



## Diffusion and Immobilization Mechanisms in Zeolites Studied by ZLC Chromatography\*

MLADEN EIČ\*\*

*Department of Chemical Engineering, University of New Brunswick, P.O. Box 4400, Fredericton, NB, Canada E3B 5A3*  
meic@unb.ca

ANDRÉ MICKE

*The BOC Group Technical Center, 100 Mountain Ave., Murray Hill, NJ 07974, USA*

MILAN KOČIRÍK

*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 8, 182 23 Prague 8, Czech Republic*

MOHAMED JAMA

*Department of Chemical Engineering, University of New Brunswick, P.O. Box 4400, Fredericton, NB, Canada E3B 5A3*

ARLETTE ZIKÁNOVÁ

*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 8, 182 23 Prague 8, Czech Republic*

**Abstract.** Zero Length Column chromatography was used to study mass transfer in zeolites involving coupled diffusion and immobilization mechanisms. A modeling based on *Volterra* integral equation technique was utilized to simulate sorption and desorption kinetic curves and compare results of the simulations with experimentally obtained curves. This approach was applied to analyze sorption kinetics in the model system: toluene/silicalite-1 (75°C–178°C). The system generally shows a non-*Fickian* behavior and can be described by diffusion coupled with immobilization.

**Keywords:** *Fickian* diffusion, immobilization, ZLC chromatography, zeolites, *Volterra* integral equation

### 1. Introduction

A number of mass transport processes involving zeolites that were studied in past were found not to follow

pure *Fickian* diffusion mechanism. Additional effects that are reflected in so called tailing of response curve are usually attributed to extra crystalline effects, such as external film resistance, bed diffusion, surface barrier etc. (Micke et al., 1994). It was also found that immobilization/mobilization mechanisms may play a central role in sorption kinetics for a number of systems

\*This paper is dedicated to Professor Zhdanov on the occasion of his 90th birthday.

\*\*To whom correspondence should be addressed.

investigated in earlier studies, i.e., n-hexane/silicalite and p-ethyltoluene/H-ZSM-5 (Micke et al., 1994; Micke and Bülow, 1994; Zikánová and Derewinski, 1995). Principal theories and theoretical analyses used to explain influence of immobilization on transport properties were discussed in Micke et al. (1994).

The specific mechanisms related to the immobilization in MFI type zeolites were studied by Zikánová and Derewinski (1995), which could be generalized for a regular matrix of zeolites and their analogues with respect to three main immobilization mechanisms:

- (i) molecules are immobilized in traps outside the channels responsible for radial transport
- (ii) immobilization proceeds via formation of strong sorbate complexes with active sites in the channels
- (iii) immobilization proceeds via chemical transformation of a molecule into a bulky or long chain complex of low mobility.

Main objective of this study is focused on investigating the role of immobilization in toluene/silicalite which is chosen as a model system. Two basic models, i.e. pure *Fickian* diffusion and diffusion coupled with immobilization were used to analyze experimental results. *Volterra* Integral Equation technique was applied to obtain numerical solutions for the models. Standard Zero Length Column (ZLC) technique was employed to obtain experimental curves (cf. Eic and Ruthven, 1989; Ruthven and Brandani, 1996). The ZLC method is based on measuring limiting diffusion coefficient at zero loading. At such very low concentration levels the immobilization effects are usually most pronounced thus allowing to study the immobilization phenomenon under the most favorable conditions (cf. Micke et al., 1994).

## 2. Modeling

The ZLC technique is based on chromatographic analysis of desorption curves obtained when a small sample of adsorbent particles is purged with an inert gas. A relatively high purge flow rate  $\dot{v}$  is used to maintain a low sorbate concentration at the external surface of the particles thus minimizing any external heat or mass transfer resistance. In general He is used as carrier and purge gas (cf. Eic and Ruthven, 1988, 1989; Ruthven and Brandani, 1996). The inlet concentration  $c_B$  is changed from  $c_0$  to  $c_\infty$  (usually  $c_\infty = 0$  is used) and the outlet concentration  $c$  is monitored as a function of time.

