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Diffusion of *p*-xylene in single and binary systems in zeolites investigated by FTIR spectroscopy

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Abstract

A novel method based on Fourier transform infrared spectroscopy (FTIR) is applied to study sorption and sorption kinetics of *p*-xylene in ZSM-5-type zeolites as a single component and in a binary-component system, in the presence of benzene under conditions close to those of a catalytic run From the change of intensities of IR bands characteristic for the adsorbates, diffusivities of *p*-xylene in the single-component system as well as in the binary-component system are determined at various temperatures and loadings In comparison with benzene measured as a single component in the same system, the diffusivities of *p*-xylene are higher by a factor of 2 to 3 This is in agreement with the literature data In the binary system, the presence of benzene reduces the diffusivities of *p*-xylene by 30 to 50% Isotherms, isosteres and isosteric heats of adsorption are determined from the measurements The isosteric heats of adsorption agree well with the literature data

Keywords diffusion, counter-diffusion, co-diffusion, sorption, *p*-xylene, benzene, H-ZSM-5

Introduction

In many cases, conversion and/or selectivity in zeolite catalysts are affected by the diffusion of reactive molecules in the pores Diffusion coefficients and activation energies for diffusion characterize the molecular transport in the zeolite channels With respect to catalysis, multi-component diffusion is particularly interesting, since even in the most simple cases of catalytic conversions inside the zeolite pore structure one sort of molecule has to travel in and another sort, the product, has to travel out However, studies of multi-component diffusion are rather scarce because there was essentially no suitable technique for such multi-component systems Recently, a novel technique for studying sorption and sorption kinetics not only of single-component systems but also of multi-component systems in porous materials was presented [1–4] This technique employs Fourier transform infrared spectroscopy (FTIR) to determine the sorbed amount of material in the zeolite In the multi-component measurements, the co- and counter-diffusion of the adsorbate molecules can be investigated Furthermore, the method provides isotherms and isosteric heats of the components in single- and multi-component systems

In the present work this technique is applied to study the sorption and sorption kinetics of *p*-xylene in H-ZSM-5 as a single component and in a binary-component system in the presence of benzene for co- and counter-diffusion

Experimental

H-ZSM-5 was used as the adsorbent. The zeolite, well crystallized (8 8 × 5 2 × 3 2 μm), was commercially produced, and kindly provided by Degussa, Wolfgang, Germany The overall Si/Al ratio was 33 5 However, ^{27}Al MAS NMR measurements indicated a significant amount (*i e*, ~30%) of

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extra-framework aluminium p-Xylene and benzene were supplied by Merck, Darmstadt, Germany, and were of spectroscopic grade and additionally purified by distillation The experimental set-up with the FTIR spectrometer, ultrahigh vacuum, mass flow control system and IR cell has been reported elsewhere [1–3] In the experiments the adsorbate was admixed to a continuous flow of helium passing the zeolite sample In the case of binary mixtures the partial pressures of the adsorbates could be changed independently Sorption into or desorption from the adsorbent was monitored through the increase or decrease of the IR bands typical of the adsorbates The IR spectra were obtained at intervals as short as 0 37 s The exact experimental procedure and the evaluation of the diffusivities have been described in refs 1–3

Results and discussion

Figure 1 presents a set of p-xylene spectra for successive states of sorption, which were obtained during 324 s The increasing intensity of the typical deformation mode of p-xylene at 1516 cm^{-1} shows the uptake of p-xylene in the sample until an equilibrium state is reached From such curves obtained in sorption and desorption experiments at various temperatures, the amount of material sorbed into or desorbed out of the zeolite pores (proportional to A and $1-A$, where A is the absorbance of the IR band under investigation) is derived as a function of the square root of time These sorption kinetics of p-xylene in H-ZSM-5 are illustrated in Fig 2 under various conditions of pressure increments and temperatures The symbols indicate the amount of adsorbed p-xylene, which was calculated from the intensities of the typical IR bands appearing in the spectra during the uptake measurements The adsorbed amount of p-xylene decreases with increasing temperature

The application of an appropriate solution of Fick's second law to the uptake curves provides the desired diffusivities D [1–3] The solid line presents the best fit of the experimental data according to the theoretical solution The obtained diffusion coefficients D were corrected according to the Darken equation using the adsorption isotherms measured by FTIR (*vide infra*) [5] The corrected diffusivities of p-xylene ($D_0 = 1\ 5 \times 10^{-9}$ cm^2/s, 395 K) agree with the literature data of $D_0 = 4 \times 10^{-9}$ cm^2/s obtained by Bulow *et al* [6] at 393 K for the same amount adsorbed ($n_\infty = 0\ 3$ mmol/g)

