Thermodynamics and Kinetics of Adsorption of Selected Monoalkylbenzenes in H-ZSM-5

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Received: May 5, 1998; In Final Form: November 27, 1998

In this study, we present the first systematic investigation of the adsorption of *n*-propylbenzene, isopropylbenzene, and *n*-butylbenzene in H-ZSM-5. Both the sorption isotherms and the rate of sorption uptake were investigated at temperatures between 315 and 425 K. The adsorption isotherms are of type I and are reasonably well described by the Langmuir−Freundlich model. It is shown that the heat of adsorption of the longer sorbate molecules depends significantly on the concentration, thus indicating an increased influence of sorbate-sorbate interaction. The uptake rates are determined by Fickian diffusion. The activation energies for the diffusion process are identical for all systems (32−36 kJ/mol). The diffusivities are also in the same order of magnitude decreasing noticeably for sorbates with longer or more complex substituents. A tentative explanation based on a simple jump-rate model for intracrystalline diffusion is given.

I. Introduction

Zeolites of the MFI-type have been investigated extensively in the past because of their application in catalysis but also for separation processes. This type of zeolites is of major interest for the processing of benzene or other smaller aromatics. This is mainly due to the fact that the kinetic diameter of the aromatic ring (5.85 Å, see ref 1) is of approximately the same magnitude as the pore diameters of the MFI-type zeolites (5.3×5.6 and 5.1×5.5 Å, see ref 2). Adsorption and diffusion of aromatic molecules are therefore generally assumed to play an important role in reactions of aromatics over MFI-type zeolites.

Particular effects are generally observed with MFI-type catalysts if the various species participating in a reaction differ in the number, shape, or position of their substituents of the aromatic ring as this generally influences diffusion and adsorption inside the zeolite crystallite. In the case of xylenes or diethylbenzenes this leads to the phenomenon of product shape selectivity.[3,4] In the case of the xylene isomers, differences of the diffusivities in MFI-type zeolites have also been used as the basis of separation processes.[5]

It is, therefore, not surprising that a large number of publications has been dedicated to the investigation of various aspects of the adsorption of alkylbenzenes in pentasil-type zeolites, and much effort has been devoted to the investigation of the intracrystalline diffusion. Results were summarized, e.g., in refs 6 and 7. Heats of adsorption and sorption isotherms have been determined (see, for example, refs 8 and 9). The structural aspects of the host−guest system have also been investigated in some detail.[10,11] However, up to now the investigations have mainly been focused on the smaller aromatics, such as benzene, toluene, and the isomers of xylene. Although the literature data concerning the transport properties are contradictory to a certain extent, a general understanding of the adsorption equilibrium of the smaller aromatics in MFI-zeolites has been reached.

Investigations of adsorption and diffusion in MFI-type zeolites have only rarely been extended to ethylbenzene and higher substituted alkylbenzenes (see, for example, refs 12 and 13 and literature cited therein). This is probably due to the fact, that they are not of primary interest in most aromatics conversion reactions over H-ZSM-5, although they usually contribute to the product spectrum. However, it seems worthwhile to investigate the sorption and diffusion properties of those aromatics, too, in order to elucidate the interaction between adsorbed aromatics and the MFI-type zeolite system in general. Of special interest might be those molecules, the lengths of which are close to the distance between two adjacent channel intersections of the MFI lattice, for example, to *n*-propylbenzene and *n*-butylbenzene. We have therefore extended our previous investigations from the adsorption of ethylbenzene in H-ZSM-5[12] to that of *n*-propylbenzene, isopropylbenzene, and *n*-butylbenzene, focusing on the influence of the substituent attached to the benzene ring on the sorption and diffusion properties in MFI-type zeolites.

II. Experimental Section

II.1. Setup. The same constant volume/variable pressure-type apparatus as in our previous study was used for the present investigations[12] (see also Figure 1). In experiments with this type of device, the equilibrium state of the system consisting of the sorbate gas phase and the adsorbed phase is changed by a sudden increase of the pressure in the sorption volume. The sorption uptake is then monitored via the pressure decrease above the zeolite sample during the subsequent equilibration of the gas/zeolite system. In our apparatus, the kinetic curve can be monitored in the sorption chamber, so that the effects of gas expansion and sorption uptake can be clearly distinguished in the sorption kinetic curves.

The sample was spread as a thin layer on the bottom of the sorption chamber to minimize extraparticle mass transfer and to expedite good heat transfer. The pressure in the gas phase could be increased in small increments of less than 10 Pa to further minimize the effect of sorption heat release. The vacuum system was contained in a thermal insulation box ensuring a homogeneous temperature in the range measured between 315 and 425 K.

