SORPTION KINETICS OF *p*-ETHYLTOLUENE IN NaH-ZSM-5 CRYSTALS – SIMULTANEOUS EFFECT OF INTRACRYSTALLINE DIFFUSION AND A MASS TRANSPORT RESISTANCE WITHIN THE CRYSTAL SURFACE

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Adsorption equilibrium and sorption uptake data have been measured for the system *p*-ethyltoluene/NaH-ZSM-5 zeolite under constant volume/variable pressure condition at elevated ambient temperature of 343 K. The equilibrium data are described by a superposition of two Langmuir isotherms. The uptake curves observed in the present paper revealed devations from the second Fick law behaviour. The experimental uptake curves are compatible with rate mechanism involving Fickian diffusion superimposed by a surface barrier. The evaluation of the model parameters was carried out by simulation of the kinetic curves that include both the interactions of the system with the apparatus and the intrinsic sorption kinetics. The dependence of the fitted model parameters on sorbent amount and pressure, respectively, is consistent with Langmuir sorption kinetics at crystal surface on one side and with the concept of molecule jumps on a system of fixed positions in the crystal bulk on the other.

Recently, several authors[1,2] reported deviations of the sorption kinetics from the second Fick law behaviour with respect to aromatics substituted on the benzene ring in MFI molecular sieves. Also theoretical papers[3–6] on the possible explanation of non-Fickian kinetic patterns with respect to sorption in zeolites exist.

In contrast to a long-term observations at constant pressure conditions reported elsewhere[1,2], the time scale of the sorption kinetics of *p*-ethyltoluene observed in a closed system is from 20 to 6 000 s. For treatment of non-stationary sorption kinetics with complex rate mechanisms, a Volterra integral equation technique has been developed[7–9] which describes the interaction of system investigated with the apparatus in addition to the intrinsic sorption kinetics. These interactions are: (i) mass conservation in a closed system with finite volume, (ii) the finite conductivity of the valve used to start the kinetic run.

There does not exist in the literature a systematic treatment of complex kinetic processes involving both the apparatus effects (closed volumes, influence of a valve) and the effect of several rate limiting steps of the transport mechanism within the crystals (e.g. surface barriers). The goal of this paper is to perform the complete analysis of the sorption kinetic process in the system *p*-ethyltoluene/NaH-ZSM-5 measured under variable pressure conditions.

EXPERIMENTAL

Sorption uptake curves were measured by a constant volume/variable pressure apparatus operated in a differential concentration mode. The experimental arrangement is schematically shown in Fig. 1. For a more detailed description of the apparatus cf. refs[10,11]. The symbols V, p and T stand for the volume, the sorbate pressure in the fluid phase and the temperature, respectively. The subscripts d, v and s refer to the dosing vessel, the sorption vessel (containing the sample) and to the sorbent, respectively. In all the measurements the temperature T_d was kept equal to T_v and the pressure p_d was monitored as a function of time t measured by a membrane manometer Baratron with a response time ≤ 25 ms. A valve with the conductivity $\kappa = \kappa(t, p_d, p_v)$ separates the vessels from each other. The mass flux from the doser vessel into the sorption vessel is limited by a finite valve conductivity κ_∞. During the opening time, $t_0 > 0$, of the valve, an additional reduction of the mass flux between the vessels acts at the beginning of the experiment. For a more detailed description of the valve effect cf. ref.[8].

DATA TREATMENT

For experimental arrangement described above, the normalized uptake curves γ_v and γ_d with respect to the pressures in doser vessel and the sorption vessel defined by

$$\gamma_i(t) = \frac{p_i(t) - p_i(0)}{p_\infty - p_i(0)} \,, \quad i = \mathrm{d,v},\ \mathrm{t} \geq 0 \,, \qquad (1)$$

can be simulated solving the system of non-linear Volterra integral equations (cf. ref.[8])