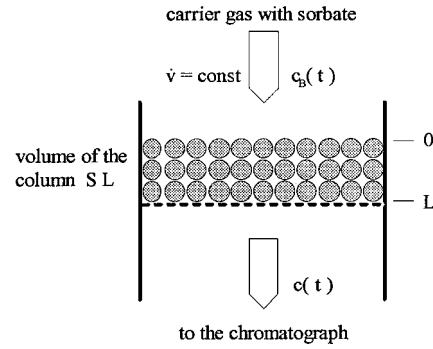


Figure 1. Experimental arrangement of a zero length column.

The mass balance for such an experimental arrangement as shown in Fig. 1 is given by

$$c_B - c = \frac{1}{\beta} \left( \frac{d}{dt} c + \frac{1 - \varepsilon}{\varepsilon} \frac{d}{dt} \bar{a} \right) \quad (1)$$

Therein  $c_B$  and  $c$  are inlet and outlet concentrations of the zero length column and  $\bar{a}$

$$\bar{a}(t) = \frac{1}{|V_s|} \int_{V_s} a(t; x) dx, \quad |V_s| = \int_{V_s} dx, \quad (2)$$

stands for the average concentration of sorbing species within the adsorbent which is presented by the volume  $V_s$ . The quantity  $a$  denotes the local concentration within a sorbing particle. The constants  $\beta$  and  $\varepsilon$  are defined as

$$\beta = \frac{\dot{v}}{S L \varepsilon} = \frac{u}{L}, \quad \varepsilon = 1 - \frac{|V_s|}{S L} \quad (3)$$

respectively,  $\dot{v}$  is the flow rate of the fluid phase,  $u$  is the interstitial velocity of the fluid phase,  $S$  is the cross section of the column and  $L$  the length of the sorbent layer.

The mass transport within the sorbent can be described by the Fick's second law and the mass balance for the overlaid immobilization process is:

$$\begin{aligned} \frac{\partial}{\partial t} a_{\text{mob}} &= D \Delta a_{\text{mob}} - \frac{\partial}{\partial t} a_{\text{immob}}, \quad t > 0, x \in V_s. \\ \frac{\partial}{\partial t} a_{\text{immob}} &= \lambda a_{\text{mob}} - \mu a_{\text{immob}} \end{aligned} \quad (4)$$

Here,  $D$  represents the intracrystalline diffusivity which is presumed to be constant with respect to the

considered concentration range. The quantities  $a_{\text{mob}}$  and  $a_{\text{immob}}$  denote the respective amounts of mobile and immobile molecules of the sorbate, while the constants  $\lambda$  and  $\mu$  are the rate constants of immobilization and mobilization, respectively (cf. Crank, 1956, p. 121). The total sorbate concentration is

$$a = a_{\text{mob}} + a_{\text{immob}}. \quad (5)$$

For  $\lambda = 0$  the transport Eq. (4) describes pure Fickian diffusion.

The boundary conditions for the sorbent are given by the sorption isotherm

$$\begin{aligned} a_s &= f_{\text{mob+immob}}(c) = a_{\text{mob}}^s(c) + a_{\text{immob}}^s(c) \\ &= f_{\text{mob}}(c) + f_{\text{immob}}(c) = Kc. \end{aligned} \quad (6)$$

where  $a_s, a_{\text{mob}}^s, a_{\text{immob}}^s$  are the respective concentrations of the species at the sorbent surface of the area  $\Gamma_{V_s}$ , and  $K$  is the Henry constant for total adsorbed amount.

