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Configurational-bias Monte Carlo simulation of *n*-butane in NaY zeolite has been reported at different temperatures and loadings. In contrast to *n*-butane in silicalite, the *gauche* conformer population is always found to be higher in zeolite NaY than in pure fluid at the same density. Normally, an increase in adsorbate concentration in gases such as methane, rare gases, etc. leads to an increase in population near the cage centre. In contrast, we find that an increase in *n*-butane concentration gives rise to an increase in population near the periphery of the cage. Enhancement in *gauche* conformer population observed for NaY zeolite is attributed to the surface curvature of the α-cavity. © *1996 American Institute of Physics.* [S0021-9606(96)50140-6]

I. INTRODUCTION

Adsorption and diffusion of alkanes in the pores of zeolites is important both fundamentally and industrially. In recent times there have been several attempts to understand the thermodynamic, structural and diffusion properties of alkanes adsorbed in zeolites by computer simulation.[1-4] Theodorou and coworkers[1] have investigated *n*-hexane and *n*-butane adsorbed in silicalite. Hernandez and Catlow[2] have carried out extensive molecular dynamics studies to understand dependence of diffusion and conformation of these molecules in different channels of silicalite.

In this work we investigate the dependence of conformation of *n*-butane in zeolite NaY at two different temperatures and loadings. Our aim is first to obtain the nature of dependence of *n*-butane conformation on the type of zeolite in which it is confined or adsorbed. Second, our aim is to isolate and identify factors responsible for the observed behaviour obtained from the simulation.

II. METHODOLOGIES

A. Structure of zeolite NaY

The crystal structure of zeolite NaY recently obtained from neutron diffraction by Fitch *et al.*[5] has been employed in this study. The composition of one unit cell of zeolite NaY is $Na_{48}Si_{144}Al_{48}O_{384}$, and it belongs to the cubic space group $Fd\bar{3}m$ with $a=25.8536$ Å. A Si/Al ratio of three has been chosen since for this particular ratio the extra framework sodium ions occupy completely the sites SI and SII. Pore structure of zeolite Y consists of sodalite and α-cages, also known as supercages. There are eight α-cages in one unit cell which are tetrahedrally placed with respect to each other and are interconnected via twelve-ring windows of diameter ~ 8 Å. Alkane molecules however, are unable to enter the sodalite cages due to their large size.

B. The potential model

n-butane molecules have been modelled in terms of united-atom interaction sites, each representing either a CH$_3$ or a CH$_2$ group. For simplicity, the bond lengths are kept fixed at 1.53 Å. Bond bending interactions are modelled in terms of a harmonic potential[6]

$$\Phi_b(\theta) = \tfrac{1}{2}k_\theta(\theta-\theta_0)^2, \tag{1}$$

where the equilibrium bond angle $\theta_0=114°$ and the force constant $k_\theta = 6.25 \times 10^4$ K rad^{-2}. A torsional potential, governing rotation about non-terminal bonds is expressed in terms of Jorgensen's model[7]

$$\Phi_t(\phi) = a_1(1+\cos\ \phi)+a_2(1-\cos(2\phi))$$
$$+ a_3(1+\cos(3\phi)) \tag{2}$$

with $a_1=355.03$ K, $a_2=-68.19$ K, $a_3=791.32$ K. The interactions between sites in different *n*-butane molecules are modelled in terms of pairwise (12-6) Lennard-Jones form

$$\Phi_{ss}(r_{ss}) = 4\epsilon_{ss}\left[\left(\frac{\sigma_{ss}}{r_{ss}}\right)^{12}-\left(\frac{\sigma_{ss}}{r_{ss}}\right)^6\right]. \tag{3}$$

The parameters used are $\sigma_{CH_3} = \sigma_{CH_2}=3.93$ Å, $\epsilon_{CH_3}=114$ K, $\epsilon_{CH_2}=47$ K.

