SORPTION AND SORPTION KINETICS OF ETHYLBENZENE IN MFI-TYPE ZEOLITES STUDIED BY A BAROMETRIC TECHNIQUE

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The sorption and sorption kinetics of ethylbenzene in H-ZSM-5 zeolites was studied varying the experimental conditions over a broad range of temperature and concentration. Isotherms and heats of adsorption as well as intracrystalline diffusivities have been determined. The isosteric heat of adsorption decreases with increasing sorbate loading due to repulsive sorbate–sorbate interaction. The diffusivity remains independent of sorbate concentration at loadings lower than a critical value of about four molecules per unit cell, while a sharp decrease is observed at higher loadings. The critical concentration slightly depends on the temperature. The relationship between diffusivity, concentration and temperature can be tentatively interpreted in terms of a complex sorbate–sorbent interaction.

Key words: Sorption; Diffusion; Ethylbenzene; Zeolites; Hydrocarbons.

Sorption and sorption kinetics of hydrocarbons in zeolites are of considerable scientific as well as industrial interest due to the relevance in catalysis and in separation processes. Especially conversion processes of aromatics within ZSM-5 zeolites are assumed to be largely influenced by transport phenomena.

A considerable amount of work has been spent on the investigation of sorption and sorption kinetics of light paraffins as well as smaller aromatic molecules in MFI-type zeolites such as benzene, toluene and the xylene isomers. The investigations have occasionally also been extended to higher substituted aromatics. Results for aromatics adsorption in MFI-type zeolites are summarized in refs[1–3], for example.

For the sorption of ethylbenzene in MFI-type zeolites, Thamm[4] has published a calorimetric investigation. Diffusivity data were first reported by Wu *et al.*[5]. In the more actual literature investigations of the transport processes with various techniques have been reported by Ruthven *et al.*[6] (zero-length chromatography, ZLC), Niessen *et al.*[7] (FTIR sorption uptake) and Rees and Shen[8] (frequency response). Each of the four publications mainly deals with the temperature dependence of the diffusivity and the comparison with different sorbates, not investigating the concentration dependence in great detail.

It is the aim of our present study to investigate the concentration dependence of the intracrystalline diffusivity of ethylbenzene in MFI-type zeolites more closely focussing on the concentration dependence. Therefore, we have measured the sorption and sorption kinetics of ethylbenzene for loadings up to about four molecules per unit cell and for temperatures between 315 and 425 K.

EXPERIMENTAL

Apparatus

The experiments were conducted with a barometric device similar to those used in refs[9–11]. The barometric principle is based on the idea of producing a pressure step in the gas phase surrounding a sorbent sample and monitoring the subsequent pressure decrease due to the sorption process. In order to produce a pressure step, the gas phase of the apparatus is separated into two parts interconnected by a fast-opening valve as shown in Fig. 1. The sorbent is placed in the sample volume, whereas a well-defined quantity of gas is expanded from the dosing volume by opening the valve. In our apparatus, the pressure can be simultaneously monitored in the dosing volume and the sample volume. The membrane pressure sensors used are of type 617-00100 and 317-00010, respectively, purchased from MKS Instruments, Munich, Germany.

Compared to previous experiments based on the barometric principle[10,11], monitoring of the pressure in the sample volume offers the opportunity to distinguish directly between the pressure rise due to the gas expansion and the pressure decrease due to the sorption process, which is more difficult if the pressure can be monitored in the dosing volume only. The expansion of the sorbate gas does not occur infinitely fast. In the literature, this has been referred to as the valve effect (see, *e.g.*, ref.[12]). The theoretical limit of this method is therefore

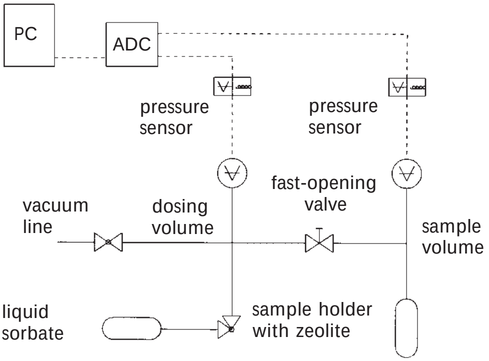

FIG. 1
Barometric apparatus

given by the finite time of gas expansion, which can be determined by blank experiments. The valve effect has to be taken into account for the evaluation of kinetics curves as described below.

