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Liquid Phase Counter-Diffusion Measurements of Aromatics in Silicalite Using the ZLC Method

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Abstract. We have developed a liquid phase Zero Length Column apparatus in order to study the counter-diffusion of aromatic compounds, benzene, toluene, m-, o- and p-xylene, in silicalite crystals. Our results show ZLC desorption curves that are consistent with the model of Brandani and Ruthven (1995). The apparent diffusivities fall in a narrow range of approximately 1 order of magnitude for all the investigated molecules. The results for o-xylene led us to investigate in detail possible mechanisms that can give erroneous results when applying the liquid ZLC technique. We have derived solutions to models for valve leakage and obtained an explanation to the experimental results.

Keywords: diffusion in zeolites, silicalite, xylenes, ZLC method

Introduction

Among the many contributions to the field of adsorption science made by Professor D.M. Ruthven, the Zero Length Column (ZLC) method to measure diffusion in zeolites represents an example of his insight in translating a concept of chemical reactor design to a useful tool for the characterisation of molecular transport in zeolites. The original idea for the ZLC system dates back to the late 1970s (Ruthven, personal communication), but it was not until the late 1980s that the well-known Eic and Ruthven (1988) paper appeared. Since then more than 50 scientific papers (ISI Jan. 2001) have been reported on the subject and almost all have dealt with gaseous systems. After the first application to liquid phase (Ruthven and Stapleton, 1993), the liquid phase ZLC has been applied only to few systems (Boulicaut et al., 1998; Rodriguez et al., 1998). Therefore, while for gas phase we can say that the ZLC is a well-established technique and that it is well understood, the same cannot be stated for the liquid phase counterpart. We have assembled a liquid ZLC system in our labs and have chosen to investigate the behaviour of aromatic compounds in silicalite for the reasons outlined below.

In a recent study (Boulicaut et al., 1998) of liquid phase diffusion in silicalite, it was shown that intracrystalline diffusion coefficients for single and double-branched paraffins were quite similar and up to two orders of magnitude larger than previous gas phase measurements (Cavalcante and Ruthven, 1995). The possible explanation given for this difference was that relaxation of the crystal lattice under saturated conditions led to a loss in kinetic selectivity for these critically sized molecules. Liquid phase counter-diffusion coefficients of aromatic compounds should show a similar behaviour and in particular the main interest is on the xylene isomers, since these molecules are critically sized (Gates, 1991). Under normal gas phase conditions only p-xylene diffuses at appreciable rates in silicalite (Brandani et al., 2000), and one would expect that m-xylene could diffuse in an enlarged lattice, while o-xylene should not diffuse into silicalite unless a dramatic effect is present. From a macroscopic measurement it could be possible, in principle, to detect the

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behaviour of the zeolite framework at the microscopic level.

Experimental

Measurements were carried out using $200 \times 50 \times 50$ μm silicalite crystals, equivalent radius 28 μm, synthesized by Prof. David Hayhurst and previously used by Boulicaut et al. (1998). The ZLC column was packed with 5.4 mg of crystals, while blank runs were performed with an empty column and one packed with 5.2 mg glass beads, with an average radius of 26 μm. Chemicals used were n-Hexane, m-, p- and o-xylene HPLC grade purchased from Sigma, and Benzene, analytical reagent grade, and toluene hyper-solvent grade purchased from Merck. The purge and carrier liquids were degassed for 30 min using an Ultra Wave ultrasonic bath prior to each series of experiments. The experimental setup consisted of two HPLC pumps, a Jasco Model PU1560 and a Waters model 510. All tubing and connectors from the pumps are stainless steel Swagelok parts. The schematic diagram of the ZLC system is shown in Fig. 1. The highlighted section of tubing was designed in order to minimise any dead volume. The water bath temperature was controlled using a Haake D3 temperature controller and both valve and column were placed in the thermostated fluid.