To model the sorption behaviour, i.e. to determine the gas phase concentration curve  $c$  with respect to time, one has to solve the equation system which consists of the external mass balance (1), the averaging formula (2), the transport equation (4), the isotherm (6) and the initial conditions represented as:

$$\begin{aligned} c_B(t) &= c(t) = c_0 & a(0; x) &= a_0 = f(c_0) \\ t < 0 & & x &\in V_s, \\ a(t, x) &= a_s(t) = f(c(t)), & t \geq 0, \quad x &\in \Gamma_{V_s}. \end{aligned} \quad (7)$$

For idealized conditions as given one can solve this system explicitly (cf. Micke et al., 1994). In general the solution requires numerical techniques. A very efficient way to treat this system, is the application of the principle of superposition (cf. Courant and Hilbert, 1937) which is represented by:

$$\bar{a}(t) - \bar{a}_0 = \int_0^t \bar{H}'(t-s)(a_s(s) - \bar{a}_0) ds, \quad (8)$$

where  $\bar{H}$  denotes the normed average concentration for constant boundary conditions, i.e. it is the system response to an unit step in surface concentration ( $a_s$  changes from  $a_{0-}$  to  $a_{0+}$ ),

$$\bar{H}(t) = \frac{\bar{a}(t) - a_{0-}}{a_{0+} - a_{0-}}, \quad (9)$$

It can be shown that  $\bar{H}$  is of the form (Micke et al., 1994):

$$\bar{H}(t) = \bar{H}_{\text{mob}}(t) - \frac{\lambda}{\lambda + \mu} \bar{G}_{\mu}(t), \quad t \geq 0, \quad (10)$$

where  $R$  stands for the characteristic dimension of the zeolite crystal. The normed average concentration for the mobile sorbate  $\bar{H}_{\text{mob}}$  is given by

$$\begin{aligned} \bar{H}_{\text{mob}}(t) &= 1 - (\theta + 1) \sum_{n=0}^{\infty} \frac{2}{k_n^2} \left( \frac{k_n^2 - l_{n2}}{l_{n1} - l_{n2}} e^{-l_{n1}\tau} \right. \\ &\quad \left. + \frac{l_{n1} - k_n^2}{l_{n1} - l_{n2}} e^{-l_{n2}\tau} \right), \quad \tau = \frac{tD}{R^2}. \end{aligned} \quad (11)$$

The convolution function  $\bar{G}_{\mu}$  can be calculated by

$$\bar{G}_{\mu}(t) = 2(\theta + 1) \sum_{n=0}^{\infty} \frac{e^{-l_{n2}\tau} - e^{-l_{n1}\tau}}{l_{n1} - l_{n2}}, \quad \tau = \frac{tD}{R^2}. \quad (12)$$

where

$$l_{1/2} = \frac{\lambda + \mu + k^2}{2} \pm \sqrt{\left( \frac{\lambda + \mu + k^2}{2} \right)^2 - \mu k^2}. \quad (13)$$

Therein the values  $k$  are the eigenvalues of the equation

$$\begin{aligned} \cos(k_n) &= 0 & \text{for } \theta &= 0 \\ J_0(k_n) &= 0 & \text{for } \theta &= 1 \\ \sin(k_n) &= 0 & \text{for } \theta &= 2, \end{aligned} \quad (14)$$

which depends on the sorbent geometry ( $\theta = 0$ , plate;  $\theta = 1$ , cylinder;  $\theta = 2$  sphere). Introducing the normalized concentrations

$$\begin{aligned} \gamma_c(t) &= \frac{c(t) - c_0}{c_{\infty} - c_0}; & \gamma_{c_B}(t) &= \frac{c_B(t) - c_0}{c_{\infty} - c_0}, \\ c_{\infty} &= \lim_{t \rightarrow \infty} c_B(t), \end{aligned} \quad (15)$$

equations (1–4) and (6) can be rewritten as:

$$\begin{aligned} \gamma_c(t) &+ \alpha \int_0^t \bar{H}'(t-s) \gamma_c(s) ds \\ &= \beta \int_0^t (\gamma_{c_B}(s) - \gamma_c(s)) ds, \quad \alpha = \frac{1 - \varepsilon}{\varepsilon} K. \end{aligned} \quad (16)$$

This reduces the determination of concentration  $c$  (i.e.  $\gamma_C$ ) to the solution of a single Volterra integral equation.

