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# Diffusion of aromatic hydrocarbons in silicalite/HZSM-5

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**Abstract** Diffusion of benzene and the xylene isomers in silicalite/HZSM-5 has been studied by a wide range of different experimental techniques. The available data are reviewed in an attempt to draw general conclusions concerning the intracrystalline diffusion process. The results for benzene are remarkably consistent, and the conformity between transport and tracer diffusion and between single crystal membrane and ZLC and frequency response data suggests that diffusion is essentially isotropic with no significant difference between the self and "corrected" transport diffusivity. The situation is more complex for p-xylene which shows clear evidence of non-isotropic behavior and a significant difference between tracer and transport diffusivities.

**Abbreviations**

| | |
|---|---|
| b | Langmuir equilibrium constant |
| D | Diffusivity |
| $\overline{D}$ | Average value of D |
| $D_o$ | Thermodynamically corrected diffusivity |
| $D_i$ | Diffusivity in direction i where i = x, y or z |
| $\mathscr{D}$ | Tracer or self-diffusivity |
| K | Henry constant |
| $\ell$ | Thickness of membrane |
| p | Partial pressure of sorbate |
| $q_s$ | Saturation capacity |
| x, y, z | Half-width, half-thickness or half-length of crystal |

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## 1 Introduction

Stimulated by the goal of developing a cost effective separation process, the adsorption and diffusion of single ring aromatics in silicalite has been widely studied by several different experimental techniques. A detailed review of these data provides a generally coherent picture of the behavior and comparisons between the diffusivities determined by different experimental techniques yield some interesting insights which are not apparent from the individual studies.

## 2 Benzene

Many years ago Riekert (Beschmann et al. 1987) showed that carefully measured uptake curves for benzene-silicalite, even when measured over a large (integral) concentration step, are consistent with the simple Fickian diffusion model. More recently measurements have been made by a variety of different techniques for both silicalite (Si/Al > 1000) and HZSM5 (Si/Al < 30). The results, which are summarized in Fig. 1, are broadly consistent. It is evident that diffusion in silicalite is significantly faster than in HZSM5 but the activation energies are almost the same (27–28 kJ/mole).

Recent ZLC and tracer ZLC (TZLC) measurements show that the self diffusivity ($\mathscr{D}$) is almost independent of loading and close to the limiting (or corrected) transport diffusivity ($D_o$) (Brandani et al. 2000). Frequency response (FR) measurements are broadly consistent although they suggest that $D_o$ decreases at higher loadings (Song and Rees 2000) (see Fig. 2). Diffusion of benzene in the direction of the z-axis (the longest axis) has been measured by Shah and Liou (1994) in an oriented single crystal membrane. Unfortunately the measurements were carried out at high loadings such that the thermodynamic correction factor is

