



Effect of variation of the size of CH_3 and CH_2 groups on cage-to-cage migration of *n*-butane in zeolite NaCaA

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Abstract

Configurational bias Monte Carlo (CBMC) technique has been employed to investigate the cage-to-cage migration of *n*-butane molecules in zeolite NaCaA. Three different sets of parameters for the size or diameter of methyl (CH_3) and methylene (CH_2) groups have been used and the simulations were carried out at a low sorbate concentration of one *n*-butane per α -cage of the zeolite. It has been observed that only a 5% change in size of CH_3 or CH_2 groups can drastically alter the cage-to-cage migration and hence the transport properties of *n*-butane in zeolite NaCaA. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Transport properties of fluids adsorbed in microporous materials are significantly different from those of bulk fluids. Zeolites belong to this class of materials which are widely used as molecular sieves in different industrial processes, such as, separation of mixtures, catalysis, purification etc. [1]. Proper knowledge of the transport behaviours of fluids in zeolites is extremely important to obtain a better understanding of the mechanisms of such processes. There are several factors such as, molecular geometry or shape, Si/Al ratio, presence of extraframework cations, Bronsted acid sites, sorbate-zeolite interactions, etc. which are known to influence the

sorption and diffusion characteristics of sorbates within zeolites [1,2]. Diffusion of alkanes in zeolites is rather complex and study of such behaviour is a real challenge in petrochemical industries [2]. Although, there are a large number of experimental investigations on alkanes adsorbed in zeolite pores [3–6], but because of technical difficulties involved in experimental measurements, our understanding is still at a rudimentary level. Computer simulation studies can provide a powerful alternative way to study such systems. During past few years several workers have reported different simulation studies of alkanes in zeolites [7–16].

Karger and coworkers [17,18] have observed from PFG NMR studies that for propane and higher *n*-alkanes the diffusivities in zeolite NaCaA are much smaller than in zeolite NaX, although structurally these two zeolites are quite similar, both contain large α -cages or supercages which are intercon-

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nected by smaller windows [19,20]. For example, at room temperature diffusivity of *n*-butane in zeolite NaX is of the order of 10^{-8} m²/s, whereas it is of the order of 10^{-13} m²/s in zeolite NaCaA. The diffusivity of alkanes in these zeolites arise from migration of the *n*-alkane molecules from one cage to another. One of the reasons for low diffusivity in zeolite NaCaA is the presence of narrow windows. A proper choice of the size or diameter (σ_{ss}) of the methyl or methylene groups is extremely important to verify the experimental results from computer simulation studies. This becomes particularly crucial, as different parameters are available in literature to model alkane molecules [10,13,21]. In this work we have employed configurational bias Monte Carlo (CBMC) technique as proposed by Smit and Siepmann [13] and used different parameter sets [10,13,21] to investigate the influence of σ_{ss} on cage-to-cage migration of *n*-butane in zeolite NaCaA.

2. Structure and models

2.1. Structure of zeolite A

The crystal structure of zeolite NaCaA reported in the literature [19] has been employed in the present work. One unit cell of zeolite A has a composition Na₃₂Ca₃₂Si₉₆Al₉₆O₃₈₄. It belongs to the cubic space group Fm $\bar{3}$ c with lattice parameter $a = 24.555$ Å. Zeolite A consists of sodalite and α -cages or supercages. The sodalite cages have much smaller openings and the *n*-butane molecules are unable to enter these cages. There are in all eight α -cages in one unit cell of zeolite A. The approximate diameter of each α -cage is about 11.4 Å [1,19]. The α -cages are interconnected in an octahedral fashion via eight-ring windows of diameter, $\sigma_w = 4.5$ Å. The sodium and calcium atoms occupy positions close to the center of the six-ring windows.