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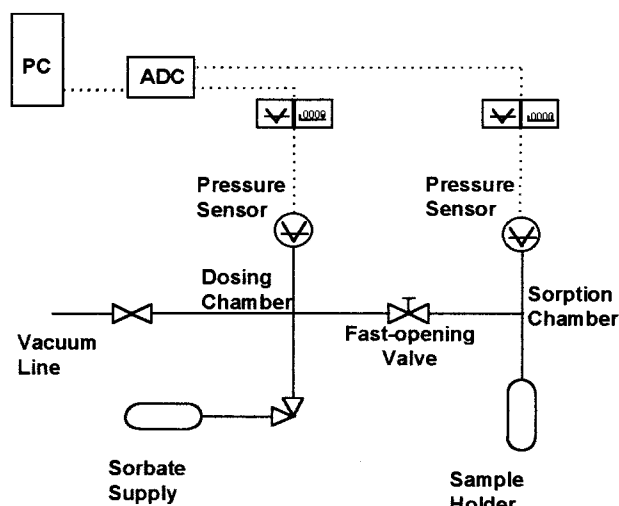
Figure 1. Apparatus of the barometric (volumetric) type used for this investigation.

This method offers the advantage of obtaining both the sorption equilibrium and the sorption kinetics data in the same experiment.

II.2. Evaluation. Adsorbed amounts were calculated from the pressure decrease taking into account the known volumes of dosing and sorption chambers. Plotting the adsorbed amount as a function of the equilibrium pressure at a constant adsorption temperature provided the adsorption isotherms. For each system, sorption isosteres were derived from the intersections between isotherms of different temperatures and lines of constant loading q. The heats of adsorption ΔH_{ads} were calculated from this data as a function of sorbate concentration according to

$$\Delta H_{ads} = \frac{d \ln(p)}{d(1/T)_{q=const}} \tag{1}$$

The curves of sorption kinetics were evaluated by fitting the analytical solution of Fick's second law under appropriate boundary conditions to the experimental data. The valve effect was taken into account as described in ref 14 to compensate for the finite rate of gas expansion in a real experiment. The Fickian diffusivities determined therefrom were corrected by Darken's correction.[15]

II.3. Samples. *N*-Propylbenzene, isopropylbenzene, and *n*-butylbenzene were purchased from Fluka Chemie at the highest available purity of >99.5%. The sorbates were further purified chromatographically utilizing activated Al_2O_3 as an adsorbent in order to remove oxidized species. Prior to the experiments, at least five freeze−pump−thaw cycles were performed with each sorbate to remove all impurities with a higher volatility.

The zeolite sample used for these investigations was a H-ZSM-5 synthesized by H. K. Beyer, Budapest. The n_{Si}/n_{Al} ratio was 34, and the average diameter of the crystallites 2.0 μm. The crystallinity of the sample was checked by XRD. Before each experimental run, the sample was heated in vacuum in the barometric apparatus. The heating rate was 2 K/min up to a temperature of 675 K, at which the sample was kept for 4 h.

III. Results

III.1. Sorption Equilibrium. The sorption isotherms obtained for the investigated systems are of type I according to the IUPAC classification. As shown in Figure 2a−c, the Langmuir−
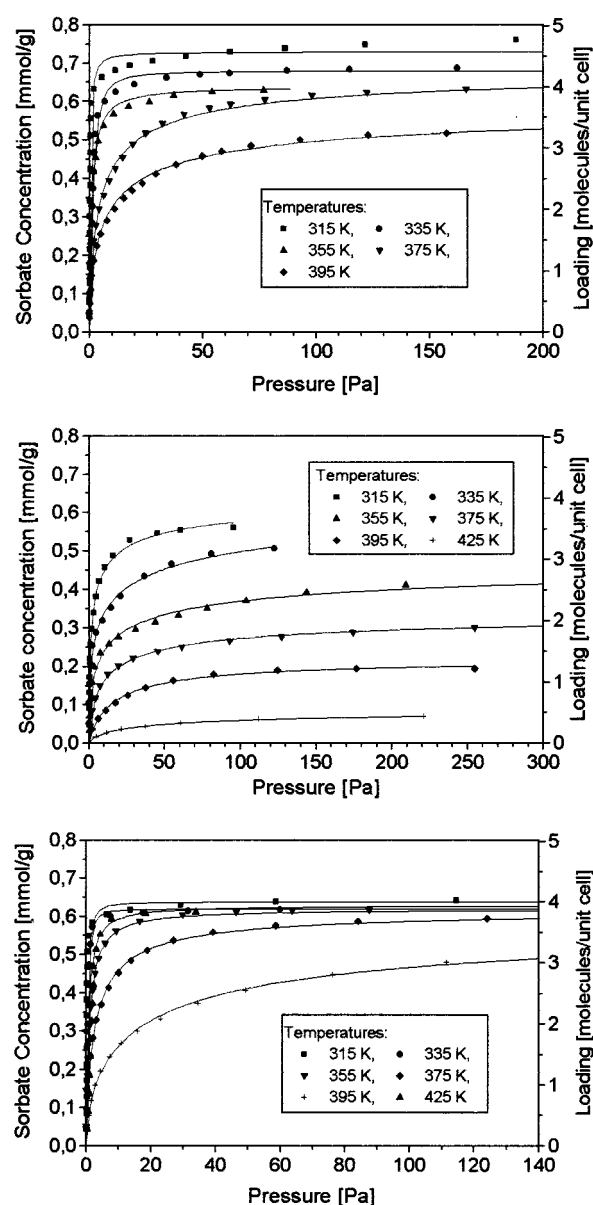

