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Separation of Alkane Isomers by Exploiting Entropy Effects during Adsorption on Silicalite-1: A Configurational-Bias Monte Carlo Simulation Study

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We discuss and develop an entropy-driven principle for separating isomers of alkanes in the five to seven carbon atom range by adsorption on silicalite-1. The normal alkanes are preferentially adsorbed because of configurational entropy effects; they "pack" more efficiently within the channel structures of silicalite. To demonstrate the separation principle we carried out CBMC simulations to determine the isotherms of various mixtures of linear and branched alkanes in silicalite-1. We show that the configurational entropy effects manifest at loadings greater than 4 molecules/unit cell and the sorption favors the linear alkanes while the branched alkanes are virtually excluded from the silicalite matrix. Validation of the entropy-based separation principle is obtained by analyzing the silicalite membrane permeation data published in the literature.

Introduction

The separation of isomers of alkanes is a problem that is growing in industrial importance. New reformulated gasoline specifications are forcing petroleum refiners to reduce the amount of olefins and aromatics in gasoline, and consequently, there is a greater need in the refining industry for catalytic isomerization for converting straight chain hydrocarbons to branched hydrocarbons. Branched hydrocarbons are preferred to straight-chain hydrocarbons as ingredients in gasoline because branched hydrocarbons burn more efficiently and have a higher octane number. Consider, for example, the isomers of hexane; *n*-hexane has a RON (research octane number) = 30 whereas the corresponding RON values for its isomers are the following: 2-methylpentane (2MP), 74.5; 3-methylpentane (3MP), 75.5; 2,2-dimethylbutane (22DMB), 94; 2,3-dimethylbutane (23DMB), 105. In the catalytic isomerization process, straight-chain hydrocarbons are converted to their mono- or dibranched structures. However, the product of catalytic isomerization is a mixture of linear and branched hydrocarbons that are in thermodynamic equilibrium and the separation of linear hydrocarbons from their branched isomers becomes necessary. The separation of the hydrocarbon isomers is usually carried out using adsorption in a bed of zeolite 5A particles[1,2] in which the principle of separation is that of molecular sieving. Only the linear paraffin is capable of entering the pores of 5A zeolite, and the branched isomers are excluded. One important disadvantage of sorption separation using 5A zeolite is that the diffusivities, and hence the fluxes, are very low. Therefore equipment sizes are large.

Our research focus is the separation of alkane isomers by exploiting subtle entropy effects. A careful examination of the physical properties of linear and branched alkanes[3] shows that the largest difference between the properties of alkanes isomers is with respect to the freezing point. When a mixture of, for example, nC_6 and 2MP is cooled, the first crystals to form will be that of the linear isomer. The reason is that the linear paraffin molecules "stack" more easily. Branching destroys the symmetry required for crystal formation. In other words the differences in the freezing points is due to differences in "ordering" or "packing" efficiencies. The major drawback in applying this principle to separate linear and branched alkanes in the gasoline boiling range is that the temperatures to which the mixtures must be cooled is very low, of the order of 120−180 K. Therefore freeze crystallization is not a viable technological solution for separation of isomers in the 4−7 C atom range. Ideally we would like to be able to exploit packing efficiency, or configurational entropy, differences without the need to cool to such low temperatures required for crystallization. To achieve this goal we consider adsorption of the alkane isomers inside the matrix of an ordered structure, such as that of silicalite-1. Silicalite consists of straight channels and zigzag channels, which cross each other at intersections. The length of the normal hexane molecule, for example, is commensurate with the length of the zigzag channel, between two intersections.[4] That the linear molecules pack more efficiently within the silicalite structure is also evidenced by the differences in the saturation loadings, expressed in molecules/unit cell, between linear and branched alkanes in silicalite; see Figure 1. We aim to demonstrate in this paper that, for mixtures of linear and branched alkanes, such differences in "packing" efficiencies could cause an almost total exclusion of the branched isomer.

To demonstrate our entropy-driven sorption separation of alkane isomers using medium pore-size silicalite, we need to be able to estimate the sorption characteristics of various mixtures of linear and branched alkanes in the 5−7 carbon atom range, of interest as components in gasoline. While there is a considerable amount of published experimental data on *pure* component isotherms for various alkanes and isoalkanes,[5−9] there is little or no experimental data on *mixture* isotherms. This lack of mixture isotherm data is most probably due to the

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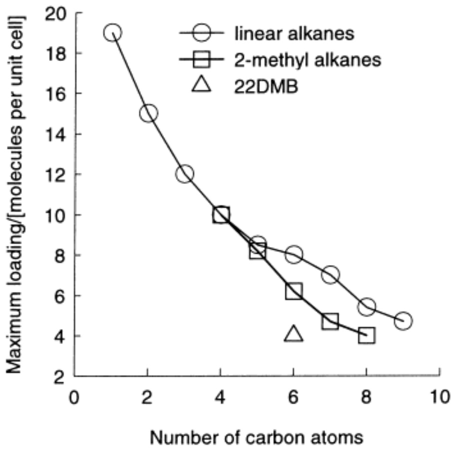

Figure 1. Saturation loadings (molecules/unit cell) of alkanes in silicalite-1 obtained from CBMC simulations at $T = 300$ K.

difficulty of experimentation. In this paper we discuss a strategy for generating the required mixture isotherms using configurational-bias Monte Carlo (CBMC) simulations. The study reported here is not only of technological importance in the context of isomer separation but emphasizes some new scientific principles governing sorption of molecules in confined environments such as zeolites and other nanoporous materials.

There are several factors which determine the sorption behavior of mixtures: (1) There are differences in chain lengths (i.e. number of carbon atoms) of the components. In general, the longer the chain length, the higher is the adsorption strength. This is illustrated in Figure 2 which shows the sorption isotherms of (a) linear alkanes and (b) branched alkanes in silicalite at $T = 300$ K. (2) Another factor is the inflection behavior of the components. All branched alkanes show inflection behavior at a loading of 4 molecules/unit cell. Linear alkanes show pronounced inflection behavior for C atoms exceeding 6. Inflection behavior is caused by configurational effects, causing preferential siting of molecules at certain positions in silicalite. Interesting effects, such as selectivity reversal and exclusion of the branched alkane, can be expected to arise when one of the components in the mixture exhibits inflection behavior; this is often the case for a mixture of linear and branched alkanes.[10] (3) A final factor is differences in maximum molecular loadings of the components. The maximum loadings for linear and 2-methyl alkanes are shown in Figure 1 as a function of the number of C atoms; the maximum loading decreases with increasing C number. This is a size entropy effect. For example, for a mixture of methane and propane, size entropy effects tends to favor methane at high loadings.[11,12] This is because the smaller methane molecule finds it easier to fill in the "gaps" at high loadings within the zeolite.

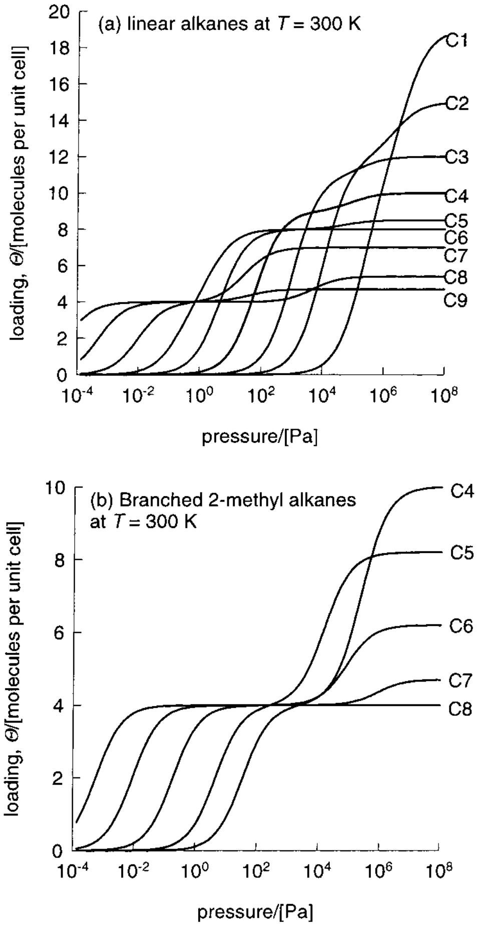

Figure 2. Pure component isotherms for (a) linear and (b) 2-methylalkanes in silicalite-1 at 300 K calculated using CBMC.

It is worthwhile describing the overall structure and strategy to be adopted in this paper to give some perspective to the individual sections. First, we describe the details of the CBMC technique. Then pure component isotherms are simulated and compared with experimental data to demonstrate the accuracy of CBMC simulations. Subsequently, the entropy-driven separation principle is demonstrated by carrying out mixture simulations for isomers. We seek verification of the entropy separation principle by analyzing published silicalite membrane permeation data of Funke et al.[13] and Gump et al.[14] Subsequently, we examine mixtures of linear and branched alkanes where the constituents have different number of carbon atoms.