The experiments are carried out by initially saturating the column with the carrier stream, which is typically a 0.05% w/w solute-n-hexane mixture, and then switching to the pure n-hexane solvent purge stream. The desorption curve is monitored using a data acquisition system.

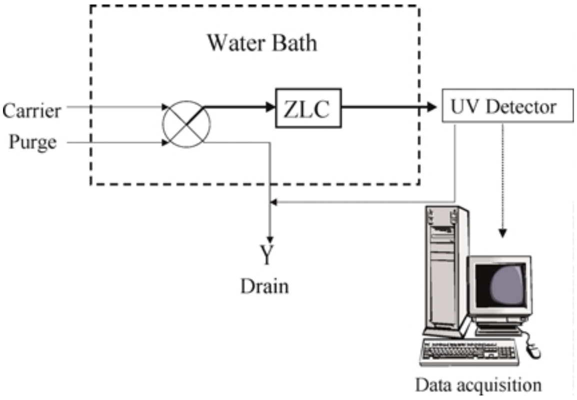


Figure 1. Schematic representation of the liquid ZLC setup.

Table 1. Summary of experimental conditions.

Solute	Temperatures (°C)	Flow rates (ml/min)
Benzene	20, 30, 40	0.1, 0.3, 0.5, 1.0
Toluene	0, 20, 30, 40	0.1, 0.3, 0.5, 1.0, 1.5, 2.0
p-Xylene	20, 30, 40	0.1, 0.3, 0.5, 1.0
m-Xylene	20, 30, 40	0.1, 0.3, 0.5, 1.0
o-Xylene	20, 30, 40	0.1, 0.3, 0.5, 1.0

The set of experimental conditions used in the present study is summarized in Table 1.

The series of experiments carried out using toluene at 0°C was performed using ice in the tank. This temperature level was abandoned from the experimental programme since the valve used was only rated to 10°C and showed appreciable leakage at a lower temperature.

Experimental Results

The experimental desorption curves were analyzed using the analytical solution to the liquid ZLC model developed by Brandani and Ruthven (1995).

$$\frac{c}{c_o} = \sum \frac{2L\exp\left(-\beta_n^2\tau\right)}{\beta_n^2 + \left(1 - L + \gamma\beta_n^2\right)^2 + L - 1 + \gamma\beta_n^2} \tag{1}$$

where β_n are the positive roots of

$$\beta_n \cot \beta_n + L - 1 - \gamma\beta_n^2 = 0 \tag{2}$$

and the model parameters are

$$L = \frac{1}{3}\frac{FR^2}{KV_S D} \quad \gamma = \frac{1}{3}\frac{V_F}{KV_S} \quad \tau = \frac{D}{R^2}t$$

with F the flowrate, K the equilibrium constant, V_F the fluid volume and V_S the solid volume. The three model parameters can be extracted from the experimental curves in two different ways. The simple analysis of the asymptotic behaviour shows that in the short time Eq. (1) reduces to Brandani and Ruthven (1995)

