

Equilibrium adsorption of linear and branched C₆ alkanes on silicalite-1 studied by the tapered element oscillating microbalance

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Received 26th January 2001, Accepted 28th February 2001

First published as an Advance Article on the web 22nd March 2001

The equilibrium adsorption of linear and branched C₆ alkanes n-hexane, 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane on silicalite-1 has been investigated using a novel technique—the tapered element oscillating microbalance (TEOM). For n-hexane, a small “kink” in the isotherm is observed at about 4 molecule (unit cell of silicalite-1)^{−1}. The measured isotherms of both 2-methylpentane and 3-methylpentane at 303 K for the first time show a second-step adsorption at loadings over 4 molecule (unit cell)^{−1}. A two-step adsorption behavior is confirmed for single branched C₆ alkanes. This observation is in good agreement with the picture of two distinct adsorption locations for single branched alkanes in silicalite-1 indicated by other techniques. The maximum loading for 2,3-dimethylbutane is about 4 molecule (unit cell)^{−1} under the conditions investigated and the molecules reside completely in the intersections. A dual-site Langmuir expression appropriately describes the equilibrium data for n-hexane, 2-methylpentane and 3-methylpentane, while the isotherms of 2,3-dimethylbutane can be described by the Langmuir model. The derived thermodynamic properties such as adsorption enthalpy and entropy agree with those available, determined by other techniques. The observed two-step adsorption behavior for single branched C₆ alkanes on silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the channel intersections and in the zigzag channels.

Introduction

One of the main applications of zeolitic materials is in the separation of mixtures based on different mechanisms, such as steric, equilibrium, and kinetic ones.¹ In the equilibrium mechanism zeolites have micropores with different abilities to accommodate different molecules. In general, the stronger adsorbing species are preferentially removed by the adsorbent.

Silicalite-1 is the aluminium-free form of the ZSM-5 zeolite. Therefore it is hydrophobic.² This characteristic can be used to selectively adsorb nonpolar hydrocarbon molecules in water for environmental applications.³ It is also considered as a good model adsorbent for testing adsorption isotherm models, based on gas–solid molecular interactions.⁴

Branched hydrocarbons are preferred to straight-chain ones as ingredients in gasoline because branched hydrocarbons have a higher octane number. Catalytic isomerization has been used to convert straight-chain hydrocarbons to their mono- or di-branched structures. However, the product of catalytic isomerization is a mixture of linear and branched hydrocarbons in thermodynamic equilibrium, and the separation of linear hydrocarbons from their branched isomers becomes necessary. Recently, separations of linear and branched C₆ mixtures through silicalite membranes have been carried out by Noble and co-workers^{5–7} and Matsufuji *et al.*⁸ A very high selectivity for normal hexane over branched isomers has been reported. Furthermore, at elevated temperatures the flux of branched isomers exhibited a curious maximum with increasing partial pressure. Krishna and Paschek⁹ used configurational bias Monte Carlo (CBMC) simulations to calculate the pure component and mixture isotherms at various temperatures. By applying the Maxwell–Stefan theory for zeolite diffusion, they provided a nearly quantitative explanation of the separation data through the

silicalite-1 membranes. The high selectivity for the separation of n-hexane from branched isomers is primarily caused by the exclusion of the branched molecules. The reason for this exclusion was to be found in configurational entropic effects, *i.e.* for the branched isomers on silicalite-1 there is a large difference in the adsorption entropy between the molecular locations in the intersections and in the channels. Indeed, an extensive study by CBMC simulations shows a two-step adsorption behavior for branched alkanes on silicalite-1.^{10–14}

Two distinct adsorption sites for branched alkanes, one within the channel interiors and one at the intersections of the straight and zigzag channels, have been confirmed using FT-Raman spectroscopy¹⁵ and temperature-programmed desorption.^{16–18} Sun *et al.*¹⁹ and Zhu *et al.*²⁰ measured the isotherms of isobutane on silicalite-1 and reported a step at 4 molecule (unit cell)^{−1}. This observation is in good agreement with the results obtained by CBMC simulations. The adsorption properties of n-hexane on silicalite-1 have been extensively studied, and there are many isotherm data available in the open literature.^{2,3,21–25} However, adsorption of the branched alkanes has received much less attention. The reported isotherms of the branched isomers were only measured at relatively high temperatures and low pressures and did not show the two-step adsorption behavior predicted by the molecular simulations.

In this paper we present the isotherm data for n-hexane (NC6), 2-methylpentane (2MP), 3-methylpentane (3MP) and 2,3-dimethylbutane (23DMB) on silicalite-1, determined by a novel technique, the tapered element oscillating microbalance (TEOM).²⁶ We also use the concept proposed in a previous paper:²⁷ a volume filling process with two different spaces, to interpret the adsorption. A dual-site Langmuir expression is used to describe the isotherm data. In addition, thermodynamic properties such as adsorption enthalpy and entropy are

derived to characterize interactions between adsorptive and adsorbent.

