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Can alkane isomers be separated? Adsorption equilibrium and kinetic data for hexane isomers and their binary mixtures on MFI

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Abstract In this study we present a global overview of the adsorption behavior of hexane isomers on MFI. With an experimental approach that couples a manometric technique with Near Infrared (NIR) spectroscopy, which has been recently developed, we did address adsorption kinetic properties of *n*-hexane, 2-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane, and their binary mixtures. The adsorption equilibrium properties of the binary mixtures were also assessed using the same technique. Whereas the adsorption isotherms and heats of adsorption for single components have been studied by a manometric technique coupled with a micro calorimeter. The differential heats of adsorption of *n*-hexane increase slightly with loading, on the other hand the heat of adsorption of branched hexanes exhibits a decrease with loading. The diffusion rates on MFI of *n*-hexane, 2-methylpentane and 2,3-dimethylbutane are in the same order of magnitude. However, the diffusion rate of 2,2-dimethylbutane is two orders of magnitude lower than rates of the other isomers. In the binary mixtures the components interact and the difference between the diffusion rates of the components decreases. The MFI zeolite presents equilibrium selectivity towards the less branched isomers. In conclusion, a separation process for linear/mono-branched alkanes + double-branched alkanes, has to be based on its equilibrium properties and not based on adsorption kinetics.

Keywords Zeolites · Alkanes · Isotherms · Differential heat of adsorption

Abbreviations

D	diffusivity, $m^2 \cdot s^{-1}$
D_c	uptake diffusivity, $m^2 \cdot s^{-1}$
D/r^2	diffusion time constant, s^{-1}
K_C	adsorption equilibrium constant in the channels, kPa^{-1}
K_I	adsorption equilibrium constant in the intersections, kPa^{-1}
K_H	Henry's Law constant, $mmol \cdot g^{-1} \cdot kPa^{-1}$
p	pressure (adsorbate concentration in the gas phase), Pa
Q_0	initial heat of adsorption, $kJ \cdot mol^{-1}$
q	loading (adsorbate concentration in the particles), $mmol \cdot g^{-1}$
$q_{sat,C}$	saturation loading in the channels, $mmol \cdot g^{-1}$
$q_{sat,I}$	saturation loading in the intersections, $mmol \cdot g^{-1}$
q_t	adsorbed amount at time t, $mmol \cdot g^{-1}$
q_{inf}	adsorbed amount at equilibrium, $mmol \cdot g^{-1}$
r	particle radius, m
V_s	the volume of the sample, cm^3
V_g	the volume of apparatus, cm^3
α	$K_c V_s / V_g$, (−)

1 Introduction

The diffusion of molecular species inside the intra-crystalline network of zeolites, is both relevant to the field of adsorptive separation and to the area of catalytic conversion. At present we address the adsorption and diffusion behavior of linear and branched alkanes in view of the potential of developing an adsorption based separation process. How do molecules move inside zeolites and how does the intra-crystalline channel network of a zeolite influence the movement and the reaction pathway of organic molecules,

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are necessarily important questions in the design and application of shape selective catalysts (Chen 1994). The influence of the zeolite's structure depends critically on the pore topology, resulting in large differences in catalytic selectivity between pore topologies. These differences can be studied by analyzing the adsorption behavior of all molecules involved (Schenk 2003). Therefore, adsorption data are relevant to the catalytic isomerization in the zeolite. The adsorption equilibrium and kinetic data are also essential to the development of adsorption based separation methods. Isomerization of linear hydrocarbons and separation of linear and branched hydrocarbons is a problem with industrial importance, because of its potential for octane number enhancement (Gener et al. 2002). Branched alkanes have higher octane numbers than linear alkanes, thus the former are preferred as ingredients in the gasoline.

Several authors have studied the adsorption of linear hexane (e.g. Arik et al. 2003), but the adsorption of branched hexane isomers has received far less attention (Gener et al. 2002; Cavalcante and Ruthven 1995; Yang and Rees 1997; Stach et al. 1986, Zhu et al. 2001a, 2001b; Denayer et al. 1998; Bellat et al. 2005). The hexane adsorption isotherm exhibits a step at a loading around 4 molecules per unit cell; the reason for this is the two different sites available to hexane molecules within the MFI structure, the channels and the intersections. This behaviour is also predicted for the mono-branched hexane isomers (Schenk 2003; Vlugt 2000), but the reported isotherms were mainly measured at high temperatures and relatively low pressures (Zhu et al. 2001b), and therefore did not exhibit the two-step adsorption isotherm predicted by the simulations. The results of Zhu et al. (2001b) for mono-branched hexanes (2-methylpentane, 3-methylpentane) do present the typical "kink" of a two-step adsorption behavior. For 2,3-dimethylbutane Zhu et al. (2001b) reported results with a single-step isotherm, a maximum capacity at about 4 molecules per unit cell, which is also in accordance with simulation results (Schenk 2003). Equilibrium and kinetic adsorption data for mixtures of hexane isomers are almost nonexistent in the literature, and some diffusion results for single component hexane isomers are presented by some authors (Gener et al. 2002; Zhu et al. 2001a).

