Micro-imaging of transient guest profiles in nanoporous host systems of cylindrical symmetry

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Nanoporous host materials giving rise to transient guest profiles of cylindrical symmetry during molecular uptake and release are shown to provide particularly advantageous conditions for the study of guest diffusion by micro-imaging. Considering zeolites of structure type DDR (Deca-dodecasil 3R) as a host system and short-chain length hydrocarbons as guest molecules, the benefits thus attainable in micro-imaging studies using interference microscopy are shown to include the determination of transient concentration profiles with improved accuracy, the option to overcome the disturbing impact of surface imperfections, and easy access to concentration-dependent diffusivities. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4762849]

I. INTRODUCTION

Although the crucial role of guest diffusion in the application of nanoporous materials for catalytic conversion¹ and mass separation² has been well recognized since the very beginning of their technological use, it was only during the last few decades that researchers became aware of the fact that, depending on the length scale of observation, the diffusivities determined by different measuring techniques may differ quite substantially from each other.^{3,4} For many systems, the diffusivities tend to be smaller when measured over longer distances. One therefore has to conclude that, in addition to its "genuine" pore structure, the material may be traversed by further transport resistances which become "invisible" when the diffusion path lengths observed by the given measuring technique are significantly smaller than the distances between these "barriers." This type of information was, in particular, provided by the pulsed field gradient technique of NMR (PFG NMR) which allows a controlled variation of the observation distance from less than 100 nm up to several tens of μ m.^{4–6}

However, in contrast to the situation that prevails during catalytic conversion and separation processes, diffusion measurements by PFG NMR are carried out under equilibrium conditions. This limitation has been overcome by the recent application of micro-imaging to diffusion studies with nanoporous materials,^{7,8} notably by the application of interference microscopy (IFM) and IR micro-imaging (IRM). By recording the optical density (in interference microscopy) and the absorbance at a characteristic frequency (in IRM), these techniques yield, as primary data, a quantity directly proportional to the integral $\int_0^{L(x,y)} c(x, y, z) dz$ in the observation direction over the guest concentration inside the material (the nanoporous crystal) under study. L(x, y) denotes the crystal thickness at position x, y in the observation plane.

Particularly favorable conditions for the application of these micro-imaging techniques are provided by host systems in which the guest concentration may be assumed to be uniform in the observation direction (the z-direction) since the concentration integral then simplifies to the product c(x, y) $\times L(x, y)$. Hence, for crystals of constant thickness L, the data accessible by micro-imaging are immediately proportional to the local concentration. Systems which give rise to such a situation include nanoporous materials with pore systems extended in only one dimension (such as metal-organic frameworks (MOFs) of type Zn(tbip)^{9,10} and manganese formate¹¹ with a channel-like pore system) or in two dimensions (such as zeolite ferrierite,⁸ containing mutually intersecting channels).

Being sensitive to a characteristic frequency of a guest molecule (using it as a "fingerprint"), IRM is able to distinguish between different molecular species. This ability opens up new routes for the exploration of multicomponent diffusion⁷ and permeation^{12–14} through nanoporous materials. However, the cost is a loss of spatial resolution (pixel size of the order of 3 μ m) in comparison with about 0.5 μ m in IFM. The accuracy of transient concentration profiles attainable during molecular uptake and release may be further enhanced if, as a consequence of the pore architecture of the host system, local guest concentrations become a function of only one rather than of two coordinates. In this case, the accuracy of the recorded concentration profiles may be greatly enhanced by taking the average over the concentrations of all positions where, according to the host symmetry, the local concentrations are expected to coincide.

A particularly simple case is provided by onedimensional (i.e., channel-like) pore arrangements. Here, during molecular uptake and release, the local concentration is a function of only the coordinate in the channel direction, while all concentrations perpendicular to the channel direction are identical. The benefit offered by this option, however, could not really be exploited hitherto because in the crystals

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studied (manganese formate¹¹ and MOFs of type Zn(tbip)⁹) the direction of the channels coincides with the longest axis of the crystal and in the perpendicular directions the dimensions are too small to provide useful concentration averaging. Moreover, the option of averaging was often additionally impaired by imperfections in the channel structure.