Figure 2. (a) Isotherms of adsorption for n-propylbenzene in H-ZSM-5. (b) Isotherms of adsorption for i-propylbenzene in H-ZSM-5. (c) Isotherms of adsorption for n-butylbenzene in H-ZSM-5.

Freundlich model (eq 2) generally gives a good description of the experimental observations:

$$n_{ads} = n_\infty \frac{bp^m}{1 + bp^m} \tag{2}$$

where n_{ads} is the amount adsorbed at a pressure p and a given temperature and n_∞ the final adsorption capacity. The coefficients for the model isotherms are given in Table 1. It can be derived from the presented data that the sorption capacity is approximately four molecules per unit cell or one molecule per channel intersection. For isopropylbenzene the isotherms are less steep (Figure 2b) and saturation does not seem to be reached, so that the respective values for n_∞ in Table 1 are extrapolated over a broad range and must be considered to be formal values. In particular, for *n*-propylbenzene and *n*-butylbenzene, the final capacities of about four molecules per unit cell seem to have been reached at the maximum pressures employed. This is in complete agreement with the proposal that the aromatic ring of benzene derivatives adsorbed in MFI-type

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J. Phys. Chem. B, Vol. 103, No. 9, 1999 **1479**

TABLE 1: Coefficients of Langmuir–Freundlich Model for the Isotherms of Adsorption

	n-propylbenzene			isopropylbenzene			*n*-butylbenzene		
T [K]	n_∞ [mmol/g]	b [Pa^{-m}]	m	n_∞ [mmol/g]	b [Pa^{-m}]	m	n_∞ [mmol/g]	b [Pa^{-m}]	m
315	0.76	3.8	1.1	0.66	0.66	0.51	0.63	3.6	1.5
335	0.68	0.53	1.5	0.64	0.35	0.39	0.62	2.8	1.7
355	0.62	1.2	1.0	0.51	0.31	0.48	0.65	1.1	1.0
375	0.69	0.34	0.67	0.28	0.24	0.78	0.62	1.0	1.0
395	0.60	0.29	0.61	0.24	0.085	0.85	0.62	0.45	0.8
425				0.092	0.079	0.68	0.62	0.18	0.62

zeolites is preferably located in the channel intersection.[10] Unfortunately, the data for isopropylbenzene is limited to lower loadings and is therefore less conclusive in this respect.

In order to achieve a deeper understanding of the observations, the heats of adsorption where calculated from the slope of the sorption isosteres. The plots of the isosteres are shown in Figure 3a–c, the heats of adsorption are given in Figure 3. The data reported previously for ethylbenzene[12] is also included for comparison. The reliability of this method was shown by the excellent agreement of the data determined for ethylbenzene with those reported from the microcalorimetric measurements of Thamm[8] and the microcalorimetric and isosteric measurements of Niessen et al.[16] Unfortunately, evaluation of the isosteric plots becomes somewhat more difficult for adsorbates, such as *n*-propylbenzene and *n*-butylbenzene, where the sorption isotherms are relatively steep in the initial region. As the isotherms for those two systems are relatively close to each other, which is in fact a consequence of the low heat of adsorption, the evaluation of the sorption isosteres becomes even more difficult. Therefore, the relative uncertainty of the heats of adsorption runs up to about 60% for some data points and an evaluation was impossible for loadings lower than 1 molecules per unit cell (cf. Figure 4). Nevertheless, the qualitative results are not affected by the undesirably high experimental uncertainty of the data. The investigated systems can obviously be divided into two different groups. Whereas the heat of adsorption remains more or less independent of sorbate loading for the shorter molecules, ethylbenzene and isopropylbenzene, the heat of adsorption increases with sorbate loading for the longer molecules, *n*-propylbenzene and *n*-butylbenzene. It can also be seen that the initial heat of adsorption becomes lower as the length of the substituents increases. The heats of adsorption of ethylbenzene and isopropylbenzene are both around 75–80 kJ/mol, while the initial heats of adsorption rather seem to be about 40–50 kJ/mol and about 10 kJ/mol for *n*-propylbenzene and *n*-butylbenzene, respectively.