In this work we have studied the adsorption equilibrium and heats of adsorption of hexane isomers on MFI, measured directly by a manometric set-up coupled with a micro-calorimeter, at 423 K. With an experimental approach that couples a manometric technique with Near Infrared (NIR) spectroscopy we addressed adsorption kinetic properties of *n*-hexane, 2-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane, and their binary mixtures, at 423 K. The adsorption equilibrium properties of the binary mixtures were also assessed using the same technique. Furthermore, Henry's Constants and Initial Heats of Adsorption were derived in order to give a better insight over the adsorption process of linear and branched alkanes on MFI.

2 Experimental

In the present work the adsorption properties of hexane isomers (*n*-hexane, 2-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane) on MFI are being studied. Adsorption isotherms and differential heats of adsorption are assessed directly by a manometric set-up combined with a micro-calorimeter. The adsorption uptake rates of the components and their binary mixtures, as well as the adsorption equilibria of the binary mixtures, are assessed using an experimental approach that couples a manometric technique with NIR spectroscopy.

2.1 Manometric + calorimetric set-up

Single component adsorption experiments were performed in a micro-calorimeter (Calvet C80, Setaram) connected to a home built manometric apparatus, to address single component equilibrium data and heats of adsorption. Figure 1 shows a scheme of the experimental setup.

The calorimeter used for these experiments is of the Calvet type, it can be operated isothermally at a fixed temperature. A detailed description of the experimental system is given in previous work (Ferreira et al. 2006).

2.2 Manometric + NIR spectrometer set-up

In this study the adsorption diffusion time constant of hexane isomers and their binary mixtures, on MFI are also studied using a manometric technique coupled with Near Infrared (NIR) spectroscopy. The adsorption equilibrium properties of the binary mixtures were also assessed using this technique.

Figure 2 shows the experimental setup. A constructed in-house manometric apparatus coupled with a NIR spectrometer (Perkin Elmer, FT-IR system, GX Spectrum) was used. The volume of the Gas Cell chamber is of 204 cm^3, and the Sample Holder chamber has a volume of 24.4 cm^3. A more detailed description of this experimental system is given in previous work (Ferreira et al. 2004, 2005).

2.3 Materials

Commercial MFI from Zeolyst (Zeolyst International) was used as adsorbent material, with a silica alumina ratio (Si/Al) of 100, the mean size of the particles is 2.0 μm. The sample was calcined for 6 h at 873 K under Argon flow.

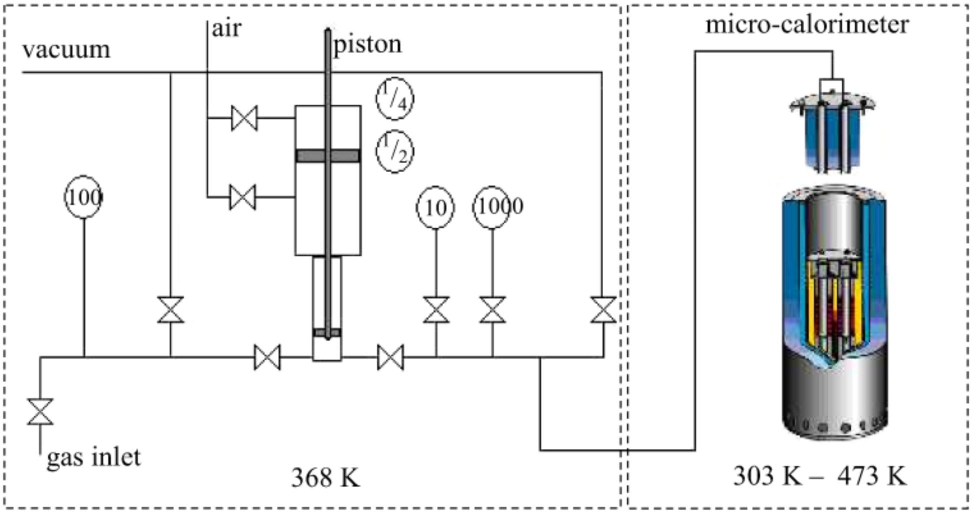

Fig. 1 Scheme of the manometric + calorimetric set-up

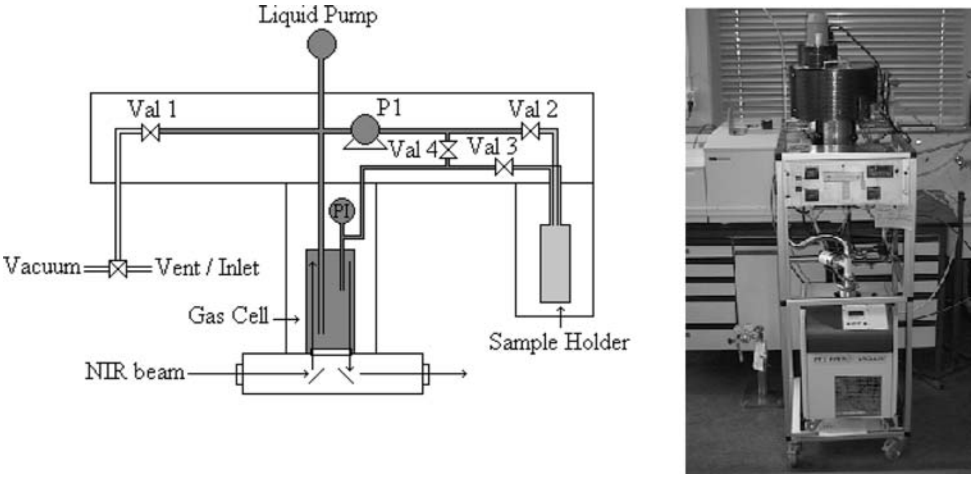

Fig. 2 Volumetric technique + NIR (*scheme* and *photo*)

The adsorbates used were *n*-hexane 99+% from Merck, 2-methylpentane 99+%, 2,3-dimethylbutane 98+% and 2,2-dimethylbutane 98%, the last three components were from Acros Organics. These liquids were vaporized, and then fed into the system without any further treatment.