Sorbate and Sample

The H-ZSM-5 zeolite sample used in the present study was provided by Dr H. K. Beyer, Budapest. The crystallites were of approximately spherical shape with an average diameter of $2R = 2.0$ µm. The Si/Al ratio determined by AAS was 34. Each sample was activated for four hours at 670 K prior to each experimental run.

Ethylbenzene was purchased from Fluka with purity of spectroscopic grade. To remove oxidized species, the sorbate was further purified chromatographically by passing it through an adsorption column (Al_2O_3) and by several freeze-pump-thaw cycles.

Methods and Evaluation

The experimental determination of transport coefficients by sorption kinetic methods consists of two independent steps. Besides monitoring sorption uptake rates as described above, a suitable method of evaluation for determining the transport coefficients has to be chosen.

The model used in the present study is essentially based on Fick's second law of diffusion for the sorbate concentration, *c*, within a spherical sorbent with radius *R*, where *r*, *t* and *D* are the space and time coordinates and the diffusivity, respectively:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right); \qquad 0 \le r \le R . \tag{1}$$

The boundary condition at the outer surface of the sphere is given by Henry's law relating the gas phase pressure *p* and the sorbate concentration at the outer surface of the crystallite:

$$p(t)/RT = Kc(r = R,t) . \tag{2}$$

For symmetry reasons, the boundary condition at the centre of the sphere is given by

$$\left.\frac{\partial c}{\partial r}\right|_{r=0} = 0 . \tag{3}$$

An additional equation is necessary for the description of the finite rate of gas expansion within the expansion time t_δ, *viz*.

$$\left[V_{\text{gas}}\ \dot{p}(t)/RT + V_{\text{sorbent}}\ \dot{\bar{c}}(t)\right] = \varphi_0 \times \begin{cases} 0; & t < 0 \\ \dfrac{1}{t_\delta}; & 0 \le t \le t_\delta \\ 0; & t_\delta \le t \end{cases} . \tag{4}$$

Equation (*4*) expresses the fact that the total amount of sorbing species in the sample volume increases by the value φ_0 within $t = 0$ and $t = t_\delta$, but remains constant afterwards.

This set of equations can be solved by analytical methods. Details of the derivation will be published elsewhere[13]. The solution is:

$$p(t) = p_\mathrm{v} + \frac{p_0 - p_\mathrm{v}}{1+\alpha} \times \begin{cases} 0 & ; \quad t < 0 \\ \dfrac{1}{\beta t_\delta} \times \left[\dfrac{\alpha}{15(1+\alpha)} + \beta t - \displaystyle\sum_{n=1}^{\infty} a_n \mathrm{e}^{-u_n^2 \beta t} \right] & ; \quad 0 \le t \le t_\delta \\ 1 + \dfrac{1+\alpha}{\beta t_\delta} \displaystyle\sum_{n=1}^{\infty} a_n \mathrm{e}^{-u_n^2 \beta (t - t_\delta)} \times (\mathrm{e}^{-u_n^2 \beta t_\delta} - 1) & ; \quad t_\delta \le t \end{cases} \qquad (5)$$

In Eq. (*5*) p_v denotes the pressure of sorbing species in the sample volume prior to the beginning of the kinetic run, p_0 stands for pressure which would be established in the gas phase after time t_δ in the absence of the sorbent and a_n and u_n are given as:

$$a_n = \frac{6\alpha(1+\alpha)}{9\alpha(1+\alpha)u_n^2 + u_n^4} \quad \text{and} \qquad (6)$$

$$\tan(u_n) = \frac{u_n}{1 + u_n^2 / 3\alpha} , \qquad (7)$$

and

$$\alpha = K \frac{V_\mathrm{sorbent}}{V_\mathrm{gas}} ; \qquad \beta = \frac{D}{R^2} . \qquad (8a,\ 8b)$$

In each experimental run, the quantities p_v and p_0 can be determined by direct measurement, while t_δ is known from blank experiments performed previously. The parameter α can be calculated from known quantities, while β is determined by fitting Eq. (*5*) to the experimental data.