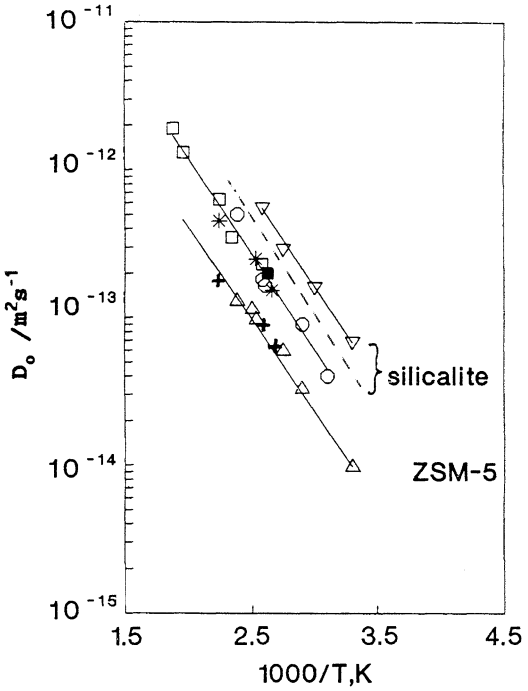


**Fig. 1** Arrhenius plot showing temperature dependence of corrected diffusivity ($D_o$) for benzene in silicalite and HZSM-5 as measured by different experimental techniques. □, van den Begin et al. (square wave) (van den Begin et al. 1989); o, Eic and Ruthven (ZLC) (Eic and Ruthven 1989); p, △, Zikanova et al. (piezometric) (Zikanova et al. 1987); +, Shen and Rees (square wave) (Shen and Rees 1991); ■, Förste et al. (NMR tracer exchange) (Förste et al. 1990); —- Brandani et al. (ZLC/TZLC) (Brandani et al. 2000)

large. However, re-analysis of these data making due allowance for the thermodynamic factor (Ruthven in press) yields values which are consistent with the extrapolation of the ZLC/TZLC data to 298 K (see Fig. 3).

If diffusion in silicalite is non-isotropic with a smaller diffusivity in the z-direction, as might be expected from the channel geometry, ZLC or FR measurements will yield a diffusivity close to the average of the diffusivities in the y (straight) channel and x (sinusoidal channel) directions (see the Appendix), whereas the single crystal membrane technique yields, unequivocally, the diffusivity in the z-direction. The observation that, for benzene in silicalite, these values coincide implies that, for this system, diffusion must be close to isotropic. This suggests that, at each channel intersection, the benzene molecule has equal probability of moving into any of the four intersecting channels, i.e. the molecule can either continue along the straight (or sinusoidal) channel or change direction from straight to sinusoidal channels (or vice versa) with equal probability. Such a model also explains the observed coincidence between $D_o$ and $\mathcal{D}$ from ZLC and TZLC data (Brandani et al. 2000). Thus, for diffusion of benzene, the experimental results appear to be broadly consistent with this simple picture.

## 3 p-xylene

The diffusional behavior of p-xylene is evidently more complex than that of benzene. Riekert's integral uptake rate measurements (Beschmann et al. 1987) show clearly that (in contrast to benzene) the adsorption of p-xylene in silicalite does not conform to the simple Fickian model. These measurements were, however, carried out at 298 K (below the monoclinic-rhombic transition) and differential measurements at higher temperatures (Ruthven et al. 1991) suggest consistency with the Fickian model, albeit with a concentration dependent diffusivity. There is some evidence that the phase transition is stimulated by adsorption of p-xylene (Fyfe et al. 1989; Kokotailo et al. 1989), which would explain the complexity of the uptake behavior at low temperatures (Karsli et al. 1992).

In contrast to benzene the ZLC/TZLC data for p-xylene (Brandani et al. 2000) show that the self-diffusivity is significantly smaller than the corrected transport diffusivity ($\mathcal{D} \approx D_o/3$), as shown in Fig. 3. The actual diffusivities (in the z-direction), as measured by Shah and Liou (1994) lie somewhat above the extrapolation of the $D_o$ values derived from ZLC measurements but when the thermodynamic factor is allowed for the values derived for the corrected diffusivity in the z-direction lie close to the extrapolation of the self-diffusivity data (Ruthven in press). This observation can be explained if it is assumed that (in contrast to benzene) the longer p-xylene molecules can jump between the straight and sinusoidal channels only with some difficulty. Self-diffusion requires jumps between the two channel systems (for the molecules to pass each other) and transport diffusion in the z-direction also requires such jumps. It is therefore to be expected that these processes will occur at similar rates, so the observation that $D_{oz} \approx \mathcal{D} \approx D_{xy}/3$ is understandable.