III.2. Sorption Kinetics. As can be seen from Figure 5a–c, the sorption uptake of the alkylbenzenes was in close agreement with the Fickian model of diffusion. In particular, deviations in the long-time region as reported in refs 7 and 17 were not observed in these experiments. However, in some experimental runs, the rate of adsorption was too high to be evaluated due to the relatively steep sorption isotherms. Therefore, the range of concentration in which diffusivities could be determined is slightly more limited than in our previous investigations.[12] As can be seen from Figure 6a–c, the Darken-corrected diffusivity is independent of sorbate concentration at lower loadings, i.e., distinctly below the critical value of four molecules per unit cell and decreases dramatically at loadings close to it. Whereas the temperature dependence of the critical concentration was very pronounced in the case of ethylbenzene (see ref 12), it is still obvious for *n*-propylbenzene and also occurs, to a lesser extent, with *n*-butylbenzene.

The energy of activation for the diffusion could be determined (see Figure 7 and Table 2; data from ref 12 is also included)

TABLE 2: Intracrystalline Diffusivity Data (Data from ref 12 included)

	energy of activation E_A [kJ/mol]	diffusivity at $T = 375$ K D [cm^2/s]
ethylbenzene	34 ± 3	$(1.3 \pm 0.2) \times 10^{-10}$
n-propylbenzene	36 ± 6	$(3.4 \pm 0.2) \times 10^{-11}$
n-butylbenzene	32 ± 6	$(1.9 \pm 0.5) \times 10^{-11}$
isopropylbenzene	35 ± 2	$(8.9 \pm 0.3) \times 10^{-12}$

from the data in that concentration range where constant diffusivity was observed. It is evident that the activation energies are identical within the limits of experimental uncertainty. From Figure 6 it is also obvious that the absolute values of the diffusivities vary slightly but systematically. Table 2 shows the data of the Darken-corrected diffusivities of the different systems at 375 K for comparison.

IV. Discussion

The equilibrium properties of the systems MFI/adsorbed alkylaromatics may be best explained on the basis of the concentration dependence of the heat of adsorption. As mentioned above, the four systems can be easily subdivided into two groups.

In principle, the observations should be correlated to the structural properties of the sorbate molecule and the zeolite. Unfortunately, no crystallographic data is available for these host–guest systems. Therefore, the position of the guest molecules inside the zeolite framework is not precisely known. For the smaller aromatic sorbates such as benzene, toluene, and p-xylene, however, it is well-known that the aromatic ring is located in the channel intersections of the MFI-framework, at least at sorbate concentrations below four molecules per unit cell (see, for example, ref 10). It is therefore at least likely that this is also true for the sorbates investigated here. This would mean that the more compact molecules of ethylbenzene and isopropylbenzene are more or less restricted to the region of the channel intersections. As the distance between the channel intersections is too large, direct sorbate–sorbate interaction cannot occur. The heat of adsorption is essentially determined by the interaction with the zeolite lattice and does not change much with the sorbate concentration.