2.2. Models

n-Butane molecules have been modelled in terms of united-atom interaction sites or beads, i.e., methyl (CH₃) and methylene (CH₂) groups are represented as single interaction centers, the site of interaction coinciding with position of the C atom. The distance

between these interaction sites are the same as the C–C bond lengths viz., 1.53 Å. This model has been found to be successful in modelling liquid *n*-butane [13,14,22]. Bond bending interactions between three adjacent sites are modelled in terms of a harmonic potential [23]

$$\phi_b(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \quad (1)$$

where θ_0 is the equilibrium bond angle and k_θ is the force constant. The values of θ_0 and k_θ are 114° and 6.25×10^4 K rad⁻² respectively. A torsional potential is expressed in terms of a model proposed by Jorgensen [21]

$$\begin{aligned} \phi_t(\phi) = & a_1(1 + \cos\phi) + a_2(1 - \cos(2\phi)) \\ & + a_3(1 + \cos(3\phi)) \end{aligned} \quad (2)$$

with $a_1 = 355.03$ K, $a_2 = -68.19$ K, $a_3 = 791.32$ K.

The intermolecular interactions between *n*-butane molecules as well as between the zeolite atoms and the *n*-butane molecules are modelled in terms of united-atom model consisting of site-site pairwise (12-6) Lennard-Jones interactions of the form

$$\phi_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

Interactions between the sorbate molecules and the framework Si/Al atoms are not included since the close approach of the sorbates is prevented by the surrounding bulkier oxygens. The self-interaction parameters of the zeolite atoms used in this study are $\sigma_O = 2.79$ Å, $\sigma_{Na} = 3.26$ Å, $\sigma_{Ca} = 3.35$ Å, $\epsilon_O = 211.8$ K, $\epsilon_{Na} = 10.7$ K, $\epsilon_{Ca} = 1148.1$ K [24].

Three different sets of calculations have been carried out with three different sets of the diameter σ_{ss} of CH₃ or CH₂ groups. Parameters for Set I are taken from the work of Smit and Siepmann [13] which have been employed in our earlier works [15,16,25]. Jorgensen and coworkers [21] have determined optimal intermolecular potential parameters for hydrocarbons which is used in Set II. Goodbody et al. [10] have used a slightly smaller value of σ for methyl or methylene groups, which is used in Set III. We define a parameter $\rho = \sigma_{ss}/\sigma_w$, ratio between the sorbate and the window diameters, which are listed in Table 1 alongwith the different values of σ_{ss} used. The self-interaction parameter (ϵ) for CH₃ and

Table 1

Diameter σ_{ss} for CH₃ and CH₂ groups ($\sigma_{\text{CH}_3} = \sigma_{\text{CH}_2}$) for different set of calculations and the ratio (ρ) between σ_{ss} and σ_w

Set	σ_{ss} (Å)	ρ
I	3.930	0.873
II	3.905	0.868
III	3.730	0.829

CH₂ groups are kept same in all the three sets to that used by Smit and Siepmann [13] in order to understand the influence of the diameter of CH₃ and CH₂ groups have on intercage migration. In all the cases, the cross-interaction parameters between CH₃ and CH₂ groups with the zeolite atoms are obtained from the well-known Lorentz-Berthelot combination rules [26]. The total potential energy of interaction U_{tot} is the summation over the contributions from all the above-mentioned interactions. We have not included the induction interactions between *n*-butane and the zeolite atoms. The reason being that, the polarizability of methyl group is quite small and therefore contribution due to induction will be insignificant (less than 1–3%). Since the computation of induction term is rather involved, we decided to exclude these terms from our calculations.

3. Computational details

Monte Carlo (MC) calculations have been carried out in the canonical ensemble at fixed (N, V, T). Cubic periodic boundary conditions were employed [26]. An attempt is made to displace a molecule randomly, rotate it by a random amount around a randomly chosen axis and finally, to regrow either a part or whole of it. N such attempts comprise a MC cycle during which the molecule itself is selected randomly. CBMC technique has been employed to break and regrow the molecules. This technique has been found to be extremely efficient in simulating various systems where ordinary Monte Carlo (MC) method fails, such as, *n*-alkanes [27–29], phase equilibria of long chain molecules [30] etc. We have employed CBMC method in this work as well as our earlier calculations [15,16,25] on *n*-alkanes in zeolites, as proposed by Smit and Siepmann [13]. These Calculations were carried out on one unit cell of

zeolite NaCaA consisting of eight α -cages. Simulations have been performed on eight *n*-butane molecules corresponding to a sorbate concentration of 1 *n*-butane/ α -cage. Set I simulations were carried out at three different temperatures of 200, 300 and 400 K, whereas for Set II and Set III, simulations were performed only at 200 K. Equilibration was carried out over 2500 MC cycles, followed by production runs of 10⁵ MC cycles. A spherical cut-off of 12 Å has been employed in evaluating the intermolecular interactions.

