ADSORPTION OF LINEAR AND BRANCHED ALKANES IN FERRIERITE: A COMPUTATIONAL STUDY

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ABSTRACT

Molecular simulations using the Configurational-bias Monte Carlo technique were performed to calculate the adsorption behavior of linear and branched alkanes (carbon numbers ranging from 4 to 6), and their 50%-50% mixtures on Ferrierite. It was found that small molecules (up to C_4 backbone) can occupy both channels of Ferrierite while larger molecules (from C_6 backbone) can only reside in the 10-ring channels of Ferrierite. As a consequence, the isotherms of n-pentane and 2-methylpentane exhibit inflection points. The probability distribution of branched alkanes along the 10-ring channel was found to be discontinuous, while this distribution is continuous for linear molecules. This is confirmed by the calculation of free energy profiles in the zeolite. The possible consequences for the diffusion mechanism and catalysis are briefly discussed. It was found that mixture isotherms can be rationalised on the basis of the pure component isotherms.

INTRODUCTION

Understanding the adsorption of hydrocarbons in zeolites is a prerequisite for optimizing catalytic processes using these materials [1, 2]. The focus of most experimental and theoretical studies has been to characterize the adsorption of linear alkanes [3–6]. Despite the importance of branched alkanes as special-purpose lubricant or as high-octane-number fuel, our knowledge on the sorption of branched alkanes is far less [7–9]. In this paper, we report a computational study on the adsorption behavior of linear and branched alkanes and their mixtures in Ferrierite, where previous studies were focussed only on n-alkanes [10–14]. Ferrierite is used as a commercial isomerisation catalyst for the production of iso-butene from n-butene, which is a intermediate for the production of tert-butyl ether.

SIMULATION TECHNIQUE

To investigate the adsorption behavior, molecular simulations using the Configurational-bias Monte Carlo (CBMC) technique [15–19] in the grand-canonical ensemble [18, 20] have been performed. This type of simulation mimics a zeolite in contact

with a large reservoir of particles which fixes the chemical potential and the temperature of the system. In addition to molecule displacements, trial moves are performed to insert or to remove molecules from the zeolite for which the CBMC technique is used. In the simulations presented here we used the united atom representation for alkanes, in which the CH_3, CH_2 and CH groups are considered as pseudo-atoms [21]. Our model uses a fixed C-C bond-length and flexible bond-bending and torsion angles. Non-bonded interactions are described with a Lennard-Jones (12-6) potential with parameters taken from ref. [22]. These parameters have been optimized to reproduce the vapor-liquid curve of the phase diagram of several linear and branched alkanes. Following Kiselev and co-workers [23], the zeolite is assumed to be rigid. This allows the use of special interpolation techniques [8] to compute the alkane-zeolite interactions efficiently. Since in this work we focus on thermodynamic properties, this is a reasonable approximation. The interactions of the alkane with the zeolite are assumed to be dominated by the oxygen atoms of the zeolite. The alkane-zeolite interactions are also described by a Lennard-Jones potential, with parameters taken from previous work [9, 24]. These parameters have been optimized to reproduce Henry coefficients and heats of adsorption of various alkanes on another zeolite, Silicalite. Here, we assume that these parameters can also describe the alkane interactions with Ferrierite. Several details about the implementation of various tricks to speed up the calculations can be found in ref. [25].

RESULTS

In figure 1 (left), several calculated adsorption isotherms of pure components are presented. The isotherms of n-pentane and 2-methylpentane exhibit inflection points at a loading of approximately 0.7 mmol/g (1 molecule per unit cell corresponds to 0.462 mmol/g), while the other isotherms have a monotonic approach to saturation. The maximum loading of small molecules like n-butane, 2-methylpropane and 2-methylbutane is found to be much larger than the maximum loading of n-hexane.