Experimental

A Rupprecht and Patashnick TEOM 1500 mass analyzer (100 mg sample volume) was used in an experimental set-up designed for measurements of equilibrium, transient adsorption and desorption on microporous materials. A detailed description of the TEOM operating principles is given elsewhere,²⁶ and the validity of the TEOM technique to accurately measure isotherm data has been verified in a previous paper.²⁰

Based on the operating principles, the TEOM yields information about mass changes rather than absolute sample masses. The total mass change measured consists of the amount adsorbed and the mass change caused by the change in the gas density in the tapered sample tube. The change in the gas density depends on the type of gas and the operating conditions. To correct for the mass change caused by the change in the density of the gas phase, reference experiments have to be performed. As mentioned in our previous papers,^{20,26} the relationship between the mass change in the reference runs and the partial pressure of an adsorbing gas is almost linear. If equilibrium adsorption for strong adsorptives is operated at very low partial pressures, this mass change caused by the density change in the gas phase will become negligible.

The supply rates of the liquid were controlled by a so-called μ -Flow mass-flow meter (Bronkhorst, High-Tech B.V.). At room temperature, the liquid, for instance n-hexane, 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane, was drawn from a pressurized container with an inert gas blanket and measured by the liquid mass-flow meter. The required flow rate was controlled to the set-point value by a control valve (C) forming an integral part of the liquid flow and carrier gas mixing valve (M). Then the formed mixture was subsequently led into the evaporator to achieve total evaporation (E). This explains the abbreviation "CEM" viz.: Controller-Evaporation-Mixing, the three basic functions of the liquid delivery system, shown schematically in Fig. 1. The main features of this liquid delivery system are (a) accurately controlled gas-liquid mixture, (b) fast response, (c) high reproducibility, (d) very stable vapor flow and (e) flexible selection of gas : liquid ratio.

The silicalite-1 crystals with a ratio Si/Al > 1300 were synthesized in-house. The template inside the silicalite-1 crystals was removed by calcination at 873 K for 12 h. The apparent density of the sample was 1.76 g cm⁻³ and the adsorption of N₂ indicated an accessible microporous void volume of 0.179 cm³ g⁻¹ and a microporous area of 372 m² g⁻¹. The silicalite-1 crystals had a uniform shape and size of about 120 × 50 × 50 μ m ($L \times H \times W$), as determined by scanning electron microscopy (SEM).²⁰

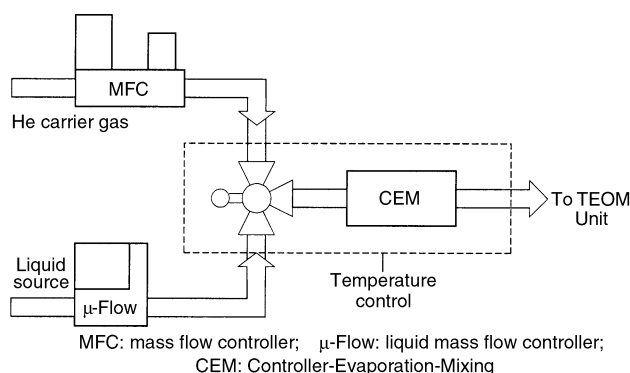


Fig. 1 Schematic diagram for the liquid-vapor delivery system.

Prior to the experiments the crystals were outgassed in the following way. After a temperature rise with a rate of 10 K min⁻¹ *in situ* in a helium flow of 200 cm³ (NTP) min⁻¹ (NTP: room temperature and 101.3 kPa), the sample was heated at 573 K for 12 h in order to remove adsorbed impurities.

Helium was obtained as an ultra-high purity gas (>99.999%). The liquid adsorptives such as n-hexane, 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane were obtained from Alfa Aesar or Aldrich, with specified purities over 99%, and were used without further purification.

The isotherm data were measured in the temperature range from 303 to 408 K for n-hexane, 2-methylpentane, 3-methylpentane and from 303 to 473 K for 2,3-dimethylbutane. At least four temperatures were used for each adsorptive to reduce the uncertainty in the derived thermodynamic properties. Most experiments were duplicated, and both adsorption and desorption experiments were performed to confirm reversibility.

Results and discussion

Isotherms

Experimental adsorption data for linear and branched C₆ alkanes on silicalite-1 are given in Fig. 2–5. The measured isotherm data for NC6 at 303 K have a constant value of 8 molecule (unit cell)⁻¹, see Fig. 2. For the single branched alkanes, a two-step adsorption behavior can be clearly seen in Fig. 3 and 4. In addition, both single branched alkanes show very similar adsorption trends. It is interesting to note constant isotherm data measured with a value of 4 molecule (unit cell)⁻¹ for 23DMB at 303 K and at the pressure range investigated, presented in Fig. 5.

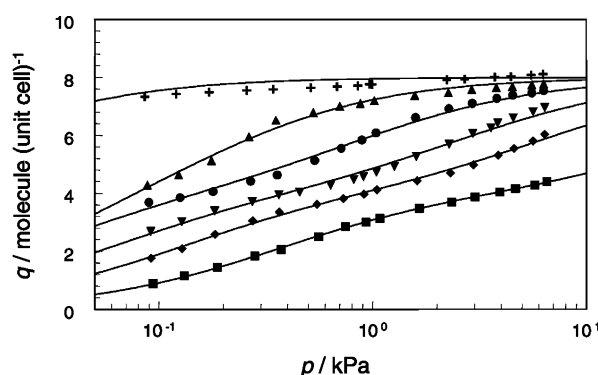


Fig. 2 Isotherms of NC6 on silicalite-1. Lines are the DSL isotherm model fits. (+) 303, (▲) 338, (●) 353, (▼) 373, (◆) 388 and (■) 408 K.