It is important to remark here that we had first introduced the entropy-driven separation concept in an earlier short communication;[10] the current article represents a fuller account of this concept and demonstrates its generic character. Furthermore, since the publication of our short communication, new experimental data on permeation of alkane isomers across a silicalite membrane have been published by Gump et al.[14] To rationalize their experimental data, we performed many more simulations with various mixtures under a variety of temperature, pressures and compositions. Our simulations offer a fundamental explanation of their experimental results which is different from that presented by Gump et al.[14] The generic character of our approach is also demonstrated by considering the sorption of isomers of decane on two types of zeolitic structures: silicalite and MEL.

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Configurational-Bias Monte Carlo (CBMC) Simulation Technique

The linear and branched alkanes are described with a united-atom model, in which CH_3, CH_2, and CH groups are considered as single interaction centers. When these pseudoatoms belong to different molecules or to the same molecule but separated by more than three bonds, the interaction is given by a Lennard-Jones potential. The Lennard-Jones parameters are chosen to reproduce the vapor−liquid curve of the phase diagram as shown in Siepmann et al.[15] The bonded interactions include bond-bending and torsion potentials. Details for the alkane model can be found in Vlugt et al.[16]

All the simulations have been performed in zeolite silicalite (MFI). Silicalite has both straight elliptical channels and zigzag channels that cross at the intersections. Following Kiselev and co-workers,[17] we consider the zeolite lattice to be rigid and we assume that interactions of an alkane with the zeolite are dominated by the dispersive forces between alkane pseudoatoms and the oxygen atoms of the zeolite. These interactions are described by a Lennard-Jones potential, which parameters are given in ref 16.

Adsorption isotherms are conveniently computed using a Monte Carlo simulation in the grand-canonical ensemble.[18] In this ensemble the temperature and chemical potentials are imposed. The number of adsorbed molecules per unit cell of the zeolite follows from the simulations. The characteristics of these type of simulations is that during the calculations attempts are made to change the total number of particles by making attempts to insert molecule into or remove molecules from the zeolite. To make these types of moves possible for the long chain alkanes, we use the configurational-bias Monte Carlo (CBMC) technique.[18,19] Instead of inserting a molecule at a random position, in a CBMC simulation a molecule is grown atom by atom in such a way that the “empty spots” in the zeolite are found. This growing scheme gives a bias that is removed exactly by adjusting the acceptance rules.[18,19]

These simulations were performed in cycles, and in each cycle, an attempt to perform one of the following moves was made: (1) Displacement of a randomly selected chain was attempted. The maximum displacement was adjusted to an overall acceptance of 50%. (2) Rotation of a chain around its center of mass was attempted. The chain is chosen at random and the maximum rotation angle is selected to accept 50% of the moves. (3) Partly regrowing of a chain was tried; a chain is selected at random and part of the molecule is regrown using the CBMC scheme. It is decided at random which part of the chain is regrown and with which segment the regrowing is started. For branched alkanes, the approach in Vlugt et al.[16] was used. (4) Regrowing of the entire chain (only for NVT simulations) was attempted. A chain selected at random is completely regrown at a random position. (5) Exchange with a reservoir (only in grand-canonical simulations) was tried. It is decided at random whether to add or to remove a molecule from the zeolite following the acceptance rules derived in Vlugt et al.[16] and Smit.[20] (6) Finally, a change of identity (only in the case of mixtures) was tried; one of the components is selected at random and an attempt is made to change its identity (Martin and Siepmann[21]). The acceptance rules for these trial moves can be found in Frenkel and Smit[18] and Smit.[20]

For the pure components adsorption isotherm, 2×10^5 Monte Carlo cycles were performed, and for the mixture adsorption isotherms, the number of cycles was 3×10^7. The relative probabilities for attempting these moves were such that in the NVT simulations 10% of the total number of moves were displacements, 10% rotations, 10% partial regrowths, and 70% regrowths of the entire molecule. For the case of grand-canonical simulations of the pure components the relative probabilities of moves were the following: 15% displacements; 15% rotations; 15% partial regrowths; 55% exchanges with the reservoir. For the mixture the number of exchanges was reduced to 50% and the remaining 5% of the moves were attempts to change the identity of a molecule. The number of trial orientations in the configurational-bias Monte Carlo scheme was six for all molecules. In addition, we used the multiple first bead scheme[22] with 15 trial positions for the first bead.

CBMC Simulation Results for Pure Components and Mixtures

Pure Component Isotherms of Hexane Isomers. We first consider the isomers *n*-hexane (nC_6), 2-methylpentane (2MP), 3-methylpentane (3MP), and 2,2-dimethylbutane (22DMB). The pure component isotherms at various temperatures are shown in Figure 3a−d. A good description of the pure component isotherms can be obtained with the dual-site Langmuir (DSL) model.[11] In this model the loading, $\Theta_i^0(P)$, expressed in molecules/unit cell, is represented as a function of the pressure P as follows:

$$\Theta_i^0(P) = \frac{\Theta_{i,\mathrm{sat,A}} b_{i,\mathrm{A}} P}{1 + b_{i,\mathrm{A}} P} + \frac{\Theta_{i,\mathrm{sat,B}} b_{i,B} P}{1 + b_{i,\mathrm{B}} P} \tag{1}$$

The superscript 0 on $\Theta^0 i(P)$ is used to emphasize that the relation is for *pure* component loadings. In eq 1 $b_{1,\mathrm{A}}$ and $b_{1,\mathrm{B}}$ represent the DSL model parameters expressed in Pa^{-1} and the subscripts A and B refer to two sorption sites within the silicalite structure, with different sorption capacities and sorption strengths. $\Theta_{i,\mathrm{sat,A}}$ and $\Theta_{i,\mathrm{sat,B}}$ represent the saturation capacities of sites A and B, respectively. The fitted parameters for the pure component isotherms are listed in Table 1. It is to be noted that the total saturation loading $\Theta_{i,\mathrm{sat}} = \Theta_{i,\mathrm{sat,A}} + \Theta_{i,\mathrm{sat,B}}$ is not a fitted parameter but taken from the final plateau value of the sorption isotherm, estimated from CBMC simulations. Figure 3 also shows the fitted DSL model. It is to be observed that nC6 shows a slight inflection at $\Theta = 4$ due to commensurate freezing.[4] The branched isomers 2MP and 3MP also show an inflection at $\Theta = 4$ for some temperatures because these molecules prefer the intersections between the straight and zigzag channels of silicalite; to push them into the channel interiors requires an extra “push”, leading to inflection behavior. The isomer 22DMB is so bulky that it can be located only at the

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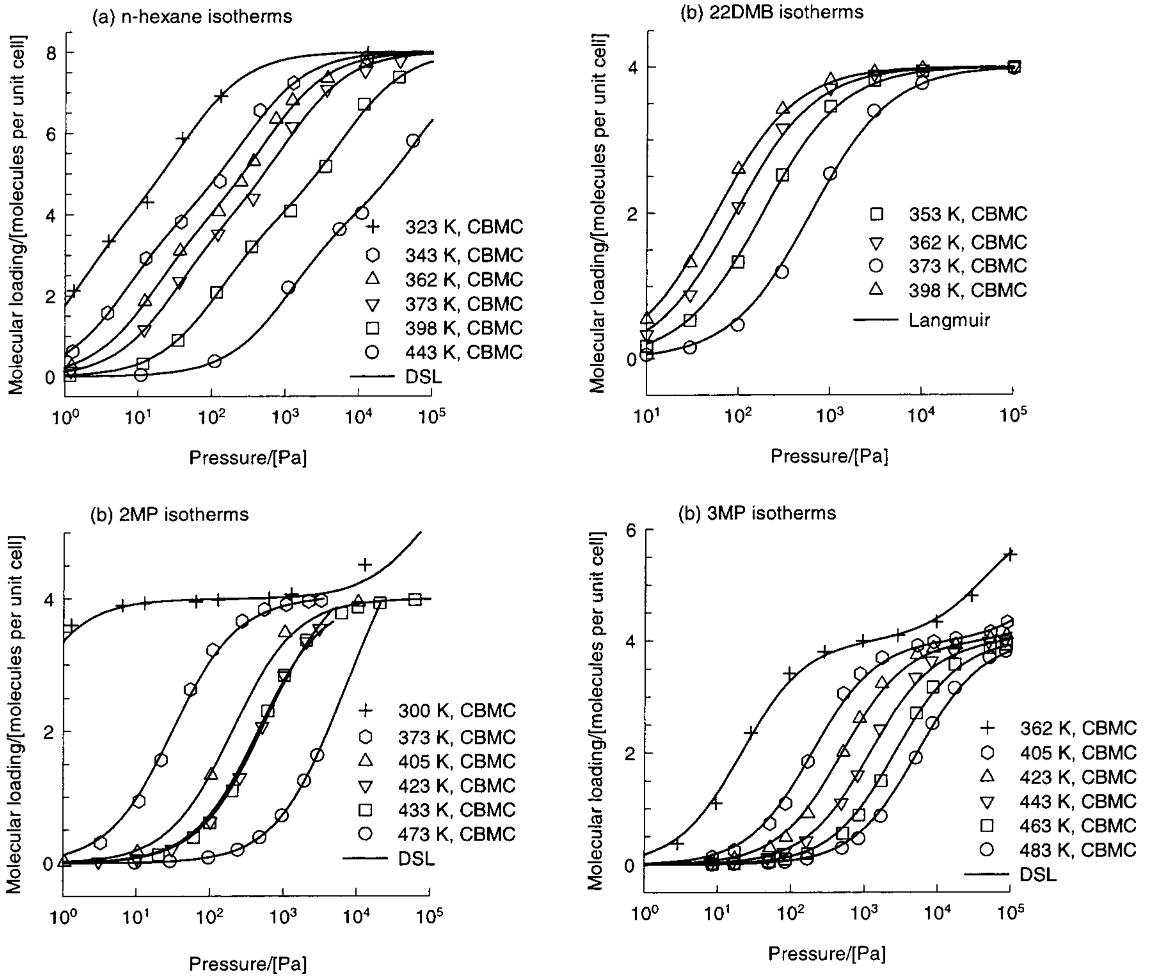