Ferrierite has a two dimensional channel structure where large 10-ring channels (5.4 Å$\times$ 4.2 Å) channels are connected via small 8-ring channels (4.8 Å$\times$ 3.5 Å). It is interesting to look at the distribution of molecules along the channels. In figure 2, the probability distributions of n-butane (a), 2-methylpropane (b), 2-methylpentane at low pressure (c) and 2-methylpentane at high pressure (d) are presented. The differences are striking. n-Butane and 2-methylpropane occupy both the 10-ring and the 8-ring channels. The distribution of molecules in the 10-ring channel is completely different, where the distribution of n-butane is continuous and 2-methylpropane is trapped

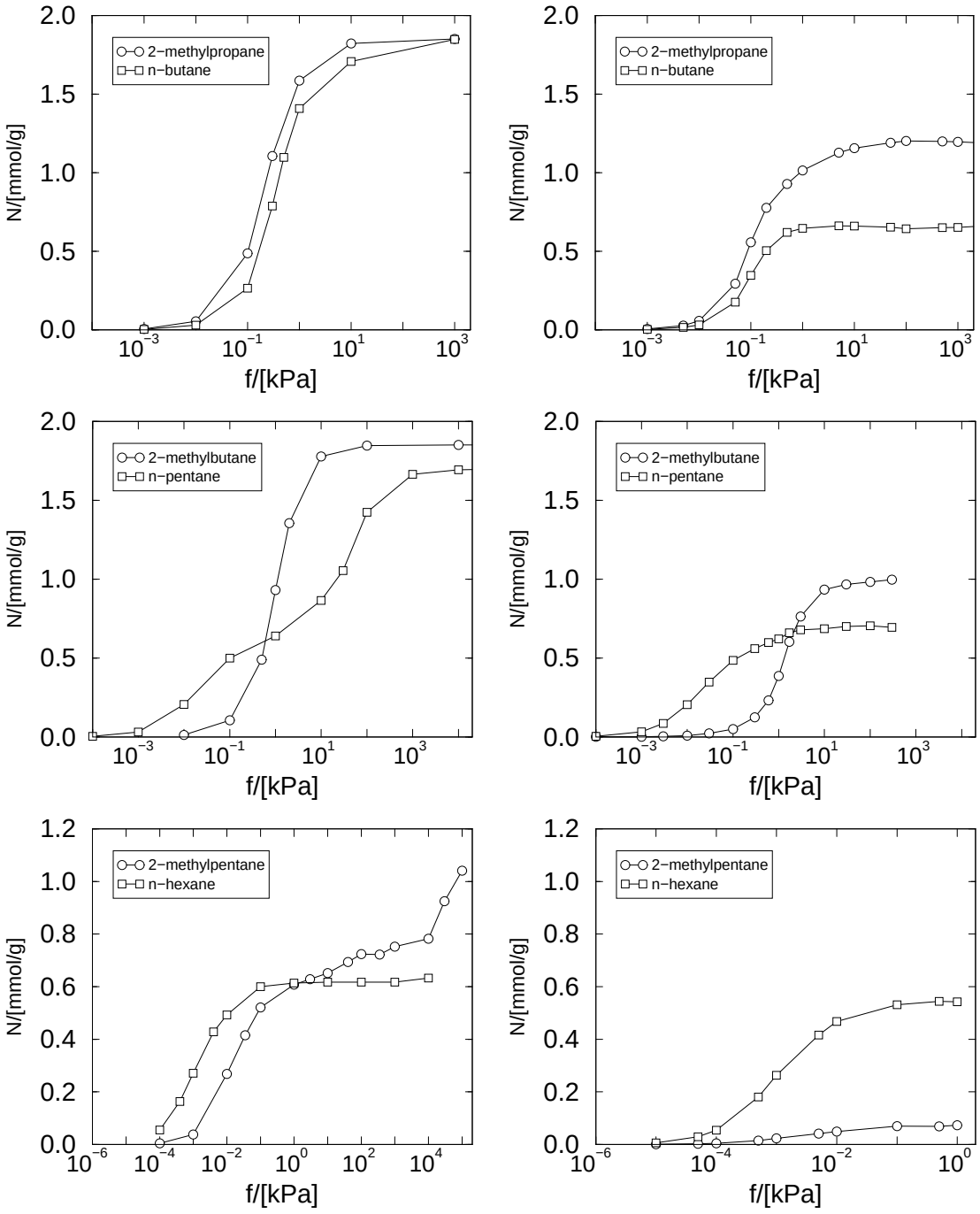

Figure 1: Calculated adsorption isotherms of pure components (left) and 50%-50% mixtures (right) of C_4, C_5 and C_6 hydrocarbons on Ferrierite. For mixtures, the x-axis represents the fugacity of each component. At a low fugacity, the fugacity is equal to the pressure. T=300K.

