Microporous and Mesoporous Materials 130 (2010) 92–96

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Investigating the reasons for the significant influence of lattice flexibility on self-diffusivity of ethane in Zn(tbip)

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ARTICLE INFO

Article history:
Received 1 August 2009
Received in revised form 15 October 2009
Accepted 22 October 2009
Available online 28 October 2009

Keywords:
Self-diffusivity
Molecular dynamics
Lattice flexibility
Ethane
Metal-organic frameworks

ABSTRACT

Published molecular dynamics simulations of the self-diffusivity, D_S, of ethane within the one-dimensional 4.5 Å channels of Zn(tbip) (H_2tbip = 5-tert-butyl isophthalic acid) have shown not only quantitative, but also qualitative, differences in the D_S values for fixed and flexible lattices when the concentration of molecules, *c*, is increased. The reasons for these differences are investigated with the aid of probability density plots, free energy landscapes and barriers, along with a determination of the structural changes accompanying increasing *c*. It is found that for flexible lattices, the tighter, more constrained parts of the channels become wider at higher *c*; this allows more molecules to diffuse in the central region of the channels.

1. Introduction

Metal-organic frameworks (MOFs) are a new class of porous materials that consist of metal atoms that are connected by organic linkers. In recent years, there has been a significant increase in research on MOFs in view of several potential applications in the field of storage, separation and catalysis [1–4]. For the development of separation and catalytic technologies utilizing MOFs, it is essential to have data and insights into the diffusion of guest molecules. Many MOFs possess soft dynamic frameworks whose cell dimensions change in a reversible manner in response to external stimuli. For example, IRMOF-1 exhibits negative thermal expansion [5]. Mesh adjustable molecular sieves (MAMS) allow the pore size to be precisely tailored for a given separation application by adjusting the temperature [3]. MIL-53 exhibits breathing effects initiated by either temperature or adsorption of guest molecules such as CO_2 and H_2O [6]. Lattice flexibility of IRMOF-1, that has large size cavities, has been found to increase the diffusivity by about 20–50% [7]. It is to be expected that lattice flexibility will have a greater influence when the molecule is more tightly constrained within a MOF framework. One example of a MOF with narrow pores is Zn(tbip) (H_2tbip = 5-tert-butyl isophthalic acid) that has one-dimensional 4.5 Å channels. Zn(tbip) has narrow channels that exclude large bulky molecules such as aromatics and branched alkanes, while allowing access to linear alkanes and alcohols. It has therefore been suggested for gas separation applications [8–10].

Sorption experiments with short-length alkanes, Zn(tbip)-type crystals allowed the recording of transient concentration profiles with inprecedented options for the measurement of intracrystalline diffusivities [10] and surface permeabilities [11].

In a recent investigation using molecular dynamics (MD) using the fixed lattice assumption it was found that the self-diffusivity of ethane in Zn(tbip) the self-diffusivity, D_S, decreases monotonically with concentration, *c* [12]; see Fig. 1. In sharp contrast, MD simulations with a flexible-lattice displays a qualitatively different characteristic. D_S, firstly decreases with *c* till a loading of six molecules per unit cell is reached; this value corresponds to a loading of one molecule per channel segment (for an indication of a channel segment see the pore potential landscape in Fig. 2). Interestingly, for $c > 6$, the D_S increases until it reaches a maximum and then decreases thereafter. The major objective of the present communication is to examine in detail the reasons behind the differences in the D_S vs. *c* characteristics of fixed and flexible-lattices.