$$\ln\frac{c}{c_o} = -\frac{F}{V_F}t \tag{3}$$

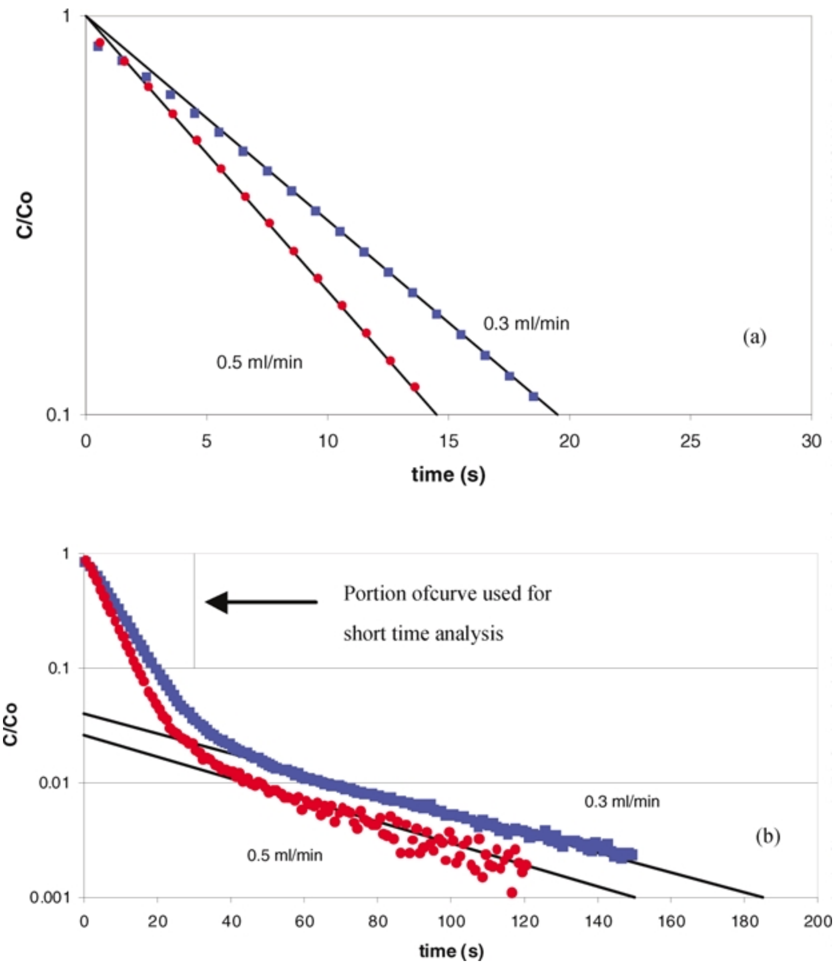


Figure 2. Short (a) and long (b) time asymptotes for o-xylene at 40°C.

while, in the long time region

$$\ln\frac{c}{c_o} = \ln\left[\frac{2L}{\beta_1^2 + \left(1 - L + \gamma\beta_1^2\right)^2 + L - 1 + \gamma\beta_1^2}\right] - \beta_1^2\tau \qquad (4)$$

Therefore, in a semilog plot, from the slope of the short time asymptote and the intercept and slope of the long time asymptote the three model parameters may be found. Alternatively direct numerical fit of the experimental curves can be carried out using a nonlinear regression algorithm (Brandani and Ruthven, 1995). The model parameters were all obtained from the simultaneous analysis of experiments carried out at two different flowrates. Figure 2 shows an example of the simplified procedure, while Fig. 3 shows the results of the full curve fitting procedure, with the solid lines representing the curves obtained from Eq. (1). Both methods yield consistent values for the physical parameters. Table 2 shows a summary of the results at 20°C.

From this table it can be seen that there is a trend in the diffusion coefficients, but surprisingly there is a small difference between the values of the different isomers, with o-xylene diffusing at a significant rate. This is clearly shown in Fig. 4, which also presents a comparison with the extrapolated values obtained from gas phase experiments (Brandani et al., 2000).

Table 2. Summary of experimental results at 20°C.