This procedure offers the opportunity to check the experimental data for additional processes which might disturb the principal mechanism of sorption. Thus, curves severely influenced by such effects like intercrystalline diffusion or extensive sorption heat release can be identified on the basis of deviations between the experimental and theoretical curves. As the crystallite size is known from electron microscopical data, a value for the intracrystalline diffusivity can be calculated. The diffusivity is assumed to be constant during a single uptake step, which is reasonable as only small pressure steps (<10 Pa) were applied and the sorbate concentration did not change significantly during a single experimental run. Corrected intracrystalline diffusivities have been determined *via* Darken's equation[14].

RESULTS

Sorption Equilibrium

From the observed data, sorption isotherms can be determined with little effort. Results are presented in Fig. 2 for six different temperatures between 315 and 425 K. All the isotherms are obviously of type I according to IUPAC classification[15].

Experimental data does not follow a simple Langmuir model, while a Langmuir–Freundlich equation gives a reasonable description of the data. From the experimental data it is obvious that the coverage clearly decreases with increasing temperature. The maximum loading achieved in our experiments never exceeded six molecules per unit cell. From comparison with the sorption experiments with *p*-xylene a saturation capacity of eight molecules per unit cell would have been expected. Although a capacity of six molecules would be in agreement with the results of Thamm[4], limitations of our apparatus do not permit experiments at higher pressures, so that no statement on the saturation capacity for ethylbenzene can be made on the basis of our own experiments.

From the data given in Fig. 2, sorption isosteres have been determined and the corresponding isosteric heats of adsorption have been evaluated. These are displayed in Fig. 3. The calorimetric data of Thamm (*cf.* ref.[4]) and

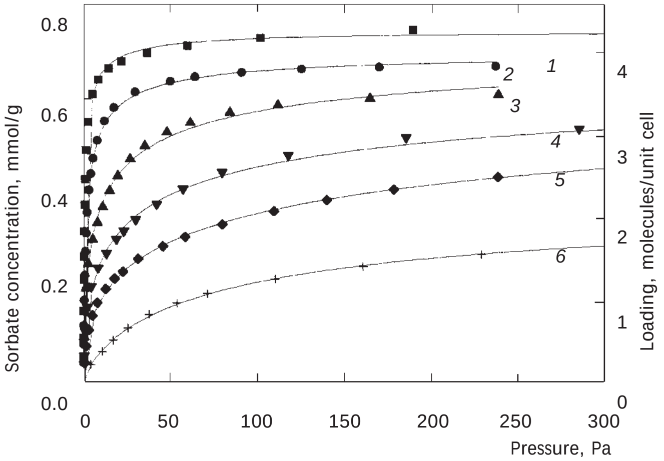

FIG. 2
Isotherms of adsorption. *1* 315 K, *2* 335 K, *3* 355 K, *4* 375 K, *5* 395 K, *6* 425 K

the values reported by Niessen *et al.* are quantitatively confirmed[7]. Nevertheless, the overall dependence on the sorbate loading is clearly confirmed.