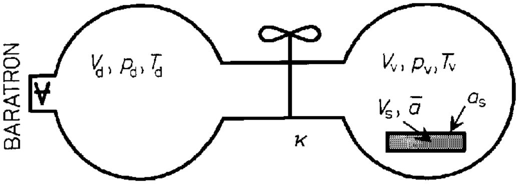

FIG. 1
Principle scheme of the experimental arrangement

$$\gamma_v(t) - (1+\mu)\gamma_d(t) + \mu \int_0^t \overline{H}'(t-s)\, F(\gamma_v(s))\, \mathrm{d}s = 0 \qquad t \geq 0 \qquad (2)$$

$$\gamma_d(t) + \int_0^t k(s,\gamma_d(s),\gamma_v(s))\, \mathrm{d}s = 0$$

with

$$\mu = \boldsymbol{R}T \frac{|V_s|}{|V_v|} \frac{f(p_\infty) - f(p_v(0))}{p_\infty - p_v(0)} , \quad |V| = \int_V \mathrm{d}x$$

$$F(\gamma_v(t)) = \frac{f(p_v(t)) - f(p_v(0))}{f(p_\infty) - f(p_v(0))} \qquad (3)$$

$$k(s,\gamma_d(s),\gamma_v(s)) = \frac{\boldsymbol{R}T}{|V_d|\,(p_\infty - p_d(0))}\, \kappa(s,p_d(s),p_v(s)) \ .$$

Therein the function $\overline{H}$ stands for the response (normed average concentration) of the system crystal/sorbate to an unit jump of the surface concentration a_s. The function f denotes the adsorption isotherm ($a_s = f(p)$). A laminar flow is assumed for the mass flux through the valve. It can be described by the function κ with

$$\kappa(t,p_d,p_v) = \kappa_t(t)\kappa_2(p_d(t)^2 - p_v(t)^2) , \quad 0 \leq \kappa_t \leq 1 \ . \qquad (4)$$

The time dependent function κ_t simulates the external control of valve during its opening. It is a dimensionless quantity with $0 \leq \kappa_t \leq 1$. The time-dependent function κ_t and the constant κ_2 have to be determined in blank experiments.

All the procedures of data treatment herein were carried out by means of the program package ZEUS (Zeolite Uptake Simulator, cf. ref.[12]) on a standard personal computer. The experimental uptake curves were fitted by selection optimum values of kinetics data with a minimum value of standard deviation of experimental data and simulated curve γ_d.

The sorption equilibrium isotherm was calculated from the set of final states of individual kinetic runs. The NaH-ZSM-5 crystals used were synthesized by Mostovicz (Warsaw). The shape of the crystals is approximately that of an epiped with the dimensions 14 μm × 6.5 μm × 4.5 μm and ratio of Si/Al ≈ 35. The crystals are twined. The crystal density based on both chemical composition and crystallographic data is $\rho \approx$

1.82 g cm^{-3}. For the simulations the crystal shape was approximated by a circumscribing sphere with radius of ≈ 4.0 μm based on the equivalence of the ratio between the surface and the volume, where the transport across 110 plane of the epiped is neglected.

The sorbate used was *p*-ethyltoluene product of Merck–Schuchard (Art. 820046) with a GC purity of 99.2%.

The following values of the apparatus constants have been determined for the reported series of experiments: $V_d = 123.5$ cm^3, $V_v = 79.1$ cm^3, $\kappa_2 = 1.3 \cdot 10^{-8}$ mol Pa^{-2} s^{-1}. For a satisfactory description of valve opening process, it is sufficient to use a piece-wise linear function κ_t. The delay time of the valve amounts $t_0 = 0.5$ s. In this time the useful valve capacity increase linearly (cf. ref.[8]).

Uptake measurements were performed with sample crystals arranged in a monolayer formed at plane bottom of ≈ 20 cm^2. The mass of the crystals amounted to 14 mg. The uptake curves were measured at the temperature of 343 K. The values of the initial pressure $p_d(0)$ ranged from about 1 Pa up to 250 Pa. After the equilibration of the system, the valve was closed and the pressure $p_d(0)$ in the doser vessel was increased over a differential step. After such a dosing step, the valve was opened and the pressure p_d in the doser vessel was monitored up to subsequent equilibrium state.

RESULTS AND DISCUSSION

The equilibrium data from the measurements are summarized in the form of the adsorption isotherm in Fig. 2.