The larger molecules on the other hand do not completely fit into the channel intersections. At least part of the alkylgroups will be located in the channels. Considering the fact that the alkylgroups do not form straight radial lines from the center of the benzene ring, but have a more complicated geometrical structure due to the nature of the C–C bonds, it is plausible that the molecules fit less efficiently into the MFI-structure, the longer their substituting group is. Apparently, parts of the adsorbed molecules are so close to the walls of the zeolite channels that the repulsive part of the interaction potential becomes operative. As the repulsive part of the interaction potential is extremely steep, even small structural misfits can lead to major contributions to the sorption energy. Some energy has to be spent on the deformation of the sorbate molecule (for
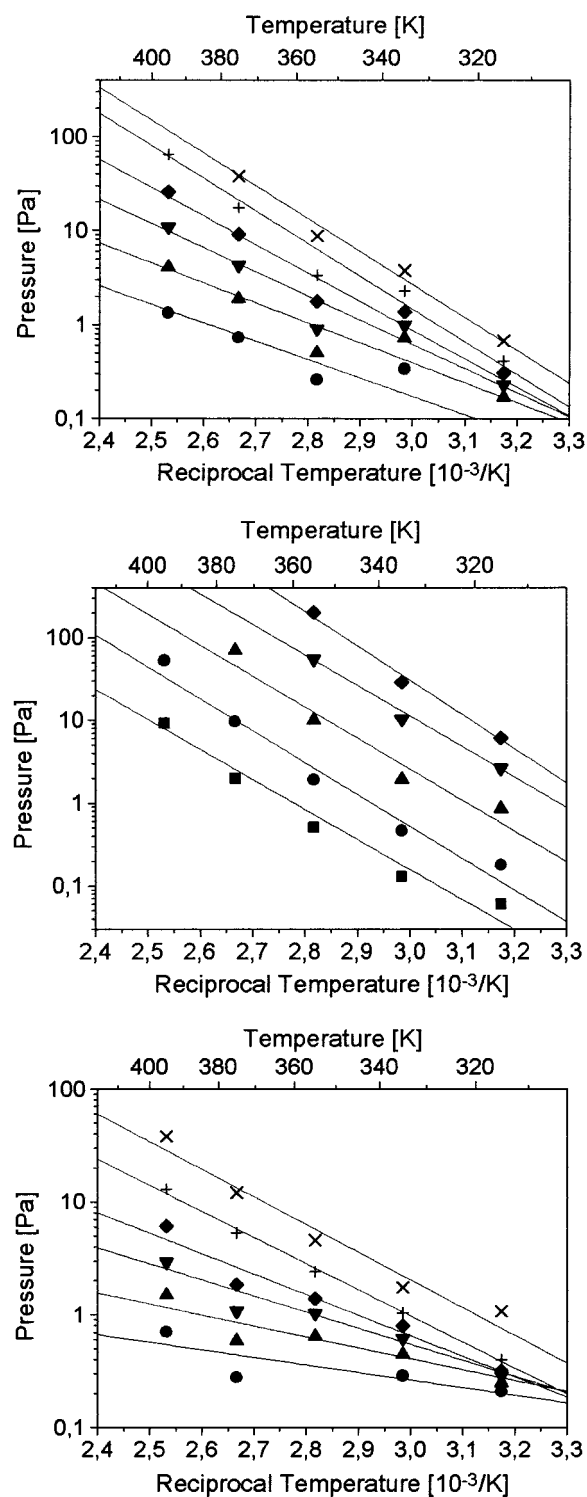
Figure 4. Concentration dependence of the heats of adsorption determined from the isotherms of adsorption of the various sorbates in H-ZSM-5. Data from ref 12 is included. Error bars indicate absolute uncertainty.

it is known that interaction of the methyl groups with the system of π-electrons of the sorbate molecules plays a role in the adsorption of p-xylene at higher loadings.[11] Because of the length of the *n*-propyl and the *n*-butyl group a similar interaction seems to be possible. Possibly this is the molecular basis for the observed increase of the heat of adsorption upon increasing loading with *n*-propylbenzene and *n*-butylbenzene.

This view is supported by a simple estimate of the geometrical proportions of the investigated sorbate molecules and the channel system of the MFI-type structure. The distance between the channel intersections of the MFI-structure is approximately 1.0 nm for both types of channels, straight as well as sinusoidal.[2] The length of the sorbate molecules can be estimated from the data for bond lengths, bond angles, and van der Waals radii. This results in a length of 0.90 nm for ethylbenzene and *n*-propylbenzene, 1.02 nm for *n*-propylbenzene, and 1.15 nm for *n*-butylbenzene. Apparently this is not sufficient for a noticable sorbate−sorbate interaction in the case of the shorter molecules but is enough to render interactions of the longer molecules possible in the adsorbed phase.

One of the well-established technical applications of zeolites is their use as adsorbents for separation or purification purposes. This is of particular interest when isomers have to be separated since their boiling points are often very similar. In the case of the propylbenzene isomers the boiling points differ by only about 7 K, so that their separation by distillation is tedious. It seems to be interesting to explore the potential of MFI-type zeolites for the separation of *n*-propylbenzene and isopropylbenzene as a preliminary step in the industrial phenol process.[18] Comparing the sorption equilibria of the propylbenzene isomers, two differences are obvious. Firstly, in the initial regions the isotherms of *n*-propylbenzene are much steeper; secondly, the heat of adsorption is clearly higher for isopropylbenzene. This means that at low pressures the isopropylbenzene isomer is likely to be preferentially adsorbed from the mixture. Assuming, for example, that a gas mixture with the ratio of 0.1 Pa *n*-propylbenzene/10 Pa isopropylbenzene (i.e., an impurity of 1%) was used, the hypothetical concentration ratio in the adsorbed phase can be calculated on the basis of the single-component isotherms. The data in Table 3 shows that under these conditions the ratio of the concentrations of *n*-propylbenzene vs isopropylbenzene is higher by a factor of about 30 in the adsorbate compared to the gas phase. However, this holds true only in the case where the overall sorbate concentration inside the zeolite is significantly lower than the sorption capacity. Oth-

Figure 3. (a) Adsorption isosteres for *n*-propylbenzene in H-ZSM-5. Loading: (■) 0.5, (●) 1.0, (▲) 1.5, (▼) 2.0, (◆) 2.5, +3.0, ×3.5 molecules/unit cell. (b) Adsorption isosteres for isopropylbenzene in H-ZSM-5. Symbols as in a. (c) Adsorption isosteres for *n*-butylbenzene in H-ZSM-5. Symbols as in a.

example, alteration of bond angles or bond lengths, change of conformation). This would explain the remarkably low value of the heat of adsorption for *n*-butylbenzene and *n*-propylbenzene.

