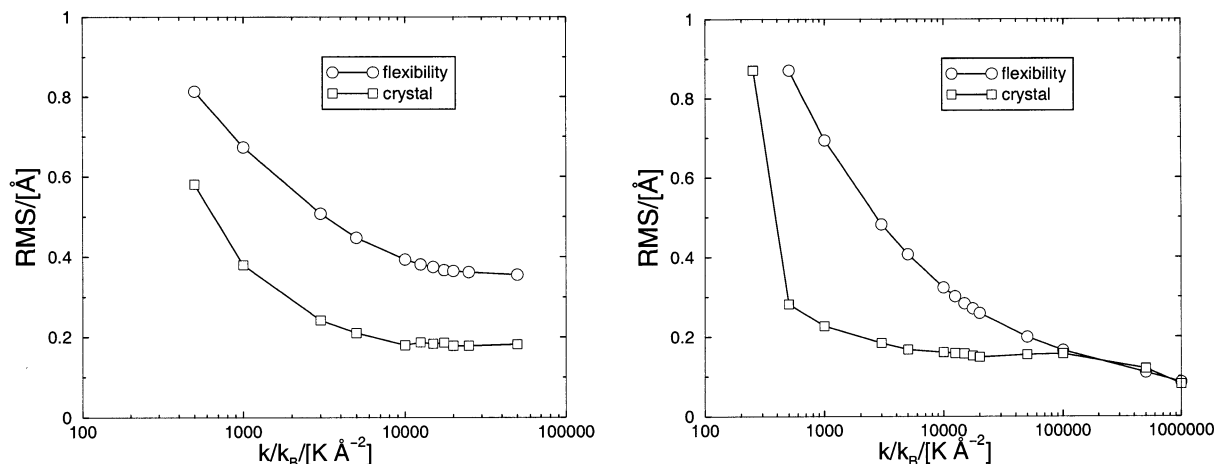
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Figure 2. Root-mean-square differences and fluctuations for the original model of Demontis (left) and the new model (right) as a function of the flexibility k/k_B. (○): rms deviation from the average position. (□): rms difference between the crystal structure and the average structure in the simulation. The average structure was computed using a fixed center of mass (see ref 44). $T = 300$ K.

(without the zeolite). For the simulation of adsorption isotherms, we use a grand canonical simulation (μVT ensemble) in which trial moves are made to exchange particles from an infinitely large particle reservoir. To have a high acceptance rate for these exchanges, we used the configurational-bias Monte Carlo technique.[44,55-58] We have included trial moves that attempt to displace, rotate, or (partially) regrow a hydrocarbon molecule. For the simulation of mixtures, we included identity changes.[59] All simulations have been performed at $T = 300$ K.

To simulate a flexible zeolite, we have included MC trial moves that attempt to give a randomly selected zeolite atom a random displacement. The maximum displacement of zeolite atoms was adjusted in such a way that 50% of all displacements were accepted. As the number of zeolite atoms is much larger than the number of hydrocarbon molecules in the zeolite, the number of attempted zeolite displacements was chosen in such a way that it was 2 orders of magnitude larger than the number of attempts to displace a hydrocarbon molecule. It is important to note that the volume of our simulation box is constant (i.e., we neglect the influence of flexibility on the equilibrium framework density). We have taken the crystal structure of silicalite ($2 \times 2 \times 4$ units cells) from the Cerius[2] package,[60] resulting in 4608 zeolite atoms. A typical simulation took at least 10 times more CPU time than that for a rigid zeolite.