2. Model and simulations

The MD simulations are carried out with a periodic simulation box comprising of six one-dimensional channels. Each channel has five double three-leafed clover topology segments linearly linked together through the windows having the effective diameter

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doi:10.1016/j.micromeso.2009.10.017

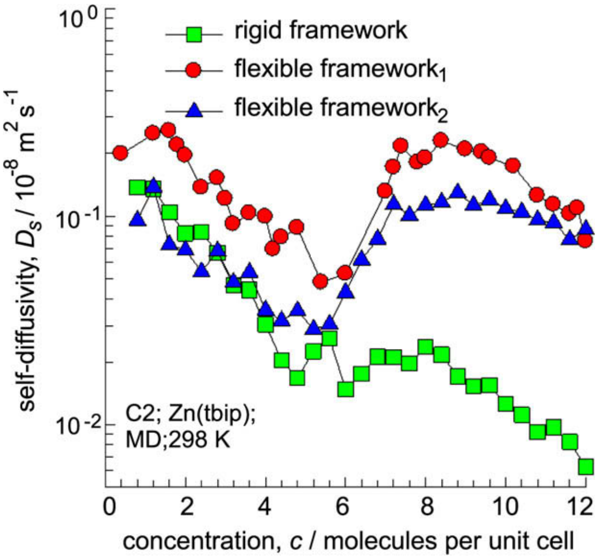

Fig. 1. The self-diffusion coefficients of different loadings of ethane in the flexible and rigid framework. The self-diffusion coefficients are calculated at 298 K in the NVT ensemble.

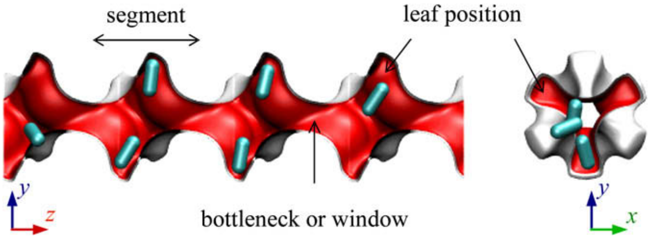

Fig. 2. Snapshots showing the location of ethane molecules within the one-dimensional channels of Zn(tbip) at a loading of 12 molecules per unit cell. The view shows 4 unit cells in the z-direction. Also shown is the side-on view of the channels.

of 4.5 Å. The simulation box is the same as in Ref. [12] and corresponds to five unit cells. Each unit cell consists of 1044 lattice atoms with a stoichiometric composition of C:H:O:Zn = 12:12:4:1. One ethane molecule per unit cell would mean a loading of 0.0973 mmol/g of MOF. The unit cell has dimensions of $28.863 \times 49.992 \times 7.977$ Å. For more structural details see Refs. [9,13].

The force fields used in these simulations are the same as in Ref. [12]. They are described in detail in the supplementary material to [12] which is available in the Web.

For each loading, every channel of Zn(tbip) is firstly loaded with an equal number of ethane molecules before being randomly added with the remainders. The MD runs are performed in the canonical (NVT) ensemble at a temperature of 298 K using Nosé–Hoover thermostat. To ensure that the effect is not influenced by the thermostat, also MD simulations using the NVE ensemble have been performed and gave equivalent results. The equations of motion are integrated with a time step of 1 fs. The starting configuration for each run of MD simulations with rigid and flexible-lattice is relaxed by an initial thermalizing part of the run of 1–2 ns before evaluations start. After that, the production runs are stored every 100 fs for further analyses.

An illustrative quantity that helps to understand structural and dynamical properties of adsorbed particles is the average reversible work to bring a particle to a given site against the resistance of external forces (lattice) and those originating from other particles. In generalization of the Helmholtz free energy this quantity has been named local free energy by Chandler [14] and is now widely used [15]. The average reversible work to bring a particle to a given site and its relation to the logarithm of the local density, Eq. (1), is explained e.g. in Ref. [16].

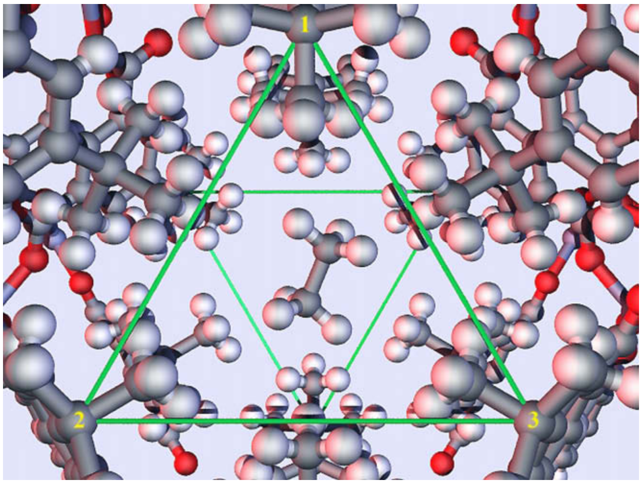

Fig. 3. The two window areas in the Zn(tbip) framework which look like triangles.