at the intersection of the 10-ring and 8-ring channels. A continuous probability distribution in the 10-ring channel was found for all linear alkanes. Our observations

may have significant consequences for the diffusion mechanism of n-butane and 2-methylpropane. n-Butane will move gradually through the 10-ring channel while 2-methylpropane will hop once in a while from one adsorption site to another. This may even provide an explanation why Ferrierite is used as an isomerisation catalyst. When a branched molecule is formed it will stay there for some time because there is a large energy barrier to hop to another site. This will block the pore for linear molecules, resulting in a longer residence time which causes them to isomerise. However, trapped reaction products can also "back-react", resulting in a lower conversion.

The situation for 2-methylpentane at low pressure (c) is different from n-butane (a), because the 8-ring channels are not occupied. Apparently these channels are energetically unfavorable for 2-methylpentane. At high pressure (d) this situation changes. Apparently a large driving force (pressure) is needed to push 2-methylpentane into the 8-ring channels which causes the inflection point in the isotherm. Such an effect has also been observed for 2-methylpropane in Silicalite [9]. As the isotherm has a large influence on the concentration dependency of the diffusivity [2], we expect curious behavior at the inflection point. A similar but less pronounced inflection behavior is observed for n-pentane. Larger chains like n-hexane have a lower maximum loading because they can not reside in the 8-ring channels. This is in agreement with the recent experiments and molecular simulations by van Well *et al.* [12–14].

For the purpose of separation it is interesting to compute mixture isotherms. In figure 1 (right), we present the mixture isotherms of 50%-50% mixtures of 2-methylpropane/n-butane, 2-methylbutane/n-pentane, and 2-methylpentane/n-hexane. For 2-methylpropane/n-butane we find that 2-methylpentane is preferentially adsorbed because the Henry coefficient of 2-methylpropane is larger. Both components can adsorb in the 10-ring and the 8-ring channel, so there is a competition in both channels. For 2-methylpentane/n-hexane, the situation slightly changes because both components can not occupy the 8-ring channels at low pressure. This means that 2-methylpentane and n-hexane have a competition to adsorb in the 10-ring channels. Because the Henry coefficient of n-hexane is much larger, hardly any 2-methylpentane is adsorbed. For 2-methylbutane/pentane we find a cross-over in the isotherm. The reason for this is that n-pentane has a larger Henry coefficent but a smaller maximum loading than 2-methylbutane.

Although small branched alkanes can be located in the 8-ring channel, there might be a high free energy barrier for diffusion. Such a barrier will lead to a very low diffusion