### 3. Experimental

#### 3.1. ZLC Chromatographic Technique

To obtain the transport coefficients from a desorption curve several numerical techniques have been developed depending on the assumptions made. The following assumptions are often used:

- (i) step change of the inlet gas concentration  $c_B$
- (ii) pure *Fickian* diffusion
- (iii) negligible accumulation term
- (iv) linearity of the isotherm
- (v) constancy of the transport parameter

Under these conditions the model equations (mass balance, *Fick* diffusion equation) permit to determine the solution  $c/c_0$  explicitly (cf. Eic and Ruthven, 1988). The standard moment analysis (cf. Ko  r  k and Zik  nov  , 1970, 1974) can be directly used to calculate diffusivity coefficient. However, if the above assumptions are not valid, these methods are not applicable, thus it remains to be verified whether the conditions stated in (17) are fulfilled.

Conditions (iv) and (v) of (17) can always be satisfied if the change in concentration  $c_0 - c_\infty$  is sufficiently small. Accumulation (iii) can be eliminated by choosing a sufficiently high purge flow rate  $\dot{v}$ . The inlet concentration  $c_B$  is determined in blank experiments and can be compared directly with the monitored outlet concentration  $c$ . If the kinetic process is sufficiently slow the time delay due to the imperfect step shape of  $c_B$  can be neglected (cf. Micke et al., 1993).

A minimum conditions for a transport process to follow the second *Fick's* law requires that the full process behavior is explained by such model, i.e. the desorption vs. time curve must fully reflect the predicted behavior using *Fickian* diffusion equation (total curve fitting method, cf. B  low and Micke, 1995). However, a total curve fit requires a more complex approach involving iterative numerical methods which were carried out in Micke and B  low (1995), Micke et al. (1993, 1994).

In the case of conditions (ii) and (iv) as stated in (17), two parameters have to be fitted from an experimental desorption curve, the diffusion coefficient  $D$  and the equilibrium constant  $K$  (which is *Henry* constant in

case of  $c_\infty = 0$ ). These constants can be determined by using the least square difference fit between the experimental results and the model solution, i.e.

$$\int_0^\infty |c_{\text{measured}}(t) - c_{\text{model}}(t)|^2 dt \rightarrow \min \text{ for optimum } D, K \quad (18)$$

Carrying out the moment analysis, the equilibrium constant  $K$  can be directly determined satisfying the equality of the first moments, i.e.

$$\int_0^\infty c_{\text{measured}}(t) dt = \int_0^\infty c_{\text{model}}(t) dt. \quad (19)$$

The first moment of the measured desorption curve (left hand side of Eq. (19)) can be approximated by the finite integral  $\int_0^{t_{\text{end}}} c dt$  where  $t_{\text{end}}$  denotes the time the experiment is terminated (truncation). For slow sorption processes the truncation error  $\int_{t_{\text{end}}}^\infty c dt$  is not negligible. This term which represents the residue sorbate amount may be determined using temperature programmed desorption (TPD). However, diffusion of toluene in silicalite (system chosen in this study) is relatively fast, and the approximate solution for the first moment, as discussed above, was used (truncation error was considered negligible).

In all the runs the mass of the sample was held between 1.7 and 2.2 mg. Furthermore, to verify consistency of the experimental results for a number of selected runs different purge flow rates, i.e., 70–120 cm<sup>3</sup>/min range, were used. Void fraction of the ZLC bed was found to be about 0.5. The samples were activated in situ in a stream of helium (5–10 cm<sup>3</sup>/min) at 623 K for 24 hours. The same procedure was repeated after each experimental run.

To account for the apparatus effects, the inlet concentration vs. time curves  $c_B$  were measured in the absence of adsorbent under isothermal conditions (blank curves). These curves were used both for the kinetic simulations (cf. Ko  r  k and Zik  nov  , 1974 (change to normal script) and Ko  r  k and Zik  nov  , 1970) and to correct the integral balance of the moment analysis (cf. Micke and B  low, 1995).

#### 3.2. System Investigated

The experimental model system selected to analyze different gas/solid interactions was toluene/silicalite-1, where the specific sites for interaction with aromatics are mainly weak acid OH groups (internal silanols).