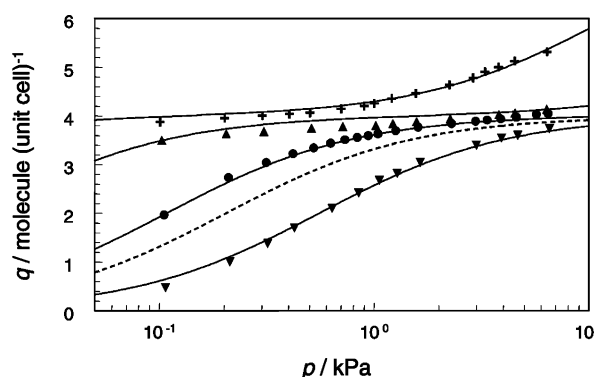


Fig. 3 Isotherms of 2MP on silicalite-1. Solid lines are the DSL isotherm model fits. (+) 303, (▲) 338, (●) 373 and (▼) 408 K. The dashed line is the fitted isotherm from Cavalcante and Ruthven³⁰ at 373 K.

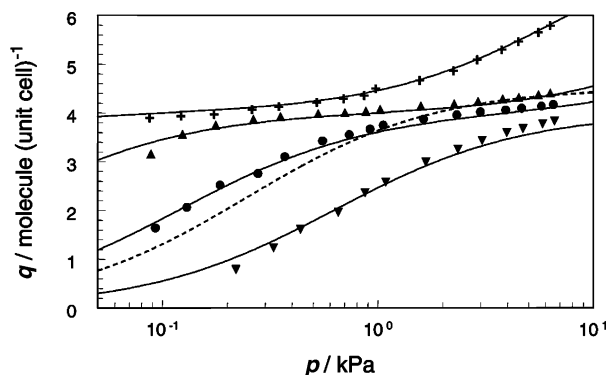


Fig. 4 Isotherms of 3MP on silicalite-1. Solid lines are the DSL isotherm model fits. (+) 303, (▲) 338, (●) 373 and (▼) 408 K. The dashed line is the fitted isotherm from Cavalcante and Ruthven³⁰ at 373 K.

Isotherm model. The adsorption of NC6 on MFI zeolites has been extensively studied by both experiments and molecular simulation techniques. Generally speaking, the isotherm data obtained by both methods are consistent. The determined saturation amount adsorbed for NC6 on silicalite-1 is about 8 molecule (unit cell)⁻¹. The experimental data for the maximum loading, reported in the literature and measured in this study, for NC6 are summarized in Table 1. The agreement can be considered to be very good.

Molecular simulations suggest the occurrence of a kind of phase transition in the adsorption of NC6 on silicalite-1.²⁸ It is shown that NC6 molecules first take an ordered arrangement in the zigzag channels before loadings above approximately half the maximum loading (4 molecule (unit cell)⁻¹)

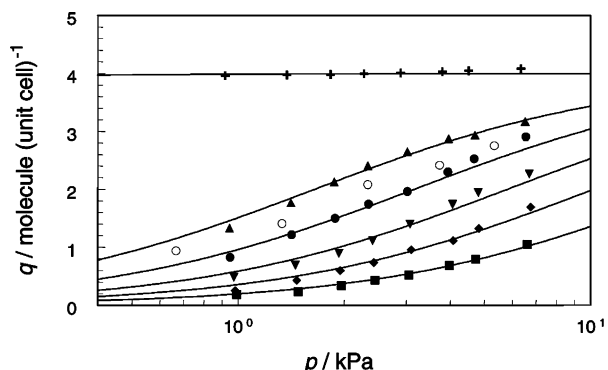


Fig. 5 Isotherms of 23DMB on silicalite-1. Lines are the Langmuir isotherm model fits. (+) 303, (▲) 408, (●) 423, (▼) 438, (◆) 453 and (■) 473 K. (○) data from Cavalcante and Ruthven³⁰ at 423 K.

Table 1 Comparison of maximum loadings measured with the literature data for the adsorption of linear and branched C₆ isomers on silicalite-1

Adsorptive	T/K	p/kPa	$q_{\max}^a$	Ref.
NC6	303	1.313	8.27	3
	295	2	7.79	25
	—	—	8.11	24
	303	6.29	8.11	This study
2MP	373	2	3.89	30
	293	2	5.03	25
	303	6.40	5.21	This study
3MP	373	2	4.36	30
	293	2	5.64	25
	303	6.32	5.79	This study
23DMB	383	3.33	2.85	30
	303	6.35	4.08	This study

^a Molecule (unit cell)⁻¹.

can be reached. Due to the additional loss of entropy, an increased pressure is needed to “freeze” the molecules in the channels. This increase in pressure is reflected as a step in the adsorption isotherms. Van Well *et al.*¹⁸ and Millot *et al.*²⁹ have proposed that there are two distinct adsorption sites available on silicalite-1 for NC6, based on temperature-programmed desorption results.