2.4 Experimental procedures

2.4.1 Single component isotherms and heats of adsorption (manometric + calorimetric set-up)

Blank measurements have been performed to correct for the non-ideality of the gases. These measurements were carried out by introducing a known amount of gas into the empty sample holder and register the final pressure. The blanks were performed for the hexane isomers at 423 K. To calculate the amount adsorbed, the blank curves are used with a correction for the volume occupied by the zeolite sample itself. The zeolite sample was outgassed at 573 K during 6 hours under a vacuum better than 5×10^{-7} mbar. Isotherms and heat fluxes have been measured in a continuous way for the 4 gases at 423 K. For pressures up to 1 kPa a small amount of gas was introduced (piston in the $1/4$ of a stroke position, admission pressure of 10 kPa), this allows measuring several adsorption equilibrium points in the low pressure region—the Henry region. Then, the introduction pressure and volume are increased; the piston introduces $1/2$ of stroke, with a pressure of 50 kPa, until an equilibrium pressure of 9.8 kPa. The final equilibrium points (equilibrium pressure between 9.8 kPa and 200 kPa) were measured with the piston on the full stroke position and an admission pressure of 100 kPa.

2.4.2 Mixtures equilibrium data and diffusion time constants (manometric + NIR spectrometer set-up)

This experimental technique uses Near Infra-Red (NIR) spectroscopy to monitor the bulk composition. Therefore, single and multi component calibration models are necessary. To build these models NIR spectra (average of 10 scans with 4 cm^{-1} of resolution) of pure gases are recorded at 423 K, for different pressures. The data are treated as explained in previous work (Ferreira et al. 2005).

All sorption experiments were performed at 423 K. To perform an adsorption experiment vapor is fed into the gas cell while valves 2 and 3 are closed, in order to isolate the sample. After introduction of the gas, valves 1, 2 and 3 are kept closed during an initial period, keeping the pressure constant at its initial value. Spectral data acquisition is started during this initial period. When valves 2 and 3 are opened, and valve 4 is closed simultaneously, the adsorption process starts, at this moment a pressure drop is observed. Spectra are recorded in time, so the adsorption uptake can be computed as a function of time for every single equilibrium point. This procedure is repeated several times to obtain a full adsorption isotherm.

3 Theory

3.1 Isotherm models

MFI type zeolites are widely used in many areas of chemical industry. The MFI topology consists of intersecting straight and sinusoidal channels. The straight channels have an elliptical cross section with diameters equal to 0.52 nm and 0.58 nm, while the zigzag channels have a nearly circular shape, with diameter of 0.54 nm (Kärger 1992). The intersections have a diameter of roughly 0.9 nm (Zhu et al. 1998). Molecules have the tendency to adsorb in the smaller channels to maximize the attractive interactions with walls. However, geometric constraints can appear if the molecular diameter is too large, leading to preferential adsorption on the larger intersections. Simulations of adsorbate spatial distribution show that the side groups in the branched alkanes force these to sit in the channel intersections, while the linear alkanes prefer to reside in the channels (June et al. 1990). This means that there are two different possible adsorption sites on MFI. Therefore, a two-site Langmuir model would be required to describe the adsorption on MFI-type structures.

$$q = q_{sat,C}\frac{K_C p}{1+K_C p} + q_{sat,I}\frac{K_I p}{1+K_I p}, \quad C\text{—}Channel,\ I\text{—}Intersection, \tag{1}$$

where q is loading (adsorbate concentration in the particles) and p is pressure (adsorbate concentration in the gas phase). Two different saturation loadings are used in (1), and are indicated by $q_{sat,C}$ and $q_{sat,I}$. K_C and K_I are the adsorption equilibrium constants for the two sites.

When one of the sites is inaccessible to the adsorbate molecules, the double Langmuir model simplifies to the well-known Langmuir model.

$$q = q_{sat}\frac{Kp}{1+Kp}. \tag{2}$$

3.2 Henry's Law region

Langmuir isotherm model reproduces the general shape of a Type I isotherm. Thus, at low pressure where $K \cdot p$ may be neglected in comparison with unity, equation simplifies to:

$$q = K_H p. \tag{3}$$

Equation (3) is only valid for the region where adsorption is directly proportional to the pressure; this region is known as Henry's Law region. K_H is the Henry's Law constant. In the Henry's Law region ($p \to 0$), the Langmuir model must still be observed, thus the right side of (2) and (3) must be equal, obtaining in this way (4).

$$K_H = q_{sat} K. \tag{4}$$

The K_H values can be obtained directly by fitting the linear part of the isotherm to (3) and forcing it to pass by through origin. Another way of computing K_H is to plot $\ln(q)/\ln(p)$ versus $1/\ln(p)$ for the points belonging to the Henry's Law region. The obtained line must be straight, with slope $\ln(K_H)$ and intercept 1.