Results and Discussion

Zeolite Structure. To study the different models for zeolite flexibility, we have performed simulations of a flexible zeolite without any hydrocarbon molecules adsorbed. The starting point of these simulations was the original crystal structure. To avoid large structural fluctuations, we performed our simulations using a fixed center of mass. In Figure 2, we have plotted the rms fluctuations of the oxygen atoms around their average positions as well as the rms deviation between the crystal structure and the average zeolite structure as a function of the flexibility k/k_B. The rms fluctuations are smaller than a typical bond length between zeolite atoms. For the Demontis model with fixed equilibrium bond lengths, the rms fluctuations are approximately constant when $k/k_B > 10\,000$ KÅ^{-2}, whereas these fluctuations go to zero for large values of k/k_B for the modified Demontis model. Therefore, it seems that the Demontis model still has some flexibility even for very large values of k/k_B, whereas for the modified Demontis model, the flexibility can be easily tuned without changing the rms difference of the crystal structure too
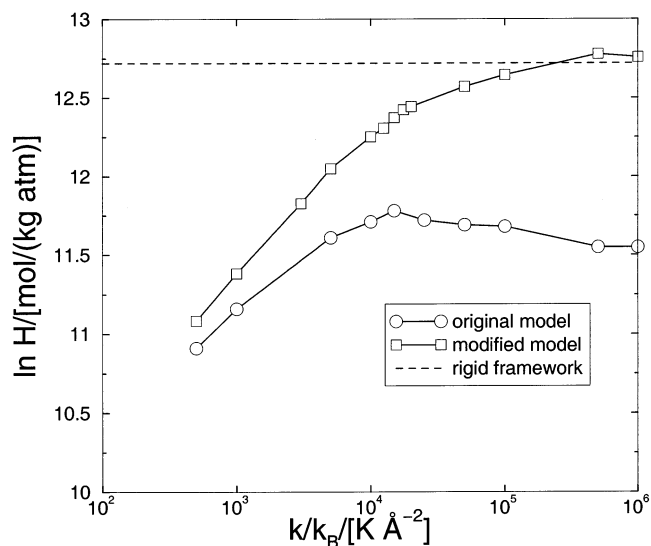

Figure 3. Henry coefficient H of n-hexane for various models as a function of the framework flexibility. (○): Model of Demontis et al. (original parameter: $k/k_B = 2.6 \times 10^4$ KÅ^{-2} from ref 45). (□): Modified Demontis model. The dashed line represents the Henry coefficient for a rigid zeolite. $T = 300$ K.

much. Furthermore, in the limit of $k/k_B \rightarrow \infty$ (or $T \rightarrow 0$), the average structure of the Demontis model does not converge to the exact crystal structure. For low values of k/k_B (<1000 KÅ^{-2}), the differences between the average structure and the crystal structure become very large. At these conditions, adsorption data are no longer meaningful.