The sorbate-zeolite interactions $\Phi_{sz}(r_{sz})$ are also modelled in terms of pairwise (12-6) Lennard-Jones form and interaction parameters are σ_{sz} and ϵ_{sz}, where s=CH$_3$ or CH$_2$ and z=O, Na. Interactions between the sorbate molecule and the framework Si/Al atom are not included since the close approach of the sorbates is prevented by the surrounding bulkier oxygens. The interaction parameters between *n*-butane and the zeolite atoms employed in this work are listed in Table I. Here $A_{sz} = 4\epsilon_{sz}\sigma_{sz}^6$ and $B_{sz} = \epsilon_{sz}\sigma_{sz}^{12}$. The corresponding interaction energies for each of the above four types of interactions are obtained by summing over the contributions from individual molecules and their mutual interactions and interactions with the zeolite atoms. The total potential energy is therefore

$$U_{tot} = U_b+U_t+U_{ss}+U_{sz}. \tag{4}$$

TABLE I. Potential parameters for sorbate-zeolite interactions.

| Type	A_{sz} (10^3 kJ/mol Å^6)	B_{sz} (10^6 kJ/mol Å^{12})
CH$_3$-O	5.0898	5.8592
CH$_3$-Na	1.8230	4.3085
CH$_2$-O	3.2681	3.7622
CH$_2$-Na	1.1705	2.7664

C. Computational details

Monte Carlo (MC) calculations were carried out in the canonical ensemble at fixed (N,V,T). Cubic periodic boundary conditions were employed.[8] A MC cycle consists of three types of moves, viz. randomly selected attempts to displace a molecule, to rotate a molecule as a whole, and to regrow either the entire molecule or a part of it attempted once over each of the N molecules selected randomly. The configurational-bias Monte Carlo (CBMC) technique proposed by Smit and Siepmann[3] has been employed in this study to regrow the molecules. Calculations have been performed on 8 and 40 n-butane molecules in one unit cell of zeolite NaY corresponding to a sorbate loading of one and five n-butane molecules per α-cage at 200 and 400 K. Equilibration was performed over 2500 MC cycles, followed by production runs of 10^5 MC cycles at a loading of $c=1$ n-butane per α-cage and 2.5×10^4 MC cycles at a loading of $c=5$ n-butane per α-cage. A spherical cut-off of 12 Å has been employed in evaluating both sorbate-sorbate and sorbate-zeolite interaction energies.

III. RESULTS AND DISCUSSION

Table II lists the average values of butane-butane interactions (U_{ss}), butane-zeolite interactions (U_{sz}), bond bending interactions (U_b), torsional interactions (U_t), total interaction energy (U_{tot}) and the isosteric heat of adsorption (q_{st}) at 200 and 400 K for one n-butane per α-cage, and at 400 K for five n-butane per α-cage.

Figure 1 gives the dihedral angle distribution $f(\phi)$ for n-butane in zeolite Y for $T=200$ and 400 K and 1 n-butane/cage and $T=400$ K at 5 n-butane/cage. The *trans* population under these conditions are respectively 76.8%, 57.0% and 48.9%. These are listed in Table III. Note that for 1 n-butane/cage when the temperature is increased from 200 to 400 K the *gauche* population increases from 23.2 to 43.0%. This may be compared with the increase in the *gauche* population from 5.6% to 15.04% in silicalite when the temperature was increased from 200 to 400 K at an adsorbate loading
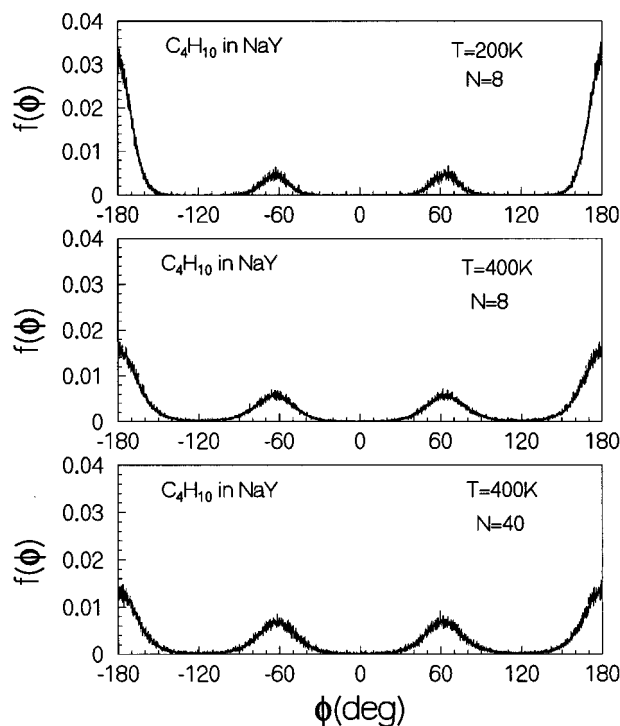
FIG. 1. Dihedral angle distribution $f(\phi)$ in n-butane confined in the α-cages of zeolite NaY at different temperatures and loadings.