Sorption Kinetics

For most of our experiments, sorption kinetics was clearly identified to be limited by Fickian diffusion. An example is presented in Fig. 4. Only at

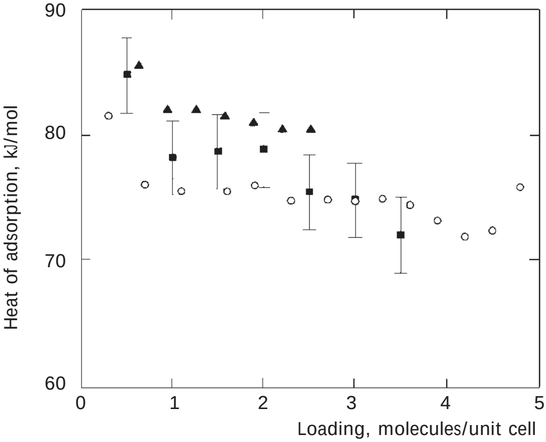

FIG. 3
Concentration dependence of the isosteric heat of adsorption. ■ This work, ▲ Niessen *et al.*[7], ❍ Thamm[4]

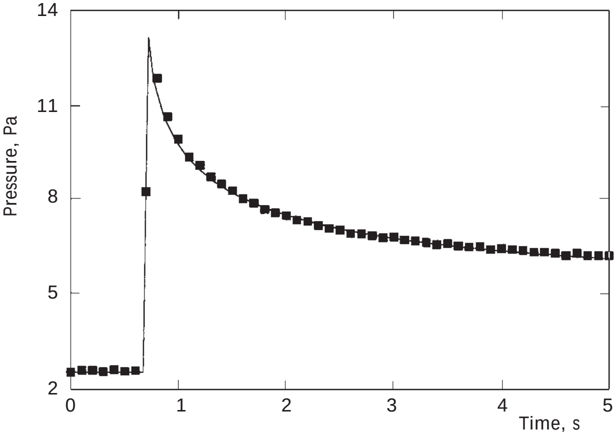

FIG. 4
Experimental uptake curve

coverages clearly below one molecule per unit cell, deviations from the expected behaviour were observed which are most likely caused by intercrystalline transport processes not carrying any information about the transport of sorbate molecules within the zeolite. The numerical values of the diffusivities are presented in Fig. 5.

Obviously, the intracrystalline diffusivity is independent of sorbate concentration for a broad range of loadings. However, a sharp decrease is observed when the sorbate concentration exceeds a critical value. Thus, as far as the concentration dependence of the sorption kinetics is concerned, the system ethylbenzene/ZSM-5 clearly belongs to type II according to the classification by Kärger and Pfeifer[16].

It is remarkable that the critical concentration clearly depends on the temperature at which the experiment was conducted.

Figure 6 shows the temperature dependence of the diffusivity at concentrations below the critical loading. The experimental data closely follows Arrhenius' law. The activation energy can be determined to be 34 ± 3 kJ/mol which is in satisfactory agreement with the values of 31 kJ/mol published by Niessen *et al.*[7] and 30 kJ/mol reported by Ruthven *et al.*[6], but considerably higher than the value of 24 ± 2 kJ/mol given by Rees and Shen[8]. Differences between the individual values might be due to differences of the individual samples used (*e.g.*, crystallinity, Si/Al ratio, amount of extra-framework species).

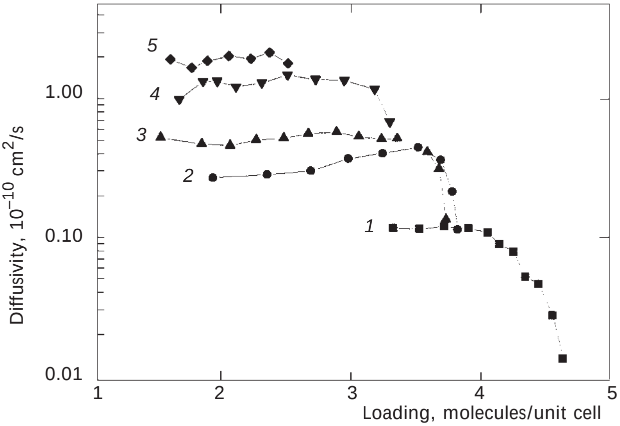

FIG. 5

Concentration and temperature dependence of the intracrystalline diffusivity. *1* 315 K, *2* 335 K, *3* 355 K, *4* 375 K, *5* 395 K