In analogy to the adsorption experiments, the desorption measurements for the same temperatures and pressure jumps are illustrated in Fig 3 In all cases where the final pressure is not zero,

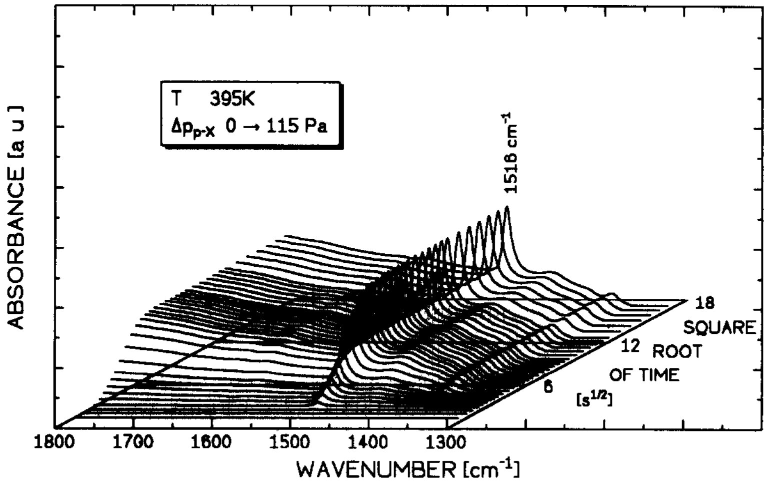

Fig 1 Single-component diffusion Set of p-xylene spectra for successive states of adsorption in H-ZSM-5-type zeolite obtained during 324 s

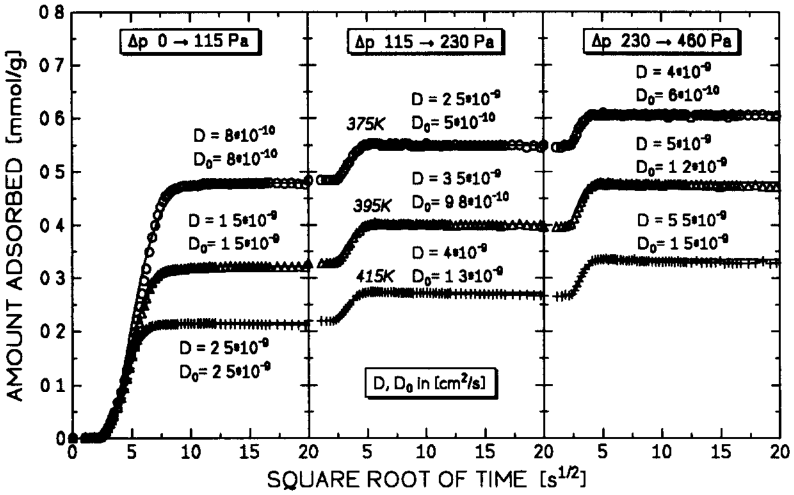

Fig 2 Diffusion of *p*-xylene in H-ZSM-5 Adsorption curves as a function of the square root of time, *D* Fickian diffusivity, D_0 diffusivity corrected according to the Darken equation

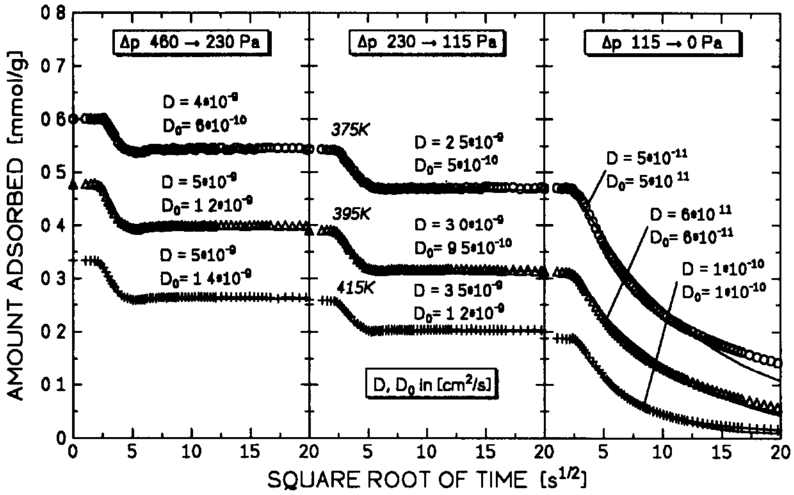

Fig 3 Diffusion of *p*-xylene in H-ZSM-5 Desorption curves as a function of the square root of time, *D* Fickian diffusivity, D_0 corrected diffusivity according to the Darken equation

the diffusivities calculated from the desorption measurements agree with those obtained by the adsorption measurements The deviation of the diffusivities when the partial pressure jump started with or reached zero can be explained with respect to the heterogeneity of the internal zeolite surface Sites with very high adsorption potential affect the rate of desorption more strongly than that of the reverse process