For single branched alkanes 2MP and 3MP on silicalite-1, the CBMC simulations have confirmed that these molecules prefer to reside in the channel intersections but can also occupy the channel space, resulting in a two-step adsorption behavior. Fig. 6 shows a comparison of 2MP isotherm data in this study with the data from the simulation.¹⁰ Some deviations between experiment and simulation can be seen, but both results agree reasonably and show a two-step adsorption behavior. Experimentally, the equilibrium adsorption data of 2MP and 3MP have to be measured at relatively low pressures. The measured maximum loadings for these two single branched alkanes, from the literature and from this study, are listed in Table 1.

For 23DMB adsorption on silicalite-1, only isotherm data at 383, 423 and 473 K are reported in the literature.^{30,31} The measured maximum loadings from the literature and this study are included in Table 1.

Theories of adsorption on heterogeneous surfaces or sites are usually based on the concept of independent sites or patches, so that the total amount adsorbed is simply a summation over the various parts:

$$q(T, p) = \sum_i q_i(T, p, E_i) \quad (1)$$

$q_i(T, p, E_i)$ is called the local adsorption isotherm with energy of adsorption (E_i) at site i . $q(T, p)$ is the overall single-component isotherm measured experimentally. If one assumes that the local adsorption isotherm is given by the Langmuir model, the total adsorption isotherm for the bimodal two-site discrete distribution in eqn. (1) can be expressed

$$q = q_a^{\text{sat}} \frac{K_A p}{1 + K_A p} + q_b^{\text{sat}} \frac{K_B p}{1 + K_B p} \quad (2)$$

where q_a^{sat} and K_A are the saturation capacity and the affinity parameter and equilibrium constant on the first set of sites, respectively, and q_b^{sat} and K_B are the analogous parameters on the second set of sites. By convention, we assume that the first set of sites has the larger affinity parameter, *i.e.*, $K_A > K_B$.

Following the concept in a previous paper,²⁷ the saturation capacities in the two sets of sites are prior defined for the adsorption of linear and branched C₆ isomers on silicalite-1. Richards and Rees²¹ proposed that the saturation amount could be split into the numbers of molecules located in two representative adsorption sites. q_A^{sat} and q_B^{sat} have the same

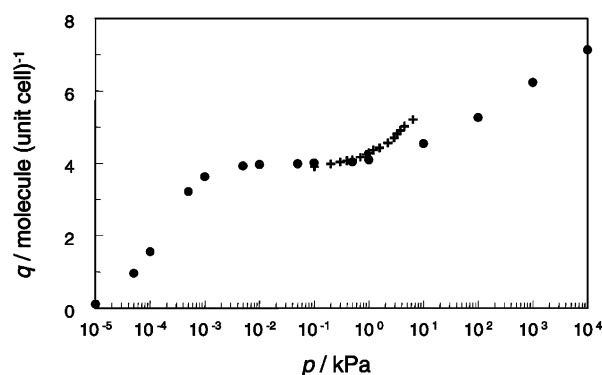


Fig. 6 Comparison of 2MP isotherm data with data from the literature. (+) This study at 303 K and (●) CBMC-simulation data from Vlught *et al.*¹⁰ at 303 K.

value of 4 molecule (unit cell)⁻¹, based on the length of the channels and of the intersections as well as on the adsorptive molecular size. The number, 4 molecule (unit cell)⁻¹, is called the “magic” number by Olson and Reischman,³² because it represents the number of intersections, the number of straight channels and the number of zigzag channels per unit cell in silicalite-1. Thus a four-parameter isotherm model in eqn. (2) is simplified to a two-parameter isotherm model as follows:

$$q = 4 \frac{K_A p}{1 + K_A p} + 4 \frac{K_B p}{1 + K_B p} \quad (3)$$

The combined fitting by the above dual-site Langmuir (DSL) isotherm model is given by the solid lines for NC6, 2MP and 3MP in Fig. 2–4. For 23DMB, the experimentally adsorbed amounts did not indicate a distinction between channels and intersections (Fig. 5). The measured amount adsorbed is almost independent of the pressure investigated at 303 K, and these determined isotherm data have the same value of 4 molecule (unit cell)⁻¹, which is equal to that of the theoretical value in the intersections. Therefore, a simple Langmuir expression was used with the intersection adsorption capacity for fitting the isotherms at 303–473 K for the 23DMB/silicalite-1 system, also shown in Fig. 5.

$$q = 4 \frac{K_A p}{1 + K_A p} \quad (4)$$

For the other adsorptives higher loadings were obtained. For NC6 the observed capacity was in agreement with the theoretical value.

The estimated values of the adsorption equilibrium constants for each temperature, K_A and K_B , are listed in Table 2 for all the systems studied. These values were obtained by non-linear regression of the experimental data on either the DSL model or the Langmuir isotherm using the fixed values of the saturation loadings.

