Mass transfer in one-dimensional nanoporous crystals with different surface permeabilities

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Abstract

The use of optical techniques, such as interference microscopy and IR micro-imaging, has enabled the direct observation of transient concentration profiles. In a one-dimensional crystal, surface permeabilities on opposing crystal faces are usually equal, so that mass transfer occurs symmetrically and the fluxes through both crystal faces are identical. If the surface permeabilities on opposing crystal faces are different from each other, mass transfer is not symmetrical anymore. We are going to show that the fraction of molecular uptake (or release) through a given host face is inversely proportional to the time constant of uptake/release via this crystal face. This finding permits a straightforward estimate of the influence of asymmetry on overall uptake.

Keywords

Diffusion, surface permeation, unsymmetrical mass transfer

Introduction

The performance of nanoporous materials [1-3] in their technological application is often controlled by the rate of mass transfer of the guest molecules involved in these processes. Apart from the magnitude and the concentration dependence of the transport parameters, it may be crucial to know the pathways, i.e. the crystal faces and channel systems through which molecules are predominately entering (or leaving) the crystals during uptake (or release).

In the present paper, mass transfer processes in one-dimensional crystals (this means, in crystals with one-dimensional pore systems) are studied where the permeabilities of the surfaces on opposing sites are different from each other. Different surface permeabilities may be caused, for instance, by
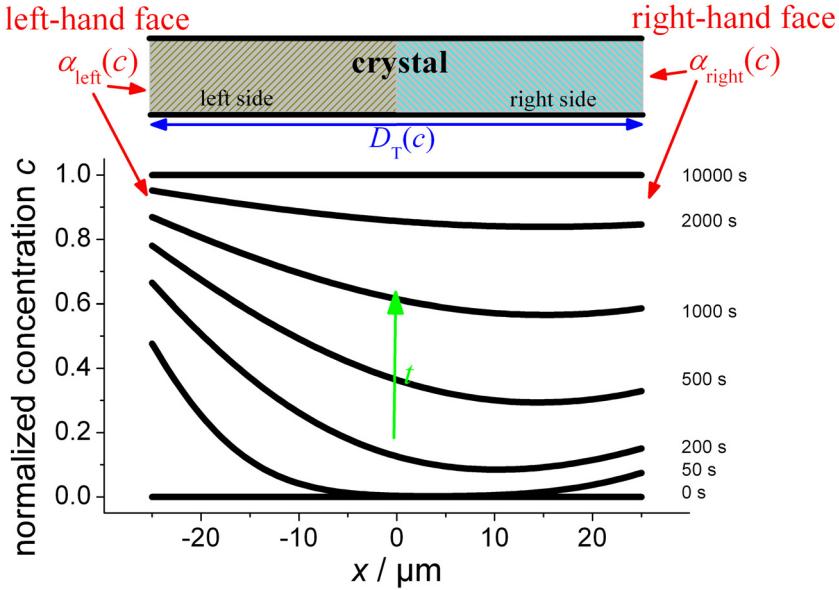
Figure 1: Sketch of mass transfer in a one-dimensional crystal (with $\alpha_{left} = 10$ $\alpha_{right} = 5$ D l, $D = 10^{-13}$ m^2 s^{-1}, $l = 25$ μm). The times after uptake onset are given on the right-hand side.

breaking the crystal (and by, hence, producing a new surface), by different aging of the surfaces or by coating only one crystal face. The fluxes of guest molecules are estimated from the knowledge of the transport parameters, which can be determined by analysis of transient intracrystalline concentration profiles [4, 5]. Transient concentration profiles evolve during uptake (or release) and may be recorded by interference microscopy [6, 7] and by IR micro-imaging [8] as well as by optical and fluorescence microscopy [9].

Since the transport equations are independent of the absolute values of the concentration, only the normalized concentrations, with an initial concentration $c_0 = 0$ and an equilibrium concentration $c_{eq} = 1$, will be considered. An example of the situation considered in our calculation is given in Figure 1.