3.3 Diffusion model

The uptake rate can be easily obtained by monitoring the pressure in a constant volume apparatus after making a step in the gas phase pressure. However, it is necessary to use a sensitive and rapid pressure acquisition system to monitor the pressure. In this study, NIR spectroscopy was used for this propose, it has the advantage of not only being able to follow the total pressure with time, but also the partial pressures in the case of alkane isomers mixtures. In the manometric case, opposite to the gravimetric, the relative volume of the apparatus to the sample must be small enough such that pressure changes with time can be recorded.

A description of adsorption rates requires an understanding of how the concentration changes within the crystal particle as a function of time. By performing a mass balance to the adsorbed phase concentration, q, in the zeolite, we obtain the Fick's second law (Chen 1994) (5), where D_c is the uptake diffusivity.

$$\frac{\partial q}{\partial t} = D_c(c)\frac{\partial^2 q}{\partial x^2}. \tag{5}$$

For isothermal particles and absence of other transport resistances, like the fluid film resistance surrounding the particles, the solution of Fick's second law equation may be used to calculate the transient uptake diffusivity.

For short times and low fractional uptakes a simplified solution has been provided for the manometric case (Chen 1994):

$$\frac{q_t}{q_{\inf}} = \frac{6(1+\alpha)}{\sqrt{\pi}}\sqrt{\frac{Dt}{r^2}} \tag{6}$$

where $\alpha = K_c V_s / V_g$; K_c is the adsorption equilibrium constant; V_s is the volume of the sample; V_g is the volume of apparatus, and q_t and $q_{\inf}$ are the adsorbed amounts at time t and at equilibrium, respectively.

The overall diffusion can be affected by heat effects or by a wide particle size distribution. The short time response is less susceptible to thermal effects and/or wide crystal size distribution (Kärger 1992), so it was used in this study for the calculation of diffusivity coefficients.

4 Results and discussion

4.1 Single component equilibrium adsorption data

Experimental data on single component adsorption isotherms and differential heats of adsorption, of n-hexane, 2-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane, on MFI zeolite, at 423 K, for a pressure range from 0.01 kPa to 250 kPa, were obtained.

The isotherms of the C_6-isomers are shown in Fig. 3. Branched hexane isomers present a Type I isotherm behaviour (Rouquerol 1999), therefore the classical Langmuir model given by (2) was used to fit the data. On other hand, n-hexane equilibrium data are better fitted by a dual site Langmuir model (1). The differential heats of adsorption as a function of coverage for the four isomers at 423 K are plotted in Fig. 4. For n-hexane the heat of adsorption presents an initial plateau with constant value, until adsorption loading value of 0.60 mmol·g^{-1}, afterwards presents a slight increase. This increase can be explained by adsorbate–adsorbate interactions. The heats of adsorption for the branched isomers present a continuous decrease with adsorption loading. This decrease is more pronounced for the case of 2,2-dimethylbutane. However, it can be generalized that the heats of adsorption have a "plateau" like behaviour, and the length of this "plateau" depends on the nature of the adsorbate. The final abrupt decrease of the differential heat of adsorption, presented by the four isomers, essentially corresponds to pore condensation. Gener et al. (2002) presents similar behaviour for the heats of adsorption of the C_6 isomers.

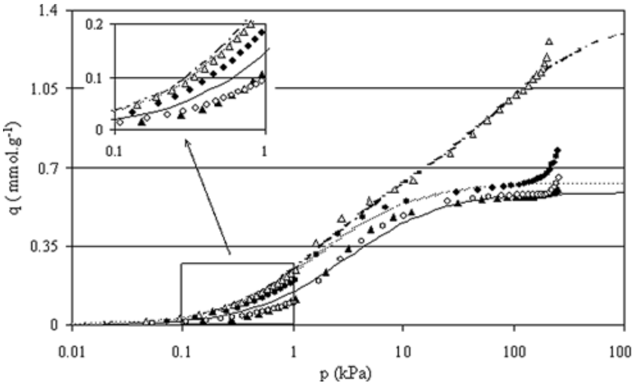

Fig. 3 Adsorption isotherms on MFI at 423 K. (△) n-hexane, (●) 2-methylpentane, (○) 2,3-dimethylbutane and (▲) 2,2-dimethylbutane. Lines are the isotherm model fits by (1) for n-hexane and (2) for branched isomers

By extrapolating the heat of adsorption (Fig. 4), Q, to zero coverage one gets an initial heat of adsorption Q_0, the values for the two isomers are summarized in Table 1.

The range of the experimental heats of adsorption presented by Vlugt (2000) for n-hexane is 60 kJ·mol^{-1} to 82 kJ·mol^{-1}, for 2-methylpentane is between 62 kJ·mol^{-1} and 90 kJ·mol^{-1}. These data are in agreement with the values presented in this study. Zhu et al. (2001b) reports estimated adsorption enthalpy for n-hexane, 2-methylpentane, and 2,3-dimethylbutane in silicalite-1 that are in agreement with ones presented by this study.