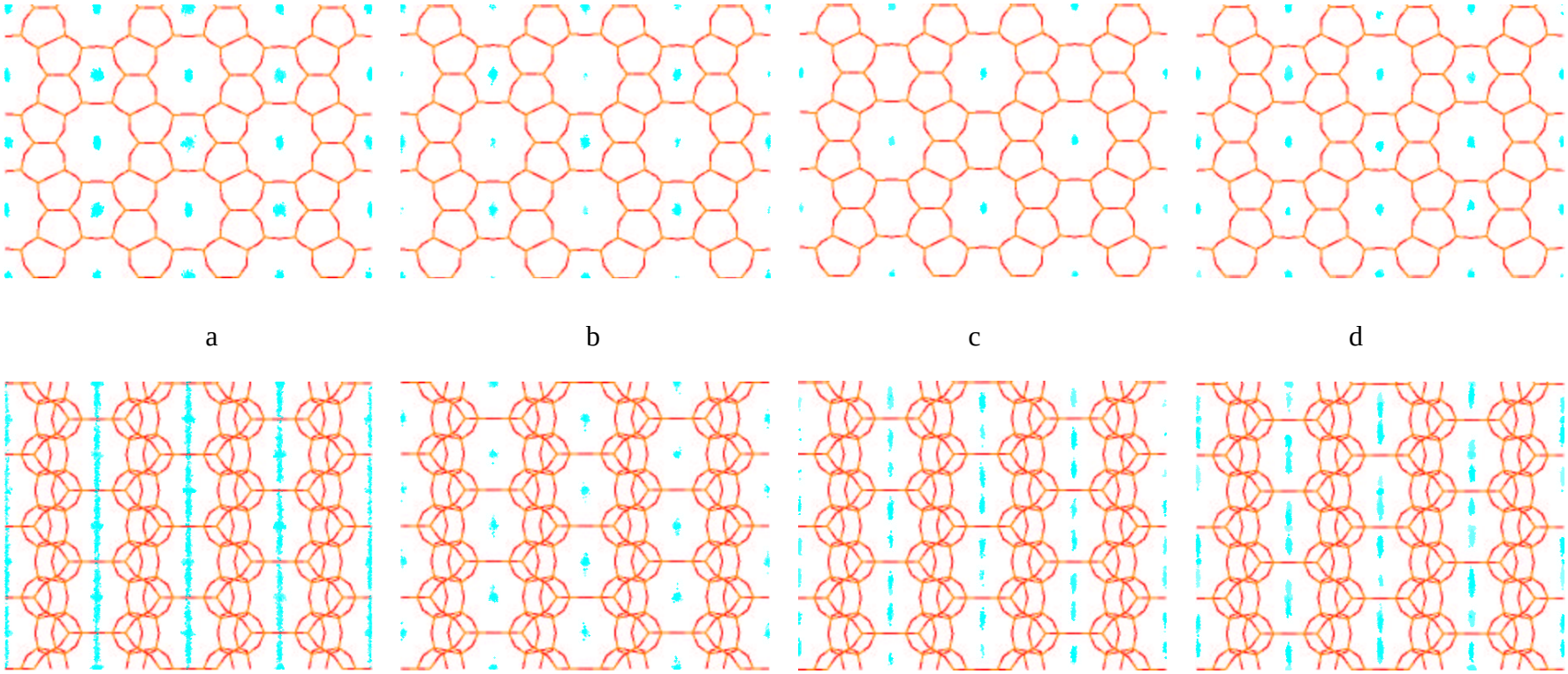

Figure 2: Probability distributions of n-butane (a), 2-methylpropane (b), 2-methylpentane at low pressures (c), 2-methylpentane at high pressures (d). The upper figures are the xy-plane and the lower figures are the xz-plane. The 10-ring channels are parallel to [001] and the 8-ring channels are parallel to [010]. This figures were obtained by plotting the center of mass of the molecules every 100 Monte Carlo cycles. T=300K.