Figure 3. Pure component isotherms of hexane isomers obtained at various temperatures using CBMC simulations.

Table 1. Pure Component Sorption Parameters for Dual-Site Langmuir Model Applied to Silicalite

		dual-site Langmuir params (eq 1)			
		site A		site B	
component i	temp/K	$b_{i,\mathrm{A}}$/Pa^{-1}	$\Theta_{i,\mathrm{sat,A}}$/molecules per unit cell	$b_{i,\mathrm{B}}$/Pa^{-1}	$\Theta_{i,\mathrm{sat,B}}$/molecules per unit cell
nC5	310	0.25	4	0.06	4
	433	2.43×10^{-4}	4	3.24×10^{-5}	4
nC6	300	4.62	4	0.422	4
	323	0.73	4	2.2×10^{-2}	4
	343	0.158	4	3.4×10^{-3}	4
	353	0.12	4	3.5×10^{-3}	4
	362	6.32×10^{-2}	4	1.7×10^{-3}	4
	373	3.21×10^{-2}	4	8.8×10^{-4}	4
	398	8.24×10^{-3}	4	1.56×10^{-5}	4
	433	1.44×10^{-3}	4	2.16×10^{-5}	4
	443	8.9×10^{-4}	4	1.44×10^{-5}	4
2MB	310	0.25	4	1×10^{-4}	4
2MP	433	2.17×10^{-3}	4		
3MP	362	4.75×10^{-2}	4	2.27×10^{-5}	2.3
	403	5.2×10^{-3}	4	1.9×10^{-6}	2.3
	423	2.02×10^{-3}	4	7.14×10^{-7}	2.3
	443	8.45×10^{-4}	4	3.4×10^{-7}	2.3
	463	3.85×10^{-4}	4	1.18×10^{-7}	2.3
	483	1.91×10^{-4}	4	6.41×10^{-8}	2.3
22DMB	362	0.011	4		
	373	5.43×10^{-3}	4		
	398	1.75×10^{-3}	4		
nC7	374	0.15	4	3×10^{-5}	2.9
2MH	374	0.17	4	2×10^{-9}	0.7
	433	0.01	4		

intersections; there is no inflection for this component for the range of temperatures and pressures studied.

To verify the accuracy of our CBMC technique, we compared the CBMC simulation results for pure component isotherms with the experimental measurements of Cavalcante and Ruthven[6] and Millot et al.;[7] see Figure 4. The agreement between CBMC simulations and experimental data fits of these authors can be considered to be good for a wide range of pressures and temperatures.

Pure Component Permeation Selectivities across Silicalite Membrane. Further verification of the pure component CBMC simulations will now be obtained by examining experimental results on permeation of pure components across a silicalite membrane. Funke et al.[13] have presented data on the ratio of permeation fluxes of (1) nC6 and (2) 3MP at 362 and 405 K, keeping the upstream hydrocarbon pressures at 15 kPa; see Table 3 of their paper. They observed the nC$_6$/3MP permeation selectivities to be 1.3 and 1.9, respectively. Let us first try to rationalize these experimental findings. The permeation flux of component 1, e.g., is expected to be proportional to the Fick diffusivity, D_1, inside the zeolite matrix and the driving force for transport across the membrane, $\Delta\Theta_1$, which is the difference between the molecular loadings in the upstream and downstream faces of the membrane. In their membrane experiments the downstream membrane compartment is purged with inert gas, keeping the partial pressures to near zero values. Therefore the driving force $\Delta\Theta_1$ can be taken to be the loading corresponding to the upstream pressure conditions, i.e., $\Delta\Theta_1 = \Theta_1$ corresponding to p_1. The flux of any component is therefore proportional to the diffusivity of that component and its molecular loading at the upstream pressure conditions. The sorption

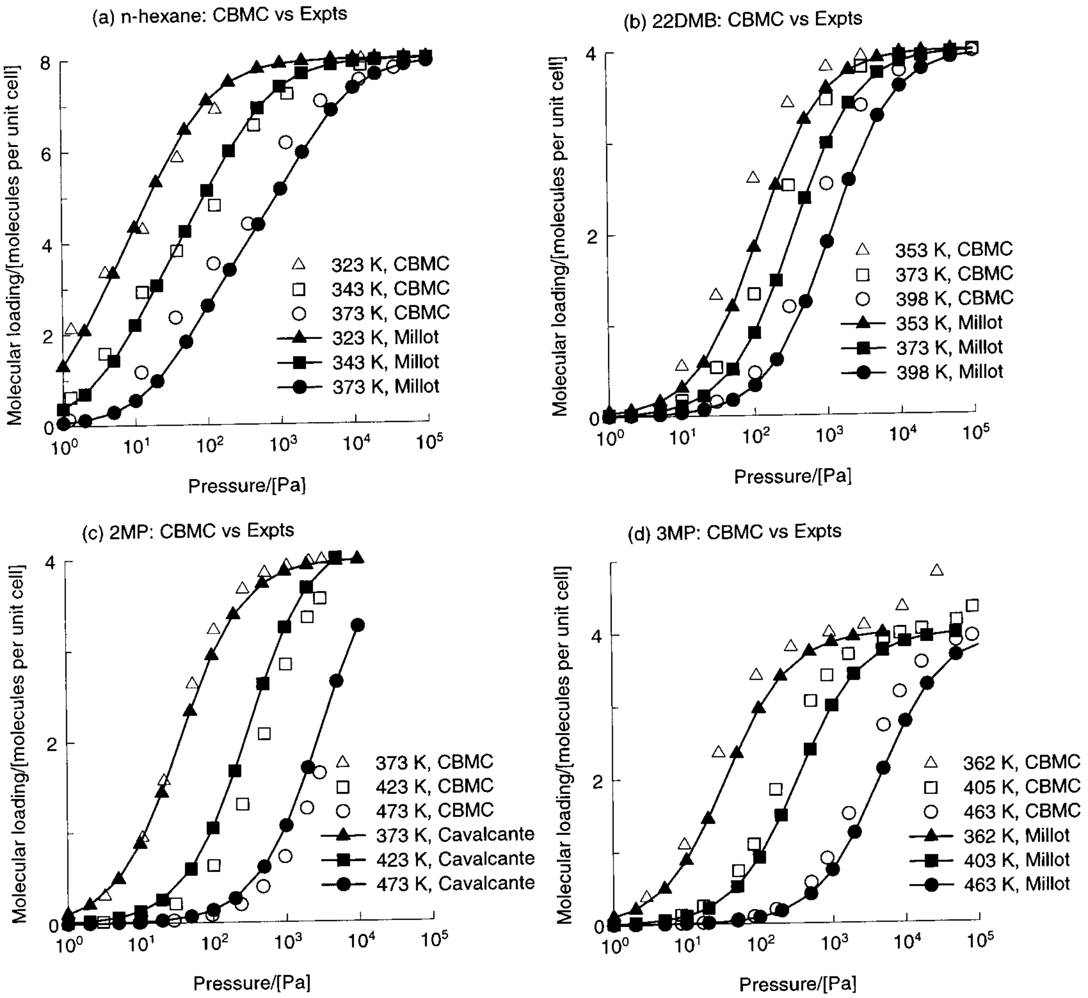


Figure 4. Comparison of experimental data with CBMC simulations for pure component isotherms of hexane isomers obtained at various temperatures.

isotherm is therefore an important determinant in the permeation behavior across a membrane. From the experimental data on the pure component permeations in two separate experiments, the permeation selectivity S_P can be calculated as follows:

$$S_P = \frac{D_1}{D_2}\frac{\Theta_1}{\Theta_2}\frac{p_2}{p_1} \tag{2}$$

In Figure 5 a the measured values of S_P are compared with the sorption selectivity S

$$S = \frac{\Theta_1}{\Theta_2}\frac{p_2}{p_1} \tag{3}$$

determined from CBMC simulations. The values of S_P and S are quite close to one another, suggesting that the ratio of Fick diffusivities D_1/D_2 of the linear and branched isomers, nC_6 and 3MP, is close to unity. It is noteworthy that the ratio of pure Fick diffusivities measured by Cavalcante and Ruthven[6] for nC6 and 3MP is much higher than unity. The precise reasons behind this discrepancy is not known. It appears that to interpret membrane permeation data one must measure the pure component Fick diffusivities using the same membrane and not rely on single-crystal or chromatographic studies for this information.