At the same coverage, the molecules of *n*-propylbenzene and *n*-butylbenzene will fill the void volume to a much larger extent than, for example, ethylbenzene and, therefore, direct sorbate−sorbate interaction is also likely. For the system *p*-xylene/MFI,
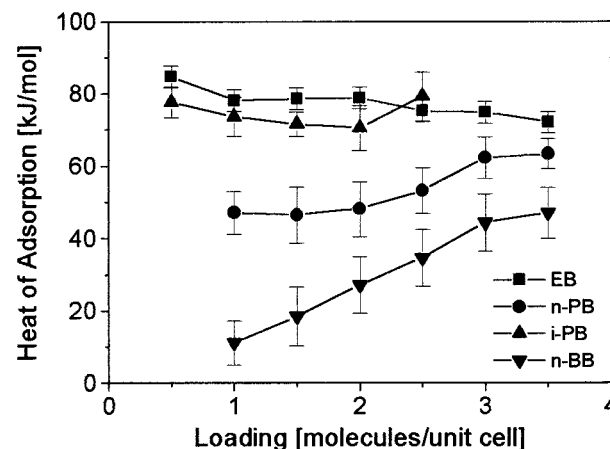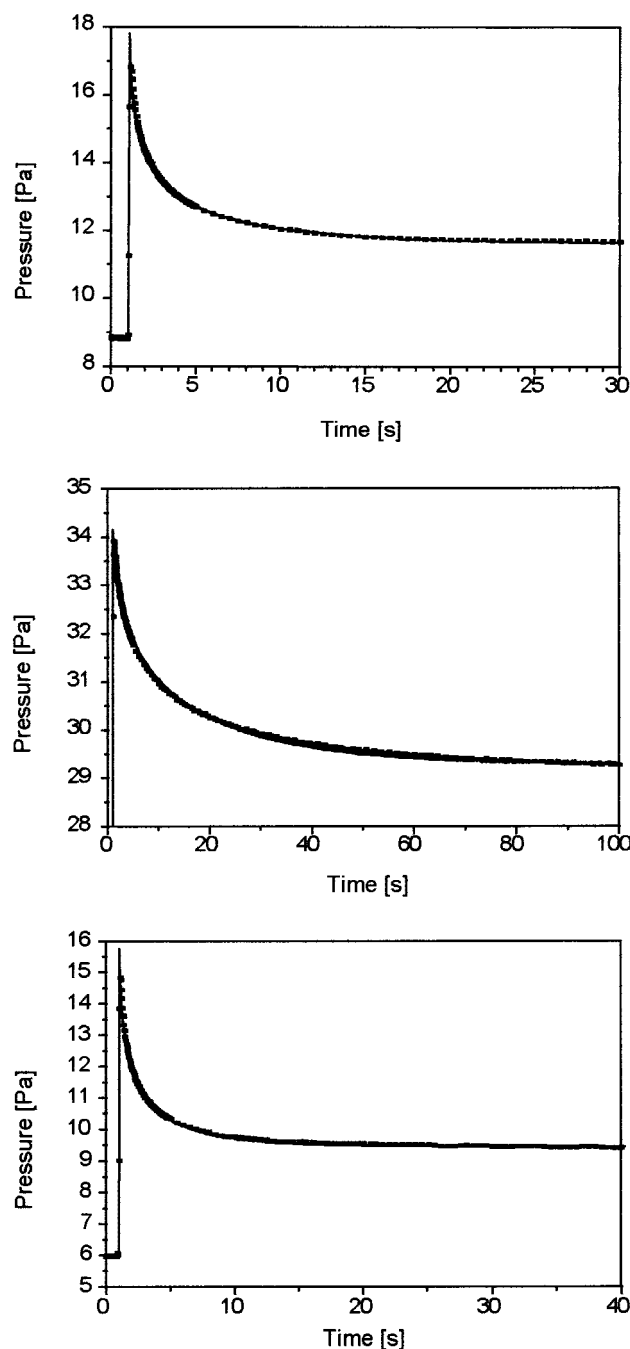
Figure 5. (a) Kinetic curve for *n*-propylbenzene adsorption into H-ZSM-5. $T = 395$ K. Solid curve corresponds to the solution of Fick's second law. (b) Kinetic curve for isopropylbenzene adsorption into H-ZSM-5. $T = 395$ K. Solid curve corresponds to the solution of Fick's second law. (c) Kinetic curve for n-butylbenzene adsorption into H-ZSM-5. $T = 425$ K. Solid curve corresponds to the solution of Fick's second law.

erwise the component with the higher heat of adsorption will prevail over the component with the lower heat of adsorption and no purification will be achieved. Thus, a separation of the propylbenzenes over MFI-type zeolites has to be conducted either at low partial pressures or at higher temperatures. In fact, this could mean that separation is technically possible but economically unfavorable.