An alternative to these systems of one-dimensional channel structure is provided by host systems that give rise to transient guest profiles of cylindrical symmetry. In this case, local concentrations become a function of only the radial distance (r) from the axis of symmetry. Zeolites of structure type DDR (Deca-dodecasil 3R)^{15,16} offer this possibility. The DDR structure does not contain coherent channels but rather it consists of cages interconnected through windows. The crystal structure is built by corner-sharing SiO₄ tetrahedra that are connected to pseudohexagonal layers of face-sharing pentagonal dodecahedra (5¹² cages). These layers are stacked in an ABCABC sequence and are interconnected by additional SiO₄ tetrahedra that form six-membered rings between the layers. Thus, two new types of cages arise, a small decahedron, $4^35^66^1$ cage, and a large 19-hedron, $4^{3}5^{12}6^{1}8^{3}$ cage. By connecting the 19-hedra cavities through the 8-ring windows with an aperture of 0.44 nm \times 0.36 nm, a two-dimensional porous system is formed in which each cage is connected with three neighbours. Mean apertures of 0.26 nm in axial direction are too small to allow diffusion of small hydrocarbons in *c*-direction. Following recent macroscopic studies of molecular uptake and release with such systems^{17,18} the present paper reports the first investigations of molecular uptake and release by micro-imaging, exploiting the options provided by this type of zeolite for the generation of transient concentration profiles of cylindrical symmetry.

II. EXPERIMENTAL

The IFM measurements were carried out using the interference microscope Jenamap p dyn (Carl Zeiss GmbH) controlled by a personal computer, a CCD camera (SenSys KAF 0400, Photometrics), and a vacuum system. The variation in local concentration was determined by recording the change in the optical path length in the crystal under study in comparison with the surrounding atmosphere. All measurements were performed at room temperature and initiated by stepwise variation of the external pressure which, afterwards, was kept constant until equilibrium was established. The attainable resolutions in time and space (i.e., in the *x*-*y* plane, perpendicular to the direction of observation) were about 15 s and 0.5 μ m, respectively. Further details of the equipment and the measuring procedure may be found in Refs. 19 and 20.

We had access to two different samples of DDR-type zeolites. The sample designated as DDR II was similar to the sample with the same designation studied by Vidoni,^{17,18} but the sample designated here as DDR I was not the same as Vidoni's DDR I. The SEM photomicrographs in Figure 1 show typical examples of the crystals under study. Both samples are seen to be of hexagonal prismatic shape, with sample I (DDR I) having a somewhat larger diameter (mean value: 48 μ m, in comparison with about 40 μ m for DDR II) and with more perfectly formed side faces. The height of the prisms is of the order of 34 μ m and 28 μ m, respectively. The crystallographic structure of both samples was confirmed to coincide with the genuine structure of zeolite DDR, in this case the all-silica analogue of ZSM-58,15,16,21 firstly synthesized by ExxonMobil²² which is known to be of hexagonal symmetry, with cavities trigonally connected through "8-ring" (siliconoxygen) windows of elliptical shape, with principal diameters of about 0.36 nm and 0.44 nm, leading to isotropic twodimensional diffusion in the radial direction with no transport in the axial direction.

The critical diameters of the probe molecules (defined as the diameter of the smallest cylinder that can circumscribe the molecule in its most favorable equilibrium conformation) are approximately: methane ~0.34 nm, ethane ~0.37 nm, propylene ~0.43 nm. These values are calculated from the wellknown bond lengths and bond angles assuming the effective diameter of a hydrogen atom to be 0.166 nm.²⁴ There is, however, considerable uncertainty as to the effective size of a hydrogen atom. With the as well used value of about 0.23 nm, e.g., correspondingly larger estimates for the critical diameters are obtained.²³



FIG. 1. SEM images of typical crystals from sample I (a) and sample II (b), referred to as DDR I and DDR II, respectively, showing their hexagonal prismatic shape.