Examples of the obtained Fickian diffusivities and corrected diffusivities (*D* and D_0) of *p*-xylene in adsorption and desorption measurements at several temperatures and coverages are given in Table 1 The diffusivities D_0 increase with temperature while the equilibrium coverages n_∞ decrease with temperature

p-Xylene shows diffusivities which were by a factor of 2 to 3 higher than those obtained for benzene with the novel FTIR method [1–4] ($D_0 = 1\ 5\times10^{-9}$ cm²/s for *p*-xylene and $D_0 =$

TABLE 1

Diffusivities of *p*-xylene as a single component in adsorption and desorption measurements[a]

T (K)	n_∞ (mmol/g)	Adsorption		Desorption	
		D (cm^2/s)	D_0 (cm^2/s)	D (cm^2/s)	D_0 (cm^2/s)
		Δp 0→115 Pa		Δp 115→0 Pa	
375	0 48	8×10^{-10}	8×10^{-10}	5×10^{-11}	5×10^{-11}
395	0 33	$1\ 5\times10^{-9}$	$1\ 5\times10^{-9}$	6×10^{-11}	6×10^{-11}
415	0 21	$2\ 5\times10^{-9}$	$2\ 5\times10^{-9}$	1×10^{-10}	1×10^{-10}
		Δp 115→230 Pa		Δp 230→115 Pa	
375	0 55	$2\ 5\times10^{-9}$	$5\ 0\times10^{-10}$	$2\ 0\times10^{-9}$	$5\ 0\times10^{-10}$
395	0 40	$3\ 5\times10^{-9}$	$9\ 8\times10^{-10}$	$3\ 0\times10^{-9}$	$9\ 5\times10^{-10}$
415	0 28	$4\ 0\times10^{-9}$	$1\ 3\times10^{-9}$	$3\ 5\times10^{-9}$	$1\ 2\times10^{-9}$

[a] D, Fickian diffusivities, D_0, corrected diffusivities, n_∞, equilibrium coverage

$6\ 8\times10^{-10}$ cm^2/s for benzene at 395 K) This is similar to results reported in the literature where diffusivities of $D_0=4\ 1\times10^{-9}$ cm^2/s at 373 K for *p*-xylene and $D_0=(5\text{–}9)\times10^{-10}$ cm^2/s at 393 K for benzene have been reported by Ruthven *et al* [7] and Forste *et al* [8] In Table 2 a comparison between the diffusion coefficients of *p*-xylene and benzene obtained at various temperatures with the novel FTIR method is given Differences between both components up to more than two orders of magnitude measured with the frequency response method by Rees and Shen [9] were not obtained

The activation energy for diffusion of *p*-xylene in H-ZSM-5 ($E_A=30$ kJ/mol) is in good agreement with the literature data, where the same value of $E_A=30$ kJ/mol was obtained [7] Benzene, the second component in the binary system, showed a lower activation energy of $E_A=23$ kJ/mol for diffusion in ZSM-5-type zeolites [1–4,10] Adsorption isotherms could also be derived from the uptake measurements (Figs 2 and 3) From the stationary coverages after various pressure jumps, adsorption isotherms were constructed at three given adsorption temperatures as shown in Fig 4 The solid lines represent the best fit of the experimental data by a combination of a Langmuir isotherm and a Freundlich isotherm after the expression

$$n=n_0\times b\times p^m/(1+b\times p^m)$$

where n = coverage, n_0 = maximum coverage, p = equilibrium partial pressure, m,b = specific constants [5]

From such a set of isotherms as shown in Fig 4 the diffusivities could be corrected according to the Darken equation [5] and the isosteric heats of adsorption, Q_{isost}, could be evaluated The isosteric heats of adsorption of *p*-xylene ($Q_{\text{isost}}=80$ kJ/mol) were in good agreement with the literature data of $Q_{\text{isost}}=80$ kJ/mol reported by Rees and Shen [9] In comparison with benzene ($Q_{\text{isost}}=64$ kJ/mol [3–4]), the isosteric heats of *p*-xylene are higher