Free energy profiles were estimated from equilibrium MD simulation by using the histogram method [17,15]. Using this method, the histogram is directly obtained from the particle positions according to the MD trajectory data. First, the probability $P(z)$ to find an ethane at the particular value of the reaction coordinate z is computed. Then the free energy profile is obtained by using

$$F(z) = -k_B T \ln P(z), \tag{1}$$

where k_B is Boltzmanns constant.

3. Results and discussions

In Ref. [12], the self-diffusivities (D_s) of ethane have been examined in a rigid framework and in a flexible framework of Zn(tbip). We will call the parameter set used for the flexible framework in Ref. [12] flexible framework$_1$. To eliminate some possible reasons for the observed maximum (see Fig. 1) we first carried out test calculations without thermostat using final situations of thermalised runs as starting situations. Of course, these runs did not proceed exactly at the temperature of the thermalised run but, gave equivalent results, so that artefacts connected with the thermostat could be discarded as reason for the maximum in D_s.

We made an additional trial with respect to the interaction parameters of the metal atom in Zn(tbip) to examine whether the Zn atoms have much influence on the self-diffusivity of ethane molecules. The interaction parameters of Zn atoms were modified to have rather strong interaction with ethane molecules using $\epsilon_{Zn-Zn} = 0.9696$ kJ/mol and $\sigma_{Zn-Zn} = 3.02$ Å. The resulting self-diffusion coefficients were found to be equivalent to the unmodified ones suggesting that Zn atoms are well shielded in the lattice framework and difficult to be accessible to ethane molecules.

The size of the open channel windows connecting between adjacent segments was another trial we considered since the molecules have to diffuse from segment to another segment through these narrow windows (or bottlenecks). Instead of using atomistic interactions, as shown in Fig. 3, the CH_3 groups were modeled as spherical united atoms having interaction parameters exactly the same as the CH_3 groups of ethane. This modified flexible-lattice will be called flexible framework$_2$ in this study. By using these parameters, the cross sections of the bottlenecks become slightly narrower as compared to the unmodified ones leading to the significantly smaller self-diffusion coefficients. We found that ethane molecules only displace themselves in the same segment when they were confined in the rigid-lattice framework$_2$. When using flexible framework$_2$ model, the intersegment diffusion of ethane molecules could, however, be observed. The plot of self-diffusion coefficients as a function of loading shows the same trend as found in the unmodified flexible framework$_1$ (see Fig. 1). The results for all models that we used are presented in Fig. 1, that includes the MD results of all models investigated.

Fig. 1 shows that in both of the flexible framework models a maximum appears at about 7–9 molecules per unit cell and a minimum at about six molecules per unit cell. For a loading of 6, in average each segment of framework is occupied by one ethane. When the loading is more than six molecules per unit cell, some segments will be occupied frequently by two or even more ethane molecules. The repulsive interactions between ethane molecules in these segments will lead to stronger forces on the flexible-lattice that can cause an enlargement of the narrow parts of the channel. This would result in an increase of the self-diffusion coefficient. At very high concentrations of guest molecules all segments will be filled with guest molecules and, of course, their mutual hindrance will lead to a decrease of the self-diffusion with increasing loading.

In the following we call the narrow sites (bottlenecks) in the channel ‘windows’. In order to calculate the cross section area of such a window, adjacent lattice atoms are connected by lines that form triangles as shown in Fig. 3. The reported cross section area of the window as a function of loading was calculated as the triangular area shown in Fig. 4 and averaged over 100,000 configurations of the Zn(tbip) lattice. Note, that there are two triangles each for one of two adjacent segments. In Fig. 4, it can be seen that the window is noticeably opened at loadings higher than six molecules per unit cell (some segments are occupied by two ethane molecules).