Gump et al.[14] have presented experimental results for the permeation fluxes of pure components nC_6 and 22DMB across a silicalite membrane at 353 K and at various upstream pressures; see Figure 4 of their paper. We calculated the permeation selectivities S_P for these experiments and compared them with the sorption selectivities S using the pure component CBMC simulations at 353 K; the comparison between S_P and S is shown in Figure 5b. We again note the close agreement between the permeation and sorption selectivities. The values of S_P are consistently higher than that of S suggesting that the ratio of Fick diffusivities D_1/D_2 of the linear and branched isomers, nC_6 and 22DMB, is only slightly higher than unity. It is again to be noted that the ratio of pure Fick diffusivities of nC_6 and 22DMB measured by Boulicaut et al.[5] is a few orders of magnitude higher than unity and the reasons behind this discrepancy remain unclear.

Funke et al.[13] also published experimental results for the permeation fluxes of pure components 3MP and 22DMB across a silicalite membrane at 362 K keeping the upstream hydrocarbon pressure at 12 kPa; see Table 5 of their paper. We calculated the permeation selectivities S_P for this experiment and compared them with the sorption selectivities S using the pure component CBMC simulations at 362 K; the comparison between S_P and S is shown in Figure 5c. Once again we note the close agreement between the permeation and sorption selectivities.

The results of Figure 5 allow us to conclude that the CBMC simulations can be used with confidence to estimate

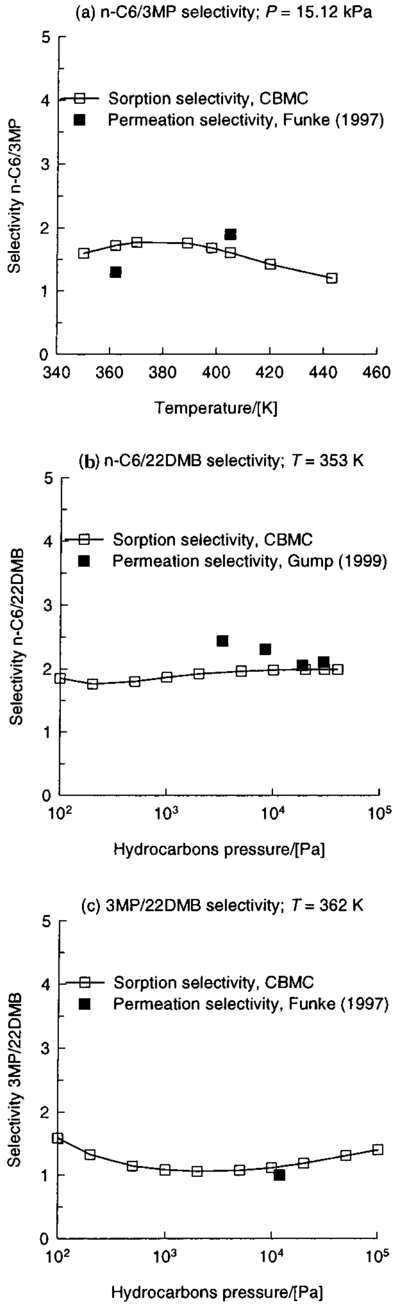


Figure 5. Comparison of experimental data with CBMC simulations for sorption selectivities based on pure component data.

the pure component permeation selectivities of hexane isomers across a silicalite membrane.

Sorption of *n-Hexane*−*3-Methylpentane Mixtures.* Let us now consider sorption of a 50−50 mixture of nC_6 and 3MP at temperatures of 362 and 443 K. CBMC simulations for the loadings in the mixture as shown in Figure 6a,b for a range of pressures. It is interesting to note the maximum in the loading of 3MP at about 100 Pa for 362 K and at about 10 000 Pa at 443 K. When the pressure is raised above these pressures, the loading of 3MP reduces virtually to zero. The nC_6 molecules fit nicely into both straight and zigzag channels[16] whereas the 3MP molecules are preferentially located at the intersections between the straight channels and the zigzag channels; see Figure 7. The nC_6 molecules have a higher packing efficiency within the silicalite matrix than the 3MP molecules. It is more efficient to obtain higher loading by "replacing" the 3MP with nC_6; this *configurational entropy* effect is the reason behind the curious maxima in the 3MP loading in the mixture.

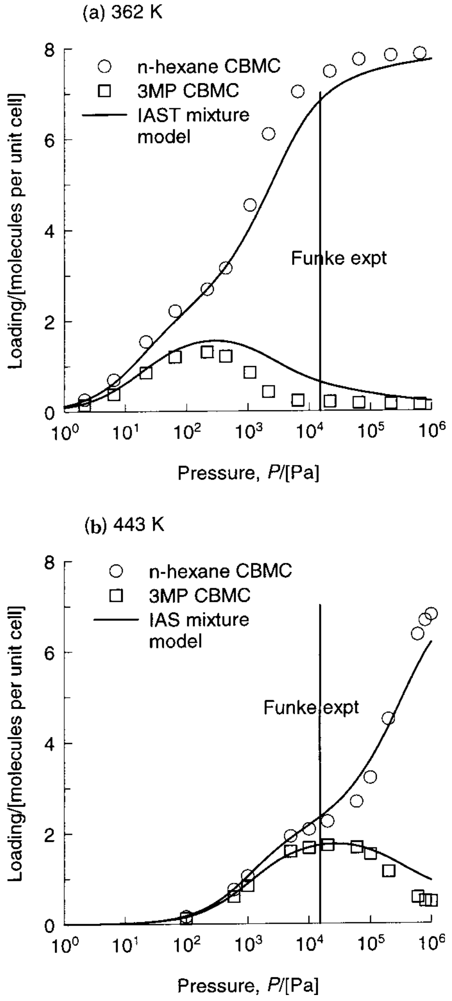


Figure 6. CBMC simulations for 50−50 mixture isotherm for nC6−3MP at 362 and 443 K.

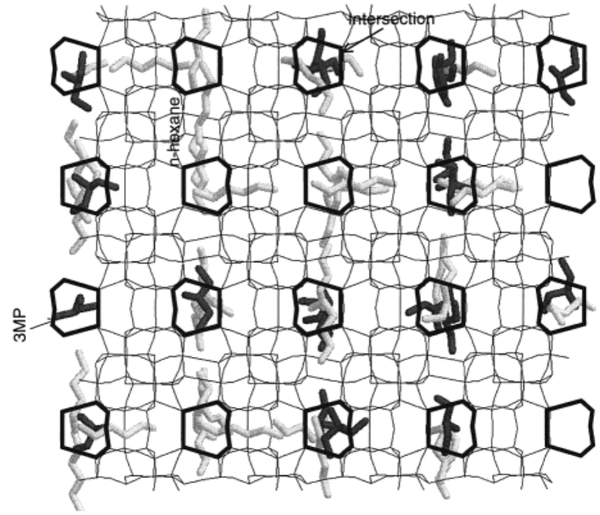
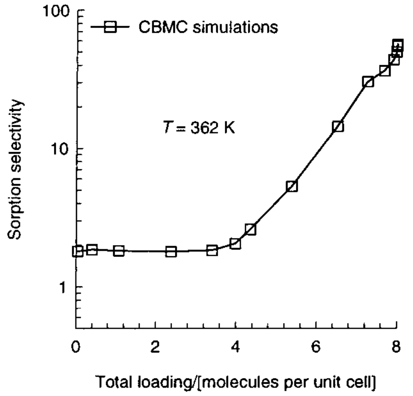


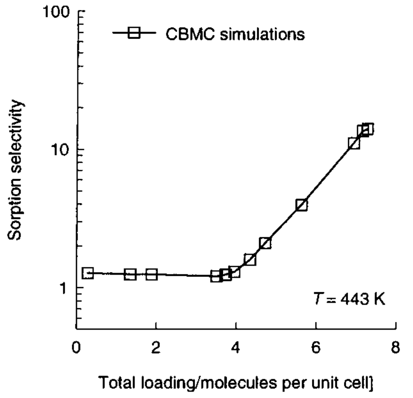
Figure 7. Typical snapshot showing the location of a 50−50 mixture of *n*-hexane (1)−3MP (2) at 362 K and 100 Pa. Preferential siting of 3 MP alkanes at the intersections between the straight and zigzag channels is evident. The linear alkane can be located at any position within the silicalite structure.

