Transport Processes

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Transport in Nanoporous Materials Including MOFs: The Applicability of Fick's Laws

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Abstract: *Diffusion in nanoporous host–guest systems is often considered to be too complicated to comply with such "simple" relationships as Fick's first and second law of diffusion. However, it is shown herein that the microscopic techniques of diffusion measurement, notably the pulsed field gradient (PFG) technique of NMR spectroscopy and microimaging by interference microscopy (IFM) and IR microscopy (IRM), provide direct experimental evidence of the applicability of Fick's laws to such systems. This remains true in many situations, even when the detailed mechanism is complex. The limitations of the diffusion model are also discussed with reference to the extensive literature on this subject.*

Thermal energy gives rise to permanent irregular molecular motion. In systems of non-homogeneously distributed molecules, this irregular movement results in fluxes that are correlated with the gradients in molecular concentration by Fick's 1st law [Eq. (1)].

$$J = D\frac{\partial c}{\partial x} \tag{1}$$

Combined with the law of matter conservation, the "continuity relation" $\partial c/\partial t = -\partial j/\partial x$, Equation (1) yields Fick's 2nd law [Eq. (2)].

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{2}$$

If the diffusivity D is independent of concentration, Equation (2) simplifies to Equation (3).

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{3}$$

Relationship (3) holds especially for the migration of labeled molecules within unlabeled surroundings under equilibrium conditions, commonly referred to as self-diffusion. This is the situation in PFG NMR diffusion studies.[1,2]

Relationships between physical quantities can only be meaningful if the quantities themselves are meaningfully defined. The fluxes and concentrations as the relevant quantities in Equations (1)–(3) must, therefore, be based on unit areas and unit volumes that are large enough that the fluxes and concentrations become homogeneous functions of the location x. Unit volumes and areas must thus notably exceed the pore size (just as, in bulk fluids, they must exceed the size of the molecules). On the other hand, differential equations such as Equations (1)–(3) are only meaningful if unit volumes and areas are small relative to the size of the system under study. With typical pore diameters on the nanometer scale and particle/crystal sizes on the micrometer scale, both requirements are generally easily fulfilled.

The concept formulated by Equations (1)–(3) has been applied to mass transfer in nanoporous materials, even from the earliest studies of adsorption and catalysis. Examples include Damköhler's pioneering papers[3,4] and the classic textbooks by Satterfield and Sherwood,[5] and Petersen.[6] The diffusivities were well defined in the context of Equations (1)–(3) but their accessibility by direct measurement was limited because, at that time, the guest concentrations and guest fluxes appearing in these equations were generally not amenable to direct observation. The diffusivities were therefore derived from observations of "macroscopic" phenomena controlled by diffusion. Examples include measurements of the rates of molecular uptake and release by beds or aggregates of nanoporous materials, and the rates of reactions subject to heterogeneous catalysis by such systems.

Theoretical models were developed to relate the measured diffusivities to more fundamental parameters such as the molecular density of the adsorbed phase, the pore diameter, the tortuosity of the pore network, and the corresponding gas- or liquid-phase diffusivities. These approaches proved to be quite successful, in many cases yielding good agreement with the macroscopic measurements, especially when the pores are large relative to the molecular diameter of the sorbate molecules.[7–9]

This approach breaks down when the pore diameter is close to the molecular diameter (the configurational diffusion regime) since the diffusivity is then determined mainly by repulsive interactions with the pore wall. Although in this region, the diffusivities cannot be related directly to other transport properties, they remain perfectly valid as fundamental parameters for characterizing the migration rate.

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It is only relatively recently, with the development of microscopic techniques for diffusion measurement, that it has become possible to directly investigate whether or not mass transfer in a given nanoporous host–guest system follows the laws of ordinary diffusion as given by Equations (1)–(3). These techniques, notably pulsed field gradient (PFG) NMR and microimaging by interference microscopy (IFM) and IR microscopy (IRM), cover diffusion paths from hundreds of nanometers to hundreds of micrometers, as required for diffusion measurement in nanoporous materials.[10] In contrast to single-molecule techniques,[11] these techniques collect, by their very nature, information about ensembles of molecules (typically from 10^{10} up to much larger numbers). Recording data for many molecules is a prerequisite for the meaningful application of Equations (1)–(3).

To rationalize the evidence that PFG NMR spectroscopy is able to provide in favor of the Fick's laws, we recall that the primary quantity accessible by PFG NMR spectroscopy, namely the attenuation of the NMR signal as a function of the intensity of the applied field-gradient pulses, is the Fourier transform of the (mean) propagator. The propagator is defined as the probability distribution $c^*(x,t)$ of an ensemble of labeled molecules (within an unlabeled, homogeneously distributed molecular entity) at time t, when at time $t=0$, all these molecules have been positioned at $x=0$. For a system following Equation (3), $c^*(x,t)$ is given by the Gaussian Equation (4).

$$c^*(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{4}$$

It follows that, if the PFG NMR data reveal a propagator of this form, the diffusion process must be Fickian [i.e., in accordance with Equations (1)–(3)].