The isotherm has been fitted by superposition of two different Langmuir isotherms,

$$a_s(p) = a_1 \frac{p}{b_1 + p} + a_2 \frac{p}{b_2 + p} \quad . \tag{5}$$

The values of the constants are fitted as follows:

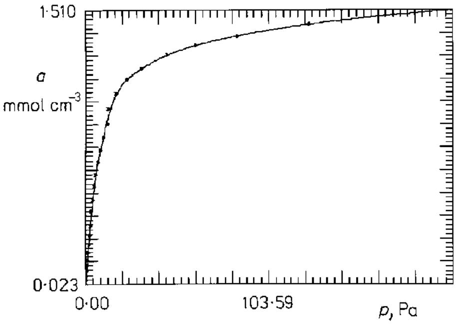

FIG. 2
Sorption isotherm for *p*-ethyltoluene on NaH-ZSM-5 ar 343 K. Δ: Experimental points; full line: result of simulation

$$a_1 = 1.275 \text{ mmol m}^{-3},\ b_1 = 6 \text{ Pa}$$

$$a_2 = 0.408 \text{ mmol m}^{-3},\ b_2 = 101 \text{ Pa}. \tag{6}$$

Thus, both the apparatus parameters and the equilibrium data of the model equation (*2*) have been determined. Optional in this equation is only the function $\overline{H}$ that describes the intrinsic intracrystalline sorption kinetics. Assuming that in the interior of the crystal the second Fick law

$$\frac{\partial}{\partial t} H = D\,\Delta H, \quad t \geq 0, x \in V_\mathrm{s} \tag{7}$$

is valid, the function

$$\overline{H}(\tau) = \frac{1}{|V_\mathrm{s}|} \int_{V_\mathrm{s}} H(\tau,x)\,\mathrm{d}x \ , \tag{8}$$

can be represented by

$$\overline{H}(t) = 1 - (\eta + 1) \sum_{n=0}^{\infty} \frac{2}{k_n^2} \Psi_n \exp\left(-k_n^2 \frac{Dt}{\boldsymbol{R}^2}\right), \quad \eta = 0, 1, 2 \tag{9}$$

($\eta = 0$ for a plate, $\eta = 1$ for a cylinder and $\eta = 2$ for a sphere). Therein D denotes the diffusivity. For pure diffusion into an isotropic particle one obtains for the constants in Eq. (*9*) the following equations

$$\Psi_n \equiv 1 \quad \text{and} \quad \begin{array}{ll} \cos(k_n) = 0 & \text{for } \eta = 0 \\ J_0(k_n) = 0 & \text{for } \eta = 1, \quad n \geq 0, \\ \sin(k_n) = 0 & \text{for } \eta = 2 \end{array} \tag{10}$$

where J_i stands for the *i*-th order Bessel function of the first kind.

It has been found, that the assumption of pure diffusion control for the sorption kinetics of *p*-ethyltoluene in NaH-ZSM-5 observed under conditions of the present paper fails in all the pressure region investigated. Typical examples of uptake curves fitted by the second Fick law solution are shown in Figs 3 and 4. Particularly, the initial part of the curves cannot be fitted by the solution of the second Fick law.

Surprisingly, no one of the known kinetic models (diffusion with heat dissipation or diffusion with immobilisation) did fit the experimental data except that with a complex mechanism comprising diffusion superimposed by a surface barrier. For this case the function $\overline{H}$ is also given by Eq. (*9*) but with the constants

$$\Psi_n = \frac{L^2}{k_n^2 + (1-\eta)L + L^2} \quad \text{and} \quad \begin{array}{l} k_n \tan(k_n) - L = 0 \ \text{ for } \eta = 0 \\ k_n \dfrac{J_1(k_n)}{J_0(k_n)} - L = 0 \ \text{ for } \eta = 1 , \quad n \geq 0 \\ k_n \cot(k_n) + L = 1 \ \text{ for } \eta = 2 \ . \end{array} \tag{11}$$

The dimensionless barrier parameter L is defined as (see ref.[13])

$$L = \alpha \frac{\boldsymbol{R}}{D} \ . \tag{12}$$

The pressure dependence of the barrier coefficient α can be derived from the Langmuir sorption kinetics at the crystal surface. Denoting with a_{s-} the actual concentration just within the crystal and with a_{s+} the concentration required to maintain equilibrium with surrounding gas phase (cf. ref.[13], p. 56), the mass balance based on the Langmuir kinetics is given as

$$\omega \frac{\mathrm{d}}{\mathrm{d}t} a_{s-} = k_a(a_\infty - a_{s-})\, p - k_d a_{s-} - j_s \ , \quad \omega = \frac{|V_{\Gamma_s}|}{|\Gamma_s|} \ , \tag{13}$$