Substantially higher diffusivities for p-xylene were reported by Song and Rees (1994, 2000) (see Fig. 4) based on their FR measurements which showed a bimodal response. They attributed the bimodal response to independent diffusion in the y (straight channel) and x (sinusoidal channel) directions. Such a model implies that there is essentially no exchange of diffusing molecules between the channel systems. However, that would require no significant diffusion in the z-direction (which requires jumps between the sinusoidal and straight channels). This is contrary to the results of the single crystal membrane measurements which show that diffusion in the z-direction is only slower by a factor of about 3 compared with the x or y directions. Sun and Bourdin showed that a bimodal response may also be produced by other mechanisms (Sun and Bourdin 1993), notably the combination of mass transfer (or diffusional) resistance and heat transfer. However, in such a model the mass transfer peak always corresponds to the faster process. Thus, although

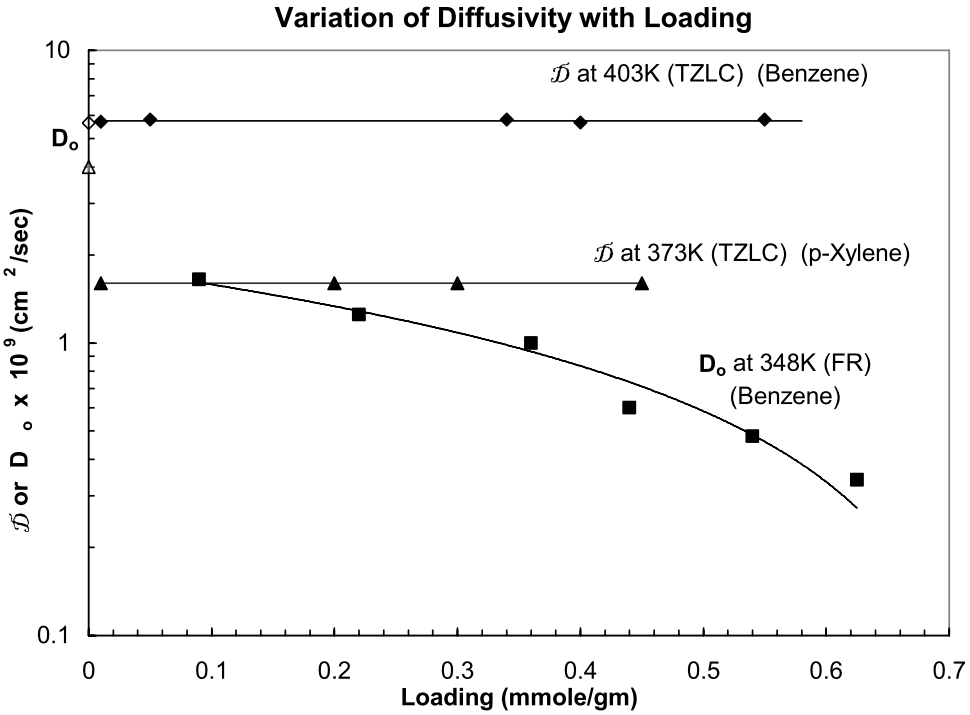


**Fig. 2** Variation of self-diffusivity ($\mathcal{D}$) and corrected diffusivity ($D_o$) with loading from TZLC (Brandani et al. 2000) and FR measurements (Song and Rees 2000). The limiting values of $D_o$ for benzene at 405 K (◊) and p-xylene at 373 K (△) derived from normal ZLC measurements are also shown