These molecules were selected as they show substantial differences in steric hindrance in the DDR pores, leading to diffusivities that vary by several orders of magnitude and thus yield uptake and release times from seconds up to days. In this way we were able to monitor in great detail the very first period of uptake and release as well as the entire uptake/release curve.

III. OBSERVING TRANSIENT CONCENTRATION PROFILES OF CYLINDRICAL SYMMETRY

Under the conditions of cylindrical symmetry, the diffusion equation (Fick's 2nd law) may be written as

$$\frac{\partial c}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial c}{\partial r} \right) = D \frac{\partial^2 c}{\partial r^2} + \frac{\mathrm{d}D}{\mathrm{d}c} \left(\frac{\partial c}{\partial r} \right)^2 + \frac{D}{r} \frac{\partial c}{\partial r},\tag{1}$$

with c and D denoting, respectively, the concentration and the diffusivity of the probe ("guest") molecules in the cylindrical "host" system under study. As a solution of this equation, guest concentration during molecular uptake, initiated by an instantaneous pressure increase in the surrounding atmosphere, is found to be²⁵

$$\frac{c(r,t)}{c_{\max}} = 1 - \frac{2}{R} \sum_{n=1}^{\infty} \frac{\exp\left(-D\alpha_n^2 t\right) J_0(r\alpha_n)}{\alpha_n J_1(R\alpha_n)}$$
(2)

with *R* denoting the radius of the host system. We have made the simplifying assumption that the concentration dependence of the diffusivity may be neglected. $J_i(x)$ denotes the Bessel function of order i and the $\alpha_n s$ are the positive roots of

$$J_0(R\alpha_n) = 0 \tag{3}$$

with c(r, t) and $c_{\max} \equiv c(R, t)$ denoting, respectively, the local concentrations at distance *r* from the system's symmetry axis and close to the external boundary (as dictated by the external pressure which is assumed to be constant during the whole process), Eq. (2) refers to the local concentrations during molecular uptake by an initially empty system. Instead, for concentrations initially different from zero but uniform, c(r, t) and c_{\max} have to be considered as the differences between the actual and the initial concentrations. Simultaneous adsorption and desorption, observable, for example, during tracer exchange, leaves the overall concentration invariant. The second term on the right-hand side of Eq. (2) is thus immediately seen to yield the transient concentration profiles during desorption from the initially uniform concentration c_{\max} .

Examples of the spatial-temporal dependence of the intracrystalline concentrations, calculated from Eq. (2), are shown in Figs. 2(b) and 2(c). The diffusivity values (assumed constant) have been chosen to yield the best possible fit of the theoretical transient intracrystalline concentration profiles to the experimental data. In order to comply with the constant diffusivity approximation we have ensured low guest concentrations by choosing methane as a guest molecule with relatively low guest pressures in the surrounding atmosphere (including the pressure step). However, these requirements for approaching constancy in the diffusivities increase the noise level of the experimental data. This is illustrated by Fig. 2(b). Figure 2(c) shows that this problem can be alleviated by taking advantage of the cylindrical symmetry of the system and by considering the average value c(r) of concentrations over all locations (pixels) at equal distance *r* from the crystal center rather than just the concentrations c(x) in a given direction.

In Fig. 2(c) the profiles c(r, t), determined in this way, are seen to show excellent agreement with the predictions of Eq. (2) with improving agreement with increasing distance from the crystal boundary. Since the influence of the different geometries (hexagonal prisms vs cylinders) and of surface-related structural defects on the concentration profiles will decrease towards the crystal center, this behavior is in complete agreement with expectation. The increasing uncertainty in the experimental data close to the crystal center is an immediate consequence of the fact that the number of pixels over which the average is taken decreases in proportion with the decreasing radius *r*.