The equilibrium points at high loadings, with heats of adsorption less than 40 kJ·mol^{-1}, represent mainly pore con-

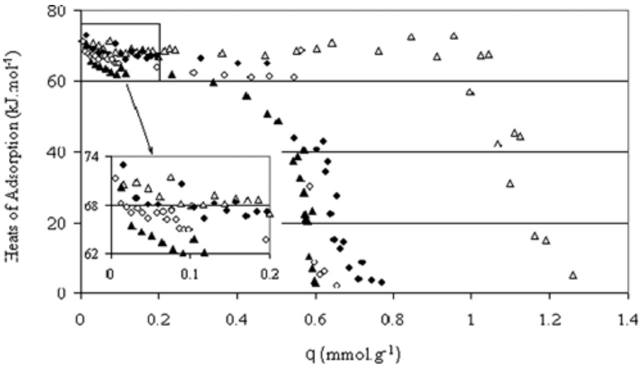

Fig. 4 Heats of adsorption on MFI at 423 K. (△) n-hexane, (●) 2-methylpentane, (○) 2,3-dimethylbutane and (▲) 2,2-dimethylbutane

Table 1 Initial heat of adsorption on MFI

Sorbate	Q_0 (kJ·mol^{-1})
n-hexane	71.0
2-methylpentane	70.7
2,3-dimethylbutane	68.2
2,2-dimethylbutane	68.0

Table 2 Langmuir K and q_{sat} parameters on MFI at 423 K

Sorbate	K_C (10^{-2} kPa^{-1})	$q_{sat,C}$ (mmol·g^{-1})	K_I (10^{-2} kPa^{-1})	$q_{sat,I}$ (mmol·g^{-1})	q_{max}[a] (m.u.c.)[c]
n-hexane	56.86	0.66	1.08	0.70	7.9
	160.13[b]	0.69[b]	2.17[b]	0.69[b]	8[b]
2-methylpentane	–	–	58.38	0.63	3.7
	0.01[b]	0.69[b]	96.91[b]	0.69[b]	8[b]
2,3-dimethylbutane	–	–	34.62	0.59	3.4
	–	–	31.98[b]	0.69[b]	4[b]
2,2-dimethylbutane	–	–	33.18	0.59	3.4

[a] Maximum amount adsorbed, $q_{max} = q_{sat,C} + q_{sat,I}$

[b] Zhu et al. (2001b)

[c] 1 molecule·(unit cell)$^{-1}$ = 0.173 mmol·g^{-1}

Table 3 Henry's Constant for hexane isomers on MFI at 423 K

Sorbate	K_H[a] (10^{-2} mmol·g^{-1}·kPa^{-1})	Kq_{sat}[b] (10^{-2} mmol·g^{-1}·kPa^{-1})
n-hexane	31.14	37.71
2-methylpentane	23.45	36.92
2,3-dimethylbutane	11.73	20.52
2,2-dimethylbutane	11.01	19.54

[a] Equation (3)

[b] Equation (4)

densation. Therefore, they weren't used in the fitting of adsorption equilibrium data to derive K and q_{sat} parameters. The parameters K and q_{sat} are reported on Table 2.

From Fig. 3 and Table 2 it can be concluded that n-hexane molecules occupy mainly the zeolite channels until a loading of 3.8 m.u.c., and then they start to be adsorbed in the intersections achieving a maximum loading of 7.9 m.u.c. When both sites are almost fully occupied, condensation on the inter-particle pores starts. On other hand, for the branched isomers the preferential site is the intersections and the maximum load tends to be lower than 4 m.u.c. Pore condensation starts straight after the intersections are almost totally occupied, not being observed adsorption on the channels (second site) like is reported by Zhu et al. (2001b) for 2-methylpentane. As expected, the saturation loading decreases with the degree of branching, but the adsorption equilibrium constant is similar for n-hexane and 2-methylpentane, and it is lower for 2,3-dimethylbutane and 2,2-dimethylbutane cases. When our experimental results are compared with Zhu et al. (2001b) results, it can be observed that value for K_I agrees on the case of 2,3-dimethylbutane only. For n-hexane and 2-methylpentane the values are in the same order of magnitude but do not agree very well. One possible reason is that Zhu et al. (2001b) consider $q_{sat,C}$ and $q_{sat,I}$ equal to 4 m.u.c., and not as fitting parameter in the Langmuir isotherm models. The value of 4 m.u.c. is the theoretical value that is derived from MFI structure and molecular simulations. Therefore, it is not introduced as parameter in the model, influencing the value of K obtained. On the inset of Fig. 3 can be observed that the Langmuir model over predicts the experimental data in the low pressures region. For n-hexane that over prediction is lower than for 2-methylpentane. Thus the value of K_I obtained for 2-methylpentane becomes similar to the value of K_C for n-hexane. The use of a fixed q_{sat} might not be correct; temperature dependence can exist due to change of the site adsorption energy with temperature and the conformational adsorption behaviour of n-hexane depends on temperature (Huang and Wang 2003).