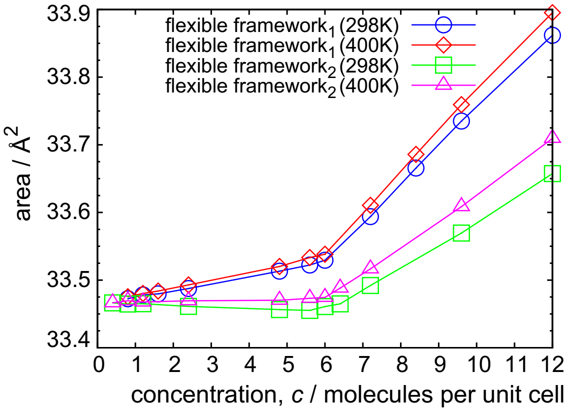

Fig. 4. The cross section area of the window as a function of loading for ethane in the Zn(tbip)flexible framework.

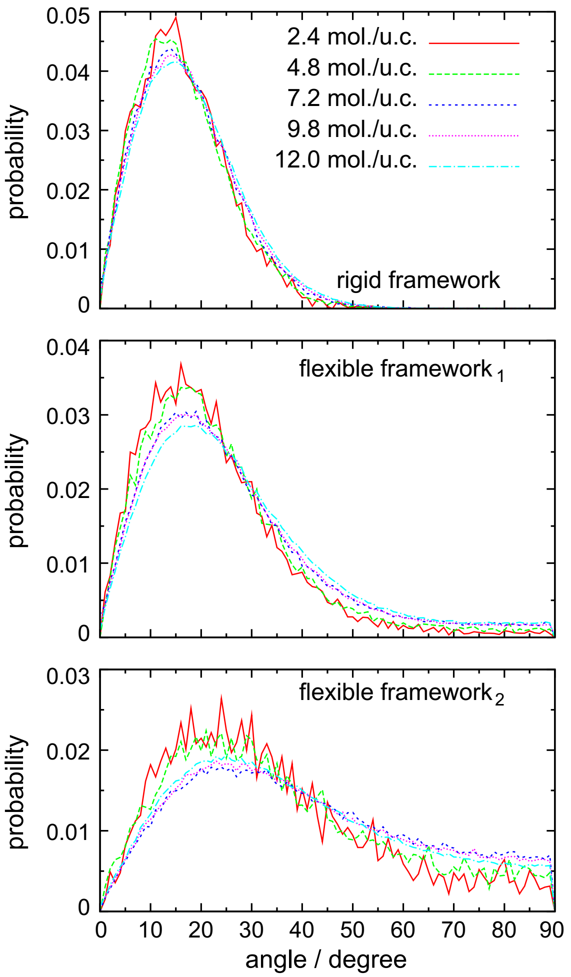

Fig. 5. Angle distribution projected in the *z*-axis for ethane moving about the window in rigid and flexible (Zn(tbip) framework at different loading.