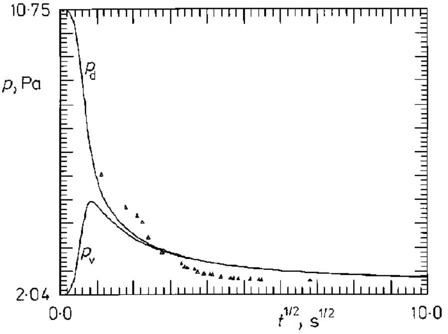

FIG. 3

Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at 343 K; $p_d(0)$ = 10.75 Pa; $p_v(0)$ = 2.04 Pa. Δ: Experimental points; full lines: result of simulation based on the best fit of the uptake curve by the second Fick law solution for spherical particles

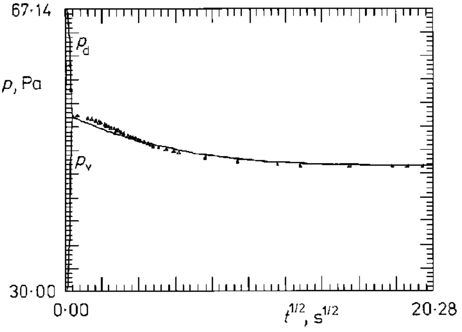

FIG. 4

Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at 343 K; $p_d(0)$ = 67.14 Pa; $p_v(0)$ = 30.0 Pa. For the notation cf. Fig. 3

where Γ_s and V_{Γ_s} denote the surface of the crystal and the corresponding volume of Γ_s, respectively. The value j_s stands for the molar flux density from the surface to the interior of the crystal. The value p denotes the sorbate pressure in the fluid phase. The constants k_a and k_d refer to the molecule transition from the gas phase to the position just behind the concentration discontinuity and in reverse direction, respectively. The value a_∞ denotes the concentration corresponding to the total sorption sites in sorbent. Further on, the concentration a_{s+} – which is given by the sorption isotherm – is reached at the equilibrium where $\frac{d}{dt} a_{s+} = 0$ and $j_s = 0$. Thus, one obtains

$$k_a(a_\infty - a_{s+})\, p - k_d a_{s+} = 0 \quad . \tag{14}$$

Subtraction of Eq. (*14*) from Eq. (*13*) yields

$$\omega \frac{d}{dt} a_{s-} = (k_a p + k_d)\,(a_{s+} - a_{s-}) - j_s = \alpha(a_{s+} - a_{s-}) - j_s \quad , \tag{15}$$

with

$$\alpha = k_a p + k_d \quad . \tag{16}$$

Due to a very small sorption capacity of the crystal interface V_{Γ_s} a quasi stationary state is attained instantaneously and

$$j_s = \alpha(a_{s+} - a_{s-}) \tag{17}$$

is valid. For the mass transport the validity of the first Fick law is assumed. Thus,

$$j_s = D \frac{\partial}{\partial x} a_{s-} \tag{18}$$

completes Eq. (*17*) to

$$D \frac{\partial}{\partial x} a_{s-} = \alpha(a_{s+} - a_{s-}) \quad . \tag{19}$$

Note that the space variable x is orientated from the interior of the particle to outside. This equation is well-known for modelling of a surface evaporation[13]. The barrier coefficient α (cf. Eq. (*16*)) is an affinely linear function of the pressure p of the sorbing species.

The measured data were fitted using the barrier model. Figures 5 – 8 present some typical examples of the fit. The fitted diffusion coefficients D plotted as a function of the equilibrium sorbed amount $a(\infty)$ of the sorbate in the crystals are given in Fig. 9. Figure 10 presents the corresponding barrier parameters α as function of equilibrium pressure p_∞ .

The pressure dependence of the barrier parameter α seems to be consistent with Eq. (*16*). The coefficients can be approached as $k_a \approx 5 \,.\, 10^{-10}$ m Pa^{-1} s^{-1} and $k_d \approx 2 \,.\, 10^{-8}$ m s^{-1}.

The behaviour of the uptake curves should be considered as an experimental finding. Only the barrier model together with a complete description of the interaction of the apparatus with the system was able to fit the measured data. At least the barrier coefficient behaves consistently with the well-known Langmuir kinetics at the surface of the crystals (affinely linear dependence on the pressure p). Consequently, the effect of surface barrier seems to be proved in this particular case. However, one can only speculate why in the system *p*-ethyltoluene/NaH-ZSM-5 the contribution to the barrier effect to the overall sorption kinetic is comparable to that of intracrystalline diffusion.