To illustrate this effect even better, in Figure 3 we have plotted the Henry coefficient of the different models as a function of the framework flexibility. Clearly, there is a significant difference between the original Demontis model and the rigid zeolite framework. We have found similar differences for the heat of adsorption. Note that as the Henry coefficient is plotted on a logarithmic scale, a small deviation from the experimental value gives a significant deviation in the adsorption isotherm. We found that for all hydrocarbons considered in this study, the Henry coefficient as well as the heat of adsorption is equal to or lower than those for a rigid zeolite framework. Because of the results presented in Figure 3, in the remainder of this paper we will consider only the modified Demontis model with equilibrium bond lengths taken directly from the crystal structure.
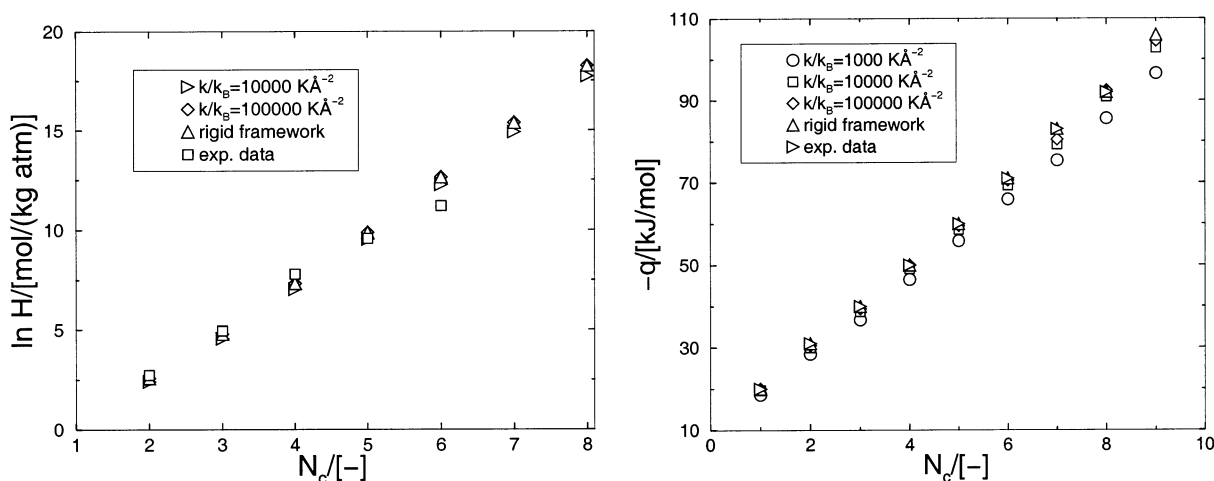
Figure 4. Henry coefficient (left) and heat of adsorption (right) for linear alkanes in silicalite as a function of the number of carbon atoms. See refs 14 and 51 for an overview of the available experimental data. $T = 300$ K.
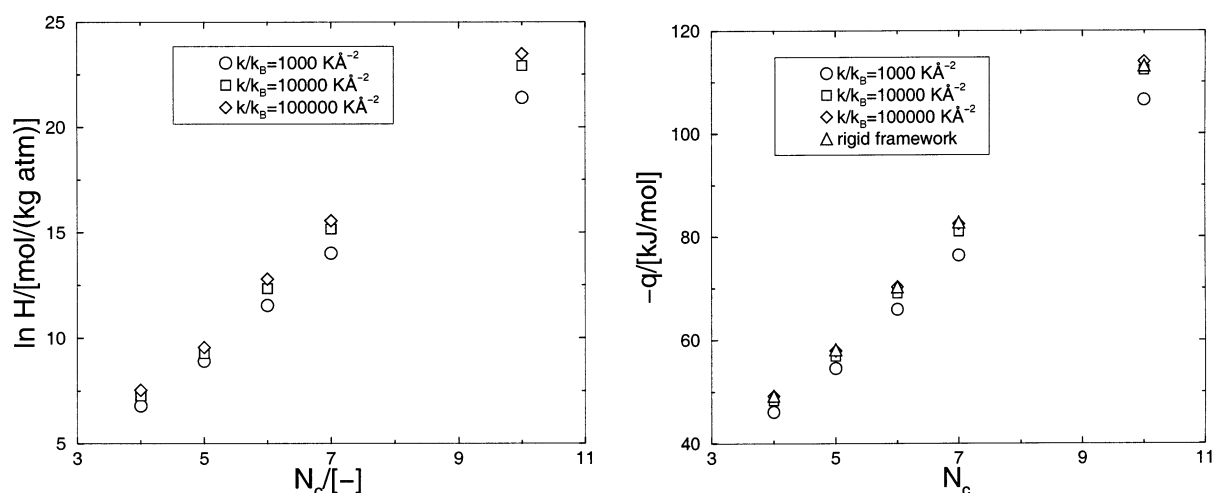

Figure 5. Henry coefficient (left) and heat of adsorption (right) for branched (2-methyl) alkanes in silicalite as a function of the number of carbon atoms. $T = 300$ K.

Henry Coefficients and Heats of Adsorption. In Figure 4, we have plotted the Henry coefficient and the heat of adsorption for linear alkanes in silicalite as a function of the number of carbon atoms for various framework flexibilities. In our plots, we have also included some experimental data taken from the overview given in refs 14,51. Clearly, we observe straight lines for all data sets except the experimental data set for the Henry coefficient. Note that for other alkane−zeolite force fields straight lines are also observed.[61] This means that we cannot attribute this earlier experimentally observed deviation from a straight line to the flexibility of the zeolite framework.[14] A possible explanation would be that at room temperature, the Henry regime for n−C_6 and longer alkanes is observed only at such low pressures that experiments become inaccurate. If one assumes a Langmuir adsorption isotherm, then computing a Henry coefficient at a pressure that is too large results in a systematic underestimation of the Henry coefficient.