	Benzene	Toluene	p-Xylene	m-Xylene	o-Xylene
D × 10^8 (cm^2/s)	1.9	1.0	1.2	1.4	0.4

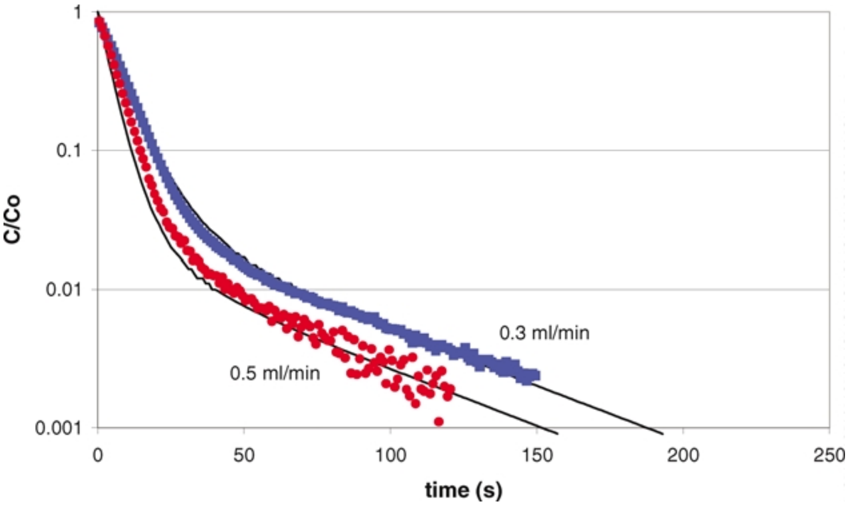


Figure 3. Results of the full curve fitting procedure.

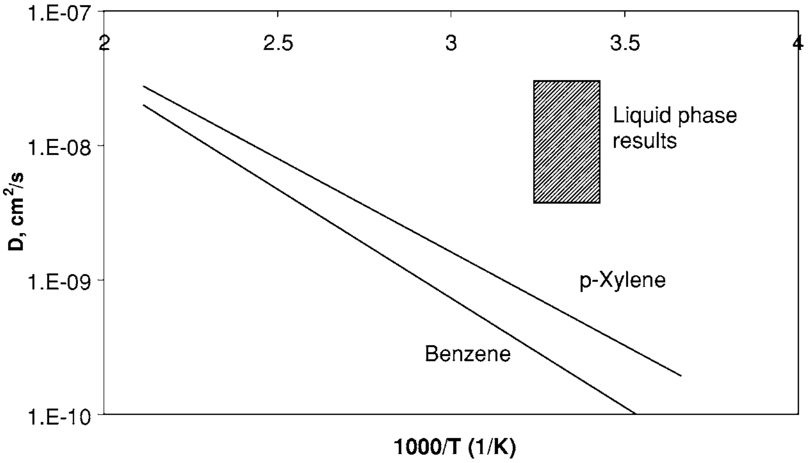


Figure 4. Comparison of liquid and gas phase results.

As found by Boulicaut et al. (1998), the liquid phase diffusivities are higher than in the gas phase. The result found for o-xylene, though, is beyond what could be expected considering the size of the molecule. The openings of the channels in silicalite are roughly elliptical with main dimensions of 5.4 × 5.6 Å for the straight channels and 5.1 × 5.5 Å for the zig-zag channels (Gates, 1991). Benzene has a critical molecular dimension of 5.13 Å (Gates, 1991). This can be taken also as the characteristic dimension for toluene and p-xylene. o-Xylene has a critical molecular dimension of 5.64 Å (Gates, 1991) and an estimate of 5.38 Å can be obtained for m-Xylene. Therefore o-Xylene should not be diffusing at an appreciable rate in silicalite. Using a column packed with glass beads of similar size as the zeolite crystals, a new series of blank experiments was carried out and the comparison of these with the o-xylene response curve is shown in Fig. 5.

Possible Explanations to the Observed Behaviour

The evidence tends to point to spurious effects that, at least for o-xylene, dominate the dynamic response of the system. As previously mentioned, in the first series of experiments using toluene the valve showed significant leakage below the rating temperature of 10°C.