Determining the fraction of uptake through a particular crystal face

We consider a one-dimensional crystal with an intracrystalline transport diffusivity $D(c)$ and surface permeabilities $\alpha_{left}(c)$ and $\alpha_{right}(c)$ on either side of the crystal. Therefore, the boundary conditions are [10]

$$j_{left\ surface} = \alpha_{left} \cdot \left(c_{eq} - c_{left\ surface}(t) \right) \tag{1}$$

and

$$j_{right\ surface} = \alpha_{right} \cdot \left(c_{eq} - c_{right\ surface}(t) \right). \tag{2}$$

Mass transfer is a function of the transport parameters (D, α_{left} and α_{right}) and of the given concentration (gradients). Hence, also the flux density through the crystal surface ($j_{\text{left surface}}$, $j_{\text{right surface}}$) generally depends on all transport parameters and on the crystal extension $2\,l$.

It is obvious that, during uptake processes limited by diffusion (i.e. $\alpha/l \gg D/l^2$), the mass transfer is symmetrical and the fluxes through both crystal faces are identical.

During transfer processes controlled by surface barriers (i.e. $\alpha/l \ll D/l^2$), the concentration profiles are essentially flat and $c_{\text{left surface}}$ equals $c_{\text{right surface}}$. Therefore, it follows directly from eqs. (1) and (2) that the flux through a surface is proportional to the respective surface permeability.

Analogously to the analysis of three-dimensional uptake or release processes [11], we imply that the relative amount of molecules entering (or leaving) through one crystal face can be estimated by

$$N_{\text{rel}}^{\text{left}} = \frac{\tau_{\text{left}}^{-1}}{\tau_{\text{left}}^{-1} + \tau_{\text{right}}^{-1}} \tag{3}$$

with

$$\tau_{\text{left/right}} = \int_0^\infty \left(1 - m_{\text{left/right}}(t)\right)\mathrm{d}t = \frac{l}{\overline{\alpha}_{\text{left/right}}} + \frac{l^2}{3 \cdot \overline{D}} \tag{4}$$

denoting the time constants for uptake (or release) by the left (or right) side of the crystal. Here, $m_{\text{left/right}}$ denotes the molecular uptake till time t if there were an impermeable membrane in the crystal centre. $\overline{\alpha}$ and $\overline{D}$ denote the mean values over the considered intervals of concentration:

$$\overline{D} = \frac{1}{c_{\text{eq}} - c_0} \int_{c_0}^{c_{\text{eq}}} D(c)\mathrm{d}c\,, \qquad\qquad \overline{\alpha} = \frac{1}{c_{\text{eq}} - c_0} \int_{c_0}^{c_{\text{eq}}} \alpha(c)\mathrm{d}c\,. \tag{5}$$

Both extreme cases – namely transfer processes controlled by surface barriers or by intracrystalline diffusion - are obviously included in eq.(3). The other methods recommended in ref. [11] can not be used, since in this case an analytical solution describing the transfer process would be required.

Checking the method

To check validity and accuracy of eq.(3), we consider mass transfer in a one-dimensional crystal with surface permeabilities differing from each other. For this purpose, a one-dimensional numerical solution of Fick's 2nd law [4] is used to calculate the transient concentration profiles.

The concentration dependences as well as the factors shifting the magnitude vary over a wide range (fig. 2), so that the derived statements may be expected to be valid for all common transfer processes of guest molecules in nanoporous materials.

By modifying the magnitude of the surface permeabilities and of the diffusivity, the crystal extension $2\,l$ can remain constant without limiting the generality of the statements. We chose to consider uptake by a crystal of 50 μm length. The lattice has 100 points.

The flux density through the surface can be calculated within these calculations by the boundary condition (eqs. (1) and (2), *method a*) or by considering the density of the diffusive flux beneath the surface by means of Fick's 1st law (*method b*),

$$j = -D \cdot \left. \frac{\partial c}{\partial x} \right|_{surface} . \tag{6}$$

In principle, methods *a* and *b* yield equal results; however, small deviations may occur due to the finite lattice size. Therefore, both methods of calculating the flux through the surface are used.

For the sets of transport parameters used in our calculation, the following three possibilities were considered:

1) All transport parameters (D, α_{left} and α_{right}) are constant.