For branched (2-methyl) alkanes, we also observe a linear relationship between the heat of adsorption and the Henry coefficient; see Figure 5. Note that there is not much difference in these properties between linear alkanes and their mono-branched isomers.

To quantify the influence of the flexibility on the thermo-dynamic data at low loadings, we have plotted the relative deviation d from the rigid framework of both the heat of

adsorption and the logarithm of the Henry coefficient (repre-sented by the function f):

$$d(k/k_B) = 1 - \frac{f(k/k_B) - f(k/k_B \rightarrow \infty)}{f(k/k_B \rightarrow \infty)} \quad (3)$$

see Figure 6. Apparently, the differences are at most around 10% for the heat of adsorption and the Henry coefficient. For the lowest value of k/k_B (here, 500 KÅ^{-2}), there is already a significant change in the zeolite structure (see Figure 2), but the heat of adsorption and Henry coefficient hardly change. Only for the Henry coefficients of ethane and long-chain hydrocarbons do these deviations seem to be somewhat larger. This is due to the fact that we compare the logarithm of the Henry coefficient. Therefore, the effect of framework flexibility on the thermo-dynamic properties at low loadings seems to be quite small, even for branched alkanes that have a tighter fit in the zeolite than linear alkanes.

Adsorption Isotherms. To investigate the effect of frame-work flexibility at high loadings, we have computed the adsorption isotherms of n−C_4, i−C_4, n−C_7, and i−C_7; see Figure 7. The differences between the isotherms are striking. For butane (top left), the isotherms show Langmuir-like behavior with a maximum loading of approximately 1.6 mmol/g. This corresponds to slightly more than 9 molecules per unit cell.
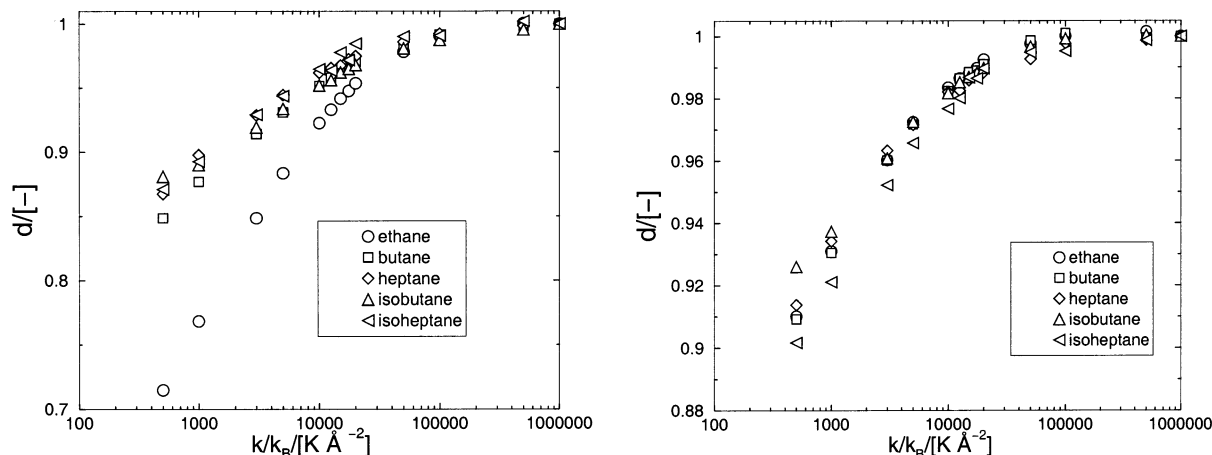
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Figure 6. Relative differences (eq 3) between the Henry coefficients (left) and heats of adsorption (right) as a function of the flexibility k/k_B. $T =$ 300 K.
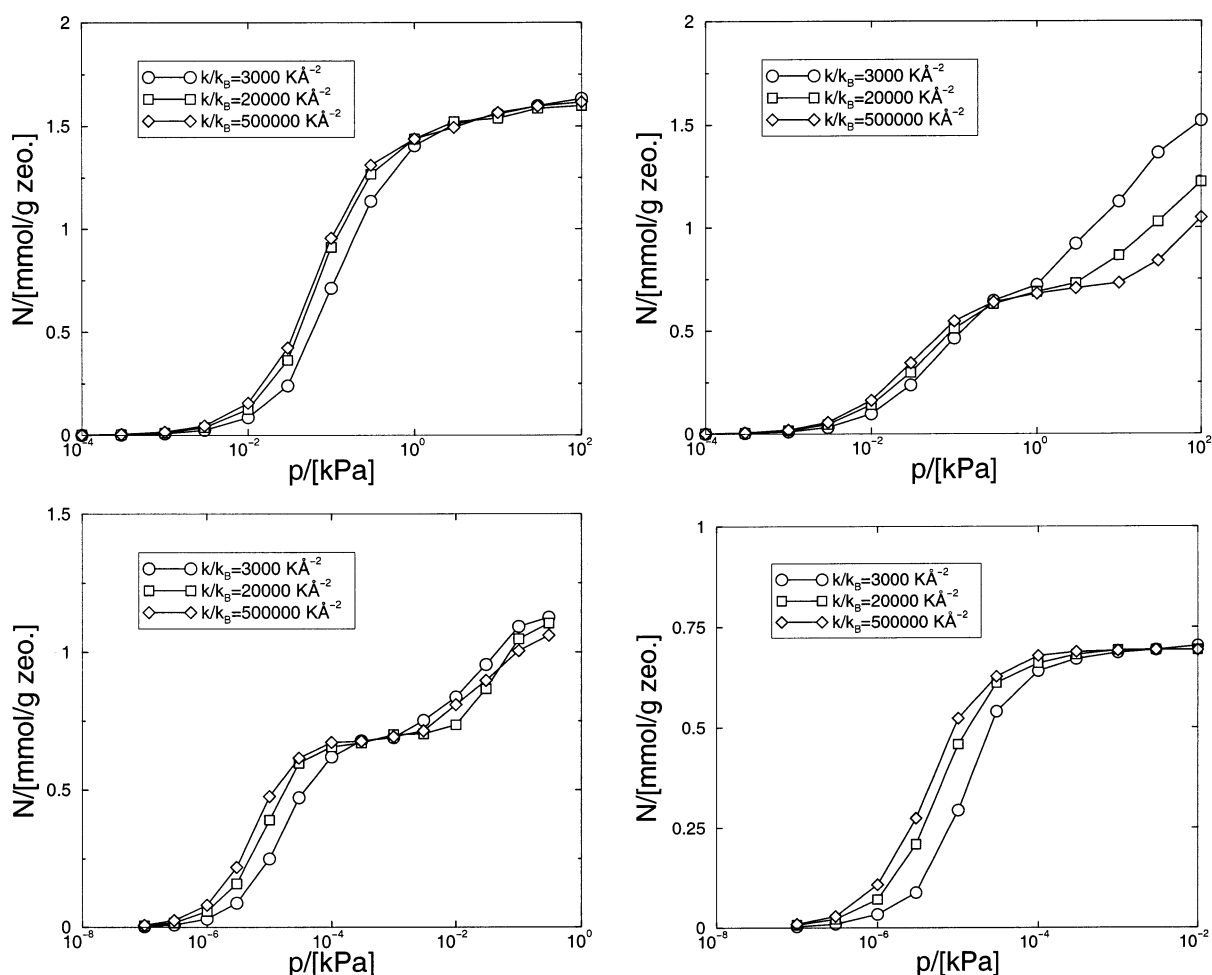

Figure 7. Adsorption isotherms of C_4 (top) and C_7 (bottom) isomers for various flexibilities. Left: *n*-alkanes. Right: branched (2-methyl) alkanes. $T =$ 300 K.