Comparing the absolute value of the diffusivity at 375 K, the present results agree excellently with the data of Niessen *et al.* ($2.5 \cdot 10^{-10}$ cm^2/s), but are slightly higher than the older value of Wu *et al.* ($5 \cdot 10^{-11}$ cm^2/s). References[6,8] report somewhat higher values of about $2 \cdot 10^{-9}$ cm^2/s. Although this might seem contradictory at first sight, it has to be kept in mind that the precise determination of diffusivities of aromatics in MFI-type zeolites remains a challenge. For the *o*-xylene diffusion, for example, the reported values in the most actual literature vary by approximately six orders of magnitude (compare refs[17,18] for details), so that the agreement of the above mentioned data must be considered satisfactory.

DISCUSSION

In the investigated range of concentrations, the temperature dependence of the diffusivity follows an Arrhenius law, so that the diffusional process can be readily interpreted as a succession of individual activated jumps.

However, above a critical concentration close to four molecules per unit cell the mutual interaction of the sorbate molecules leads to a steep decrease of the diffusivity and the temperature dependence is no longer of Arrhenius type. For the intracrystalline diffusion of aromatics in NaX crystals a similar concentration dependence was observed by Germanus *et al.*[19].

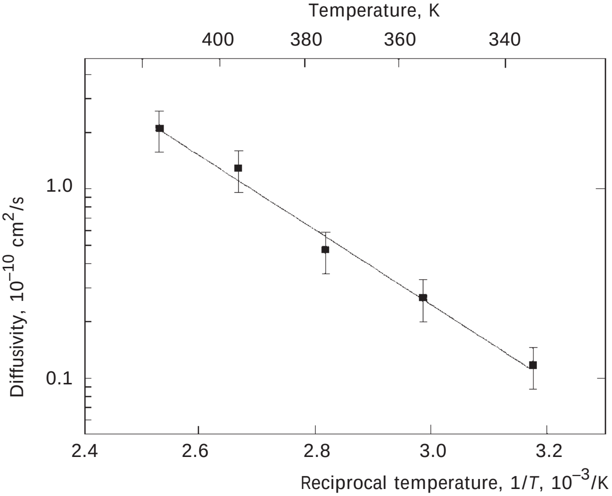

FIG. 6
Temperature dependence of the intracrystalline diffusivity

These authors found that the diffusivity was independent of the concentration for lower concentrations and decreased sharply for concentrations close to saturation. This effect can be clearly attributed to the growing importance of sorbate–sorbate interaction. In the case of MFI-zeolites it becomes very strong at loadings close to four molecules per unit cell, which corresponds to one molecule per channel intersection. An effect of saturation might therefore be expected from experiments with different aromatics.

However, not only the mobility of the sorbate molecules is affected by sorbate–sorbate interaction, but also the heat of adsorption. Our results presented above and especially the calorimetric data of Thamm (*cf.* ref.[4]) show that the repulsive interaction sets in at a loading of *ca* 3.5 molecules per unit cell. The heat of adsorption is independent of the concentration in the range below.

While, at higher loadings, direct interaction of the sorbate molecules similar to the situation in a liquid phase might be a reasonable assumption for the aromatics in more open zeolite frameworks (see, *e.g.*, ref.[20]), the aromatics sorbed in MFI-zeolites can hardly be assumed to form an independent phase. As has been pointed out by Sacerdote *et al.*[21] for the system benzene/MFI, the benzene molecules within the MFI channels form a homogeneous “benzenate”. It has been shown for various aromatic molecules (especially benzene and *p*-xylene) that they are located at well-defined sites within the MFI-framework[21–23], generally at the channel intersections for loadings lower than four molecules per unit cell. To date, similar studies have not been published for ethylbenzene, but as its size and properties are comparable to those of benzene, an analogous behaviour can be expected. This view is supported by the fact that the critical loading occurs at about four molecules per unit cell.