In contrast to the clear differences of the equilibrium properties between the two distinct groups of sorbates, their transport properties differ only gradually. For all systems the concentration dependence of the diffusivities is in agreement with the observations reported for ethylbenzene/H-ZSM-5 in
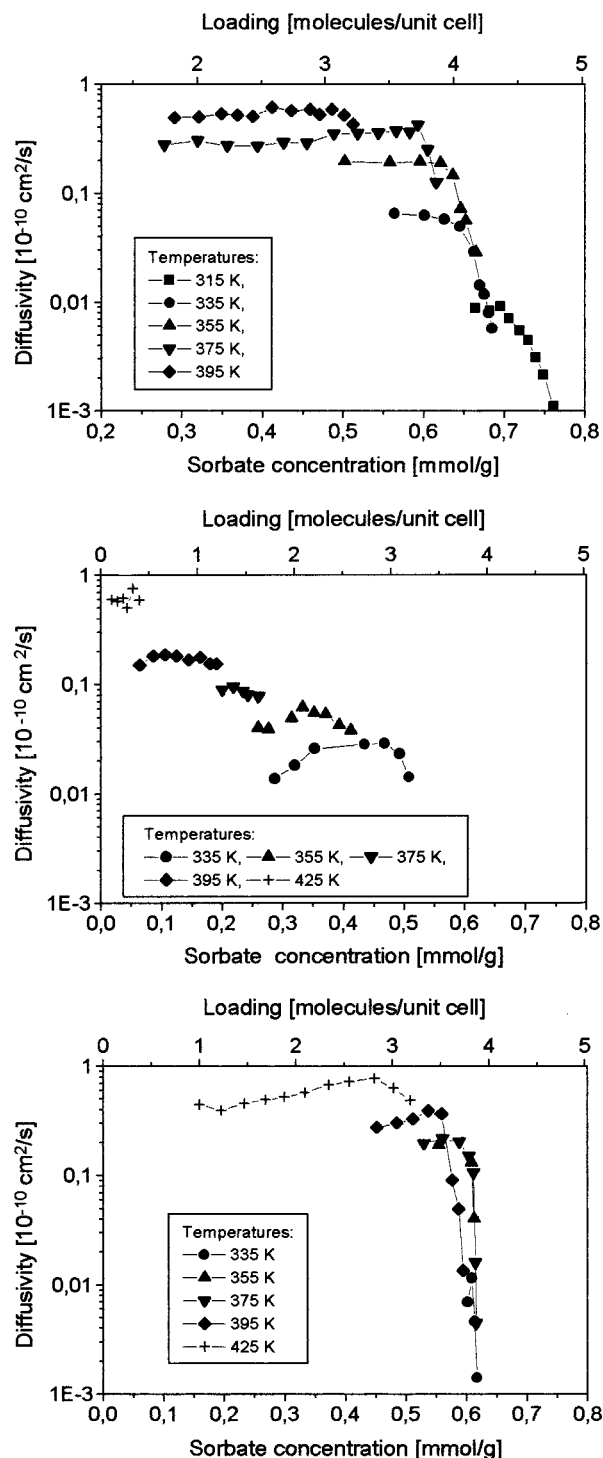

Figure 6. (a) Effect of concentration and temperature on the diffusivity of n-propylbenzene in H-ZSM-5. (b) Effect of concentration and temperature on the diffusivity of isopropylbenzene in H-ZSM-5. (c) Effect of concentration and temperature on the diffusivity of *n*-butylbenzene in H-ZSM-5.

ref 12, i.e., it is of type II according to the classification by Kärger and Pfeifer.[19] However, as the present investigations do not add any further information to that of ref 12, the concentration dependence will not be discussed in more detail.