of 4 n-butanes/unit cell.[2] However, Hernandez and Catlow find that the increase of temperature is accompanied by a substantial increase of molecules having dihedral angles in the regions between *trans* and *gauche* forms. They find that this region is found to be practically zero in intensity at lower temperatures and that the increase in intensity in this region is much larger than the increase in *gauche* conformation. We, however find no significant increase in population in the region between *trans* and *gauche* with increase in temperature. (See Figure 1).

Hernandez and Catlow have compared the *gauche* population in silicalite at 300 K which is 30% with the ideal gas value of $\sim 40\%$. It seems more appropriate to us to compare the percentage of *gauche* population in zeolite with those of pure fluid n-butane at the corresponding density rather than the ideal gas value. This is particularly important in the present context since our aim is to obtain the influence of the zeolite on the conformation of n-butane. For this reason, we would like to keep all other factors such as temperature, density, etc. identical to those of the confined fluid in zeolite. This will hopefully enable us to isolate the influence of the

TABLE II. Equilibrium thermodynamic properties of n-butane in zeolite NaY at different temperatures and sorbate loadings.

T (K)	N	U_{ss} (kJ/mol)	U_{sz} (kJ/mol)	U_b (kJ/mol)	U_t (kJ/mol)	U_{tot} (kJ/mol)	q_{st} (kJ/mol)
200	8	−4.46	−25.77	0.83	1.71	−27.70	29.36
400	8	−1.96	−22.43	1.66	3.49	−19.24	22.57
400	40	−9.76	−24.70	1.68	3.79	−28.99	32.32

TABLE III. Relative population of *trans* and *gauche* forms.

T (K)	N	ρ (gm/cc)	Confined fluid (c.f.)		Pure fluid (p.f.)		$d=$ %g (c.f.) $-$ %g (p.f.)
			%*trans*	%*gauche*	%*trans*	%*gauche*	
200	8	0.1493	76.8	23.2	81.3	18.7	4.5
400	8	0.1493	57.0	43.0	58.3	41.7	1.3
400	40	0.7466	48.9	51.1	51.7	48.3	2.8

zeolite on the equilibrium conformational population of *n*-butane. However, in order to estimate the density of *n*-butane in NaY we need to know the volume of the zeolite α-cage. We have estimated the volume of the α-cage by a method which is briefly outlined here. Different numbers, *m* of spheres of diameter equal to σ_{CH_3} was introduced into one unit cell of NaY. Minimization of total energy was carried out using the Monte Carlo method for a given number *n* of spheres per cage ($m=8n$). These calculations were repeated for several values of *n*. The intersection of the curve $U_{tot}(n)$ with the abscissa gave the number of spheres n_{op} which can be introduced into an α-cage without any unfavourable interactions. The volume of the α-cage was then estimated to be

$$V_{\alpha-cage}=n_{op}\frac{4\pi}{3}\left(\frac{\sigma_{CH_3}}{2}\right)^3. \tag{5}$$