In the binary-component system, co- and counter-diffusion were investigated In the counter-diffusion measurements benzene, which was pre-adsorbed, is partially displaced by *p*-xylene diffusing into the zeolite sample The set of spectra in

TABLE 2

Comparison between diffusivities of *p*-xylene and benzene in H-ZSM-5[a]

T (K)	*p*-Xylene		Benzene	
	n_∞ (mmol/g)	D_0 (cm^2/s)	n_∞ (mmol/g)	D_0 (cm^2/s)
Δp 0→115 Pa				
395	0 33	$1\ 5\times10^{-9}$	0 16	$6\ 8\times10^{-10}$
415	0 21	$2\ 5\times10^{-9}$	0 11	$8\ 8\times10^{-10}$
Δp 115→230 Pa				
395	0 40	$9\ 5\times10^{-10}$	0 22	$6\ 2\times10^{-10}$
415	0 28	$1\ 2\times10^{-9}$	0 15	$9\ 9\times10^{-10}$

[a] D_0, corrected diffusivities, n_∞, equilibrium coverage

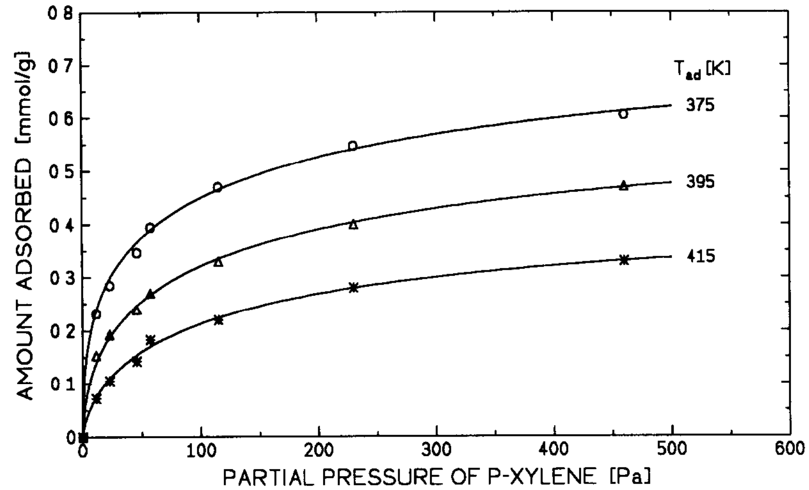

Fig 4 Isotherms of benzene adsorption on H-ZSM-5 measured by FTIR (○, △, ✳) Experimental data, (—) Langmuir–Freundlich equation

Fig 5 demonstrates the decrease of the typical benzene band at 1478 cm^{-1} when *p*-xylene is admitted to the gas stream (increasing intensity of the band at 1516 cm^{-1} typical of *p*-xylene) From such a set of spectra, uptake curves were evaluated Uptake curves for counter-diffusion of *p*-xylene *versus* benzene ($p = 115$ Pa, constant) at 395 K are shown in Figs 6a and 6b when *p*-xylene is adsorbed (Δp $0 \rightarrow 115$ Pa) and desorbed (Δp $115 \rightarrow 0$ Pa) While *p*-xylene molecules are sorbed into the zeolite pores benzene molecules are diffusing out (Fig 6a) The desorption of *p*-xylene out of the zeolite pores leads to an increase in the amount of adsorbed benzene to the same steady state as before (Fig 6b) The obtained diffusivities *D* of *p*-xylene adsorbed in the presence of benzene at 375 and 395 K were by a factor of about 2 lower than in the case of single-component diffusion (*e g*, $D_{p-X} = 1\ 5 \times 10^{-9}$ cm^2/s in single-component and $D_{p-X} = 8 \times 10^{-10}$ cm^2/s in binary-component diffusion at 395 K) At 415 K the difference in the diffusivities of *p*-xylene in single-component and