**3.2.1. Silicalite-1 Crystals and Sorbate.** Silicalite-1 crystals were synthesized according to references (Kočířík et al., 1998; Kornatowski, 1988). The sample consists of particles with average dimensions of  $207 \times 44.8 \times 41.4 \mu\text{m}$  (equivalent sphere radius  $57 \mu\text{m}$ ). The silicalite-1 crystals are  $90^\circ$ -intergrowths.

Toluene was provided by Aldrich Chemical Company, with a purity of 99.9%.

#### 4. Results and Discussion

The desorption curves for the system toluene/silicalite-1 @  $75^\circ\text{C}$ ,  $135^\circ\text{C}$ ,  $155^\circ\text{C}$  and  $178^\circ\text{C}$  were evaluated using pure *Fickian* diffusion to model the intracrystalline mass transport. Figure 2 shows the semi logarithmic plot for both the measured and the fitted desorption curves. By fitting the desorption curves over a short term range only (cf. Fig. 2), it is possible to satisfy both the integral balance (Eq. 18) and the lower limit conditions which allows a determination of the diffusion coefficient using the moment analysis. However, the long term asymptotic behavior of these simulated desorption curves does not match the experimental findings as shown in Fig. 3.

The determined diffusion coefficients under the assumption of pure *Fickian* diffusion depend on the chosen time interval where the desorption curve is fitted. An upper limit can be obtained from the arbitrarily chosen short term interval as shown in Fig. 2 while a lower limit can be obtained from the best fit over the full time region fulfilling Eq. (19) (cf. Fig. 4). This gives a wide

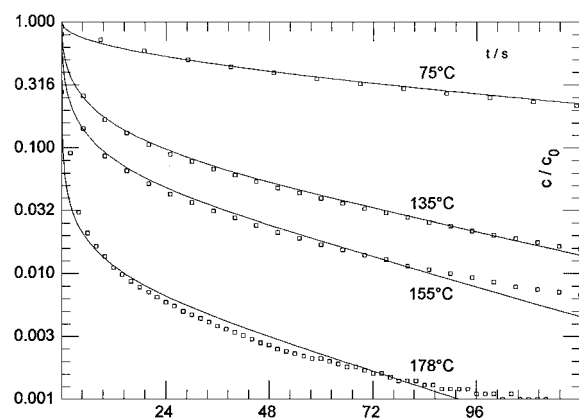


Figure 2. Short term evaluation using pure *Fickian* diffusion model @  $75^\circ\text{C}$ ,  $135^\circ\text{C}$ ,  $155^\circ\text{C}$  and  $178^\circ\text{C}$  for toluene/silicalite-1 system. In all figures the light solid lines represent simulated curves, while open symbols represent experimental data.

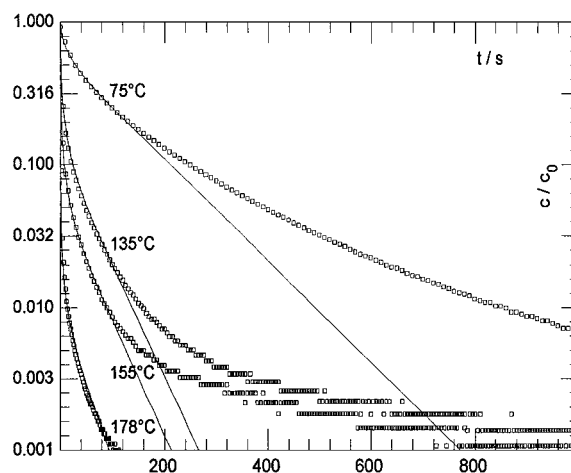


Figure 3. Short term fit of the ZLC curves for toluene/silicalite-1 using pure *Fickian* diffusion model @  $75^\circ\text{C}$ ,  $135^\circ\text{C}$ ,  $155^\circ\text{C}$  and  $178^\circ\text{C}$  in comparison with the measured desorption curves over the full time range.