Table 2 Estimated values of adsorption equilibrium constants and standard deviation of fit by combined fitting of isotherm data [eqn. (3) and (4)]

T/K	$q_{\text{A}}^{\text{sat}}$	$K_{\text{A}}/\text{kPa}^{-1}$	$q_{\text{B}}^{\text{sat}}$	$K_{\text{B}}/\text{kPa}^{-1}$	σ_{model}^b
NC6					0.163
303	4	2730	4	80.8	
338	4	171	4	4.02	
358	4	44.8	4	9.42×10^{-1}	
373	4	18.0	4	3.51×10^{-1}	
388	4	7.77	4	1.41×10^{-1}	
408	4	2.79	4	4.66×10^{-2}	
2MP					0.137
303	4	760	4	8.09×10^{-2}	
338	4	66.7	4	5.66×10^{-3}	
373	4	9.25	4	6.53×10^{-4}	
408	4	1.80	4	1.09×10^{-4}	
3MP					0.119
303	4	726	4	1.31×10^{-1}	
338	4	62.0	4	8.83×10^{-3}	
373	4	8.40	4	9.88×10^{-4}	
408	4	1.60	4	1.61×10^{-4}	
23DMB ^c					0.075
303	4	352			
408	4	0.606			
423	4	0.316			
438	4	0.172			
453	4	0.0979			
473	4	0.0515			

^a Molecule (unit cell)⁻¹. ^b Standard deviation model. ^c Fitted by a single Langmuir expression [eqn. (4)].

n-Hexane. The isotherms for NC6, shown in Fig. 2, indicate that small kinks are present at about 4 molecule (unit cell)⁻¹ in the temperature range 338–373 K. This observation is in agreement with the results from Richard and Rees,²¹ Eder³³ and Yang and Rees.²⁴ A comparison of the isotherm data with the literature data is shown in Fig. 7. These results agree well with the experimental data from Yang and Rees²⁴ and the simulation data from Vlught *et al.*¹¹ However, significant deviations from the results reported by Sun *et al.*³ can be clearly seen in Fig. 7. The reason for these deviations is uncertain, but it might be pointed out that the data from Sun *et al.*³ at higher temperatures are too low.

The idea of intracrystalline molecular rearrangement of adsorbing species has been developed by Micke *et al.*³⁴ for the system of NC6/MFI structure, based on both geometrical constraints and differences in the interaction potential topology between the straight channels and zigzag channels with the intersections within the MFI crystals. The NC6 molecules sited in the zigzag channels have less mobility than those residing in the straight channels with intersections.³⁴ From CBMC simulations, Smit *et al.*^{28,35} also observed a small two-step adsorption behavior at 4 molecule (unit cell)⁻¹ for n-hexane on silicalite-1. The molecular length of n-hexane is about 1.03 nm,²¹ which is much longer than the straight channel length (0.46 nm²¹). Therefore n-hexane molecules cannot be wholly located in the straight channel segments and they must also share the intersections. At lower loadings the hexane molecules move freely in the channels through the intersections. If a fraction of the intersections is occupied (4 segments (unit cell)⁻¹), other adsorbing molecules cannot reside in the straight channels at the same time. At high pressures, almost all the adsorbing molecules fit exactly in the zigzag channels with a length of 0.66 nm.²¹ They no longer move freely and keep their noses and tails out of the intersection. In such a configuration all the channels and the intersections can now be tightly packed with NC6 molecules. This may explain the small ‘kink’ in the adsorption isotherm; to fill the entire zeolite structure neatly, the hexane molecules located in the zigzag channels have to be frozen in these channels.²⁸ This “freezing” of the positions of the NC6 molecules implies a loss of entropy and therefore will occur only if the pressure (or gas phase chemical potential) is sufficiently high to compensate for this loss.

The configurational entropic effects lead to adsorption heterogeneity. At loadings below 4 molecule (unit cell)⁻¹, NC6 molecules can be sited in either the straight or the zigzag channels with the intersections. Globally, under these conditions a homogeneous adsorption site is considered, designated as site A. However, at loadings over 4 molecule (unit cell)⁻¹, the adsorption of the adsorbing molecules “frozen” in the zigzag channels will be energetically different. This gives rise

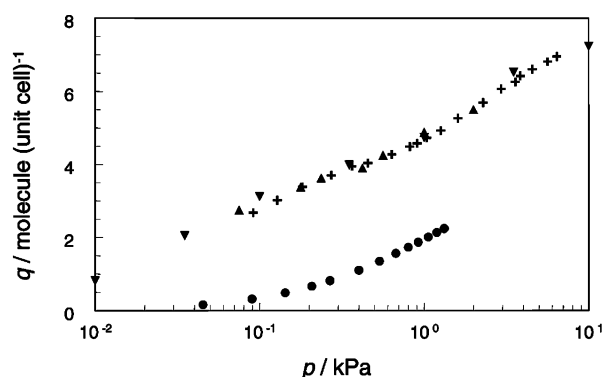


Fig. 7 Comparison of NC6 isotherm data with data from the literature. (+) This study at 373 K, (▲) data from Yang and Rees²⁴ at 373 K, (●) data from Sun *et al.*³ at 374 K and (▼) CBMC-simulation data from Vlught *et al.*¹¹ at 373 K.

to a pseudo-second-adsorption site, designated as site B. NC6 isotherm data are well described by the DSL model over the temperature and pressure range studied, as shown in Fig. 2.