Examples for which exactly this behavior has been observed include purely microporous and mesoporous zeolites,[12] activated carbon,[13] nanoporous glass,[14] and ordered mesoporous silica of type SBA-15.[15] The validity of the Fickian model and the physical meaning of the diffusivity appearing in Equation (3) do not depend on the detailed mechanism of molecular movement. Exploration of the individual steps and the mechanisms that contribute to the diffusion process, in continuation of the work of Damköhler and his successors,[4–9,16] remains a challenging task in current research.[17–22]

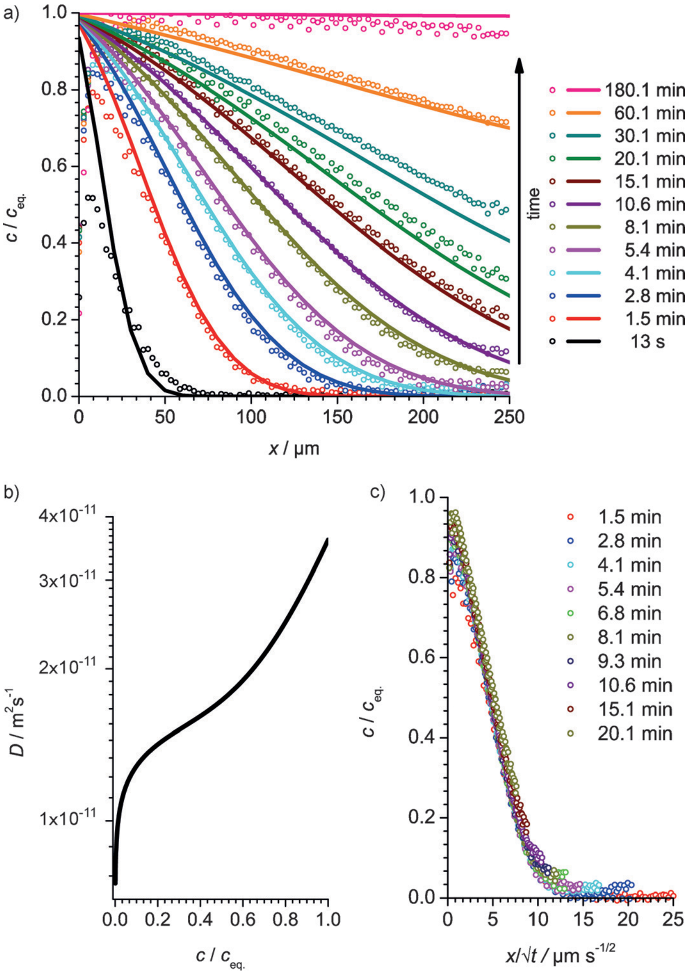

Figure 1. a) Transient concentration profiles during molecular uptake of cyclohexane by nanoporous glass induced by a pressure step from 0 to 0.1 mbar as recorded by IRM (open circles) at 298 K. The solid lines correspond to their prediction by solution of Fick's 2nd law [Eq. (2)] with the respective initial and boundary conditions and with the concentration dependency of the diffusivity as given in (b). Compatibility with Fick's diffusion laws is also documented by the Boltzmann–Matano plot in (c), where intraparticle concentrations are shown to be a unique function of $x/\sqrt{t}$. c_{eq}: equilibrium concentration.

Under non-equilibrium conditions (i.e., during uptake and release), concentrations vary with time and space. The recent advent of microimaging[23–25] has made it possible to record the evolution of such profiles with unprecedented accuracy. Figure 1a shows the concentration profiles of cyclohexane, determined in this way during uptake by a porous glass. The host material was recently applied for an in situ study of the hydrogenation of benzene to cyclohexane, and the corresponding publication also contains a detailed description of the material.[26] To reproduce the profiles through solution of the diffusion equation with the appropriate initial and boundary conditions, one must allow for the possibility that the diffusivity may be concentration dependent (in contrast to the situation in self- or tracer-diffusion measurements by PFG NMR spectroscopy). The analysis must therefore be based on Equation (2) rather than Equation (3). The results of this analysis (see Ref. [27] for details) are shown in Figure 1a by the solid lines. The concentration dependence of the diffusivity used for this fit is shown in Figure 1b. Although for individual curves, there is some deviation between theory and experiment, the fit of the entire data set with a single (concentration-dependent) diffusivity is impressive. The dramatic decrease in diffusivity at concentrations approaching zero suggests the existence of a small number of strong adsorption sites, while a distinct increase in the diffusivities at intermediate concentrations is quite common for diffusion in nanoporous materials under non-equilibrium conditions (i.e., for transport or Fickian diffusivities). It is caused by the "thermodynamic factor" $d\ln p(c)/d\ln c$, which gives rise to a driving force for diffusive