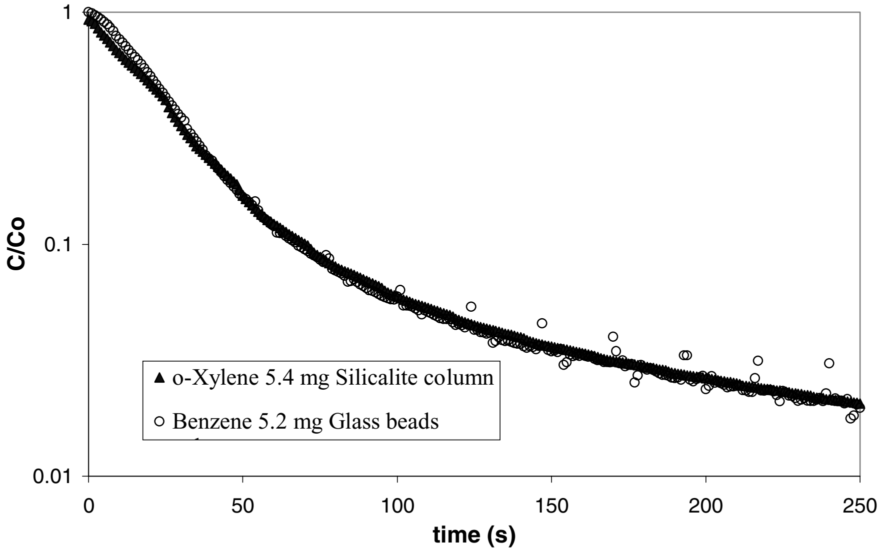


Figure 5. Comparison of o-xylene and blank benzene experiments (0.1 ml/min).

Therefore, we decided to investigate in detail the geometry of the valve and found that internally the valve includes a small 1/8″ ring, approximately 2 mm in length, which aligns the flow from the rotor.

Based on these observations there appear to be two possible explanations to the observed results for o-xylene, and these are either a leakage between the carrier and purge lines in the valve, or the existence of a side pocket of stagnant fluid through which the molecules have to diffuse in order to reach the main flow through the ZLC and the detector. Obviously a combination of the two is also possible.

Qualitatively the behaviour of a stagnant side pocket should resemble the normal liquid ZLC dynamics, as we have an accumulation volume through which mass transfer is achieved via molecular diffusion. Assuming a radius of the ring of approximately 1.5 mm we find a potential side pocket of 40 μl. If we now use the liquid phase diffusivity of Toluene in n-Hexane (Reid and Sherwood, 1964), we can have an estimate for the order of magnitude of the time constant associated with this side pocket, which is approximately 2×10^{-3} s^{-1}. This value is within the range observed and should represent a lower limit since there is a flow region and thus the diffusion path will be smaller than the entire radius of the ring.

To analyse the second possibility, i.e. the leakage through the valve, we need to develop a model for this process. Since at higher temperatures, there is no evidence of significant leakage we can assume that the gap is sufficiently small that there is only molecular diffusion through a diffusion path connecting the purge and carrier lines. In this case we can write the cell mass balance

$$V_F \frac{dc}{dt} + Fc - Fc_{IN} = 0 \tag{5}$$

the mass balance in the channel connecting the purge and carrier streams

$$\frac{\partial q}{\partial t} = D_L \frac{\partial^2 q}{\partial x^2} \tag{6}$$

with boundary conditions

$$q_{x=0} = c_o \qquad -D_L S_{Ch} \left.\frac{\partial q}{\partial x}\right|_1 = Fc_{IN} \tag{7}$$

$$\begin{aligned} q_{x=1} &= c \quad \text{Leakage directly into ZLC (model 1)} \\ q_{x=1} &= c_{IN} \quad \text{Leakage into feed flow (model 2)} \end{aligned} \tag{8}$$

Although model 2 represents the case at hand we decided to investigate model 1 as well since this would correspond to the option of placing the ZLC column directly into the valve. This option is of relevance since it would minimize the dead volume of the ZLC system. Mass transfer in the particles is not considered as we aim to provide an explanation to the o-xylene results.