On the other hand, the decrease of the diffusion coefficient D with increasing sorbed amount is in accordance with the nature of the system, i.e. with both size and shape of

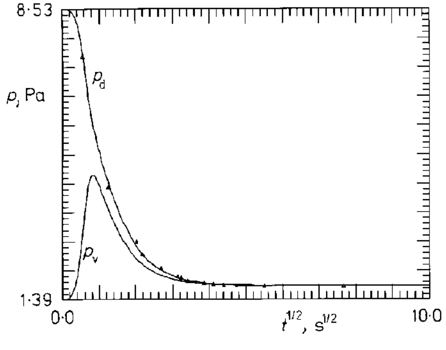

FIG. 5

Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at 343 K; $p_d(0)$ = 8.53 Pa; $p_v(0)$ = 1.39 Pa. Δ: Experimental points; full lines: result of simulation based on the best fit of the uptake curve by the model of diffusion into a spherical particle with the superimposed surface barrier

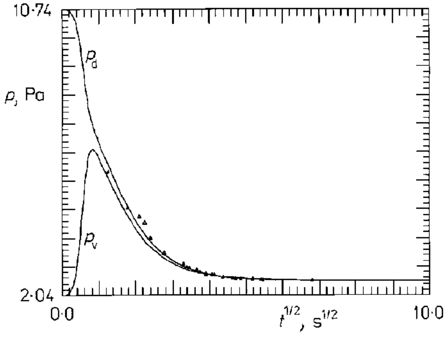

FIG. 6

Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at 343 K; $p_d(0)$ = 10.74 Pa; $p_v(0)$ = 2.04 Pa. For notation cf. Fig. 5

the sorbate molecule and the channel system. In such a system one molecule may represent an obstacle for the other. The interpretation of molecular mobility on the basis of kinetic data obtained for the reported system is essentialy restricted by serious doubts[5] that local equilibrium principle can be applied to system considered. Nevertheless, if the local equilibrium assumption is tentatively accepted at least for the system of straight channels of ZSM-5, one can express the diffusion coefficient *D* as a product of the selfdiffusion coefficient D^* and a thermodynamic factor (Darken factor)

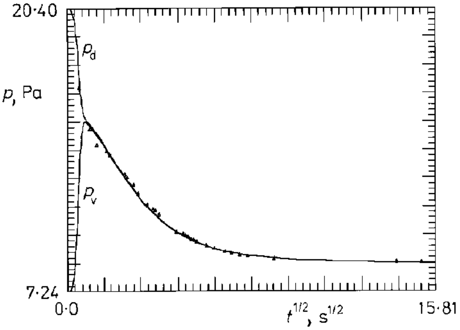

Fig. 7
Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at 343 K; $p_d(0)$ = 20.40 Pa; $p_v(0)$ = 7.24 Pa. For notation cf. Fig. 5

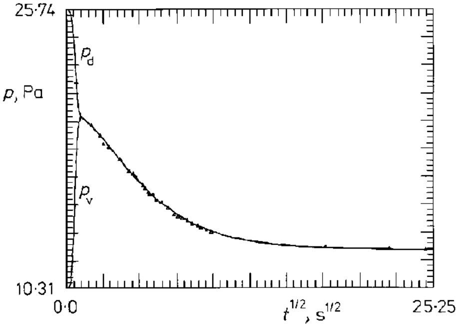

Fig. 8
Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at 343 K; $p_d(0)$ = 25.74 Pa; $p_v(0)$ = 10.31 Pa. For notation cf. Fig. 5

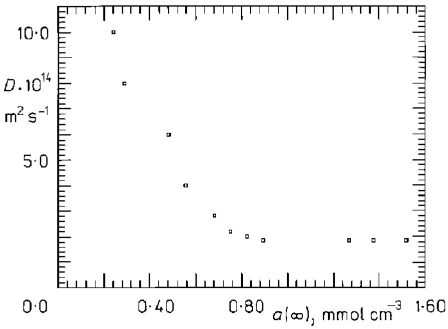

Fig. 9
Diffusion coefficients *D* (obtained from the best fits) plotted against equilibrium sorbed amount $a(\infty) = f(p_\infty)$