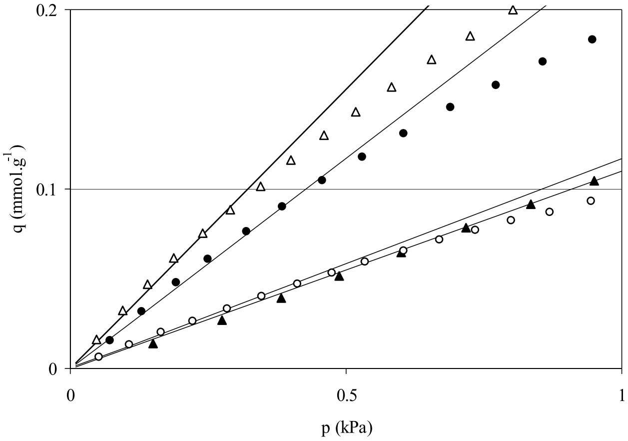

Fig. 5 Adsorption isotherms on MFI at 423 K. (△) n-hexane, (●) 2-methylpentane, (○) 2,3-dimethylbutane and (▲) 2,2-dimethylbutane at low pressures. Lines are the isotherm model fits by (3)

Henry constants were calculated by using (3) for the low-pressure data. The values derived are compared in Table 3 with ones obtained by applying the Langmuir model using the data at all pressures (4). Figure 5 presents the isotherms for the four isomers at low pressures and the fit obtain by (3) on Henry's region. It can be observed that the only the first points obey a linear relation (Henry's region). In the case of 2,2-dimethylbutane this linear behaviour is observed until higher pressures.

The Henry's constant decreases with increasing chain branching degree. The difference between the two values is due to the fact that the Langmuir isotherm models are over predicting the experimental results in the low-pressure area (see Fig. 3).

4.2 Single component transient volumetric uptake rate

Volumetric up-take results for *n*-hexane, 2-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane are presented in Fig. 6. These results are based on the spectroscopic experiments. Calibration models for single component and multicomponent cases were derived, and used to predict pressure drop in time. A more detailed description of the mathematical procedure is indicated in previous work (Ferreira et al. 2005).

The values of the diffusion time constants, defined as D/r^2, were calculated using (6). The obtained values are presented in Table 4 and compared with literature results. The calculations were performed only for the first equilibrium point (low loadings), using the short time solution (6), which reduces the influence of loading dependence and temperature effects (possible non-isothermal operation of the zeolites sample).

Table 4 Diffusion time constants for *n*-hexane isomers, on MFI, at 423 K

Sorbate	D/r^2 (s^{-1})	D/r^2 (s^{-1})[a]
n-hexane	2.51×10^{-3}	9.9×10^{-3}
2-methylpentane	2.06×10^{-3}	5.8×10^{-3}
2,3-dimethylbutane	1.54×10^{-3}	3.1×10^{-5}
2,2-dimethylbutane	4.00×10^{-5}	2.6×10^{-5}

[a] Gener et al. (2002) at 298 K

From Table 4 and Fig. 6 we can conclude that *n*-hexane, 2-methylpentane and 2,3-dimethylbutane have diffusion time constants in the same order of magnitude, but they decrease with increasing chain branching degree. It is striking that 2,2-dimethylbutane presents a diffusion time constant two orders of magnitude lower than the other 3 components. The results of Gener et al. (2002) are in agreement with ones found in this study, with exception of 2,3-dimethylbutane. For 2,3-dimethylbutane the difference between the results present in this study and the ones presented by Gener et al. (2002) is of two orders of magnitude. Based on adsorption kinetics of single component results, the separation between 2,2-dimethylbutane and the other 3 isomers would be possible.

4.3 Mixture adsorption data

Figure 7 shows adsorption equilibrium data for different binary mixtures: *n*-hexane + 2-methylpentane, *n*-hexane + 2,3-dimethylbutane, *n*-hexane + 2,2-dimethylbutane and 2-methylpentane + 2,3-dimethylbutane. The final gas composition of the mixtures is not constant, but it is about 50%–50% for the points at high pressure. This is due to the fact that the feeding mixture is 50%–50%, but as the components adsorb in different amounts, the final gas concentration in the system varies. The measurement was performed

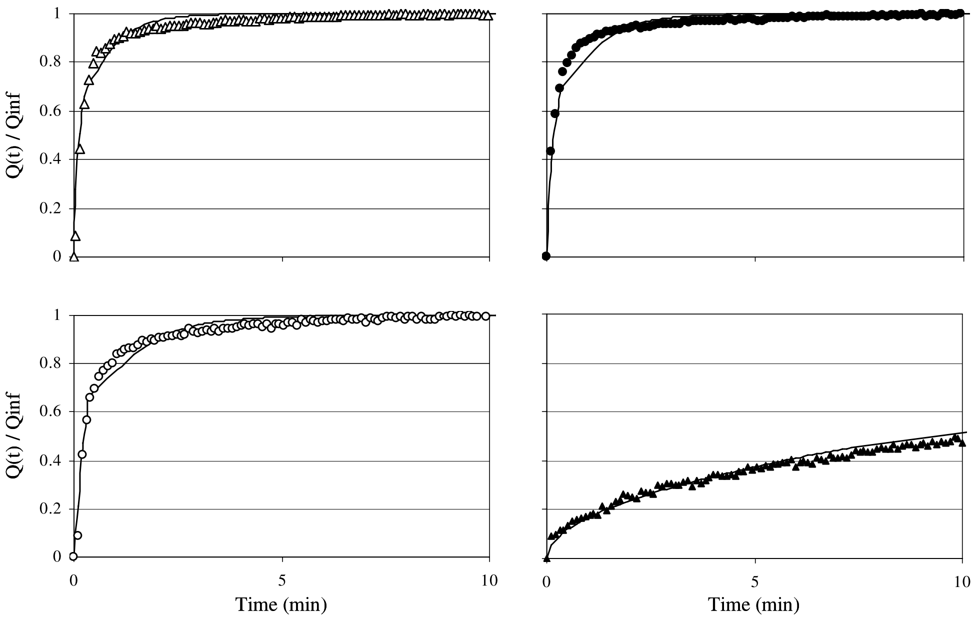

Fig. 6 Normalized Volumetric Uptake vs. time, on MFI, at 423 K. (△) *n*-hexane, (●) 2-methylpentane, (○) 2,3-dimethylbutane and (▲) 2,2-dimethylbutane. Full line is the fitted model by (6). The graphics have the same scale in both axis