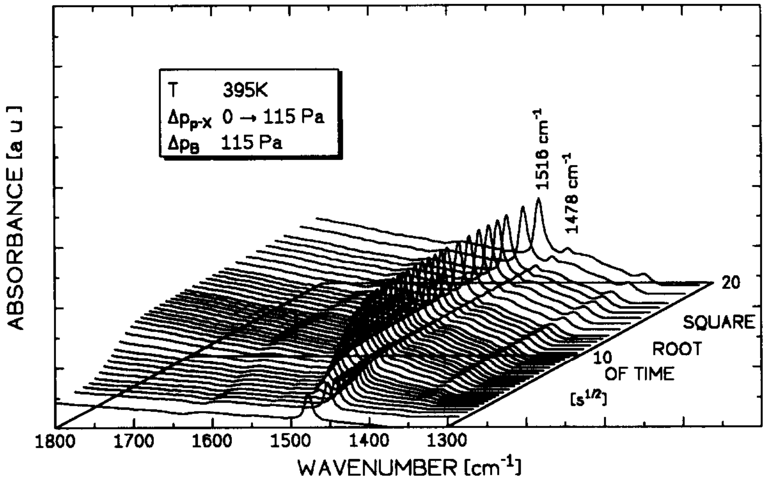

Fig 5 Binary-component diffusion (counter-diffusion) Set of spectra for successive replacement of pre-adsorbed benzene (1478 cm^{-1}) by *p*-xylene (1516 cm^{-1}) measured during 400 s

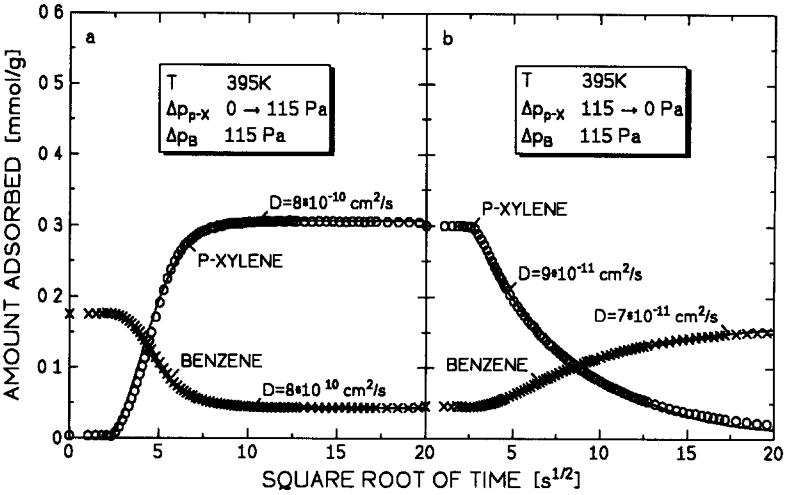

Fig 6 Counter-diffusion of *p*-xylene *versus* benzene in H-ZSM-5 Amount adsorbed from a gas mixture in adsorption (a) and desorption (b) experiments with *p*-xylene as a function of the square root of time

binary-component diffusion decreases to a factor of about 1 5 The interaction between both components in the zeolite pores leads to a slightly higher diffusion coefficient of benzene in the binary case than in the single-component diffusion Again, when the partial pressure of *p*-xylene reached zero in the binary system, the diffusivities were found to be lower than in the case of *p*-xylene adsorption Examples for diffusivities of *p*-xylene counter-diffusing *versus* benzene are given in Table 3 Benzene pre-adsorbed with a partial pressure of $p=$ 460 Pa reduced the diffusivities D of *p*-xylene subsequently adsorbed with Δp 0→115 Pa to about 50% of the values measured at a constant partial pressure of $p=115$ Pa for benzene When *p*-xylene is desorbed the partial pressure of $p=460$ Pa for benzene leads to an increase of the diffusion coefficient D of *p*-xylene by about 60% in comparison with the diffusivities measured under a constant partial pressure of $p=115$ Pa for benzene This is most likely due to the concentration dependence of the Fickian diffusion coefficient, D In the case of counter-diffusion the activation energy of *p*-xylene diffusion increased to $E_A=39$ kJ/mol when benzene is pre-adsorbed

In the co-diffusion of *p*-xylene and benzene both components were simultaneously admitted to the gas stream ($\Delta p=0\rightarrow115$ Pa) Benzene first reaches a maximum but is then partially displaced by the more strongly adsorbed *p*-xylene diffusing into the zeolite pores (see Fig 7a) The diffusivities of *p*-xylene in co-diffusion with benzene are higher than in counter-diffusion experiments, where all active

TABLE 3

Diffusivities of *p*-xylene (p-X) in counter-diffusion with benzene (B)