Before seeking experimental verification of the curious mixture behavior, let us try to estimate the mixture

(a) nC6/3MP selectivity at 362 K



(b) nC6/3MP selectivity at 443 K



(c) nC6/3MP selectivity at various *T*

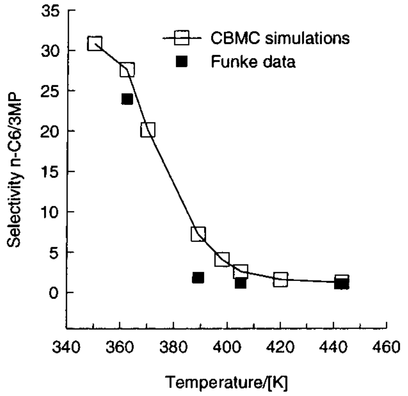


Figure 8. Sorption and permeation selectivities for 50−50 mixture of nC6−3MP at 362 and 443 K.

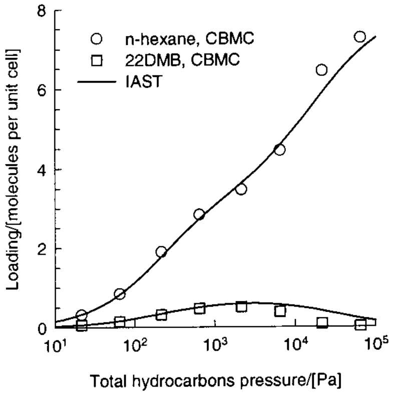
loadings from the pure component isotherms using the ideal adsorbed solution theory (IAST) of Myers and Prausnitz.[23] We have chosen the IAST in view of the recent success obtained with the description of mixture isotherms of light alkanes in silicalite.[11,12] Briefly, the basic equation of IAST theory is the analogue of Raoult's law for vapor−liquid equilibrium, i.e.

$$Py_i = P_i^0(\pi)x_i \tag{4}$$

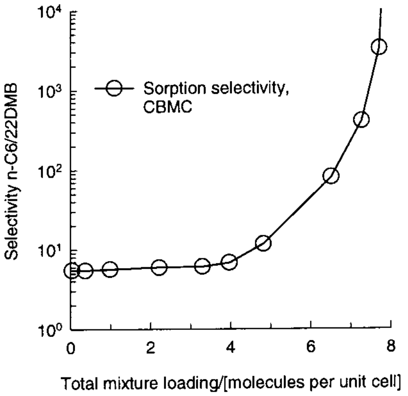
where x_i is the mole fraction in the adsorbed phase

$$x_i = \frac{\Theta_i}{\Theta_1 + \Theta_2} \tag{5}$$

(a) n-C6 and 22DMB loadings at 398 K for 50-50 mixture



(b) Selectivity at 398 K for 50-50 mixture



(c) 22DMB flux and loading at 398 K for 50-50 mixture

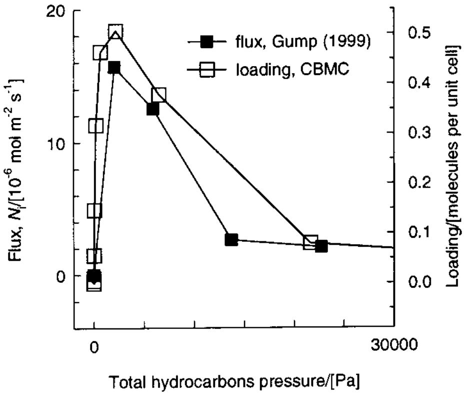


Figure 9. (a) CBMC simulations for 50−50 mixture isotherm for nC6−22DMB at 398 K. (b) Sorption selectivity from CBMC simulations. (c) Comparison of loading of 22DMB with fluxes measured by Gump et al.[14]

and $P_i^0(\pi)$ is the pressure for sorption of every pure component *i*, which yields the same spreading pressure, π, as that for the mixture. The spreading pressure is defined by the Gibbs adsorption isotherm

$$\frac{\pi A}{k_B T} = \rho \int_{P=0}^{P=P_i^0} \frac{\Theta_i^0(P)}{P} \, dP \tag{6}$$

where *A* is the surface area/m^3 of adsorbent of the adsorbent, k_B is the Boltzmann constant, ρ is the density of silicalite expressed in terms of the number of unit cells/m^3, and $\Theta_i^0(P)$ is the pure component isotherm

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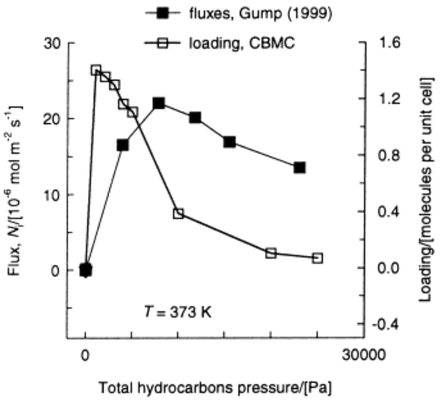
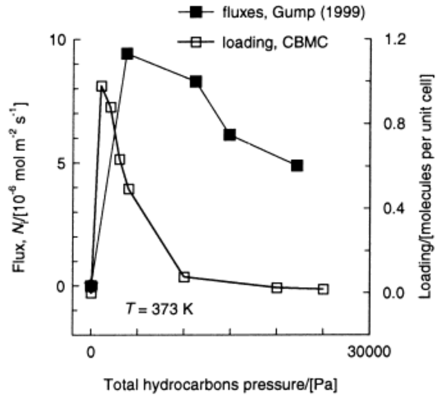
[23] Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.


(a) 22DMB flux and loading for y_1=0.2


(b) 22DMB flux and loading for y_1 = 0.3

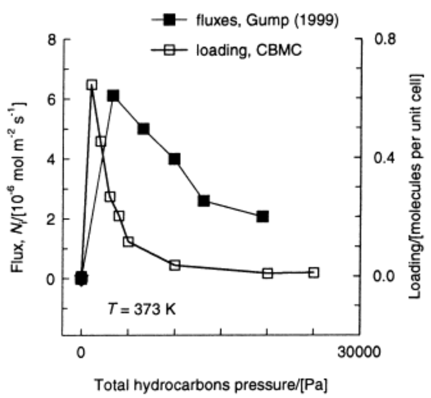

(c) 22DMB flux and loading for y_1 = 0.4

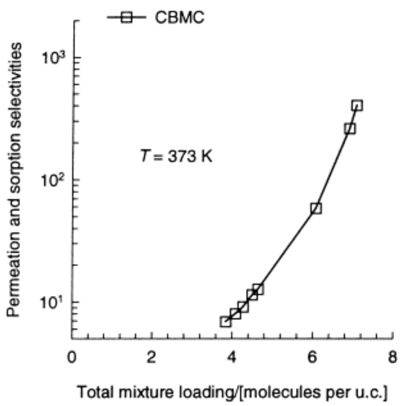
Figure 10. Comparison of CBMC simulations of loading with experimentally determined fluxes of 22DMB for mixtures of nC6−22DMB at 373 K with various composition vapor phase compositions. Experimental data are from Gump et al.[14]

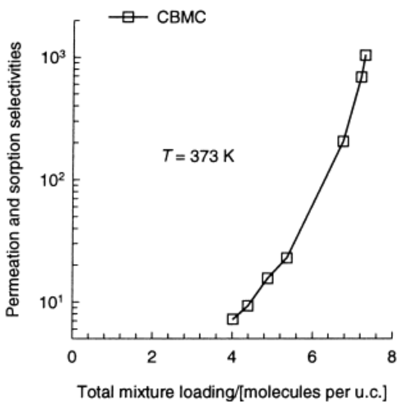
given by eq 1. The total amount adsorbed is obtained from

$$\Theta_1 + \Theta_2 = \frac{1}{\dfrac{x_1}{\Theta_1{}^0(P_1{}^0)} + \dfrac{x_2}{\Theta_2{}^0(P_2{}^0)}} \tag{7}$$

The set of eqs 1 and 4−7 need to be solved numerically to obtain the mixture loadings of components 1 and 2.