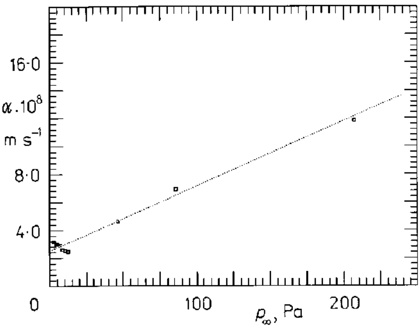

Fig. 10
Barrier coefficient α (obtained from the best fits plotted) against equilibrium pressure p_∞

$$D = D^* \frac{\partial \ln p}{\partial \ln a} \quad . \tag{20}$$

For selfdiffusion via jumps between fixed points a simple model has been presented in literature (cf. ref.[14], p. 302) which accounts for blocking the sites by adsorbed molecules:

$$D^* = \frac{\nu l^2}{q}(1 - \theta)\, e^{-\frac{E}{\boldsymbol{R}T}} \;, \quad \theta = \frac{a}{a_\infty} \quad . \tag{21}$$

Here ν, l, q, E and θ denote vibration frequency of the molecule, jump distance, number of directions into which the molecule is able to jump, activation energy of selfdiffusion and the relative loading of the sorbent, respectively.

In the low pressure region (p < 10 Pa) the sorption isotherm behaves approximately as linear one with a slope H = 120 mol $\mathrm{Pa}^{-1}\,\mathrm{m}^{-3}$. In this region $D = D^*$ is valid. This fact correlates with the empirically found asymptotic behaviour of the diffusivity

$$D = \begin{cases} D_0(1 - \theta) & \text{for } \theta << 1 \\ D_\infty & \text{for } \theta \rightarrow 1 \end{cases} \tag{22}$$

(cf. Fig. 11; $D_\infty \approx 1.8 \,.\, 10^{-14}\ \mathrm{m}^2\,\mathrm{s}^{-1}$, the approximate calculation of D_0 and a_∞ is too inaccurate). For higher concentration values the adsorption isotherm can be described by a superposition of two Langmuir isotherms with prevailing contribution of the first term (cf. fitted constants in Eq. (*6*)), the Darken factor can be approximated by $(1 - \theta)^{-1}$. In this case, the diffusion coefficient becomes independent of loading as found in Eq. (*22*) if $D_0(1 - \theta) < < D_\infty$.

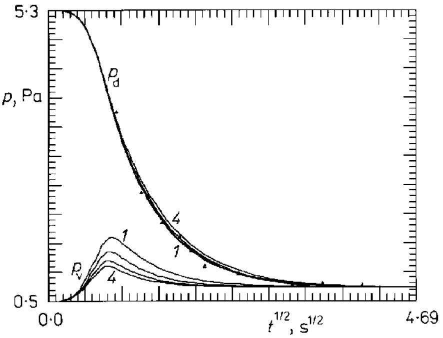

FIG. 11

Uptake curves for *p*-ethyltoluene on NaH-ZSM-5 at temtperature of 343 K; $p_d(0)$ = 5.3 Pa; $p_v(0)$ = 0.5 Pa. Δ: Experimental points; full lines: results of simulation by the model, the parameter D varies between $4 \,.\, 10^{-13}\ \mathrm{m}^2\,\mathrm{s}^{-1}$ (*1*) and $4 \,.\, 10^{-12}\ \mathrm{m}^2\,\mathrm{s}^{-1}$ (*4*). The upper curves are the pressures in the doser vessel and the lower curves the pressures in the sorption vessel

Another aspect of the data evaluation is the exact description of the system interaction with the apparatus. The influence of the valve effect on the overall kinetics is more pronounced for faster sorption kinetics. It is essential, that the pressure between the doser vessel and the sorption volume was not generally reached for times $t < t_0$ (delay time of the valve). An extreme effect is shown in Fig. 11. In this case the valve effect is very strong and the pressure p_d becomes too insensitive with respect to variations of the kinetic parameters (diffusion coefficient D). From this reason, the pressure p_d depends mainly on the valve behaviour, i.e. the mass flux through the valve is the limiting rate step, and, therefore, only a lower bound for diffusion coefficient can be estimated.

CONCLUSIONS

Sorption uptake measurements in the system *p*-ethyltoluene/NaH-ZSM-5 performed under constant volume/variable pressure conditions show kinetic patterns which are consistent with the model of simultaneous diffusion and surface barrier limitation of the overall sorption kinetics.

The analysis of kinetic patterns using Volterra integral equations approach eliminated distorting effects of the valve and gave physically reasonable dependences of barrier coefficient on pressure and diffusion coefficient on zeolite loading by sorbate.

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