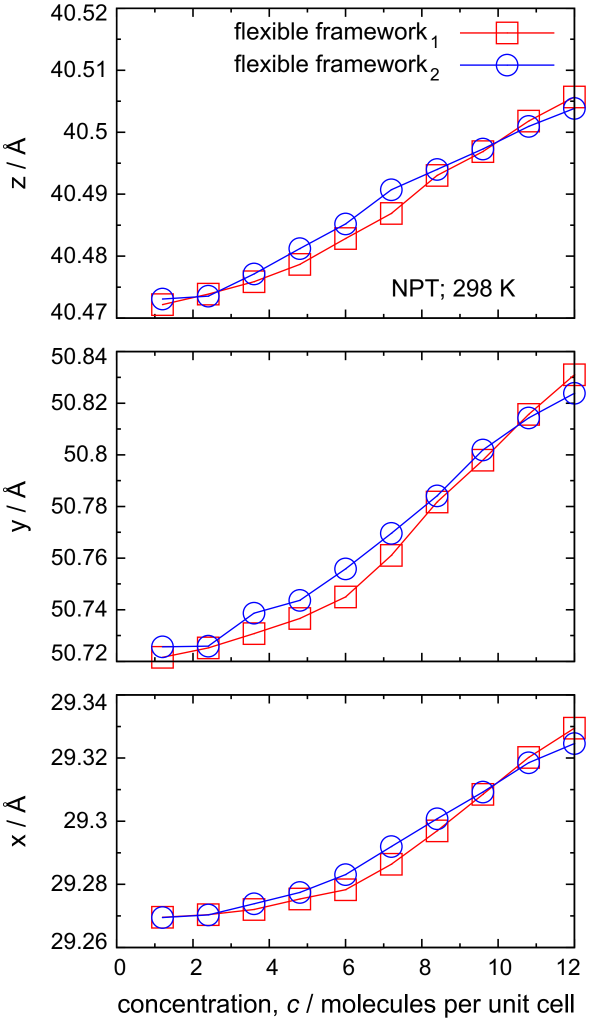

Fig. 6. Edge length of the unit cell in x, y and z direction of the framework as a function of loading for ethane in the Zn(tbip)flexible framework. The edge lengths are calculated at 298 K in the NPT ensemble.

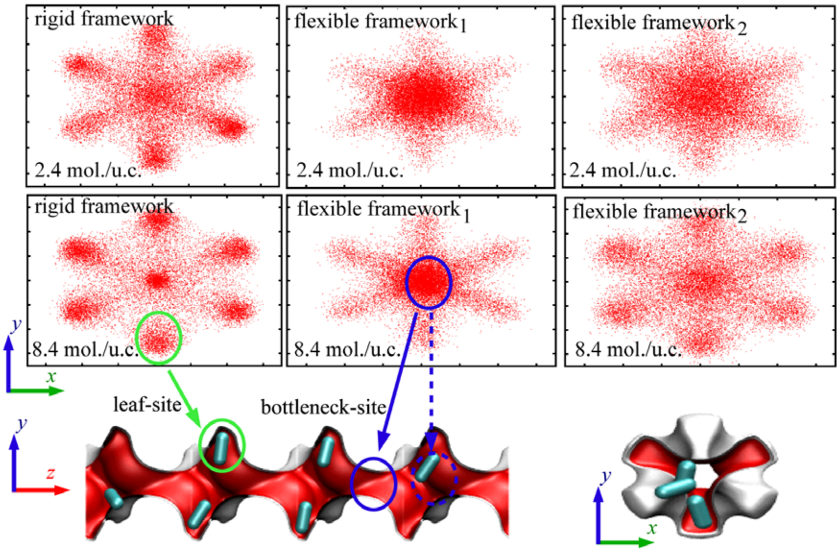

Fig. 7. Location of ethane molecule projections into the *xy* plane tracked every 0.5 ps during a simulation period of 10 ns.

This is consistent with the broadening of distribution of angles between ethane molecular axis and the channel axis at the window when increasing loading (Fig. 5). The possibility to find large angles at the window increases with increasing loading. Fig. 4 also shows that the average cross section area of the windows is more slightly increased with increasing temperature. These results can emphasize that the increasing loading in the flexible-lattice has an important effect on the diffusion behavior of ethane in Zn(tbip) framework. The flexibility and the dynamic behavior of framework thus plays an important role in increasing the self-diffusivity.

There remains one question: we have employed periodical boundary conditions with given edge length. Could it be, that this has suppressed extension of the lattice by the same forces that enlarge the bottleneck?

The framework of Zn(tbip) is much more flexible than e.g. frameworks of zeolites. Hence, the question appears whether the framework could change its size as a result of larger numbers of guest molecules. In usual MD simulations (NVE) the size of the simulation box is kept constant by definition via the periodical boundary conditions. Therefore, we carried out additional simulations at constant pressure (NPT ensemble) that allow the MD – box size to vary.