We see in Figure 6a,b that the IAST predictions are in reasonably good agreement with the CBMC mixture loadings. Some deviations are observed, especially at high loadings. These deviations are caused by mixture nonideality effects.[11]


(a) Selectivity for y_1=0.2


(b) Selectivity for y_1 = 0.3

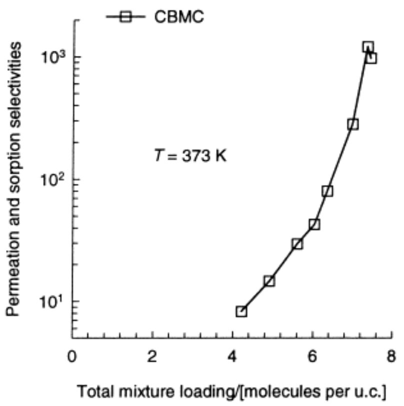
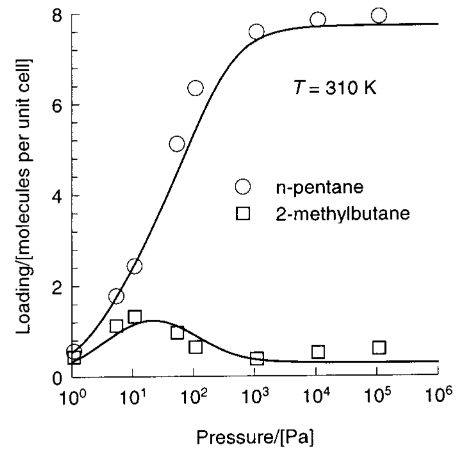
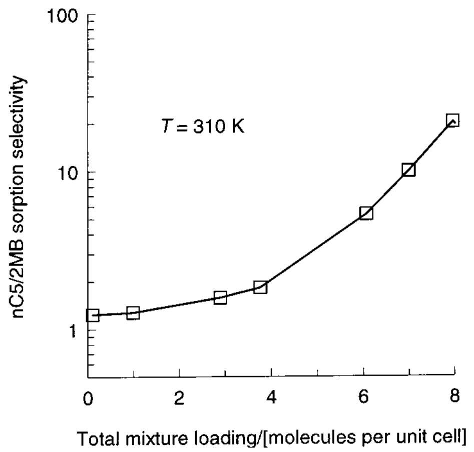

(c) Selectivity for y_1 = 0.4

Figure 11. CBMC simulations of sorption selectivity for mixtures of nC6−22DMB at 373 K with various composition vapor phase compositions.

Funke et al.[13] measured the permeation selectivities for 50−50 mixtures of nC_6 and 3MP at various temperatures, keeping the upstream hydrocarbons pressure at 15 kPa; see Table 3 of their paper. What is remarkable is that the permeation selectivity for a 50−50 mixture S_P = 24 whereas S_P = 1.3 for the pure components. This high mixture selectivity can be explained by examination of Figure 6a, where the upstream pressure (15 kPa) condition of the Funke experiment is indicated by a vertical line. The upstream pressure corresponds to a situation well beyond the pressure at which the 3MP loading exhibits a maximum and the sorption selectivity is very high. In another experiment at 443 K, the upstream pressure of



(a) 50-50 mixture isotherm for nC5 - 2MB



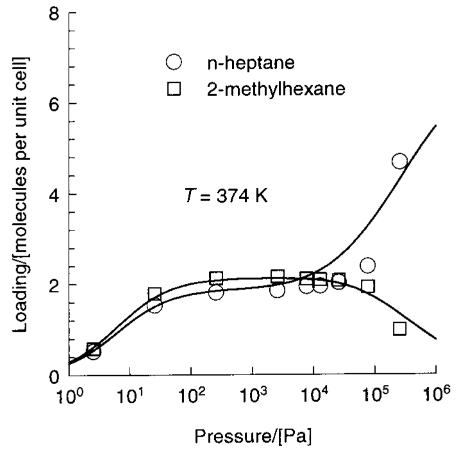
(b) Sorption selectivity for nC5 - 2MB

Figure 12. (a) CBMC simulations for 50−50 mixture isotherms for nC5−2MB at 310 K. (b) Sorption selectivity for the mixture.

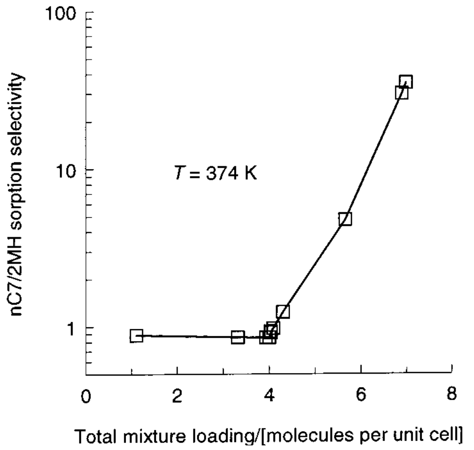
15 kPa corresponds closely to the pressure at which the loading of 3MP is at its maximum and therefore the selectivity of nC_6 is at its lowest. The CBMC simulations also show that, in order to obtain high selectivities at 443 K, the upstream pressure should be maintained at 1000 kPa. Since, at such high pressures, the hydrocarbon mixture would be in the liquid phase, one technological solution would be to operate in the pervaporation mode (upstream compartment in the liquid phase; downstream compartment in the vapor phase). Matsufuji et al.[24] have shown that high selectivities for the separation of hexane isomers can be obtained by operating in the pervaporation mode, underlining these arguments.

From the mixture isotherms presented in Figure 6a,b it becomes clear that configurational entropy effects would manifest only at higher pressures, i.e., at high mixture loadings. To stress this point, we have calculated the sorption selectivity, *S*, as a function of the total mixture loading; the results are presented in Figure 8a,b. The sorption selectivity increases sharply beyond a total loading of 4 molecules/unit cell, corresponding to the situation in which all the intersections are occupied.

The experimental permeation selectivities S_P, measured by Funke et al.,[13] are compared with the sorption selectivities *S* in Figure 8 c for a range of temperature conditions keeping the pressure constant at15 kPa. The close agreement between the two sets of results confirm the configurational entropy effects are the reasons behind the high selectivities observed at lower temperatures. Such effects diminish with increasing temperatures, when the pressure is maintained constant at 15 kPa.



(a) 50-50 mixture isotherm for nC7 - 2MH



(b) Sorption selectivity for nC7 - 2MH

Figure 13. (a) CBMC simulations for 50−50 mixture isotherms for nC7−2MH at 374 K. (b) Sorption selectivity for the mixture.

***n-Hexane−2,2-Dimethylbutane Mixtures*.** CBMC simulations carried out for a 50−50 mixture of (1) nC_6 and (2) 22DMB at 398 K also show that the double-branched is virtually excluded at higher pressures due to configurational entropy effects; see Figure 9 a. From Figure 9b we see that the sorption selectivity increases dramatically beyond a total mixture loading of 4 molecules/unit cell. Gump et al.[14] have reported the permeation fluxes of 50−50 mixtures of nC_6 and 22DMB across a silicalite membrane at 398 K for various upstream hydrocarbon pressures; see Figures 5 and 6 of their paper. Since the flux of any component is proportional to the loading at the upstream face, we would expect the flux of 22DMB to go through a maximum as the upstream compartment pressure is increased, in steps, from for example 100 to 100 kPa. This is precisely what Gump et al.[14] have observed in their experiments. The experimental fluxes of 22DMB are compared in Figure 9c with the 22DMB loadings obtained from CBMC simulations. It is heartening to note that the experimentally observed maximum flux of 22DMB is obtained at the same pressure at which the 22DMB exhibits a maximum in its loading.

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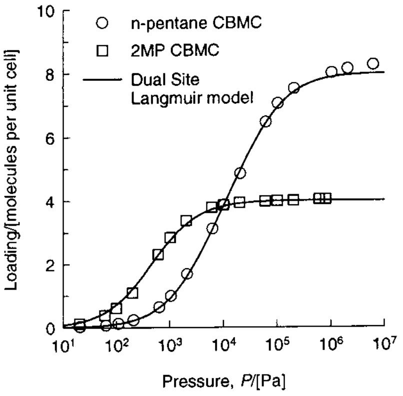
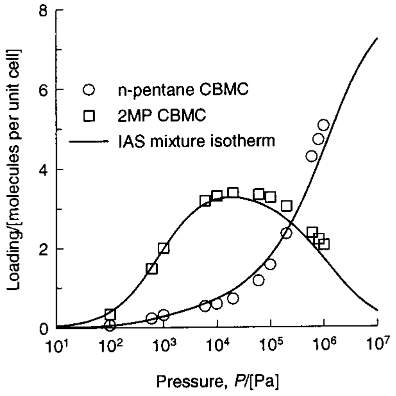
(24) Matsufuji, T.; Watanabe, K.; Nishiyama, N.; Egashira, Y.; Matsukata, M.; Ueyama, K. *Ind. Eng. Chem. Res.* **2000**, *39*, 2434.

