

Application of Boltzmann's Integration Method under non-ideal Conditions

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Abstract

Boltzmann's integration method may prove to be a very powerful tool to study the transport diffusion of guest molecules in nanoporous host systems. In many cases, however, the prerequisites for applying this method are not completely fulfilled. In the following, the consequences of these deviations on the accuracy of the obtained results are discussed. It is found that the results of Boltzmann's integration method can be corrected by different considerations. The discussion is focussed on the concentration profiles observed during the adsorption and desorption of methanol in ferrierite-type crystals as observable by interference microscopy.

Keywords: Boltzmann's integration method, diffusion, nanoporous materials

Introduction

Mass transport of guest molecules in nanoporous host materials is an important field of science with application in basic research as well as in the chemical industry. In a number of scientific works the intracrystalline diffusion is studied by analysing the integral uptake averaged over the whole sample [1-4]. The recently developed interference microscopy method [5] is able to monitor the intracrystalline concentration profiles of one single crystal with a sufficient spatial and temporal resolution. The received data provide a lot of information which can not be received by integral techniques.

To determine the relevant transport parameters, namely the diffusivity and the surface permeabilities, new methods in analysing these profiles have been introduced. The surface permeability can be calculated by relating the flux through the surface to the actual surface concentration. For determining the transport diffusivity there exists the direct way of applying Fick's 2nd law. Though this most direct access has been successfully applied in

several cases [6-8], its efficiency is limited by a couple of disadvantages. (i) Direct application of Fick's 2nd law is only possible in the central part of the profiles where the first spatial derivative of the concentration becomes zero. (ii) The accuracy of the resulting diffusivities is notably impaired by the noise of the data points. (iii) Each value in the concentration dependence of the diffusivity needs a separate calculation.

An indirect way to obtain transport diffusivities is provided by the Boltzmann transformation leading to Boltzmann's integration method [9]. This approach, however, is restricted to some restraints, viz. the diffusion has to be one-dimensional and the external surface must not exhibit any resistance to mass transfer. These restrictions are hardly strictly fulfilled. In the following, we are going to discuss the effects which small deviations from the prerequisites might have on the final results.

In particular we are going to discuss the application of Boltzmann's integration method to analyse the evolution of the concentration profiles during the uptake of methanol by ferrierite. Though this system exhibits favourable conditions for the application of this method, we shall see that the prerequisites are not completely fulfilled.

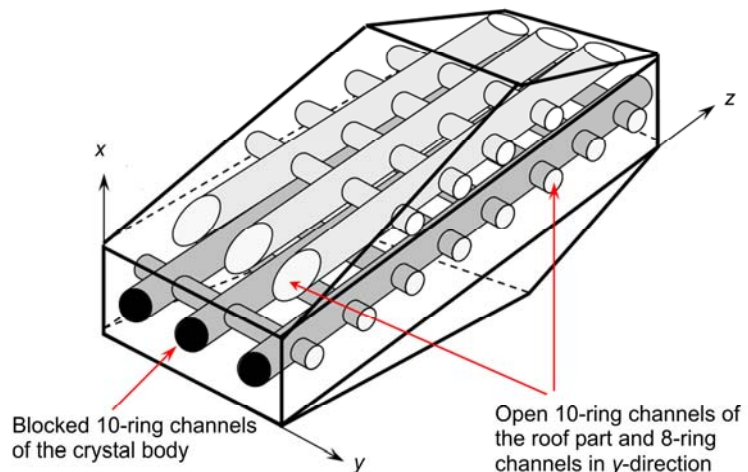
Experimental results

The ferrierite zeolite is a cation-free zeolite with two perpendicular channel systems which intersect each other [10]. One system of channels is adjusted along y -direction and is framed by eight-membered rings, this means they are formed by eight oxygen and eight silicon atoms [7]. The other channel system is along z -direction and is formed by ten-membered ring channels. Due to the larger diameter of the channels along z , a higher diffusivity can be assumed there.

The outer geometry is like a cuboid with a short side length in x -direction ($l_x = 10 \mu\text{m}$), and two long side lengths in y and z ($l_y = 50 \mu\text{m}$, $l_z = 220 \mu\text{m}$). On each of the two big side faces of the crystal there are small roof-like parts (fig. 1).