Single branched alkanes. For 2MP and 3MP on silicalite-1, a step is clearly observed for the isotherm at 303 K. At pressures below 1 kPa, the measured isotherm data are almost constant and have a value of 4 molecule (unit cell)^{−1}. At pressures above 1 kPa, the amount adsorbed starts to increase with increasing pressure. Also at 338 K the measured isotherm data do not change with pressure significantly and they have a value close to 4 molecule (unit cell)^{−1}. Only at 373 and 408 K are the isotherms of “type-I” (in Brunauer’s classification).

Compared to n-hexane much less experimental data have been reported on the adsorption of branched alkanes on silicalite-1. Adsorption isotherms have been reported for various hexane isomers by Cavalcante and Ruthven³⁰ and for 2MP and 3MP by Arbuckle *et al.*²⁵ Comparisons of the isotherms at 373 K with the literature data are also shown in Fig. 3 and 4. At higher pressures of 2MP the reported isotherm data in this study are in good agreement with the results from Cavalcante and Ruthven,³⁰ but our data are higher at low pressures. The agreement can be considered to be satisfactory for 3MP over the whole pressure range investigated.

2MP and 3MP show very similar adsorption behavior, although the amount adsorbed for 3MP is slightly higher than that for 2MP under the same conditions. This observation is in agreement with that from Cavalcante and Ruthven.³⁰ Probably, 3MP is a less asymmetric molecule than 2MP, and can pack more efficiently in silicalite-1, since the thermodynamic properties (see below) are quite similar.

A two-step adsorption behavior is more pronounced for the single branched alkanes than for NC6. A preferential packing of 4 molecule (unit cell)^{−1} for the single branched molecules corresponds to the number of intersections per unit cell in silicalite-1. For a loading above the saturation amount in the intersections the adsorbing molecules are forced at higher pressures into the channels. The DSL model, eqn. (3), implicitly describes this behavior; the intersections are filled first, followed by the channels. So, this stepwise adsorption behavior has a different cause, than for the case of NC6.

2,3-Dimethylbutane. Only very limited adsorption data have been reported for 23DMB on silicalite-1. Cavalcante and Ruthven³⁰ and Voogd and Van Bekkum³¹ reported the isotherms at high temperatures. Reasonable agreement with the data from Cavalcante and Ruthven³⁰ is found. Fig. 5 shows this comparison for 23DMB at 423 K. Unfortunately, a two-step adsorption behavior for 23DMB on silicalite-1 has not been observed due to the experimental limitation that higher loadings could not be determined.

Thermodynamic properties

The affinity parameters, K_A and K_B , quantify the adsorption interaction of a given adsorptive with an adsorbent. The magnitude of K_A and K_B depends on the properties of both the adsorptive and the adsorbent, and corresponds to the affinity of the adsorptive for the adsorbent. From the fitted K_A and K_B , the adsorption enthalpies and entropies can be obtained

via the Van’t Hoff equation, eqn. (5)

$$K_i = \exp\left(\frac{\Delta_{\text{ads}} S_i}{R}\right) \exp\left(\frac{-\Delta_{\text{ads}} H_i}{RT}\right) \quad (5)$$

where $\Delta_{\text{ads}} H_i$ and $\Delta_{\text{ads}} S_i$ are the adsorption enthalpy and entropy, respectively. $\ln K_A$ and $\ln K_B$ as a function of $1/T$ are shown graphically in Fig. 8 and 9, respectively. The linearity of these plots indicates that meaningful thermodynamic parameters result from the DSL model for NC6, 2MP and 3MP and from the Langmuir model for 23DMB. The derived values of the adsorption enthalpy and entropy are listed in Table 3.

An overview of the reported adsorption enthalpies in the literature for linear and branched C₆ isomers on silicalite-1 is presented in Table 4. For NC6 on silicalite-1, the determined values of the adsorption enthalpy cover a wide range, as seen in Table 4. However, most of the reported adsorption enthalpies for NC6 on silicalite-1 are about -70 kJ mol^{-1} . The literature enthalpy data are mostly related to adsorption techniques at low loadings and for NC6 they should therefore be compared with the adsorption enthalpy in site A. Our result is considered to be satisfactory.

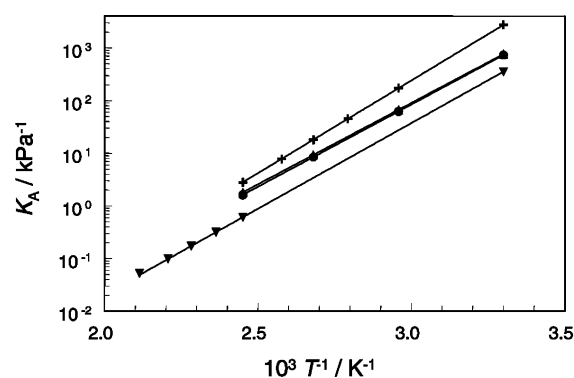


Fig. 8 $\ln K_A$ as a function of $1/T$ for the adsorption of the linear and branched C₆ isomers in site A of silicalite-1, indicated in Table 1. (+) NC6, (▲) 2MP, (●) 3MP and (▼) 23DMB.