We obtained a volume of 645.1 Å^3 which corresponds to a radius of 5.36 Å of the α-cage. We present the conformational population of pure butane in Table III. The densities at which these have been carried out are those corresponding to the density of adsorbed butane in zeolite. The simulation temperature and also all other parameters and conditions are identical to the confined fluid. A comparison between these values with those of the adsorbed fluid is interesting : the *gauche* population is always higher for the confined fluid. This difference *d* of 4.5% is particularly significant at 200 K. Clearly, the effect of confinement in zeolite NaY is to increase the *gauche* population. This is in contrast to the effect of silicalite which seems to be to decrease the *gauche* population[2] as compared to ideal gas as well as pure liquid.

The reasons for the observed enhancement of *gauche* conformers could be several. Sorbate-zeolite interaction, pore structure, sorbate-sorbate interaction among others could influence conformer population. Silicalite provides long narrow channels which constrain *n*-butane to have *trans* conformation rather than *gauche*. In zeolite NaY, the α-cages in which *n*-butane is adsorbed are large and provide considerable freedom to *n*-butane to assume different conformations. Consequently, there is no reason why there should be an enhancement of the *trans* conformation like in silicalite but then one expects no enhancement in the *gauche* conformer population either. However, there are two reasons which could lead to an enhancement of the *gauche* population. First is the pronounced curvature of the inner walls that define the α-cage (about 6 Å in radius) which could lead to a preference towards the *gauche*. Note that this is purely a steric effect. The second reason is possibly *gauche* *n*-butane

can optimize its interactions with the zeolite much better than *trans* *n*-butane. In order to see which of these two is true, we calculated the sorbate-zeolite interaction energy U_{sz} seperately for the *trans* and *gauche* conformers. These are listed in Table IV. The difference in average U_{sz} between *trans* and *gauche* conformers is insignificant. Therefore, the sorbate-zeolite interaction between *n*-butane and zeolitic wall seems to play little role in the enhancement of *gauche* conformers in the confined fluid. It is therefore clear that much of the enhancement in *gauche* population arises from the curvature of the inner wall of the α-cavity.

An increase in loading from 1 to 5 *n*-butane/cage results in an increase in the *gauche* population from just 43.0% to 51.1% at 400 K. Similar increase, for example, has been observed in silicalite by Hernandez and Catlow; on increasing the loading from 2 to 8 *n*-butane/unit cell at about 300 K they found that the *gauche* population increased from 9.3% to 11.5%. However, the increase for n-butane in zeolite NaY is around 8% which is rather large as compared to *n*-butane in silicalite ($\sim$2%). Pure fluid exhibits an increase of 6.6%. Figure 2 shows the distribution $g_{coc-com}(r)$ of the centre of mass of *n*-butane as a function of the distance from the cage centre at 200 and 400 K and $c=1$ *n*-butane/α-cage and also at 400 K and $c=5$ *n*-butane/α-cage. The curve plotted is the coc-com radial distribution function(rdf) defined as :

$$g_{coc-com}(r)=\frac{\langle n(r)\rangle}{4\pi r^2 dr\rho_b}, \tag{6}$$

where $\langle n(r)\rangle$ is the average number of sorbates between *r* and $r+dr$, ρ_b is the bulk density of the confined fluid. It is seen that at 400 K when *n*-butane loading is increased from 1 to 5 *n*-butane/α-cage, the population of butane towards the cage centre actually shows a decrease. In fact, if one calculates the actual number of molecules in the two cases ($c=1$ and 5) at about say $r=2$ Å, the decrease in intensity in $g_{coc-com}(r)$ corresponds to a decrease of nearly two orders of magnitude in intensity! Earlier simulations of ours on methane and xenon in zeolite NaY and also argon in zeolite

TABLE IV. Sorbate-zeolite interaction energy (U_{sz}) of the *trans* and *gauche* forms.