2) The transport parameters depend on concentration, however, both surface permeabilities have the same concentration dependence.

3) The concentration dependence of the different transport parameters is randomly chosen.

In each case, numerical calculations with 1000 random sets of transport parameters were performed.

The mean deviations of the relative fraction of molecular uptake through the individual crystal faces as estimated with eq.(3) from the rigorously calculated values results to be less than 4 % (Table 1). This is generally smaller than the uncertainty of the transport parameters, which are usually determined with an uncertainty of up to some 10 % [4]. Therefore, it is highly recommended to estimate the total uptake through a given crystal face by means of the respective time constants.
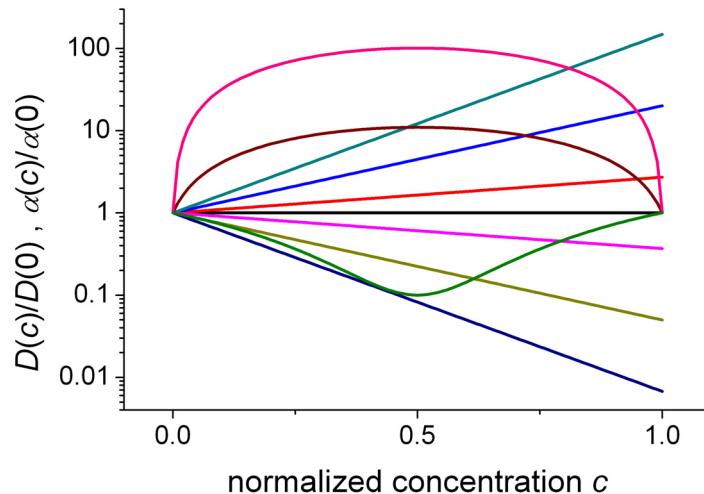

Figure 2: Representation of the different patterns of concentration dependence of the transport diffusivity and the surface permeability considered in our numerical calculations:
$D(c)/D(0)$ or $\alpha(c)/\alpha(0) =$ 1, exp(c), exp($3\,c$), exp($5\,c$), exp($-c$), exp($-3\,c$), exp($-3\,c$), $1 + 10\sin(\pi\,c)$, $1 + 100\sin(\pi\,c)$, $1 - 0.9\sin(\pi\,c)$.
At zero loading, the transport parameters were randomly chosen to assume the following values:
$D(0) = \{0.01, 0.1, 0.3, 0.5, 0.7, 1, 1.3, 1.5, 2, 5, 10, 20\} \cdot 10^{-13}$ m² s⁻¹
$\alpha(0) = \{0.01, 0.1, 0.3, 0.5, 0.7, 1, 1.3, 1.5, 2, 5, 10, 20\} \cdot 10^{-8}$ m s⁻¹.

	constant transport parameters	concentration-dependent transport parameters with $\dfrac{\alpha_{\text{left}}(c)}{\alpha_{\text{left}}(0)} = \dfrac{\alpha_{\text{right}}(c)}{\alpha_{\text{right}}(0)}$	transport parameters with different concentration-dependences
standard deviation σ to eq.(1), method a	1.9 %	2.8 %	3.8 %
standard deviation σ to eq.(6), method b	1.8 %	2.7 %	3.7 %

Table 1: Mean deviations of the magnitude of the relative uptake through a particular crystal as estimated by eq.(3) from the rigorous calculations following either Fick's 1$^{\text{st}}$ law (eq.(6)) or the boundary condition, eq.(1).

Conclusions

The performance of nanoporous materials in their technical application is often controlled by the rate of mass transfer of the involved molecules. In the present article, mass transfer in a one-dimensional crystal with different surface permeabilities on the opposing crystal faces is studied. By means of numerical calculations of a large amount of uptake processes with vastly varying transport parameters, it has been found that the fraction of uptake/release through an individual crystal face is inversely proportional to the time constant of uptake/release by this side of the crystal. This time constant follows from the transport parameters which can be determined from intracrystalline concentration profiles recorded, for instance, by interference microscopy.

Acknowledgement

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