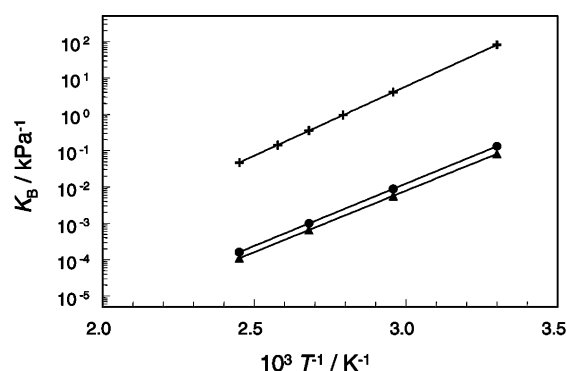


Fig. 9 $\ln K_B$ as a function of $1/T$ for the adsorption of the linear and branched C₆ isomers in site B of silicalite-1, indicated in Table 1. (+) NC6, (▲) 2MP and (●) 3MP.

Table 3 Estimated adsorption enthalpy and entropy values for linear and branched C₆ isomers in silicalite-1 for the combined fitting of the isotherm adsorption data

Adsorptive	$-\Delta_{\text{ads}} H_A / \text{kJ mol}^{-1}$	$-\Delta_{\text{ads}} H_B / \text{kJ mol}^{-1}$	$-\Delta_{\text{ads}} S_A / \text{J mol}^{-1} \text{ K}^{-1}$	$-\Delta_{\text{ads}} S_B / \text{J mol}^{-1} \text{ K}^{-1}$
NC6	67.4 ± 3.6^a	73.0 ± 1.9^a	148 ± 9^a	196 ± 5^a
2MP	59.2 ± 1.5	64.7 ± 13.3	131 ± 4	226 ± 45
3MP	59.9 ± 1.5	65.6 ± 2.2	135 ± 4	225 ± 12
23DMB	62.2 ± 1.7		148 ± 4	

^a 95% confidence error.

Table 4 Adsorption enthalpy and entropy values for linear and branched C₆ isomers on silicalite-1 taken from the literature^a

Adsorptive	$-\Delta_{\text{ads}} H/\text{kJ mol}^{-1}$	$-\Delta_{\text{ads}} S/\text{J mol}^{-1} \text{K}^{-1}$
NC6	71, ² 70, ³ 62 ^a to 84 ^{b,21} 69.8 ^a to 82 ^{b,22} 84, ³⁶ 72, ³⁷ 82, ³⁸ 70, ³⁹ 71.8 ^c and 78.2 ^{d,17}	128, ³⁷ 153, ³⁸ 85, ⁴⁰ 121.8 ^c and 187.6 ^{d,17}
2MP	61.5 ^{c,17} 62.7, ³⁰ 63 ⁴¹	116. ^{c,17}
3MP	66.8 ^c and 70.5 ^{d,16} 67.7, ³⁰ 63 ⁴¹	110 ^c and 202 ^{d,16}
23DMB	54.3 ³⁰	

^a Infinite diluted concentration in the zeolite. ^b Saturation of the zeolite. ^c Adsorption site A. ^d Adsorption site B.

Only Cavalcante and Ruthven³⁰ reported the adsorption enthalpies for 2MP and 3MP on silicalite-1, derived from the isotherms. The absolute values of the adsorption enthalpy in this study are slightly lower than those by Cavalcante and Ruthven,³⁰ especially for 3MP. There is a difference of 5 kJ mol⁻¹ in the adsorption enthalpy between 2MP and 3MP from Cavalcante and Ruthven's results. However, we found only minor differences in the adsorption enthalpy for both types of sites between two single branched C₆ alkanes. This result is supported by molecular simulations by June *et al.*,⁴¹ as indicated in Table 4. Differences in the adsorbed amounts of 2MP and 3MP are only ascribed to differences in packing efficiency.

For 23DMB, the absolute value of the adsorption enthalpy in this study is about 8 kJ mol⁻¹ higher than the data from Cavalcante and Ruthven.³⁰ The reason is not clear. In view of the intersectional space, two branched-end groups in 23DMB molecule can reside in the intersection, which leads to a more confined packing, compared to one branched-end in the intersection for 2MP and 3MP. Consequently, the interactions between the two branched-end groups and the intersection wall are enhanced and may increase the adsorption enthalpy, compared to 2MP and 3MP. Indeed our results show that the absolute value of the adsorption enthalpy for 23DMB is slightly higher than that for 2MP and 3MP. The confined packing of 23DMB in the intersection means an additional loss of entropy. From the adsorption entropy values in Table 3, we also find that 23DMB molecules have less degrees of freedom than the single branched isomers in the intersections.

Millot *et al.*^{16,17} have reported the adsorption enthalpy and entropy for NC6, 2MP and 3MP, by temperature-programmed desorption (TPD), in which equilibrium conditions are maintained. The TPD curves show two peaks for all NC6, 2MP and 3MP on silicalite-1, from which the authors^{16,17} defined two types of adsorption sites for the adsorptives. These reference data are also included in Table 4. Our results have the same trend as that reported by Millot *et al.*^{16,17} the absolute values of the adsorption enthalpy and entropy in site B are higher than those in site A. It is worth noting that our data are in fair agreement with those obtained by temperature-programmed desorption. It is logical that the absolute value of the adsorption enthalpy for the single branched isomers in site B is higher than in site A. Due to low-energy bending of the O–Si–O angle, which leads to some flexibility in the channel dimensions of silicalite-1, the branched-end group has a confined packing in the channels.⁴² This results in enhancing the interactions between the adsorptive and the channel wall.