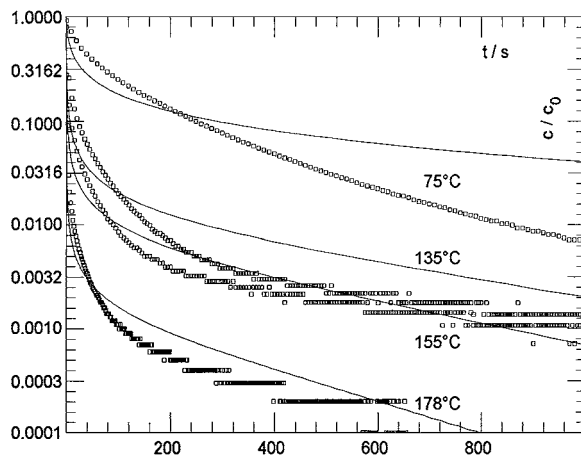
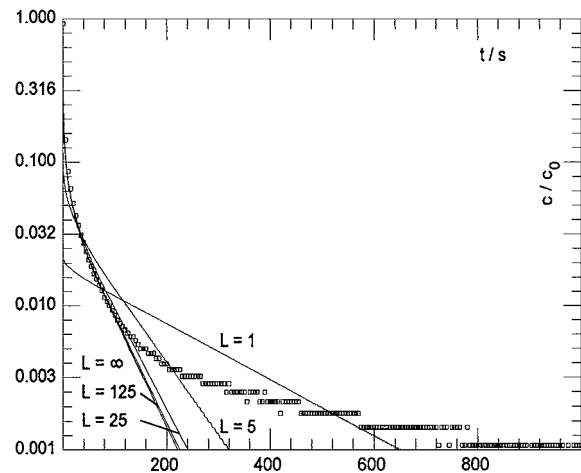
range of the diffusion values (see Table 1, columns 2 and 3). The significant deviation of the asymptotic behavior as shown in Figs. 3 and 4 indicates that a modeling using pure *Fickian* diffusion is not adequate to describe the transport process of toluene in silicalite-1. The values in Table 1 (column 3) for the *Fickian* diffusion via *Volterra* method were obtained for the fit over the full time region by satisfying the same first moment of the measured and simulated desorption curves (cf. Eq. (19)). These values do not follow the lower limit restriction as obtained from the moment analysis (column 2) in particular at lower temperatures, e.g. at  $75^\circ\text{C}$  more than one order of magnitude difference is found.

The observed tailing effects could be caused either by a surface barrier or an immobilization mechanism being superimposed to the *Fickian* transport process.

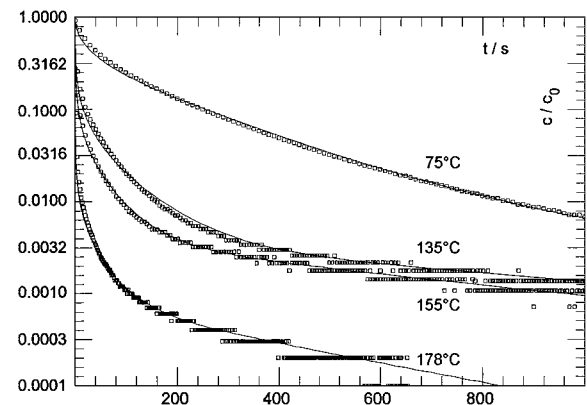
The ZLC solution for the case of a surface barrier only involves two exponential terms which produce an apparent jump at the beginning of the desorption process followed by asymptotic tailing (cf. Micke et al., 1993, Eq. (32)). A modeling involving a surface barrier superimposed to the *Fickian* diffusion smoothes such a jump behavior at the beginning of the process. However, the tailing process has a different nature as shown in Fig. 5. By simple comparison of the experimental curves with the model curves as shown in Fig. 5 it is obvious that a surface barrier superimposed to diffusion does not sufficiently represent the observed process behavior of the toluene/silicalite-1 system.

Table 1. Toluene/silicalite-1 transport properties.