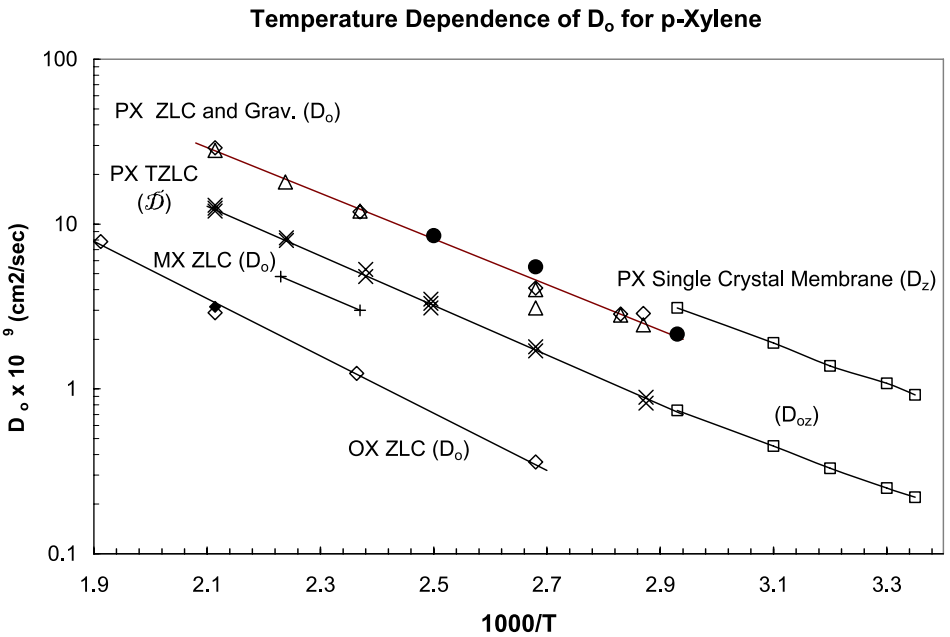


**Fig. 3** Arrhenius plot showing temperature dependence of corrected transport ($D_o$) and tracer ($\mathcal{D}$) diffusivities for p-xylene/silicalite derived from gravimetric, ZLC, TZLC (Shen and Rees 1991; Brandani et al. 2000) and single crystal membrane measurements (Shah and Liou 1994) (as reanalyzed by Ruthven (in press)). Gravimetric data are shown by *filled symbols*

the combined diffusion/heat transfer model can explain the bimodal response, it does not explain the magnitude of the faster response peak which suggests diffusivities for p-xylene which are almost two orders of magnitude greater than the values determined by other techniques. A bimodal FR response has also been reported in more recent studies of this system but the separation of the two peaks is generally smaller and the diffusivities for the fast process are correspondingly smaller than those reported by Song and Rees.

## 4 o-xylene and m-xylene

Diffusion of o and m xylenes in silicalite has been measured by both ZLC and gravimetric methods (Ruthven et al. 1991; Brandani et al. 2000). These data are included in Fig. 3 from which it may be seen that the diffusivity of o-xylene is about one order of magnitude smaller than that of p-xylene, with m-xylene having an intermediate value. This sequence is consistent with the difference in critical molecular diameters. In contrast to the ZLC measurements the single crys-

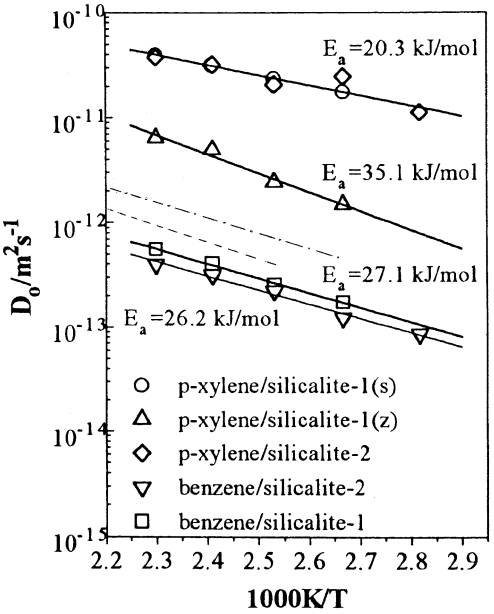


**Fig. 4** Frequency response data of Rees and co-workers (Rees 1994) for benzene and p-xylene in silicalite showing temperature dependence of the corrected diffusivity ($D_o$). Also shown are the ZLC data for benzene (- - - -) and p-xylene (-·-·-·) from Brandani et al. (2000)

tal membrane data show very little difference in diffusivity between the isomers. However, these measurements were made at very high loadings at which there may well be significant differences in the thermodynamic correction factor so similarity of the observed integral diffusivities does not necessarily imply that the $D_o$ values for the isomers are similar.