Fig. 6 shows the edge lengths in x, y and z directions of the flexible framework as a function of loading. It can be seen that the edge lengths in x, y and z directions slightly increase with increasing loading from 1 to 6 molecules per unit cell. The largest increase of the edge lengths with the concentration is observed at the interval of loadings from about 6 to 12 molecules per unit cell (high loading). The increase of the edge lengths in x and y direction (channel radius) is larger than in the z direction (channel axis).

Finally, it can be stated that the changes of the edge lengths are only about 0.1 Å. For the total edge length of the simulation box being of the order of 30 Å these 0.1 Å will not affect to self-diffusion very much.

The change of the average cross section area of the bottleneck which is directly connected to the moves of the particles can play a much more important role than the change of the edge length. In order to understand the difference between the diffusion behavior of an ethane molecules in rigid and flexible Zn(tbip) framework we have examined the spatial density distribution by marking the site of a selected diffusing molecule every 0.5 ps during a simulation period of 10 ns at loadings of 2.4 and 8.4 ethane molecules per unit cell. The results of rigid and flexible framework models are shown in Fig. 7. In the rigid framework the molecule preferably adsorbs near the center of the channel and the middle of the segments at low loadings. At loadings higher than 6 molecules per unit cell, they prefer to reside locally at the leaf positions in the outer regions of the segment center due to the intermolecular repulsion between molecules in the same segment, leading to lower probability to occupy the sites close to the windows. Contrary, the framework flexibility causes the adsorption at the leaf sites to be much less favored as compared to that in the rigid framework. Molecules prefer to be located more readily in the center region of the channel and to be adsorbed closer to the windows. Thus, they perform hops between thee segments more easily. Increased density close to the window entrance has also been found to lead to an increase of D_s with concentration in earlier work about the narrow-window-structure LTA zeolite [18].

The findings until that point rise the question how the average force field seen by a diffusing molecule would look like.

As explained above, free energy profiles will provide the potential of the mean force on a diffusing ethane molecule. Results for different loadings are shown in Fig. 8 comparing rigid and flexible Zn(tbip) framework. The results show that at low loading, for both of rigid and flexible Zn(tbip) framework models, the minima and maxima in the free energy profiles correspond to the segment and the bottleneck (or window) regions within Zn(tbip) framework, respectively. In other, there are five minima in the profiles (at about −16, −8, 0, 8, and 16 Å) that correspond to the position of centers of the five segments within our channel. The height of the free energy barrier is about $9.5k_BT$ for the flexible framework$_1$, $10.5k_BT$ for flexible framework$_2$ and $10k_BT$ for rigid framework. Because a high value of free energy corresponds to a low probability of occupying this position, conversely, a low value of free energy correspond to a high probability of occupying this position. From this reason and the form of the free energy profile, at low loading, it follows that ethane molecules are preferably adsorbed near the middle of the segments.

For comparison: at 298 K the average potential energy, which is also an estimate for the adsorption energy, per ethane molecule at high dilution is −29.1 kJ/mol.

For the flexible models, at a loading of 7.2 molecules per unit cell, the form of the free energy profiles changes; that is, it decreases noticeably from about $9.5k_BT$ down to about $7.5k_BT$ for the flexible framework$_1$ model, and from about $10.5k_BT$ down to $8.5k_BT$ for the flexible framework$_2$ model. At this high loading it can be seen that ethane molecules spend most of the time near the window and at