As shown in Figure 7 and Table 2, the activation energy of diffusion is identical for all four sorbates. This means that the energy difference between the ground state and the transition state is approximately equal for all four sorbate species. It has to be kept in mind that the activation energy is the additional amount of energy necessary for an adsorbed molecule to jump
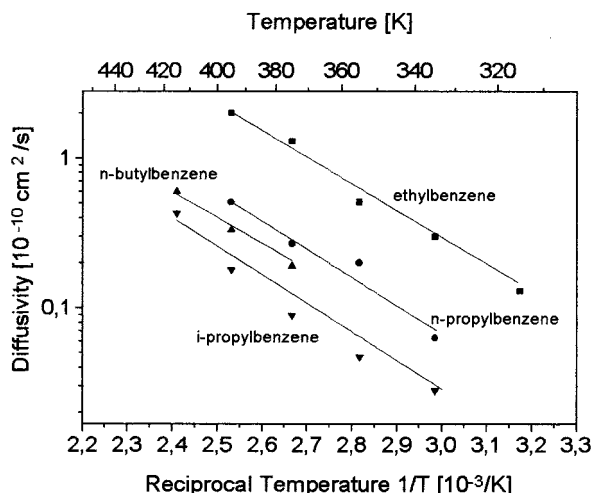
Temperature [K]

Figure 7. Comparison of the diffusivities of the investigated alkyl-benzenes in H-ZSM-5. Data of ref 12 included.

TABLE 3: Comparison of the Adsorption Properties for the Propylbenzene Isomers

temperature [K]	sorbate concentration of isopropylbenzene at a pressure of 10 Pa [mmol/g]	sorbate concentration of *n*-propylbenzene at a pressure of 0.1 Pa [mmol/g]	concentration ratio between *n*-propylbenzene and isopropylbenzene
315	0.80	0.31	0.39
335	0.61	0.20	0.32
355	0.43	0.11	0.26
375	0.30	0.084	0.28
395	0.25	0.070	0.28

from one equilibrium position to the next. There is no direct correlation between the heat of adsorption and the activation energy. For systems in which the diameters of the molecule and the zeolite channel are close, the transition state between two equilibrium states may be visualized as that configuration in which the smallest cross section of the sorbate molecule is located at the smallest cross section of the channel (see also ref 20 for the case of benzene). The activation energy is then determined by the additional energy contribution due to the interaction of the sorbate molecule with the zeolite walls in the transition state. As the kinetic diameter of all sorbates investigated is determined by the benzene ring, the additional energy contribution determining the difference between ground state and activated state is the same for all systems. In other words, a marked difference in the activation energies cannot be expected.

Considering diffusion as motion via activated jumps, the diffusivities of the investigated sorbates should also be rather similar. Closer analysis of the data shows, however, that the nature of the substituent does have a significant influence on the value of the diffusion coefficient; it affects the value of the diffusivity via the preexponential factor. In a simple jump-rate model, the preexponential factor represents the number of jump attempts which are successful, if the energy of the molecule is larger than the activation barrier.

In the jump-rate model the energy criterion, as given by the Arrhenius factor, is not the only one which has to be fulfilled for a successful jump attempt. Inside a zeolite the directions in which diffusive motion can occur are limited to the directions of the channel system. It is therefore not sufficient to raise the energy of a jumping particle over the activation barrier, but in addition the direction of motion (i.e., of the momentum of the

moving particle) must coincide with the direction of the channel. This leads to an additional decrease of the number of successful jump attempts. This effect does not depend on the temperature and is therefore not accounted for by the exponential term but rather by the preexponential factor. In principle, a quantitative estimation of the proposed effect seems to be possible assuming cylindrical pores and a cylindrical molecule. However, since neither rotation/libration of the sorbate molecule around its equilibrium position nor the atomic structure of both the molecule and the zeolite can be taken into account, this model seems to be far from applicability. Thus, the following argument is restricted to qualitative considerations.

As the angle in which translational motion of the adsorbed molecule is possible decreases with increasing length of the molecule, one may expect that the number of successful jump attempts are lower for longer adsorbed species than for shorter adsorbate molecules, even if their kinetic diameters are identical. The same argument is also valid in case of more complex structures such as isopropylbenzene where the angle of motion is also decreased.

V. Conclusions

The structure of the alkylbenzenes becomes less suited to the channel system of the MFI-framework with increasing length of the substituent. This results in a decrease of the heat of adsorption. As the length of the sorbate molecules approaches the distance between two channel intersections, this effect is partly compensated by the increasing sorbate-sorbate interaction.

Comparison of the adsorption data of ethylbenzene and isopropylbenzene shows that the structure of the substituent plays only a minor role as far as the equilibrium properties of the sorbate phase are concerned.

The diffusivities are similar for all sorbates investigated in this study. The activation energies are identical within the experimental error, thus indicating that this quantity is essentially determined by the kinetic diameters of the molecules as given by the cross section of the aromatic ring. Increasing the length or the complexity of the substituent leads to a slight decrease of the diffusivity. This can be interpreted on the basis of a simple jump-rate model, ascribing this effect to larger orientational restrictions in the case of longer molecules which lowers the preexponential factor.

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