Therefore, direct contact of the molecules can be assumed to be of minor importance for the sorbate–sorbate interaction of ethylbenzene in MFI, and a different mechanism must be responsible for the observations described above. It is well known from XRD measurements that the unit cell constants of the MFI-framework are severely distorted by sorbed molecules (see, *e.g.* ref.[24]). If the framework parameters are changed, the intracrystalline potential can not be expected to remain unchanged. If the sorbed molecule tends to expand the channel intersection where it is located, this leads to a compression of the neighboured framework. Especially the interconnecting channels will be narrowed, so that diffusional jumps will become less likely. In principle, the reverse effect is also possible, if the sorbed molecule tends to contract the channel intersection leading to an expansion of the neighbouring lattice. The mutual interaction of sorbate molecules might therefore be assumed to occur largely *via* a deformation of the crystal lattice.

Another important aspect is the temperature dependence of the critical sorbate concentration, at which the sorbate–sorbate interaction becomes relevant. One might be tempted to attribute this effect to the decrease in the sorption capacity of the zeolite as a similar effect has been reported by Barrer *et al.*[20] for various hydrocarbons sorbed in faujasite crystals. In this paper, the authors came to the conclusion that the properties of the sorbate are comparable to those of a liquid in case the density of sorbed molecules is high enough. The decrease of sorption capacity would then be analogous to the thermal expansion of a liquid.

As described above, the direct interaction of the molecules must be ruled out due to the localized adsorption of aromatics in MFI-zeolites, so that liquid-like behaviour does not seem to be an appropriate model. Instead, the deformation of the zeolite lattice by the sorbed molecules might be temperature dependent because of the following reason: The vibrational potential of the sorbate molecules is generally anharmonic, so that a higher activation of vibrational degrees of freedom increases the effective size of the molecule and the distortion of the zeolite lattice. For identical loadings, the host lattice must probably be distorted more severely at higher temperatures, which leads to the effect shown in Fig. 5, the more so as the flexibility of the structure increases with increasing temperature as well.

CONCLUSION

The collected data for the sorption and diffusion of ethylbenzene provide insight into the complex interaction of the sorbate molecules with the zeolite framework as well as into the intermolecular interaction. For a broad range of sorbate concentration, the diffusion coefficient is exclusively determined by the sorbate–zeolite interaction. Sorbate–sorbate interaction becomes operative at higher loadings close to four molecules per unit cell. The critical concentration from which on the decrease of diffusivity due to sorbate–sorbate interaction becomes noticeable slightly depends on temperature. This effect might tentatively be attributed to an increased influence of both lattice and molecular vibrations.

SYMBOLS

a_n	coefficient as defined by Eq. (*6*)
c	concentration of sorbate within the zeolite sample dependent on space and time, mol/m^3

$\bar{c}$	mean concentration averaged for full sorbent volume, mol/m^3
D	diffusivity, cm^2/s
K	coefficient defined by Eq. (*2*), Pa m^3/mol
p	gas phase pressure, Pa
p_v	pressure of sorbing species in the sample volume prior to the beginning of the kinetic run
p_0	pressure which would be established in the sample volume after time t_δ in the absence of the adsorbent, $p_0 = p_\mathrm{v} + \boldsymbol{R}T\varphi_0/V_\mathrm{gas}$, Pa
R	particle radius, cm
$\boldsymbol{R}$	ideal gas constant, 8.314 J/mol K
r	space coordinate measured from the centre of the sphere, cm
t	time coordinate, s
t_δ	time of gas expansion in a real experiment, s
u_n	*n*-th root of Eq. (*7*)
V_gas,V_sorbent	volumes of gas phase and of sorbent, respectively, m^3
α	relation between the amount of sorbate in the gas phase and in the sorbent as defined by Eq. (*8a*)
β	reciprocal to the time constant of the intracrystalline diffusion as defined by Eq. (*8b*), s^{-1}
φ_0	amount of sorbing species introduced into the sample volume during the kinetic run, mol

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