IV. SHORT-TIME ANALYSIS

At short times (before the diffusion front approaches the center of the crystal) one may treat the system as approximating diffusion into a semi-infinite medium. Under such conditions one may take advantage of the Boltzmann-Matano approach,^{8,25,26} i.e., from considering the local concentrations as a function of the ratio between the distance *x* from the crystal surface and the square root of time. Such plots lead to coinciding profiles whose functional dependence is a function of the diffusivity on the concentration. For diffusivities independent of concentration, e.g., one has²⁵

$$\frac{c}{c_{\max}} = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right). \tag{4}$$

As an example, Fig. 3(a) shows the transient concentration profiles during molecular uptake of ethane by a crystal of zeolite DDR-I at subsequent instants of time. In Fig. 3(b), the locations x of selected, special local concentrations (c/c_{max}) are plotted as a function of the square root of the observation time. The straight lines drawn through these points indicate that, for a given concentration c, the ratio x/\sqrt{t} between the location x where this concentration is recorded and the square root of time t when it is recorded is constant. Hence, as implied in the Boltzmann-Matano approach and illustrated by Fig. 3(c), the concentration profiles measured at different times become coincident when plotted as a function of x/\sqrt{t} .

Structural imperfections in the crystals under study which are most likely to occur close to the crystal boundary prevent exact localization of the crystal boundary, i.e., of the origin (position x = 0) in the spatial coordinate. With Fig. 3(b) this limitation is seen to be easily overcome by using the Boltzmann-Matano approach where, at t = 0, all concentrations $0 \le c/c_{\text{max}} \le 1$ must coincidently be found to occur at the origin. In fact, the straight lines of Fig. 3(b) are all seen to intersect in one point, with $x = -6 \mu \text{m}$ resulting as the position of the crystal boundary of the left-hand side crystal face from which, in Fig. 3(a), the concentration profiles were recorded. From Fig. 3(b) the time origin is also seen to be about -4 s rather than 0. To rationalize this observation one



FIG. 2. (a) Raw experimental data showing two-dimensional, time-dependent concentration profiles in the inner part of a crystal during adsorption of ethane in a single crystal from batch DDR-II. Comparison of the unmodified, one-dimensional profiles for methane in DDR-II (b) during adsorption (top) and desorption (bottom) with their equivalent attained by averaging over regions of equal distance *r* from the crystal center. (c) illustrates the dramatic increase in accuracy that is attained by this data averaging procedure. This is critical for small changes in guest concentration. Full lines in (c) represent the best possible fits of Eq. (2) to the experimental data resulting with the diffusivity for both adsorption (top) and desorption (bottom) chosen to be $0.96 \times 10^{-12} \text{ m}^2/\text{s}$.

must have in mind that the time origin cannot be measured exactly because it is the sequence of five individual pictures which are needed to determine, from a given interference intensity, the actual phase (and, hence, the concentration)^{19,27} and which, subsequently, are recalculated to a single concentration profile. The recording of this sequence takes about

12 s with all of the five individual pictures influencing the final outcome. Therefore, it is not unexpected that the time origin is shifted by a few seconds. The time intervals between the subsequent concentration profiles considered in our studies are clearly unaffected by this effect and, hence, exactly equal to the generally chosen and indicated interval of 15 s.



FIG. 3. One-dimensional concentration profiles of ethane uptake in DDR-I (a) providing the data for the *x*-vs- \sqrt{t} -plots shown in (b) for the left side of the crystal under study (right side not shown), exhibiting linearity between the progress of the concentration fronts and the root time. Concentration profiles plotted as *c*-vs- x/\sqrt{t} in (c) reveal the expected master plot behavior, following the Boltzmann-Matano approach.