There seems to be hardly any influence of the framework flexibility on the adsorption isotherm, except for the somewhat lower loading for $k/k_B = 3000$ KÅ^{-2}, which is due to a lower Henry coefficient. For its branched isomer isobutane (top right), however, we find an inflection in the isotherm. In earlier studies, it was found that this inflection is due to the preferential adsorption of isobutane at the intersections of silicalite;[11] see also Figure 1. At 4 molecules per unit cell, all intersections are occupied, and additional molecules can be located only in the straight and zigzag channels. However, this requires an ad-

ditional driving force that causes the inflection in the isotherm. This inflection has also been observed experimentally.[62−64] The effect of the framework flexibility on the inflection behavior is quite significant; at lower values of k/k_B, this inflection seems to disappear. Note that even for $k/k_B = 20\,000$ KÅ^{-2}, the minimum pressure to put more than 4 molecules per unit cell into the zeolite differs from the value of the rigid framework. For heptane (bottom left), there is also an inflection in the isotherm around 4 molecules per unit cell. This is due to the commensurate freezing effect discovered by Smit and Maesen.[7]
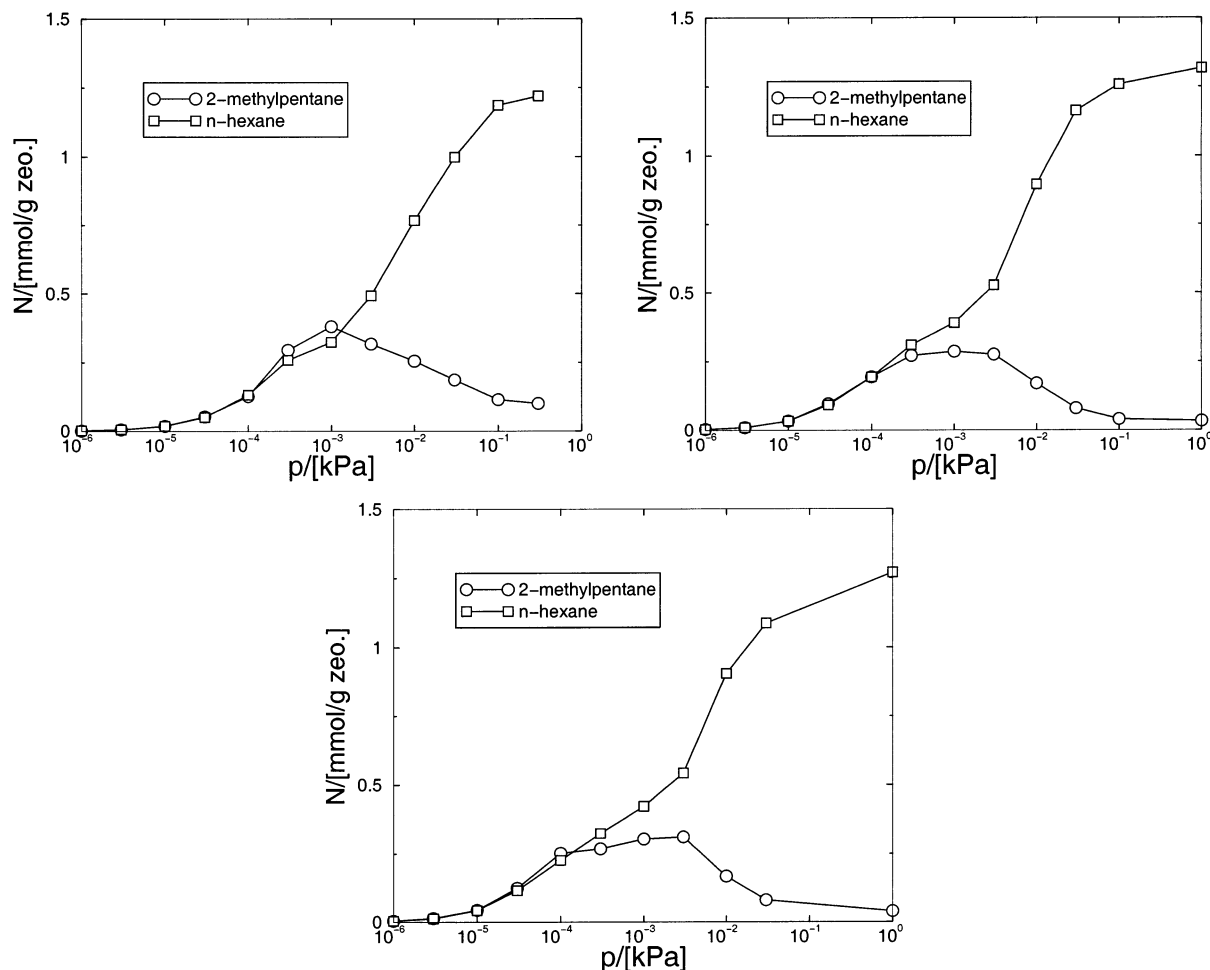
Figure 8. Adsorption isotherms of a 50%−50% mixture of 2-methylpentane and *n*-hexane. Top left: $k/k_B = 3000$ KÅ^{-2}. Top right: $k/k_B = 20\,000$ KÅ^{-2}. Bottom: $k/k_B = 500\,000$ KÅ^{-2}. $T = 300$ K.