(a) pure components at 433 K



(b) 50-50 mixture at 433 K



(c) Sorption selectivity in 50-50 mixture

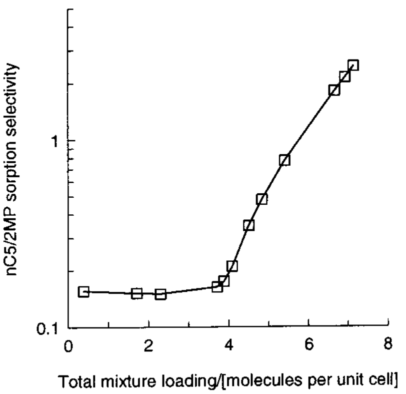
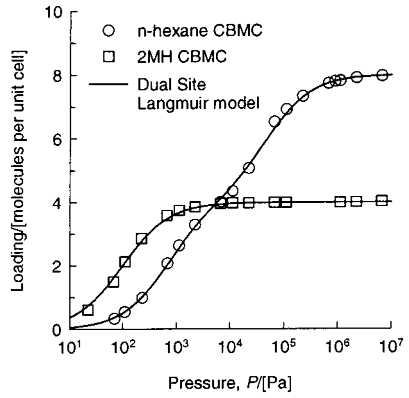


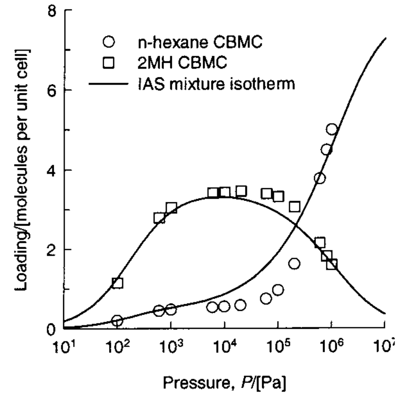
Figure 14. (a) CBMC simulations for pure component isotherms for nC5 and 2MP at 433 K. (b) CBMC simulations for 50−50 mixture isotherms for nC5−2MP at 433 K. (c) Sorption selectivity for the 50−50 mixture.

Gump et al.[14] have also reported the permeation fluxes of mixtures of nC_6 and 22DMB across a silicalite membrane at 373 K for various mixture compositions; see Figures 1 and 2 of their paper. The most intriguing results are the permeation fluxes for 22DMB which show a maximum for a set of vapor compositions $y_1 = 0.2$, 0.3, and 0.4; see Figure 2 of their paper. To understand these permeation results, the molecular loadings of nC_6 and 22DMB were determined for the same set of conditions as in the experiments. Our CBMC simulation results for 22DMB loadings are compared with the 22DMB fluxes in Figure 10a−c. For $y_1 = 0.2$, 0.3, and 0.4 the 22DMB loading exhibits a maximum at the same upstream pressure at which the flux maximum is observed. For all three mixtures, the sorption selectivities are shown in Figure 11; we see the sharp increase in the selectivity for total mixture loadings in excess of 4 molecules/unit cell.

(a) pure components at 433 K



(b) 50-50 mixture at 433 K



(c) Sorption selectivity of 50-50 mixture

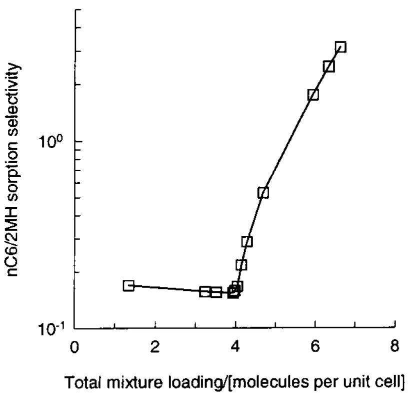


Figure 15. (a) CBMC simulations for pure component isotherms for nC6 and 2MH at 433 K. (b) CBMC simulations for 50−50 mixture isotherms for nC6−2MH at 433 K. (c) Sorption selectivity for the mixture.

From the results presented in Figures 8−10 we confirm that configurational entropy effects cause the exclusion of the branched isomer from the silicalite structure. Our explanation of the membrane permeation experiments is essentially different from that proposed by Funke et al.[13] and Gump et al.,[4] who consider the *n*-hexane to effectively "block" the permeation of branched isomers. These authors do not offer an explanation of their membrane permeation experimental results in terms of the entropy effects explained here.

Isomers of Pentane and Heptane. Configurational effects also prevail when considering mixture isotherms

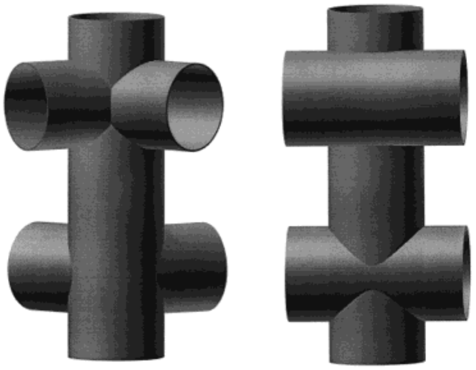


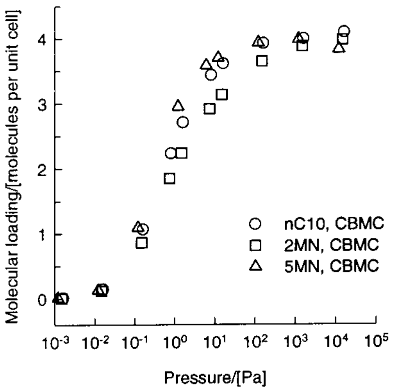
Figure 16. Schematic of silicalite (MFI) and MEL structures, shown respectively on the left and right sides.

of isomers of pentane and heptane. Figure 12a shows 50−50 mixture isotherms for *n*-pentane and 2-methylbutane. The sorption selectivity increases after a mixture loading of 4 molecules/unit cell; see Figure 12b. Figure 13a shows 50−50 mixture isotherms for *n*-heptane and 2-methylhexane (2MH), respectively. The curious table mountain loading behavior of 2MH is notable. Beyond a total mixture loading of 4 molecules/unit cell, the sorption selectivity increases dramatically in favor of the linear isomer. For the C_7 isomer mixture, reasonably high selectivities are only realized when the operating pressure is higher than e.g. 1000 kPa. At such high pressures the mixture is present in the liquid state. So, if membrane permeation is resorted to, then we should operate the membrane unit in the pervaporation model.[24] If the isomer separation is to be realized in a packed bed, then the process needs to be operated in the liquid phase. We also see from Figures 12 and 13 that the IAST provides a reasonably good description of the mixture isotherms.

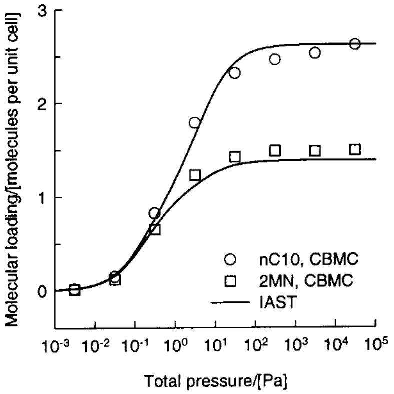
***n*-Pentane−2-Methylpentane Mixture.** The mixtures considered in the foregoing were made up of molecules with the same number of carbon atoms. In practice we also have to deal with mixtures made up of different number of C atoms. Let us now consider the characteristics of a mixture on nC_5 and 2MP. The pure component and 50−50 isotherms determined from CBMC simulations are shown respectively in Figure 14a,b. This mixture represents an interesting combination because there are two conflicting factors which determine the sorption characteristics of the mixture: (a) chain length effects, which tends to favor 2MP; (b) configurational entropy effects, which tends to favor nC_5. Since configurational entropy effects begin to play a role only at high loadings (exceeding 4 molecules/unit cell), we would expect a selectivity reversal at increased loadings. This is indeed found to be the case; see Figure 14b,c. Configurational entropy effects overrule chain length effects when the mixture loading increases beyond 4 molecules/unit cell. The IAST again provides a reasonable description of the mixture behavior and reflects the selectivity reversal phenomena adequately.

***n*-Hexane−2-Methylhexane (2MH) Mixtures.** Let us now consider the characteristics of a mixture of *n*-hexane (nC_6) and 2MH. The pure component and 50−50 isotherms determined from CBMC simulations are shown in Figure 15a,b. As in the foregoing case the mixture behavior is governed by the conflicting effects of chain length (favoring 2MH) and configurational entropy effects (favoring nC_6). The net result is that we again observe the phenomenon of selectivity reversal; see Figure 15 c. The sharp increase in the sorption selectivity beyond a total mixture loading of 4 molecules/unit cell is noteworthy. We once again find that the IAST provides a reasonable description of the mixture behavior and reflects the selectivity reversal phenomena adequately.