## 5 Oriented polycrystalline silicalite membranes

In a landmark paper (Lai et al. 2000) Tsapatsis and his co-workers reported the successful preparation of polycrystalline oriented silicalite membranes. The z-oriented membrane (the natural direction for preferential crystal growth) showed moderate permeance with a modest permselectivity in favor of p-xylene (PX/OX ∼ 2–3). These results are broadly consistent with the single crystal membrane data of Shah and Liou (1994). The y-oriented membrane, which should be the ideal crystallographic orientation with the straight channels aligned in the flow direction, showed higher permeance and a very much greater permselectivity in favor of p-xylene. Some of these data are shown in Fig. 5. Since the equilibrium is known it is in principle possible to calculate the diffusivity from the permeance ($\pi$). At high temperatures such that the loading is within the Henry's Law region:

$$\pi = \frac{D_o q_s}{\ell \Delta p} \ln(1 + bp) \approx \frac{K D_o}{\ell \Delta p}. \quad (1)$$

However, the thickness of the membrane ($\ell$) is not accurately known. We have therefore reversed this calculation and estimated the expected permeance assuming a nominal thickness of 1 μm and using the ZLC diffusivities for OX and PX (as shown in Fig. 3). For p-xylene the permeance estimated in this way is of the observed magnitude although the predicted trend with temperature is stronger. In contrast, for o-xylene the observed permeance is much smaller while the trend with temperature is as predicted.

It seems clear that the high perm-selectivity of the y-oriented membrane is not due to unusually rapid diffusion of p-xylene in the "straight" channels but rather to the substantial exclusion of o-xylene. This could be due to surface resistance which has been widely observed in silicalite crystals (Wloch 2003) and which could very well be sufficiently strong to prohibit access of the larger o-xylene molecules to the straight channels.

## 6 Binary diffusion

In an ingenious uptake experiment Garcia and Weisz (1996) showed that addition of a small amount of o-xylene had no effect on the uptake rate of p-xylene. A more detailed study of such effects has been carried out by the counter-current ZLC (CCZLC) method (Brandani et al. 2000). The results show that the diffusivity of p-xylene in counter-diffusion with either o or m xylene is essentially the same as the self-diffusivity—see Fig. 3. This is understandable on the basis of the simple model presented above since any obstruction that requires the diffusing p-xylene molecules to move between the channel systems may be expected to have a similar effect of the p-xylene diffusivity.

## 7 Conclusions

The diffusion of several different sorbates in silicalite has recently been studied in detail by interference microscopy (IFM) (Kortunov et al. 2004; Vasenkov and Kärger 2002) which allows direct measurement of the transient concentration profiles during an adsorption or desorption step. Although the diffusion of single ring aromatics has not yet been studied by this technique it is reasonable to assume that the general patterns of behavior which have been observed will apply equally to these systems. The IFM data show that most silicalite crystals have pronounced surface resistance to mass transfer which is sometimes completely dominant. These data also provide evidence of the impact of structural defects and the twin-planes. The diffusivities derived from uptake rate and membrane permeation measurements must be considered as "effective" values which may reflect significant surface resistance as well as the effects of structural