FIG. 4. Short-time concentration profiles for ethane in DDR-I crystal plotted as c/c_{max} vs x/\sqrt{t} and y/\sqrt{t} showing conformity with the Fujita model for diffusion into a semi-infinite medium with $D = D_0/(1 - 0.87c/c_{\text{max}})$ or $D_{\text{max}}/D_0 = 8$. Dashed and full line represents the calculated profiles for constant diffusivity and concentration-dependent D(c), respectively.

Figure 4 summarizes the concentration data shown in Fig. 3 for both crystal directions in one master plot. Also shown are the analytical expressions for a constant diffusivity given by Eq. (4) and for the concentration profiles calculated according to the Fujita model for a concentration-dependent diffusivity (Fujita model²⁵) of the form

$$D = \frac{D_0}{1 - \lambda c / c_{\text{max}}} \tag{5}$$

with $\lambda = 0.87$ (or, equivalently, $D_{\text{max}} \equiv D(c = c_{\text{max}}) = 8D_0$)). It is evident that the assumption that the concentration dependence is given by Eq. (5) with $\lambda = 0.87$ provides an excellent fit to the experimental data while, over the concentrations considered in this study, it is clearly impossible to represent the experimental profiles in a satisfactory manner with a constant diffusivity.

Complementing the determination of the diffusivities by seeking the best fit of the solution of Eq. (1) with an appropriately chosen analytical expression (as shown by the full



FIG. 5. Short-time concentration profiles for ethane in DDR-II (a) and propylene in DDR-I (b) plotted as c/c_{max} vs x/\sqrt{t} and y/\sqrt{t} showing conformity with the Fujita model for diffusion into a semi-infinite medium with $D = D_0/(1 - 0.71c/c_{max})$ and $D = D_0/(1 - 0.9c/c_{max})$, respectively.

line in Fig. 4), the Boltzmann-Matano method may be used to determine the diffusivities directly by using the relation^{4, 8, 26}

$$D(c) = -\frac{1}{2t} \frac{\mathrm{d}x}{\mathrm{d}c} \int_0^c x \mathrm{d}c.$$
 (6)

The diffusivities resulting from the application of this relation to the transient concentration profiles shown in Figs. 3(a) and 3(c), respectively, are summarized in Fig. 7, together with the concentration dependence following from the Fujita model (Eq. (5) and best fit to the profiles as shown in Fig. 4) and from the center-line analysis (Sec. VI), yielding satisfactory mutual agreement.

V. TRACING INDICATIONS OF DEVIATION FROM CYLINDRICAL SYMMETRY

As a remarkable feature of the presentation of Fig. 4, the concentration profiles in the y-direction (i.e., along a coordinate starting in the vertex of the hexagon – see inset) are seen to be slightly extended in comparison with those in the x-direction (i.e., along a coordinate starting in the hexagon edges). Figures 5(a) and 5(b), showing initial concentration profiles in two other cases, show a completely identical pattern.

In fact, such a behavior must indeed be expected for the initial stage of molecular uptake. Straightforward geometrical considerations show that the total boundary area at the ridge of the crystals (per cross section perpendicular to y-direction) exceeds that at the side faces (per cross section perpendicular to x-direction) by a factor of $1/\cos 30^\circ = 2/\sqrt{3} \approx 1.15$. Hence, also the total flux into the crystals and, correspondingly, the local concentrations at a given instant of time close to the "vertices" must be expected to exceed those close to the edges. This is, in fact, the behavior which, in a qualitative way, is revealed in our observations. Since the crystals under study are far from ideal and structural irregularities are particularly pronounced close to the surface, we have not endeavored any more detailed quantitative analysis of this behavior. As expected, the effect vanishes as the diffusion fronts approach the crystal center. This is the situation we consider in Sec. VI.