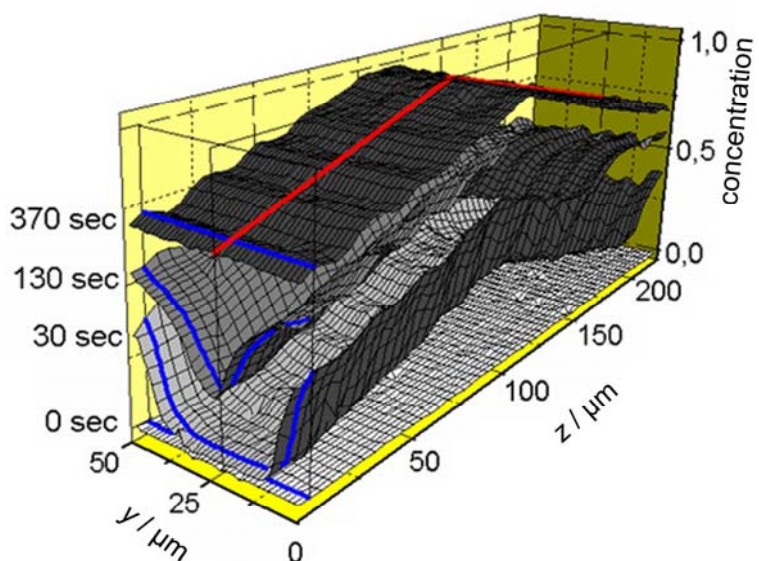
The entity of concentration profiles recorded during the uptake and release of methanol on such crystals by means of interference microscopy (IFM) is presented in [7]. These profiles have a spatial resolution of $0.5 \mu\text{m}$ and a temporal resolution of up to 10 s. The direction of monitoring the concentration profiles is along x . There are no channels in this direction, so that mass transport is excluded and concentration in the cuboid-like central part is constant in x -direction.

Figure 1: Ferrierite crystal with a two-dimensional pore structure. The figure shows partially blocked channels in z -direction in the main body of the crystal, open channels in z -direction in the roof section and open channels in y -direction [7].



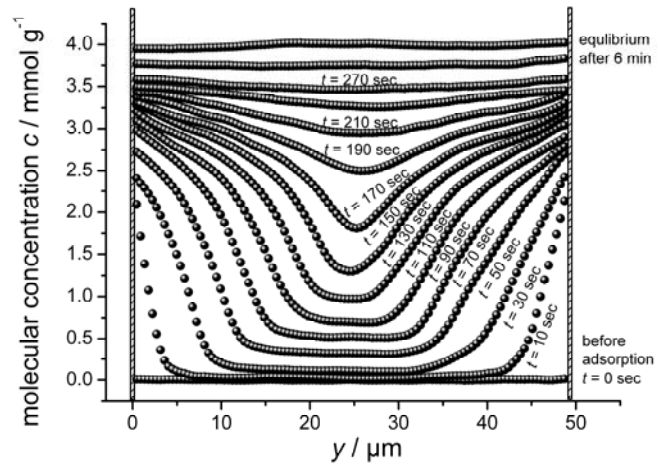
In the observed concentration profiles (fig. 2) it is visible that the concentration in the roof-like part of the crystal is built up instantaneously. Hence, this part of the concentration can easily be subtracted to yield the concentration in the central part of the crystal (fig. 3). In this cuboid-like part there exists no concentration gradient along z -direction and the concentration has not reached the equilibrium value. Consequently, the surface permeability into these big ten-membered ring channels is very low or zero. Furthermore, the concentration profiles along y -direction are curved (see fig. 3), so that the main part of the mass transport is along these channels. The concentration close to the crystal surface in y -direction is smaller than the equilibrium value. Therefore, this surface is also a resistance to the mass transport. This means the surface permeability is not infinitely large.

Figure 2: Concentration profiles measured during adsorption for the pressure step of 0 to 80 mbar. The concentration is normalized with respect to the maximum value in the roof [7].



From the slowly increasing concentration in the centre of the profiles in y -direction at small times ($t = 30 \text{ s} \dots 90 \text{ s}$ in fig. 3), without any concentration gradient along y , one has to conclude that mass transport is not completely restricted to this direction. So, taking the topology of the ferrierite into account, one may conclude that some mass transport has to proceed also along z -direction.

Figure 3: Concentration profiles in y -direction measured during adsorption for the pressure step of 0 to 80 mbar [7]. Up to 110 s after onset of adsorption the fronts of molecular concentration that have penetrated through the two apposed crystal faces in y -direction do not overlap.



To sum up, mass transport in these crystals is dominated by diffusion in y -direction, where uptake is affected both by diffusion in the channels and by a reduced surface permeability. The rate of uptake in z -direction is much smaller. It is controlled by the small surface permeability, since the diffusivity along z is very large because of the bigger channel diameter. Therefore, there exist no measurable concentration gradients in the cuboid central part, this means $c(y,z) = c(y)$.

Boltzmann's integration method

The concentration profiles measured by IFM have a sufficient spatial and temporal resolution which allows their thorough analysis. In [7], analysis of these profiles by a differential application of Fick's 2nd law has been shown to yield transport diffusivities ranging over close to two orders of magnitude. This type of analysis, however, is impaired by the significant statistical noise of the individual data points and the small number of data points used to determine the diffusivities for each particular concentration.