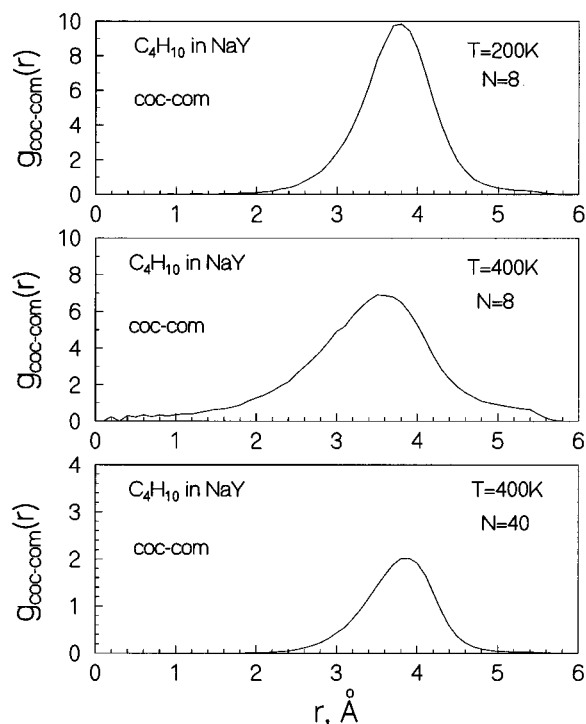| T (K)	N	U_{sz}	
		trans	*gauche*
200	8	-25.68	-26.10
400	8	-22.50	-22.33
400	40	-24.57	-24.83

FIG. 2. Distribution $g_{coc-com}(r)$ of the n-butane centre of mass as a function of the distance from the α-cage centre at different temperatures and loadings. A molecule is considered to reside in a given α-cage if the distance between the centre of the cage and the molecular centre of mass is less than 5.4 Å.

NaCaA shows that with increase in loading the population near the cage centre shows an increase.[9–11] One normally expects that at higher loadings, the adsorbates prefer to occupy regions near the cage centre due to crowding at the periphery of the cage. The present result is contrary to this and seems to arise from the fact that the additional n-butane molecules prefer to accommodate themselves near the inner surface probably due to stronger sorbate-sorbate and sorbate-zeolite interactions. We found that there is a large gain in U_{ss}: -9.76 kJ/mol at 400 K and $c=1$ as compared to -1.96 kJ/mol at 400 K and $c=5$ n-butane/α-cage. In comparison, change in U_{sz} is only a modest -2.3 kJ/mol. This suggests a strong role for sorbate-sorbate interaction in alkanes confined in NaY, especially at higher loadings. The strong preference towards regions at the periphery of the cage at high loadings in spite of the high temperature also influences the conformation of the molecules. The steric factor leads to an increase in *gauche* population; the extra cost in terms of energy due to *gauche* conformation is however offset by the large gain in the sorbate-sorbate interaction (U_{ss}). Sorbate-zeolite interaction (U_{sz}) in this case seems to play little role!

IV. CONCLUSIONS

In conclusion, we could say that the behaviour of n-butane in zeolite NaY seems to be quite the opposite of that observed when it is confined in silicalite viz., there is an enhancement of *gauche* population as compared to both ideal gas as well as pure liquid. These results along with those on silicalite obtained by earlier workers suggests strong dependence on the geometry of the zeolitic cavity. Surface curvature of the inner wall of the α-cage seems to play a dominant role. Unlike that found in the case of other adsorbates, it is observed that butane has a lower population in the region near the cage centre at higher loadings. Surprisingly, this is attributed to strong sorbate-sorbate interaction and not sorbate-zeolite interaction. Thus, the sorbate-sorbate interaction leads to significant localization of n-butane near the periphery of the cage and this coupled with the rather large curvature of inner surface leads to an increase in *gauche* conformer population. It also appears that the freedom to assume different conformations enables butane to pack better near the periphery of the α-cage.

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