VI. ANALYSING THE EVOLUTION IN THE PROFILE CENTRE

Close to the central axis of a cylindrical host system (i.e., for $r \ll R$) symmetry considerations require that $\frac{\partial c}{\partial r}|_{r=0} = 0$. Hence, in this region, the second term on the right-hand side of Eq. (1) becomes negligibly small and the Taylor expansion of the spatial concentration dependence may be approximated by $c(r) = c(0) + \frac{1}{2} \frac{\partial^2 c}{\partial r^2} r^2$ so that, for $r \ll R$, Eq. (1) assumes the simplified form

$$\frac{\partial c}{\partial t} = 2D \frac{\partial^2 c}{\partial r^2}.$$
(7)

Since both the increase with time $(\frac{\partial c}{\partial t})$ and the curvature (second derivative $\frac{\partial^2 c}{\partial r^2}$) of the concentration in the center (i.e., for r = 0) are directly accessible from the experimental data, Eq. (7) allows a straightforward calculation of the diffusivities and, by following the increase in concentration in the center of the system, of their concentration dependence.

Figure 6 provides a survey of typical concentration data in the central region of a crystal of zeolite DDR I during



FIG. 6. Center region of the mid-time adsorption profiles of ethane in DDR-I taken from Fig. 3(a). Solid lines represent parabolic fits using $c(r) = c(0) + \alpha r^2$.



FIG. 7. Variation of diffusivity with concentration for ethane in DDR-I based on Boltzmann-Matano and Eq. (6) (open symbols), mid-time regime analyzed by center-line approach (full stars), and the best fit to the complete set of profiles applying the diffusivity-concentration-dependence given by Fujita's model (solid line).

molecular uptake which have been employed for this type of analysis. The resulting diffusivities are shown in Fig. 7 and compared with the concentration dependence revealed by analyzing the initial parts of the concentration profiles as shown in Figs. 3 and 4 and with the Fujita model parameter obtained by looking for the best fit to the full set of profiles (compare Fig. 2(c)). Though there is considerable scatter in the concentration data, the general trend in the concentration dependence as expressed by Eq. (5) is found to be in fair agreement with the results of the center-line analysis presented in Fig. 6. The increasing scatter in the diffusion data with vanishing concentration resulting from the application of the Boltzmann-Matano method (Eq. (6)) is the consequence of increasing uncertainty in the factor $\frac{dx}{dc}$.

When applied to crystals from the second batch of ZSM-58 zeolites, DDR-II, the different approaches, again, provide diffusivities that are in good agreement. More precisely, the concentration dependence of the ethane diffusivity from adsorption and desorption experiments is found to be D(c)= $5.0 \times 10^{-14}/(1 - 0.67 \times c/c_{max})$ m²/s and $D(c) = 6.1 \times 10^{-14}/(1 - 0.71 \times c/c_{max})$ m²/s from center-line analysis and full profile fitting, respectively. In DDR-II, spurious uptake in *c*-direction along lattice defects prevented a reliable application of the Boltzmann-Matano method for the determination of the diffusivities, notably in the range of low concentrations.

Considering different crystal sizes, shapes, and possible (post-) synthesis treatment, a factor of about two between crystals from the different batches DDR-I and DDR-II seems fairly reasonable. Having this in mind, the present data are also in fairly good agreement with the results of previous uptake measurements with methane, ^{18,28} ethane, ¹⁷ and propylene.^{29,30} The center-line analysis is of course approximate, especially in view of the experimental scatter which makes it difficult to estimate the derivatives accurately. Furthermore, it can only be applied in the intermediate time region when the parabolic form of the central region of the profile is clear (as a prerequisite for attaining a sufficiently accurate second derivative). However, it is reasonably quick and easy and applicable to both adsorption and desorption pro-

files. Center-line analysis is therefore clearly a most useful approach for an initial estimate of the diffusivities and their concentration dependence.