$T/^{\circ}\text{C}$	Moment analysis	Volterra integral equation method full time range				
	Lower limit	Pure <i>Fickian</i> diffusion	<i>Fickian</i> diffusion with coupled immobilization			
	$D/\frac{\text{m}^2}{\text{s}}$	$D/\frac{\text{m}^2}{\text{s}}$	$D/\frac{\text{m}^2}{\text{s}}$	$\lambda/\frac{1}{\text{s}}$	$\mu/\frac{1}{\text{s}}$	$\frac{\lambda}{\mu}$
178	$>3.0 \text{ E-}12$	$1.1 \text{ E-}12$	$3.0 \text{ E-}12$	0.0080	0.0050	1.6
155	$>2.4 \text{ E-}12$	$8.0 \text{ E-}13$	$2.4 \text{ E-}12$	0.0080	0.0030	2.7
135	$>2.2 \text{ E-}12$	$6.3 \text{ E-}13$	$2.2 \text{ E-}12$	0.0045	0.0018	2.5
75	$>1.5 \text{ E-}12$	$2.0 \text{ E-}13$	$2.0 \text{ E-}12$	0.0008	0.0018	0.4

Figure 4. Evaluation of the complete ZLC curves for toluene/silicalite-1 using pure *Fickian* diffusion model @ 75°C, 135°C, 155°C and 178°C based on full time range and Eq. (19) fulfilled.Figure 5. Evaluation of the ZLC desorption curves for toluene/silicalite-1 @ 155°C using *Fickian* diffusion superimposed by a surface barrier for different settings of the surface barrier coefficient  $L = 1, 5, 25, 125, \infty$ .

Assuming an immobilization mechanism in addition to the *Fickian* diffusion, one can fit the model to the experimental findings using parameter settings as given in the last three columns of Table 1. In addition the diffusivity values determined from the moment analysis were also used. For all temperatures the desorption curves can be matched over the entire time interval of the measurement as shown in Fig. 6. However, the above approach using diffusion coupled with an immobilization process requires a three parameter fit: diffusivity  $D$ , immobilization rate  $\lambda$  and mobilization rate  $\mu$  (cf. Micke et al., 1993, Eq. (5)). Such three parameter problem cannot be solved considering a single desorption curve only, since additional information is necessary. It is shown, that the parameters  $\lambda$  and  $\mu$  must follow a certain concentration dependence (cf. Micke et al., 1994, Eqs. (15) and (16)), i.e. a full analysis requires the desorption curves for more than one concentration level. Due to limitations of the standard ZLC arrangement to operate in differential concentration mode beyond the *Henry* region, a

Figure 6. Evaluation of the complete ZLC curves for toluene/silicalite-1 using model of *Fickian* diffusion with overlaid immobilization @ 75°C, 135°C, 155°C and 178°C.

verification of such concentration dependence was not carried out.

The specific arrangement of silicalite-1-90°-intergrowths creates unique conditions during filling or emptying of the void space in the crystals. The majority of the molecules can penetrate the crystal via sinusoidal channels, which act as the transport pores for radial diffusion. The segments of straight channels can be filled instantaneously at a sufficiently high temperature from adjacent channel cross-sections. At higher temperatures the only effect associated with the filling the pockets outside the radial transport channels (i.e. straight channels) is considered to be due to a decrease in the effective coefficient of the radial diffusion (according to Eq. (12) in Micke et al., 1993). This is equivalent to a process involving equilibrium immobilization in a biporous sorbent due to instantaneous equilibrium between macropore bulk and its wall. At lower temperature there is a possibility that transition between sites in sinusoidal channels and those in straight channels are hindered according to mechanisms (i) and (ii) (or their combination) as presented in the introductory section. The presence of a barrier for transport at boundaries between the crystal domains of different crystallographic order in MFI type structure was confirmed in the study involving intracrystalline diffusion of iso-butane in silicalite-1 crystals by Geier et al. (2001). Relatively weak interactions of benzene ring with weak acid groups of silicalite-1 and/or other hydrophilic centers which were found to be present in the concentration of about 1 center per channel cross-section are not expected to contribute significantly to immobilization involving this system. At higher temperatures, i.e., 178°C the local equilibrium is established everywhere throughout the crystal and in the *Henry* region one can directly compare the corresponding estimations of  $D$  with the corrected diffusion coefficients  $D_0$ , which can be found in the literature. Results for pure *Fickian* and coupled diffusion with immobilization for higher temperatures as shown in Table 1 are in reasonable agreements. However, the condition for the lower limit, according to the moment analysis, is not fulfilled supporting earlier findings of inadequacy of using the pure *Fickian* diffusion model, especially at lower temperatures. Diffusion coefficients obtained from gravimetric measurements by Zikánová and Derewinski (1995) for benzene-silicalite-1 extrapolated to 451 K give the value of  $D_0 \cong 1.1 \text{ E-12 m}^2/\text{s}$ . A similar extrapolation of  $D_0$  data for benzene-silicalite-1 from frequency-response technique by Shen and Rees