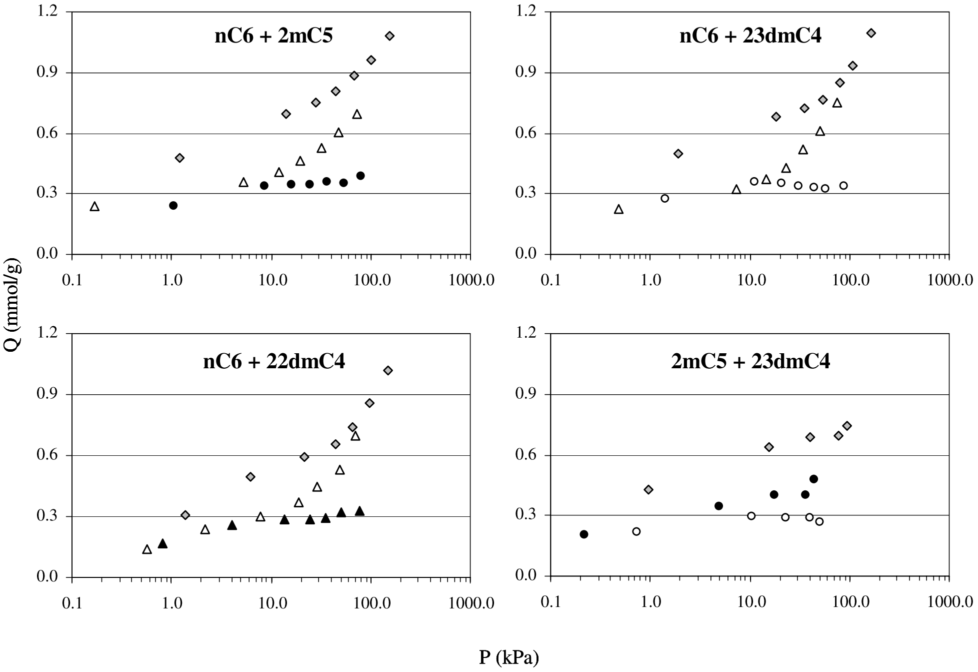

Fig. 7 Mixtures equilibrium data, on MFI, at 423 K. (△) *n*-hexane partial loading, (●) 2-methylpentane partial loading, (○) 2,3-dimethylbutane partial loading, (▲) 2,2-dimethylbutane partial loading, and (◇) total loading

in a continuous away for the 4 mixtures, so the final loading of one point is the initial loading for the following one. In the case of the mixture of *n*-hexane + 2-methylpentane, it can be observed that the amount adsorbed of 2-methyl pentane presents a plateau around 0.355 mmol/g, while *n*-hexane presents a continuous increase in the amount adsorbed. The plateau behavior for 2-methylpentane at a value lower than 0.63 mmol/g, which is the maximum loading for 2-methylpentane on the single component adsorption data, indicates that there is a competitive adsorption behavior for the two components in the mixture. The binary equilibrium selectivity for the point with total pressure of 101 kPa (total loading of 0.96 mmol/g) is 1.93. In the case of the mixture of 2,3-dimethylbutane + *n*-hexane, the amount adsorbed of 2,3-dimethylbutane does not present a plateau behaviour, but presents a maximum at around 0.355 mmol/g, decreasing afterwards with increase of (partial) pressure. However, *n*-hexane presents a continuous increase with (partial) pressure. Therefore, it can be concluded that *n*-hexane molecules can displace the 2,3-dimethylbutane molecules from the intersection at high pressures. The binary equilibrium selectivity for the point with total pressure of 109 kPa (total loading of 0.93 mmol/g) is 2.15. For the mixture of 2,2-dimethylbutane + *n*-hexane a behaviour similar to the mixture of 2-methylpentane + *n*-hexane is observed, but the amount adsorbed of 2,2-dimethylbutane achieves the plateau behaviour at higher pressures than for the case of 2-methylpentane mixture with *n*-hexane. The binary equilibrium selectivity for the point with total pressure of 98 kPa (total loading of 0.86 mmol/g) is 1.71. For these three mixtures the total loading presents a continuous increase with pressure. The increase in partial loading of 2-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane in the last equilibrium point can be explained by pore condensation, and therefore the selectivity can be affected at high pressures due to this phenomena. For the case of the mixture of branched isomers only (2-methylpentane + 2,3-dimethylbutane) the total amount adsorbed presents a plateau at the value of 0.69 mmol/g, this plateau is due to the plateau behavior observed for the amount adsorbed of both components, 0.29 mmol/g for 2,3-dimethylbutane and 0.40 mmol/g for 2-methylpentane.