From the derived values of the thermodynamic properties for the two "sites", we conclude that the difference in the adsorption enthalpy between the two types is relatively small, compared to the significant difference in the adsorption entropy for NC6. One can also recall the Gibbs energy, associated with the adsorption equilibrium constants, K_A and K_B .

$$\Delta_{\text{ads}} G_i = \Delta_{\text{ads}} H_i - T\Delta_{\text{ads}} S_i \quad (6)$$

Weaker adsorption in the range from 4–8 molecule (unit cell)⁻¹ means that $\Delta_{\text{ads}} G_B$ is less negative than $\Delta_{\text{ads}} G_A$. According to the results in Table 3, $\Delta_{\text{ads}} H_B$ becomes more negative, increasing somewhat in magnitude; this would make $\Delta_{\text{ads}} G_B$ more negative, leading to stronger adsorption. Since this adsorption is actually weaker by definition ($K_B < K_A$), $-T\Delta_{\text{ads}} S_B$ must be more positive. This implies a more ordered state for the last 4 molecules of NC6, 2MP and 3MP relative to adsorption at lower loadings.³² Since for NC6 no real distinctly different adsorption locations are present in silicalite-1 structure, the description in the DSL form is artificial. It merely reflects a change in ordering of the molecules above 4 molecule (unit cell)⁻¹, the so-called commensurate freezing.²⁸

Compared to n-hexane on silicalite-1, the difference between the adsorption entropies in the two sites is more pronounced for the single branched C₆ alkanes. The molecular size of the single branched alkanes, with a kinetic diameter of 0.5 nm,⁴³ is comparable to the diameters of the channels. On the other hand, there is more space to accommodate the branched-end group in the intersections. Thus it can be expected that the loss of entropy will be more significant if the single branched C₆ molecules are adsorbed in the smaller channels. The CBMC simulations indeed show that there is a striking difference in the probability distribution of single branched alkanes between adsorption locations in the channels and in the intersections. At loadings below 4 molecule (unit cell)⁻¹, the branched molecules only reside in the intersections due to the entropic effects.^{10,11,14}

The loss of the adsorption entropy for the single branched C₆ molecules residing in the channels is more than that for n-hexane. This also indicates that n-hexane has a higher packing efficiency than the branched alkanes within the silicalite-1 structure. Thus these entropic effects might be applied to the separation of linear and branched C₆ isomers by silicalite-1 adsorbents or membranes.⁴⁴ The initial filling of the channels by n-hexane and the intersections by the branched alkane molecules will consequently not be independent processes due to the spatial phenomena, and non-ideal behavior is expected. Unfortunately, the mixture isotherm data are rarely available, because the experimental determination of such isotherms is significantly more complicated and time-consuming than the measurements for the pure components. The mixture isomers of NC₆ and 2MP, determined by CBMC simulations,¹² show a curious maximum in the loading of 2MP; this loading decreases to almost zero with increasing pressure due to the entropic effects that the adsorbed 2MP molecules can be squeezed out by n-hexane at higher pressures, since packing efficiency is much higher for NC6 within the silicalite-1 structure. This leads to high adsorption selectivity for n-hexane. Recently reported permeation data for NC6 and 2MP mixture by a silicalite-1 membrane support this concept.⁵

Conclusion

Adsorption isotherms for linear and branched C₆ alkanes on silicalite-1 were accurately measured with the novel TEOM

technique at multiple temperatures. A two-step adsorption behavior is observed for 2-methylpentane and 3-methylpentane at 4 molecule (unit cell)⁻¹. This observation is in agreement with that predicted by CBMC simulations. A small “kink” in the isotherm at about 4 molecule (unit cell)⁻¹ is present for n-hexane adsorption. For 2,3-dimethylbutane, the measured maximum loading is limited to 4 molecule (unit cell)⁻¹ under the conditions investigated. The Langmuir model with the fixed saturation capacity in the intersections appropriately describes the isotherm data of 2,3-dimethylbutane.

The adsorption was interpreted in terms of a volume filling process with two different types of spaces for 2-methylpentane and 3-methylpentane and with two different energetic configurations for n-hexane. This can be described by a dual-site Langmuir expression. The derived thermodynamic properties like the enthalpies and entropies associated with adsorption at the two adsorption sites are physically sound and in good agreement with the available literature data. The observed two-step adsorption behavior for single branched C₆ isomers on silicalite-1 is attributed to the large difference in the adsorption entropy between the molecular locations in the intersections and in the channels. Normal hexane has a higher packing efficiency than the branched C₆ alkanes within the silicalite-1 structure. The credibility of the proposed approach is enhanced by its ability to provide meaningful thermodynamic properties.

Acknowledgement

Financial support provided to W.Z. from Delft Interdisciplinary Research Centers (DIOC) is acknowledged. W.Z. thanks Dr. T. J. H. Vlught for discussions on the CBMC simulation results.

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