The solutions to the two models are given in Eqs. (9) and (10) for model 1 and 2 respectively:

$$\frac{c}{c_o} = \sum \frac{2(L+1) + 2\beta_n^2\left(\beta_n \sin\beta_n - \cos\beta_n\left(L - \gamma\beta_n^2\right)\right)}{\beta_n^2 + \left(\gamma\beta_n^2 - L\right)^2 + L + \gamma\beta_n^2} \times \exp\left(-\beta_n^2\tau\right) \tag{9}$$

$$\frac{c}{c_o} = \sum \frac{2L(L+1) + 2L\beta_n^2(\beta_n \sin\beta_n - L\cos\beta_n)}{\left[\beta_n^2 + L(L+1)\right]\left(L - \gamma\beta_n^2\right)} \times \exp\left(-\beta_n^2\tau\right) \tag{10}$$

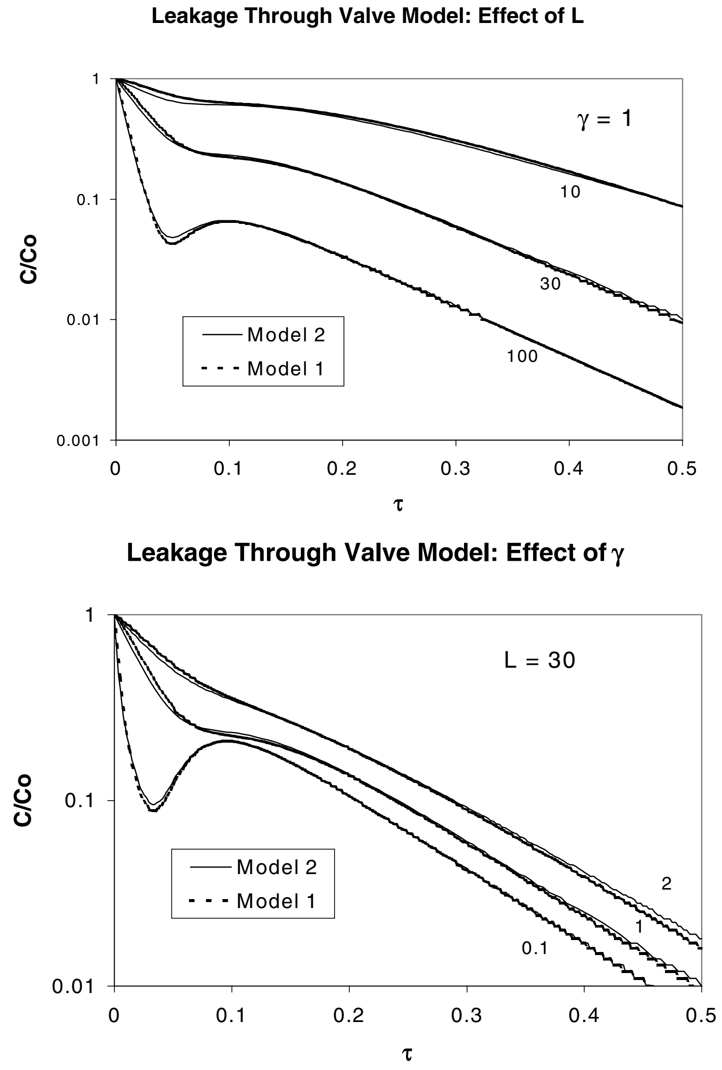
with

$$\beta_n \cot\beta_n + L - \gamma\beta_n^2 = 0 \tag{11}$$

and

$$L = \frac{Fl^2}{V_{\mathrm{Ch}}D_{\mathrm{L}}} \quad \gamma = \frac{V_{\mathrm{F}}}{V_{\mathrm{Ch}}} \quad \tau = \frac{D_{\mathrm{L}}}{l^2}t$$

Here V_{Ch} is the volume of the channel and l is its length, while D_{L} is the liquid molecular diffusivity in n-hexane. Although Eqs. (1), (9) and (10) appear to be similar, the actual response curves calculated from Eqs. (9) and (10) exhibit a characteristic double curvature behaviour, which can be seen in Fig. 6,



Leakage Through Valve Model: Effect of L

Leakage Through Valve Model: Effect of γ

Figure 6. Calculated curves from leakage through valve model.