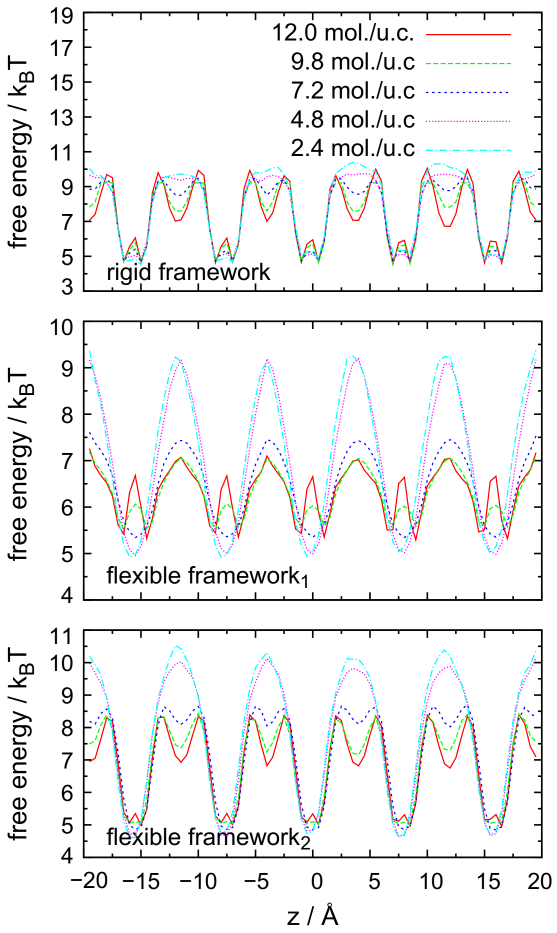

Fig. 8. Free energy profiles at different loadings of ethane in rigid and flexible Zn(tbip)framework.

the emerging sites within the window. This leads to the larger window diameter, i.e. the increase of the calculated cross section area of the window shown in Fig. 4. This significantly reduces the free energy barrier for hopping between segments, and it causes an increase in the diffusion coefficient that is consistent with the maximum in the self-diffusivity found in Fig. 1. When the loading further increases, the free energy barriers do not change much. It is also found that smaller barriers are raised between the other barriers and they grow up as loading increases. The minima at the splitting barriers also show that the ethane molecules spend more time at the leaf positions in marginal regions of the channel.

For the rigid framework model at high loading, the free energy profiles remain the same at about $10k_BT$ for the hight's barrier, however, the smaller barrier and the splitting barrier can still be observed and grow up with increasing loading. These results show that ethane molecules preferably adsorb more and more at the leaf positions when the loading is increased, this is the results of the intermolecular repulsion between molecules in the same segment. All these reasons lead to an increase of D_s with increasing concentration for the flexible framework that is missing in the rigid framework.

4. Conclusion

The framework flexibility has a significant influence on the adsorption and diffusion behavior of ethane in Zn(tbip). It allows the intermolecular repulsion between ethane molecules to extend the space at the window regions available for hopping. This results in the decrease of the free energy barrier for the intersegment hops and, hence, the self-diffusivity increases with increasing loading. Only at very high densities the mutual hindrance leads to the decrease of D_s with increasing loading as to be expected. Contrary, the mutual hindrance with increasing concentration of guest molecules is dominant over the whole range of concentrations for simulations with rigid-lattice.

For an additional, experimental confirmation of these conclusions, we are presently concerned with an enlargement of the pressure range applicable in transient infrared microscopy (IRM) measurements [10,11]. In this way, the measurement of tracer exchange and, hence, of self-diffusion, can be extended to such large concentrations which allow a reliable distinction between the flexible-lattice and the rigid-lattice patterns, namely between a minimum or a continued decay in the diffusivities with further increasing loading. Further experimental studies are as well necessitated to provide a more reliable basis for a comparison of the absolute values of the diffusivities: First measurements of the transport diffusivities of ethane in Zn(tbip) at low loadings [10,11] yield values which are by about one order of magnitude exceeded by the simulated self-diffusivities though, in the limit of sufficiently small loadings, both diffusivities should coincide. The clarification of this difference has to be left to future comparative studies.

Acknowledgments

S. Fritzsche, J. Kärger and C. Chmelik gratefully acknowledge financial support from the DFG, SPP 1362. T. Nanok thanks the DFG SPP 1155 for a postdoc position. K. Seehamart thanks the Rajamangala University of Technology Isan (RMUTI) for a Ph.D. Grant. We thank the computer center of the university Leipzig (particularly Mr. Rost who supported us) and the center for information services and high performance computing (ZIH) of Dresden University of Technology for computer facilities and CPU time. R. Krishna acknowledges the DFG for the award of a Mercator Professorship.

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