T (K)	*p*-Xylene		Benzene	
	n_∞ (mmol/g)	D (cm^2/s)	n_∞ (mmol/g)	D (cm^2/s)
	Δp_{p-X} 0→115 Pa		p_B 115 Pa (const)	
375	0 42	4 5×10^{-10}	0 06	4 0×10^{-10}
395	0 29	8 0×10^{-10}	0 05	8 0×10^{-10}
415	0 20	1 7×10^{-9}	0 04	1 7×10^{-9}
	Δp_{p-X} 115→0 Pa		p_B 115 Pa (const)	
375	→0	6×10^{-11}	0 25	4×10^{-11}
395	→0	9×10^{-11}	0 18	7×10^{-11}
415	→0	1 5×10^{-10}	0 11	1 0×10^{-10}
	Δp_{p-X} 0→115 Pa		p_B 460 Pa (const)	
375	0 37	2 5×10^{-10}	0 18	2 0×10^{-10}
395	0 24	5 5×10^{-10}	0 14	5 0×10^{-10}
415	0 16	9×10^{-10}	0 11	8 0×10^{-10}
	Δp_{p-X} 115→0 Pa		p_B 460 Pa (const)	
375	→0	9×10^{-11}	0 43	8×10^{-11}
395	→0	1 5×10^{-10}	0 28	1 0×10^{-10}
415	→0	2 5×10^{-10}	0 20	2 0×10^{-10}

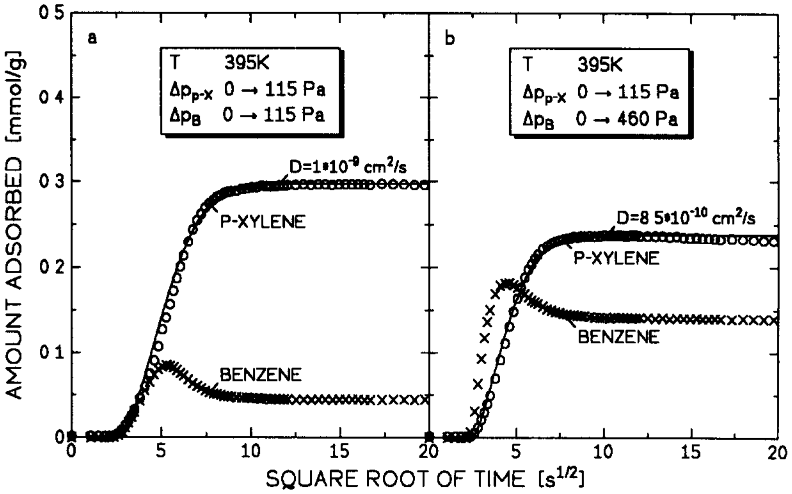

Fig 7 Co-diffusion of *p*-xylene and benzene in H-ZSM-5 Uptake from a gas mixture for two different partial pressures of benzene as a function of the square root of time

sites are occupied by pre-adsorbed benzene molecules, but lower than in the single-component system By increasing the partial pressure of the co-adsorbed benzene (Δp 0→460 Pa) the diffusivities of *p*-xylene (Δp 0→115 Pa) decrease by about 30% (Fig 7b) Diffusivities of *p*-xylene in co-diffusion with benzene are shown in Table 4

The behaviour in the system *p*-xylene–benzene in co- and counter-diffusion is predicted for two adsorbed components with different interactions to the zeolite surface by theory and is shown in binary diffusion for benzene and ethylbenzene with the same experimental set-up [1–4,11] The more strongly adsorbed component *p*-xylene replaces the more weakly adsorbed benzene

TABLE 4

Diffusivities of p-xylene (p-X) in co-diffusion with benzene (B)

T (K)	*p*-Xylene[a] n_∞ (mmol/g)	*D* (cm²/s)
	Δp_B 0→115 Pa	
375	0 43	7×10^{-10}
395	0 29	$1\ 3 \times 10^{-9}$
415	0 20	$2\ 3 \times 10^{-9}$
	Δp_B 0→460 Pa	
375	0 36	6×10^{-10}
395	0 23	$8\ 5 \times 10^{-10}$
415	0 16	$1\ 5 \times 10^{-9}$

[a] $\Delta p_{p\text{-}X}$ 0→115 Pa

Conclusions

The novel FTIR technique for the uptake and desorption measurements in zeolites as adsorbents provides reliable diffusivities for *p*-xylene not only in a single-component system but also in a binary-component system in the presence of benzene

Diffusivities in the single-component system are in agreement with the data reported in the literature

The experiments can be conducted under conditions close to those of catalytic processes

This technique enables us to study co- and counter-diffusion in porous systems, *e g*, zeolites, and to investigate the effect of coverage and derive activation energies of diffusion, isotherms, isosteres and isosteric heats of adsorption

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