VII. CONCLUSIONS

As a result of its hexagonal crystal habit coupled with the radially symmetric two-dimensional pore structure (with no transport in the axial direction), DDR (also known as ZSM-58) is particularly suitable as a model system for the study of intra-crystalline diffusion by interference microscopy. The crystal shape and symmetry of the pore system make it possible to represent this system, with good accuracy, as equivalent to diffusion in an infinite cylinder, for which (for the constant diffusivity case) a simple analytic solution is available. A further advantage of this structure is that radial averaging of the concentration profiles can be used to improve the accuracy of the experimental profiles. The value of this approach is demonstrated. By using different molecules with different critical diameters it was possible to measure both the short-time and long-time transient concentration profiles accurately and to demonstrate excellent conformity with the diffusion model.

For weakly adsorbed species (methane)²⁸ the equilibrium isotherm is essentially linear over the relevant pressure range. As a result the transient profiles for adsorption and desorption are mirror images and conform to the constant diffusivity model (Eq. (2)). In the initial region (before the concentration front has reached the center) the theoretical solution reduces to the form of a complementary error function of the single variable $x/(2\sqrt{Dt})$ (see Eq. (4)) thus allowing a straightforward determination of the diffusivity from the average profile.

The isotherms for the more strongly adsorbed species (ethane and propylene)²⁴ show increasing (Type 1) curvature. The profiles for adsorption and desorption are no longer mirror images but assume the characteristic shapes expected for a system in which the diffusivity increases with loading in accordance with the Fujita expression $D = D_0/(1 - \lambda c/c_{\text{max}})$. It is noteworthy that exactly this type of concentration dependence holds, quite generally, for host-guest systems which, as in the given case,²⁴ follow a Langmuir isotherm and where the concentration dependence of the corrected diffusivities, as observed for numerous nanoporous host-guest systems, may be assumed to be negligibly small.⁴ In the initial region the profiles are shown to conform to Fujita's analytic solution for diffusion into a semi-infinite medium with a concentration dependent diffusivity of the above form. In the longer time region (after the front has reached the center) the profiles in the central region assume a symmetric parabolic shape. In this regime the gradient of concentration at the center is zero, thus allowing a straightforward estimate of D(c) from the time dependence and curvature of the profile in accordance with Eq. (7).

At longer times the profiles conform accurately to the cylindrical diffusion model but, at short times, the difference between the longer cross sections (vertex to vertex) and the shorter sections (face to face) is clearly apparent and is shown to arise from the difference in the external area/volume ratio between the two positions.

Several different approaches to the analysis and modeling of the experimental profiles are demonstrated:

- (i) Matching of the short-time solution following the Boltzmann-Matano method as described in Ref. 8.
- (ii) Analysis of the time dependence of the center-line concentration in accordance with Eq. (7).
- (iii) Computer based fitting of the full set of concentration profiles to the basic differential equation (Eq. (1)).

The experimental data for ethane show the consistency between the diffusivity values obtained by these three approaches. It should be noted that, in the absence of a good initial estimate of the (concentration dependent) diffusivity the third approach is tedious and time consuming but the effort required is dramatically reduced by using the approximate values from (i) and (ii) as initial estimates.

Previous IFM studies^{31–35} have shown that, for many zeolite systems, the sorption kinetics are significantly affected by surface resistance. It was not possible to investigate this aspect in the present study due to the shape of the DDR crystals which precludes accurate measurements close to the external surface. However, the observed conformity of the profiles with the short time solution of the diffusion equation implies that any surface resistance must be minimal. This conclusion is further supported by the ZLC measurements^{17, 18} and breakthrough experiments.³⁰

Because of the difference in the diffusion model, precise conformity between ZLC and IFM measurements cannot be expected. Although the absolute values of the diffusivities found in this study are in fairly good agreement with the results of previous macroscopic diffusion studies by ZLC,^{17,18} thermogravimetric uptake,²⁹ and breakthrough measurements,³⁰ there appear to exist systematic deviations which we expect to be related to differences between the different samples as well as to deviations from the ideal structure as assumed in the analysis. This is currently the subject of further study.

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