As the size of a heptane molecule is commensurate with the size of the zigzag channel in silicalite (see Figure 1), we observe a freezing transition at high loading, which causes the entrapment of heptane molecules in this channel. Also, for this system, the inflection becomes more pronounced for larger values of k/k_B. For isoheptane (bottom right), the maximum loading is much lower than for heptane. The effect of the framework flexibility at medium loading is larger than that for butane because of a higher Henry coefficient.

In Figure 8, we have plotted the adsorption isotherm of a 50%−50% mixture of 2-methylpentane and *n*-hexane. In our earlier studies using a rigid zeolite, we found that at high pressures the branched component is excluded from the zeolite.[10,41] For a flexible zeolite, we find the same effect. At large flexibilities and high pressures, the adsorption of the branched component is approximately 3 times larger that for the rigid framework.

It is interesting to speculate about the reasons that the influence of framework flexibility is so large for isobutane and heptane at higher loading. These systems have two different adsorption sites that have an occupation that depends on the pressure (or loading) of the system. At high loadings, there is a subtle interplay between these adsorption sites. For example, for isobutane, there is a minimum pressure required to get a few molecules into the channel interiors. This interplay can easily be disturbed by small fluctuations of the zeolite structure. If a channel interior is a bit smaller than it is in the crystal structure, no isobutane molecule will be adsorbed at this

position. If, however, the channel interior is slightly larger, an additional isobutane molecule will be able to adsorb, and the structure will be slightly modified around this molecule to give it some extra space. This would explain the less pronounced inflection behavior of isobutane at low values of k/k_B. In the case of the 50%−50% mixture of 2-methylpentane and *n*-hexane, the preference of the branched isomer for the intersections is so strong that small changes in zeolite structure do not change the competition between linear and branched isomers too much.

Conclusions

In summary, we have investigated the influence of the flexibility of the zeolite framework on the adsorption properties of hydrocarbons in the zeolite silicalite. We found that the model of Demontis et al. influences the zeolite structure slightly even in the limit of very stiff harmonic springs. Using equilibrium bond lengths taken from the crystal structure, we were able to construct a force field in which this effect is less pronounced. At low loadings, the influence of the framework flexibility on the heat of adsorption and Henry coefficient seems to be rather small. For molecules such as isobutane and heptane with inflection behavior, the influence seems to be somewhat larger. Therefore, we expect that framework flexibility might be important for systems with different adsorption sites.

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