Another, integral approach to determine diffusivities from the concentration profiles is based on the Boltzmann-transformation [11, 12]

$$\eta = \frac{y}{\sqrt{t}}. \quad (1)$$

By using this substitution, for uptake by a semi-infinite medium without surface barrier (i.e. with infinite surface permeability) Fick's 2nd law for one-dimension

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right) = D \frac{\partial^2 c}{\partial y^2} + \frac{\partial D}{\partial c} \left(\frac{\partial c}{\partial y} \right)^2 \quad (2)$$

may be written as

$$-\eta \frac{dc}{d\eta} = 2 \frac{d}{d\eta} \left(D \frac{dc}{d\eta} \right). \quad (3)$$

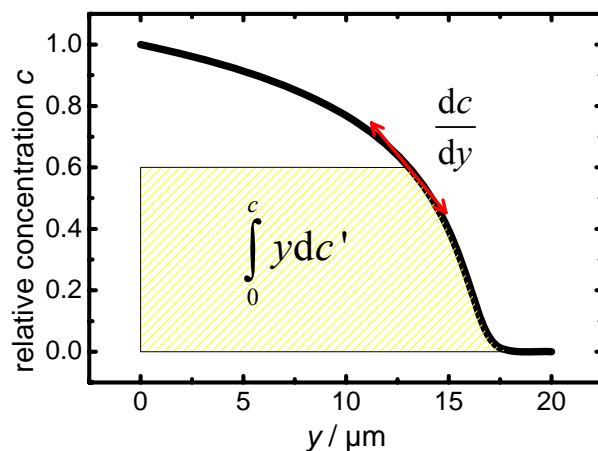
The relevant boundary and initial conditions for this transformation from y to η are $c(y=0, t) = c_{eq}$ at the crystal surface and $c(y \rightarrow \infty, t) = c(y, t=0)$.

Substitution by eq.(1) is thus found to transform the partial differential equation (2) with concentration c depending on time t and space y into an ordinary differential equation (3) where c now depends on only one variable η . The big benefit of this procedure becomes obvious after integrating eq.(3) over this new variable from $\eta = \infty$ to $\eta(c)$ and transposing to D :

$$D(\eta(c)) = -\frac{d\eta}{dc} \cdot \int_0^c \eta dc'. \quad (4)$$

This relation, after resubstitution of η , provides an equation which allows a direct calculation of the transport diffusivity D in dependence on concentration c for one concentration profile $c(y)$ measured at one sole point in time t (fig. 4):

Figure 4: Application of Boltzmann's integration method to a concentration profile ($D = \exp(5 \cdot c) 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and $t = 30 \text{ s}$). The integral (yellow area) and the derivative (red arrow) of eq. (5) are indicated for a relative concentration of 0.6.

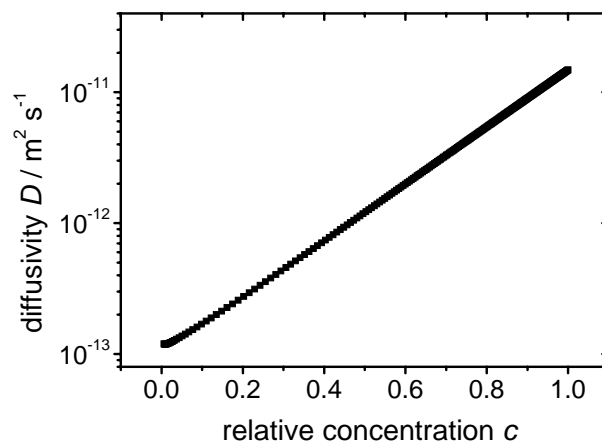


$$D(c(x,t)) = -\frac{1}{2t} \left(\frac{dc(y)}{dy} \right)^{-1} \cdot \int_0^c y(c') dc' \quad (5)$$

This method can also be used for analysing the initial period of molecular uptake by finite, one-dimensional systems, namely, if the time considered is small enough so that the concentration profiles of the molecules which penetrate through the two apposed crystal faces into the channel system do not yet overlap. In such cases, each branch of the concentration profiles can be considered as semi-infinite.

If these prerequisites are fulfilled Boltzmann's integration method yields very precise results with very low statistical noise and a large amount of data points (fig. 5). In view of the great potentials of the Boltzmann's integration method it is worthwhile to analyse in more detail the consequences of possible deviations from the required prerequisites on the final results.

Figure 5: Diffusivity from concentration profile in fig. 4 calculated with Boltzmann's integration method. This result corresponds with the original diffusivity.



Application of Boltzmann's integration method to methanol in ferrierite

The considerations of methanol transport in ferrierite have led us to fig. 6, in which only those molecules are recorded which have entered the ferrierite crystals along the channels in y -direction. Moreover, it turns out that, till about 90 seconds after the onset of the adsorption process, the thus determined normalized concentration profiles are in reasonable accordance with the initial and boundary conditions required to the application of Boltzmann's integration method (with the initial loading $c(y,t=0) = c_0$ being equal to zero). The mutual encounter of the diffusion fronts in the crystal centre after about 100 s terminates the time range of its application.