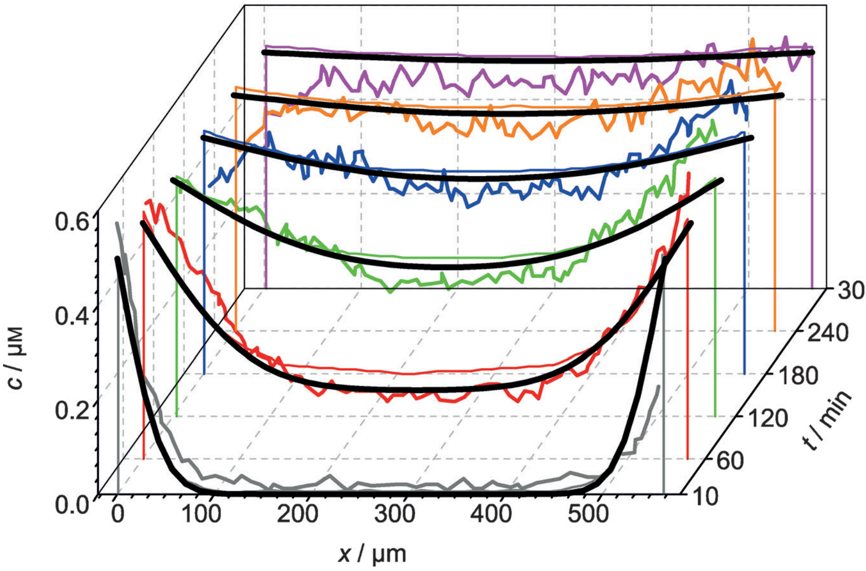

Figure 2. Concentration profiles of pyronin B (PB) upon uptake by nanoporous crystals of type MOF-5, as recorded by confocal laser scanning microscopy (experimental data of Figure 3 d of Ref. [34]) and analytical approaches to these data given in Ref. [34] (thin smooth curves) resulting from the "reaction–diffusion" equation in Ref. [34] and through the solution of the Fick's law equations (thick black curves).

fluxes under non-equilibrium conditions ($\approx 1/(1-\theta)$ for Langmuir-type isotherms) that acts in addition to mere thermal motion.[2,25,28] Self-consistency of the results in terms of Fick's 2nd law is revealed by the Boltzmann–Matano plot[29] shown in Figure 1 c. In such diagrams, all concentration profiles are plotted together as functions of $x/\sqrt{t}$. If transport resistances at the crystal surface are negligible, the profiles collapse onto a single trend line, as seen in Figure 1 c.

Mass transfer in nanoporous materials cannot always be assumed to follow the "simple" laws of ordinary diffusion. Deviations from Fickian behavior are to be expected if, during the observation time, there is no fast exchange between states of different mobility. Such behavior may be encountered in hierarchical pore systems with limited exchange between the micro- and meso-/macropores.[30] A similar situation may arise in heterogeneous adsorbents with a wide range of site energies. The behavior of such systems may often be represented by the diffusion–immobilization (diffusion–reaction) model. The general features of this model were discussed in some detail many years ago in Crank's classic textbook.[31] A wide range of different patterns of behavior is predicted depending on the ratio of the diffusional rate constant for the mobile phase and the rate constant for immobilization (or adsorption). In the limiting case of rapid equilibration, the behavior follows the Fickian model, with a diffusivity given by $D/(1+K)$, where D is the diffusivity of the mobile phase and K is the adsorption equilibrium constant.

A model of this type was used by Sherry to account for the kinetics of isotopic ion exchange in zeolite X.[32] A more recent example is provided by the data of Grzybowski and coworkers[33,34] for the uptake of pyronin B in MOF-5. Although not originally analyzed in this way, the transient concentration profiles from that study are accurately represented by the Fickian diffusion model with a constant diffusivity, as shown in Figure 2. This implies rapid equilibration with linear equilibrium between the mobile and adsorbed molecules (details are given in the Supporting Information). This result is in agreement with numerous, experimental and computational studies of the adsorption of guest molecules in MOF-type host systems,[18–22,24,25,35] where mass transfer has been observed to follow the normal diffusion model. However, the diffusion–immobilization model implies that simple Fickian behavior will be observed only if the immobilization reaction is much faster than the diffusion of the mobile molecules. When the rates of diffusion and immobilization are comparable, deviations from Fickian behavior are to be expected. The diffusion–immobilization model therefore provides a possible explanation of the non-Fickian behavior observed in a number of studies, for example, that reported in Ref. [36].

Fick's 1st and 2nd laws have been shown to provide us with excellent tools for the quantitative study of diffusional mass transfer in nanoporous materials. Today, experimental techniques are powerful enough to allow compatibility checks in numerous cases. Experimental evidence and molecular modeling verify that, despite its intrinsic complexity, mass transfer in nanoporous materials can often be described almost exactly by the Fickian diffusion laws. The relevant rate parameter which, by its use in the Fick equations, precisely fits the formal definition of a diffusion coefficient should thus be called the diffusion coefficient!

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