(a) pure component isotherms



(b) 50-50 mixture isotherm for nC10 - 2MN



(c) 50-50 mixture isotherm for nC10 - 5MN

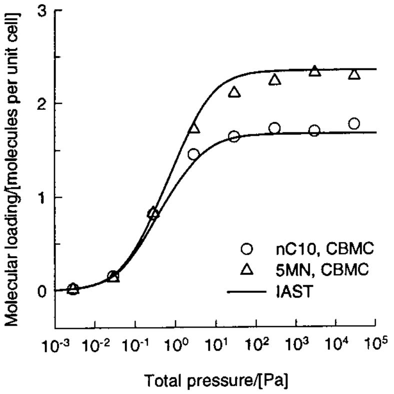
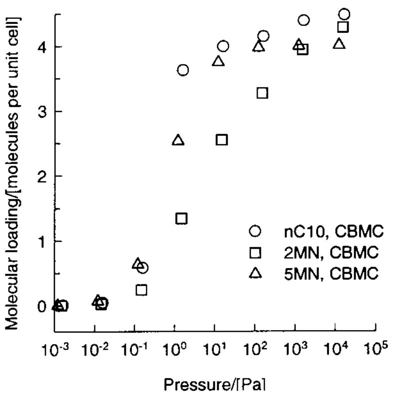
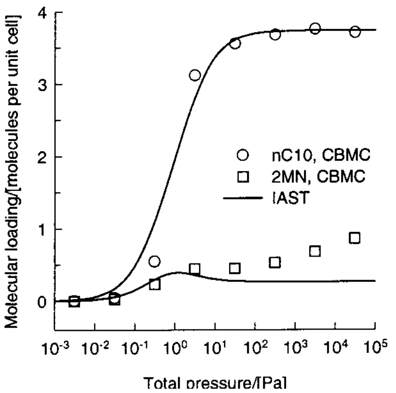


Figure 17. (a) CBMC simulations for pure component isotherms for nC10, 2MN, and 5MN at 415 K in silicalite. (b) CBMC simulations for 50−50 mixture isotherms for nC6−2MN at 415 K in silicalite. (c) CBMC simulations for 50−50 mixture isotherms for nC6−5MN at 415 K in silicalite.

Influence of Zeolite Structure

The discussions in the foregoing were restricted to the separation of alkane isomers using silicalite, or MFI, zeolite. The CBMC simulation strategy is not restricted to this zeolite nor to the variety of molecules considered above. Packing efficiency effects also manifest themselves when considering other structures and molecules. We shall illustrate this by considering pure component and 50−50 mixture isotherms for the isomers *n*-decane (nC10), 2-methylnonane (2MN), and 5-methylnonane (5MN) in two different types of zeolite structures: silicalite (MFI)


(a) pure component isotherms


(b) 50-50 mixture isotherm for nC10 - 2MN

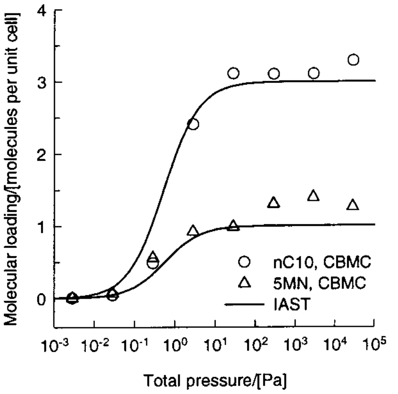

(c) 50-50 mixture isotherm for nC10 - 5MN

Figure 18. (a) CBMC simulations for pure component isotherms for nC10, 2MN, and 5MN at 415 K in MEL. (b) CBMC simulations for 50−50 mixture isotherms for nC6−2MN at 415 K in MEL. (c) CBMC simulations for 50−50 mixture isotherms for nC6−5MN at 415 K in MEL.

and MEL; see Figure 16. Hydroconversion of diesel fractions is important in practice and the distribution of 2MN and 5MN in the product fraction obtained from a nC10 feed is often taken as a measure of the performance of a zeolite catalyst such as silicalite or MEL. These zeolites have a similar pore diameter (0.55 nm) and structure. The principal difference is that MFI contains both straight and zigzag channels, while all channels in the MEL structure are straight. There is only one type of intersection in the MFI structure. In the MEL structure there are two types of intersections, small or large.

The pure component and 50−50 mixture isotherms at 415 K in silicalite are shown in Figure 17. It is interesting to note from Figure 17b that, for the 50−50 mixture, the silicalite structure favors the linear nC10 molecule to the branched 2MN molecule. However, the situation is different when the branching is symmetrically placed at the 5-position; Figure 17c shows that the 5MN molecules have a higher sorption strength in the mixture with nC10. This differences in the behavior of the two mixtures is to do with how well the three molecules pack inside the silicalite structure. The 5MN molecule can place its two “legs” in either channel quite comfortably, and this “leg room advantage” helps it win the entropic battle with the linear isomer. Snapshots of the location of 2MN and 5MN in silicalite are available on our web site;[25] these show clearly the “leg room advantage” experienced by 5MN.

Table 2. Pure Component Sorption Parameters for Isomers of Decane for MFI (Silicalite-1) and MEL Zeolites at 415 K

		dual-site Langmuir params (eq 1)			
		site A		site B	
component i	zeolite	$b_{i,\mathrm{A}}$/ Pa^{-1}	$\Theta_{i,\mathrm{sat,A}}$/ molecules per unit cell	$b_{i,\mathrm{B}}$/ Pa^{-1}	$\Theta_{i,\mathrm{sat,B}}$/ molecules per unit cell
nC10	MFI	5.8	2	0.43	2
	MEL	4	2	2	2
2MN	MFI	5.8	2	0.12	2
	MEL	2	2	0.02	2
5MN	MFI	5.8	2	0.85	2
	MEL	1	2	0.9	2

The situation is different when we consider sorption within MEL structure. The CBMC data on pure component and mixture isotherms are shown in Figure 18. Now, we note that nC10 has a higher sorption strength than either 2MN or 5MN in the 50−50 mixtures. Within the MEL structure, 5MN has no “leg room advantage” over the linear molecule. Molecular dynamics simulations of diffusion of these isomers within silicalite and MEL[26] also show that the diffusivities are significantly affected by the zeolite structure and the position of the branching. Molecular configurations affect both sorption and diffusion.

The differences in the sorption strengths and diffusivities of decane isomers in silicalite and MEL structures could provide an explanation of the striking differences in the product distributions obtained during hydrocracking of *n*-decane.[26,27] Another point to note from the results presented in Figures 17 and 18 is that the IAST mixture rule works reasonably well in the two cases (the pure component fitted data are listed in Table 2).

Concluding Remarks

We have examined the sorption characteristics of various mixtures of alkanes, in the 5−7 carbon atom range, in silicalite. The following major conclusions can be drawn: (1) CBMC simulations provide a powerful technique for determining the pure component and mixture isotherms of alkanes. The simulated pure component isotherms are in good agreement with experiment. There are no published experimental mixture isotherms, and therefore, CBMC simulations come into their own. (2) For mixtures of linear and branched alkanes with the same number of carbon atoms, the sorption selectivity increases in favor of the linear isomer for mixture loadings in excess of 4 molecules/unit cell. This is due to configurational entropy effects. This effect is so strong that the branched alkanes are virtually excluded from the silicalite matrix

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[25] http://molsim.chem.uva.nl/MFI_MEL.

[26] Webb, E. B.; Grest, G. S. *Catal. Lett.* **1998**, *56*, 95.

[27] Jacobs, P. A., Martens, J. A.; Weitkamp, J.; Bayer, H. K. *Faraday Discuss.Chem. Soc.* **1982**, *72*, 353.

and high separation factors are achievable. (3) The mixture isotherm characteristics are captured in essence by the IAS theory. (4) A characteristic feature of the configurational entropy effects for alkanes isomers is that, for mixture loadings above 4, the loading of the branched alkane *decreases* when the system pressure *increases*. This has implications when a mixture of linear and branched alkanes permeate across a silicalite membrane. At high mixture loadings, the flux of the branched alkane must *decrease* while the upstream partial pressure *increases*; this curious behavior has indeed been observed experimentally by Gump et al..[14] Their experimental results can be rationalized on the basis of our CBMC mixture simulations. (5) For sorption of mixtures of nC5−2MP and nC6−2MH within silicalite, chain length and configurational entropy effects counteract each other. At high mixture loadings, configurational entropy effects tend to mask the effect of chain length. Such selectivity reversal effects have never been stressed before in the literature.

In addition to the simulations for mixtures in silicalite, we have also shown that configurational entropy effects affect the sorption isotherms for isomers of decane; the branched isomer 5MN wins the entropic battle over nC10 within silicalite. This is because it has leg-room advantage. CBMC simulations can be helpful in screening zeolite structures for catalytic conversion.[28]

Acknowledgment. All the authors of this study have received grants from The Netherlands Organization for Scientific Research (NWO), through The Netherlands Research Council for Chemical Sciences (CW) and The Netherlands Technology Foundation (STW). S.L.V. acknowledges support from the ESF scientific program SIMU.

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[28] Maesen, T. L. M.; Schenk, M.; Vlugt, T. J. H.; de Jonge, J. P.; Smit, B. *J. Catal.* **1999**, *188*, 403.