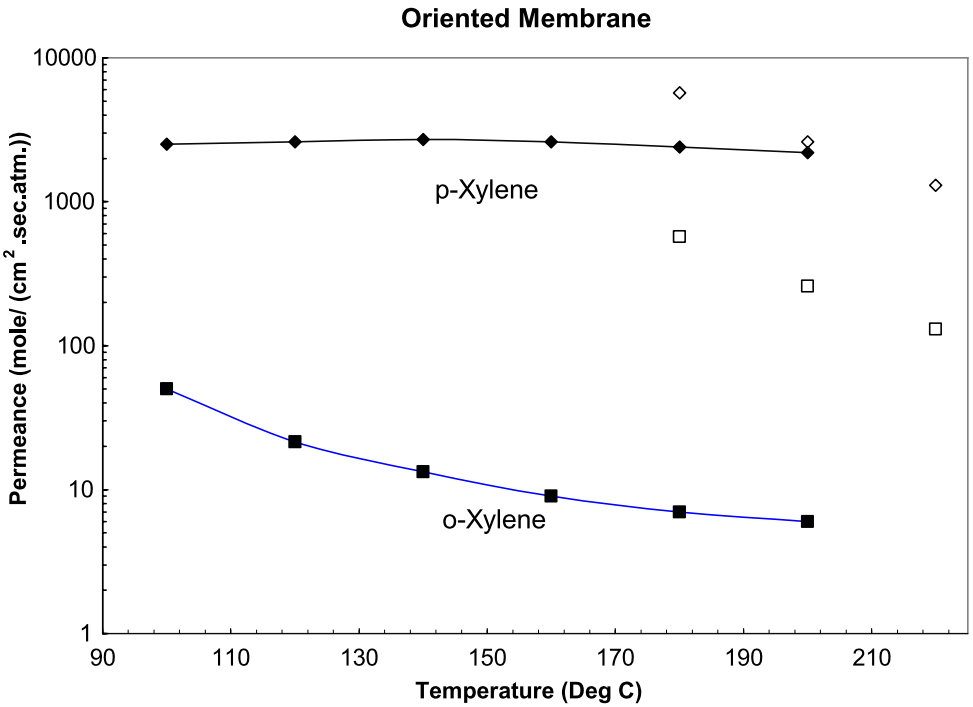


**Fig. 5** Variation of permeance with temperature for p-xylene (♦, ◊) and o-xylene (■, □) in y (b) oriented silicalite polycrystalline membrane. *Filled symbols* show values calculated from ZLC diffusivity and equilibrium data in accordance with (1)

defects. It is therefore perhaps surprising that the data summarized in this review present a fairly coherent picture that appears to be broadly consistent with structural considerations.

The following general conclusions may be drawn:

1. Diffusion of benzene appears to be essentially isotropic with the result that the tracer and corrected transport diffusivities coincide.
2. Diffusion of p-xylene appears to be modestly non-isotropic, reflecting the difficulty with which the p-xylene molecule can move between the two channel systems. This barrier appears to be entropic rather than energetic and is relatively small, leading to a self diffusivity that is about one third of the corrected transport diffusivity and a similar difference between the longitudinal and transverse diffusivities.
3. The bimodal response peaks observed by Song and Rees were interpreted as evidence of independent diffusion of p-xylene in the two channel systems, implying that exchange between the two channels is prohibited. The observation that p-xylene diffuses in the z-direction at a rate comparable with (although somewhat smaller than) diffusion in the transverse direction disproves this hypothesis. It is clear that p-xylene can indeed exchange between the channel systems, albeit with some difficulty.
4. The very rapid diffusion of p-xylene observed by Song and Rees and attributed to transport in the straight channels has not been replicated in other recent studies so it seems possible that this observation may reflect a peculiarity of the particular zeolite sample. Detailed analysis shows that the y-oriented membrane results showing high perm-selectivity for PX/OX which have been taken as support for very rapid diffusion of p-xylene in the straight channels, are actually due to the substantial exclusion or very slow diffusion of o-xylene, rather than rapid diffusion of p-xylene.

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## Appendix Non-isotropic diffusion

For a non-isotropic system:

$$\frac{\overline{D}}{R^2} \approx \frac{1}{4}\left[\frac{D_x}{x^2} + \frac{D_y}{y^2} + \frac{D_z}{z^2}\right].$$

For typical silicalite crystals $y \approx 1.2x$, $z \approx 3x$. Considering the channel geometry one may assume $D_x \sim D_y \gg D_z$ so the term $D_z/z^2$ will be small in comparison with $D_x/x^2$ and $D_y/y^2$. Therefore:

$$\frac{\overline{D}}{R^2} \approx \frac{D_{xy}}{(x+y)^2} \quad \text{where } D_{xy} = \frac{D_x + D_y}{2}.$$

The diffusional time constant measured by ZLC or FR should therefore reflect the average of the diffusivities for the straight and sinusoidal channels.

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