The diffusion time constants for the 4 mixtures were calculated from the partial loadings, only for the 1st equilibrium point, using (3). The obtained values are presented in Table 5. The diagonal values are the single component diffusion time constants. When values of Table 5 are studied closely, one can observe that *n*-hexane diffuses slower in the mixture than when alone, but branched isomers diffuse faster, when mixed with *n*-hexane. Therefore, it can be concluded that when the two components co-diffuse inside of the zeolite, they interact, and in this case the difference between their diffusion time constant decreases.

This phenomenon becomes even more clear in the case of the mixture of 2,2-dimethylbutane + *n*-hexane. Figure 8 presents the normalized volumetric uptakes of *n*-hexane and 2,2-dimethylbutane as single components and in their 50%–50% binary mixture. The diffusion time constants for these two (single) components differ in more than one order of magnitude, however in the mixture they become almost equal. The influence of the 2,2-dimethylbutane in the mixture diffusion rate is higher than the *n*-hexane (Fig. 8).

Table 5 Diffusion time constants of Sorbate 1 when co-adsorbing with Sorbate 2, on MFI, at 423 K

	Sorbate 2			
	n-hexane	2-methylbutane	2,3-dimethylbutane	2,2-dimethylbutane
Sorbate 1				
n-hexane	2.51×10^{-3}	2.30×10^{-3}	2.15×10^{-3}	8.97×10^{-5}
2-methylbutane	2.40×10^{-3}	2.06×10^{-3}	1.90×10^{-3}	–
2,3-dimethylbutane	2.38×10^{-3}	1.45×10^{-3}	1.54×10^{-3}	–
2,2-dimethylbutane	1.13×10^{-4}	–	–	4.00×10^{-5}

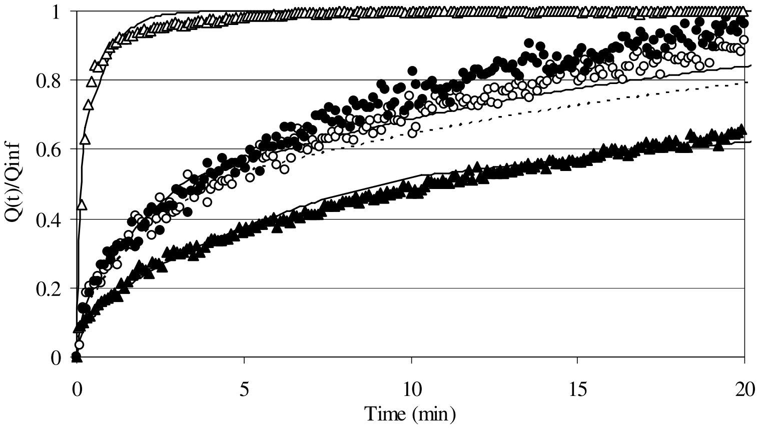

Fig. 8 Normalized volumetric uptake for *n*-hexane + 2,2-dimethylbutane mixture vs. time, compared with single components uptake, on MFI, at 423 K. (△) *n*-hexane, (●) *n*-hexane in the mixture, (○) 2,2-dimethylbutane in the mixture and (▲) 2,2-dimethylbutane. Lines are the fitted model by (6)

Even though the single component diffusion rates did point towards a possible separation of *n*-hexane from 2,2-dimethylbutane based on adsorption kinetics (e.g. RPSA), the binary mixture adsorption experiments (see Fig. 8) demonstrate the contrary. Therefore, separation factors presented in some literature based on single components data might just be a rough approximation, especially for not ideal systems. In the case of hexane isomers on MFI it will be possible to separate the mixture between linear and (mono/di) branched isomers based on adsorption equilibrium. This conclusion is supported by single and binary mixtures data (see Figs. 4 and 7).

5 Conclusions

At the temperature of 423 K the branched hexane isomers only adsorb on the intersections, while *n*-hexane adsorbs on the channels first, and only at higher coverage on the intersections. At the studied temperature, separation between *n*-hexane and its branched isomers might be possible based on equilibrium adsorption properties, however the equilibrium selectivity is only around 2. This is corroborated by the presented binary mixtures equilibrium results, where it can be observed that MFI is selective to *n*-hexane versus the hexane branched isomers. Pore condensation and/or adsorption in the non-crystalline part occur after the sites in the zeolite crystals are fully occupied.

The differential heats of adsorption when plotted against loading present a "plateau" behaviour, followed by a decrease at higher loadings. The latter is attributed to pore condensation. The diffusion time constant for *n*-hexane, 2-methylpentane and 2,3-dimethylbutane are in the same order of magnitude, but decrease with the degree of chain branching, the 2,2-dimethylbutane presents a diffusion time constant more than an order of magnitude lower than the other components. Based on the single components diffusion one could predict that 2,2-dimethylbutane could be separated from the order three components based on adsorption kinetics. However, when co-diffusion was measured in a mixture of *n*-hexane and 2,2-dimethylbutane it was observed that both diffuse at the same rate, and no separation would be possible by exploiting only adsorption kinetics. This is due to the fact that when two components co-diffuse inside of the zeolites structure (confined space with molecular dimension), they interact, and the difference between their diffusion time constants decreases.

From this work it can be concluded that for better understanding of the mixture's adsorption, followed by an accurate separation process design, one must address the real adsorption properties of the mixtures, and not use single component properties.

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