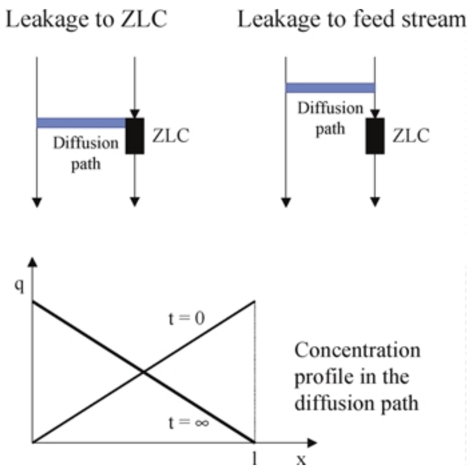


Figure 7. Schematics of valve leakage configurations and initial and final concentration profiles in the diffusion path.

and the response curves may exhibit a maximum and minimum. Figure 6(a) shows the effect of a change in flow rate, while Fig. 6(b) shows the effect of the ratio of the accumulations in the channel and ZLC void volume. To understand why this double curvature is present one needs to consider the concentration profile in the section connecting the purge and carrier streams. A schematic diagram is shown in Fig. 7. If the flow rate is sufficiently high the concentration in the ZLC column will drop to a low value before the diffusion flux through the leaking valve is established, hence there will be a minimum in the apparent desorption curve.

Since our experiments do not show the double curvature behaviour, the leakage model could provide a possible explanation to the results if the range of flow rates that we have explored is sufficiently low or if the volume of the channel is of the same order of magnitude as the void volume. It is interesting to point out that the double curvature in liquid ZLC systems can result also from the application to ion-exchange resins (Rodriguez et al., 1998).

Conclusions

We have investigated the liquid phase counter-diffusion of aromatics in silicalite and found that the diffusion coefficients follow the order: benzene $>$ toluene $\approx$ p-xylene $\approx$ m-xylene $>$ o-xylene. The apparently fast rate for o-xylene has been shown to be due to spurious effects, and our analysis has shown that these can be attributed either to a stagnant liquid volume or a valve leakage, or a combination of the two. These effects may have affected also the measurements for the other aromatics, but the observed desorption curves are sufficiently different from the blank experiments to say that at least in terms of orders of magnitude, the liquid phase diffusivities appear to be higher than the extrapolated gas phase measurements. We have not attempted to try and decouple the spurious effects from the internal diffusion process in the measurements we have carried out since the better option is to improve the experimental setup and repeat these experiments.

The analysis presented has shown that flow-mixing in liquid phase ZLC experiments plays a major role and careful design is needed to avoid the intrusion of spurious effects. Experimental curves that conform to the original liquid phase ZLC model (Brandani and Ruthven, 1995) may be obtained from side pockets of stagnant liquid or from valve leakage under low flow rate conditions. If double curvature responses are obtained at high flow rates our study shows that the most likely explanation would be a leaking valve. It is important to point out that for gaseous systems these problems could be relevant only in a poorly designed system since the solid capacity is typically two or more orders of magnitude larger than the gas phase.

As a final recommendation, any liquid ZLC study should present experimental results showing blank runs using a column packed with inert material of the same size as the adsorbent material studied.

Nomenclature

c	Concentration liquid phase (mol/m^3)
D	Diffusion coefficient (m^2/s)
D_L	Diffusion coefficient in the liquid phase (m^2/s)
F	Volumetric flow (m^3/s)
K	Dimensionless equilibrium constant
l	Length of leakage channel (m)
L	Dimensionless ZLC parameter
q	Concentration in solid phase (mol/m^3)
R	Particle radius (m)
S_{Ch}	Cross-sectional area of leakage channel (m^2)
t	Time (s)
V_F	Volume of liquid phase (m^3)
V_S	Volume of solid particles (m^3)
x	Distance along the leakage channel (m)

Greek Letters

β Roots of Eqs. (2) or (11)
γ Dimensionless group that accounts for liquid phase accumulation
τ Dimensionless time

Acknowledgments

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