(1991) gives the value  $6.0 \text{ E-13 m}^2/\text{s}$ , which is in accordance with the earlier ZLC chromatographic results for benzene-silicalite-1 by Eic and Ruthven (1989).

The actual or relative amounts of immobilized species can be estimated from temperature programmed desorption (TPD) experiment, which is normally carried out for the tail portion of the ZLC curve for an arbitrary chosen desorption time interval (after the change of the curve's slope). Results of these experiments for toluene/silicalite system were reported in our earlier publication (see, Jama et al., 1999). The largest residual amounts, that were attributed to immobilized species, were found at the lowest temperatures, i.e., at 75°C about 8% of residual species were reported, while at the higher temperatures relative amounts were much smaller, usually less than 3% (Jama et al., 1999). Further study using FTIR spectroscopy is required to determine a real nature of the residual species' interaction with the adsorbent.

## 5. Conclusions

Zero Length Column chromatography was successfully used to study combined diffusion-immobilization phenomena in selected zeolite crystals. The experimental ZLC data for toluene/silicalite-1 (75°C–178°C) could not be fully explained by *Fickian* diffusion model only. The immobilization in the case of toluene/silicalite is caused by geometrical constraints of the silicalite-1 90° intergrowth specific channel system. The ratio  $\lambda/\mu$  quantifies relative sorbate amount immobilized. This ratio remains approximately constant for the considered temperature range. Earlier intracrystalline diffusion results obtained under the assumption of pure *Fickian* diffusion processes that ignores tailing of response curves should be taken with a great caution. A superimposed immobilization process may change the 'effective diffusivity' by orders of magnitudes as follows from the relation

$$D_{\text{eff}} = \frac{D}{1 + \lambda/\mu}$$

which was derived in Micke and Bülow (1992).

To assess the full contribution of both temperature and concentration on the immobilization and to reduce uncertainties in determining the model parameters future studies should involve ZLC measurements over wider concentration range, i.e. ZLC method needs to be extended to  $c_\infty > 0$ .

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## Nomenclature

$a$	Local sorbate concentration (mol/m <sup>3</sup> )
$\bar{a}$	Average sorbate concentration (mol/m <sup>3</sup> )
$a_{\text{mob}}$	Concentration of the mobile sorbate (mol/m <sup>3</sup> )
$a_{\text{immob}}$	Concentration of the immobile sorbate (mol/m <sup>3</sup> )
$a_s$	Concentration at sorbent surface (mol/m <sup>3</sup> )
$c$	Outlet concentration (mol/m <sup>3</sup> )
$c_B$	Outlet concentration in blank experiment (mol/m <sup>3</sup> )
$c_0$	Inlet concentration (mol/m <sup>3</sup> )
$D$	Diffusivity (m <sup>2</sup> /s)
$\bar{H}$	Normed average concentration for constant boundary conditions
$J_0$	Bessel function of order zero (-)
$K$	Equilibrium constant (Henry constant for low concentration) (-)
$L$	Length of the sorbent layer (m)
$l_{n1}, l_{n2}$	Eigenvalues of Eq. (13)
$T$	Temperature (°C)
$u$	Interstitial velocity of the fluid phase (m/s)
$\dot{v}$	Volumetric flow rate (m <sup>3</sup> /s)
$V_s$	Volume of the sorbent (m <sup>3</sup> )
$\lambda$	Immobilization rate constant (1/s)
$\mu$	Mobilization rate constant (1/s)
$\Gamma_{V_s}$	Surface of the sorbent volume $V_s$ (m <sup>2</sup> )

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