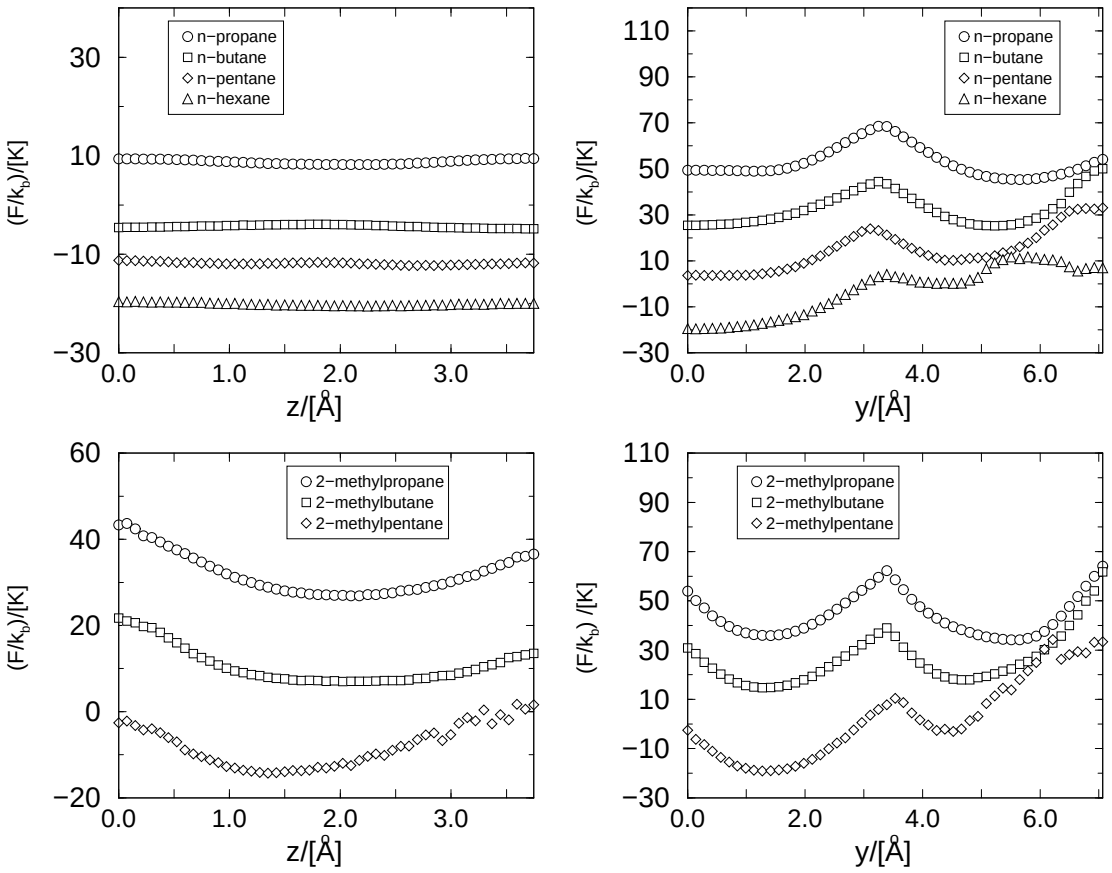

Figure 3: Relative free energies of various alkanes as a function of the position in the zeolite. Left: 10-ring channel. Right: 8-ring channel. Because of the internal symmetry of Ferrierite, we have only computed the free energy of half the pores. The lengths of the 10-ring and 8-ring channels are respectively 7.489 Å and 14.127 Å.

rate. If the diffusion into the 10-ring or 8-ring channel is an activated process, we can use the Bennett-Chandler approach [26, 27] to simulate rare events. The basic idea behind these calculations is that the hopping rate from one site to another is determined by the product of a statistical term, namely finding the molecule on top of the barrier, and a dynamical term that describes the rate at which systems at the top of the barrier move to the other valley. In this work, we only focus on the statistical term.

In figure 3, we have plotted the free energy of various linear and branched alkanes as a function of the position in the 10-ring channel (left) and the 8-ring channel (right). Details of these calculations can be found in ref. [18, 28]. It is important to note, that the free energy profiles may be significantly different for a flexible zeolite lattice. As a first order approximation, we have taken only one reaction coordinate into account (the first atom of the molecule). As can bee seen in figure 3 (left), there is no free energy

barrier for linear alkanes in the 10-ring channel, while there is a small barrier of approximately 15 k_bT for branched alkanes. This free energy barrier has the same order of magnitude as the free energy barrier for a branched alkane in Silicalite. In figure 3 (right) on can see that for linear alkanes, the barrier height to enter the 8-ring channel is increasing with the chain length. Van Well *et al.* [12–14] found experimentally that for n-pentane it is just possible to enter the 8-rings channel, which is in good agreement with the free energy plots. The free energy barrier for 2-methylpropane is significantly larger than for its linear isomer, n-butane. The same holds for 2-methylpentane.

CONCLUSIONS

In this study we have shown that there are two important effects on the sorption behavior of hydrocarbons in Ferrierite:

1. Chain branching. This changes the density distribution in the 10-ring channel from continuous to discontinuous.

2. Chain length. Small chains are preferably adsorbed in the 8-ring channels. 2-Methylpentane and n-pentane show inflection points and longer chains are only located in the 10-ring channels.

This information has been obtained by combining adsorption isotherms, free energy profiles and probability distributions. The mixture isotherms can be rationalised on the basis of the pure component isotherms.

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