4. Results and discussion

We have calculated the frequency of cage-to-cage migrations or jumps of *n*-butane molecules for all the three sets of parameters. These are listed in Table 2. By cage-to-cage migration we mean the migration of an adsorbed *n*-butane molecule from one α -cage to another neighbouring α -cage through the eight ring windows in zeolite NaCaA. There are in all eight α -cages in one unit cell [19]. The distance, r_{ic} , between the center-of-mass of the *i*-th molecule and the *c*-th cage is measured. For a particular molecule, this distance is calculated with respect to all the eight cage centers, and the molecule is assigned to that particular cage for which r_{ic} is minimum. This particular cage is called the resident cage. Whenever the resident cage at a particular MC step is different from that of the previous step, the *n*-butane molecule is considered to have undergone a cage-to-cage migration. This calculation is repeated for every *n*-butane molecule over the entire MC run. From the table it is clear that the rate of cage-to-cage migra-

Table 2

Number of cage-to-cage migrations of *n*-butane molecules for three different sets of σ_{ss} at a low sorbate concentration of 1 *n*-butane/ α -cage

Set	T (K)	Number of cage-to-cage migrations
I	200	3
	300	13
	400	45
II	200	294
III	200	1110

tion is highly sensitive to the size or diameter (σ_{ss}) of the CH₃ or CH₂ groups and a slight change of σ_{ss} can drastically alter the rate. In Set I ($\sigma_{ss} = 3.93$ Å, $\rho = 0.873$), the number of cage-to-cage migration is rather few, even at a sufficiently high temperature of 400 K. The value of σ_{ss} (3.905 Å) used in Set II is slightly smaller than that in Set I, but such a small decrease leads to a significant increase in cage-to-cage migration. The number of cage-to-cage migration observed for Set III ($\sigma_{ss} = 3.73$ Å, $\rho = 0.829$) is 1110 at 200 K, which suggests facile intercage migrations as compared to those in Set I and Set II. Note that only a 5% difference of σ_{ss} or ρ can lead to drastic change in number of intercage migrations of *n*-butane molecules. These suggest that choice of σ_{ss} is extremely crucial in modelling the transport properties of alkanes in zeolites. This is particularly important for sorbate-zeolite systems, where the size of the sorbates and the dimension of the narrow windows separating large cages are almost identical, such as *n*-butane in zeolite A. The present results support the recent MD studies of Fritzsche et al. [31,32], where they have shown that properties, such as, diffusion coefficients of methane in zeolite of type LTA depend sensitively on the choice of the Lennard-Jones parameter σ .

In summary, one of the most important and sometimes difficult issue in computer simulation studies is the accuracy of the chosen potential parameters. A proper choice of such parameters is important to obtain results in consistent with experimental findings. This is particularly crucial for complicated systems, such as, the study of adsorption and transport properties of alkanes confined within the restricted regions of microporous materials, such as zeolites. In the literature different workers have suggested different parameters of σ_{ss} for CH₃ or CH₂ groups in alkanes. It is not clear which are the most appropriate values. In this article we have shown that only a 5% difference in σ_{ss} can drastically alter the intercage migration and hence the transport properties of *n*-butanes in zeolite NaCaA. Of-course, the use of rigid framework model in the present study might have some influence on the outcome of the rate of cage-to-cage migrations. It is also necessary to obtain accurate experimental data which seems to be lacking particularly on the rate of intercage migrations. By comparison with these experimental data

and a reasonable flexible framework model for the zeolite it should be possible to discriminate between the different values of σ_{ss} and choose the best. In view of tremendous importance both from the point of view of understanding and for practical applications, this problem needs to be investigated in detail.

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