Significance of Concentration-Dependent Intracrystalline Diffusion and Surface Permeation for Overall Mass Transfer

Lars Heinke

Fakultät für Physik und Geowissenschaften, Abteilung Grenzflächenphysik, Linnéstr. 5, 04103 Leipzig, Germany

E-Mail: Heinke@physik.uni-leipzig.de

Abstract

The intracrystalline concentration profiles evolving during molecular uptake and release by nanoporous materials as accessible by interference microscopy contain a lot of hidden information. For concentration-independent transport parameter, the influence of surface resistances to overall mass transfer can be calculated by correlating the actual surface concentration with the overall uptake. By using a numerical solution of Fick's 2nd law and considering a large variety of concentration dependencies of the transport diffusivity and the surface permeability, we show that the factor by which the transport process is retarded by the surface resistance may reasonably well be estimated by the type of correlation between the actual boundary concentration and the total uptake at a given time. In this way, a novel technique of uptake analysis which may analytically be shown to hold for constant diffusivities and surface permeabilities, is shown to be quite generally applicable.

Keywords

diffusion, surface resistance, concentration dependence

1. Introduction

Diffusion and adsorption of guest molecules in nanoporous host materials is an important field of science. The recently developed interference microscopy [1] allows a direct monitoring of the evolution of the intracrystalline concentration profiles during transient sorption experiments. With a spatial resolution of down to the range of micrometers, interference microscopy has thus proved to be the first "microscopic" technique applicable to the study of molecular diffusion in nanoporous host-guest systems under non-equilibrium conditions. This peculiarity, in particular, opened up the option to monitor the evolution of concentration profiles close to the crystal boundary. As a most remarkable finding of the measurements by this technique, for many host-guest systems under transient conditions the boundary concentration close to the particle surfaces were found to notably deviate from the equilibrium value corresponding to the pressure of the guest molecules in the surrounding atmosphere. These differences indicate the presence of transport resistances at the external surface of the host systems, since any essential influence of heat release may be excluded, owing to the fact that the measurements are performed with single crystals ensuring a sufficiently large surface-to-volume ratio [2, 3]. The discussion of the relative contributions of diffusion and surface barriers on the overall kinetics of molecular uptake and release with nanoporous materials, accessible by interference microscopy, is in the focus of [4]. The aim of this work is to investigate the influence of the concentration dependency of the transport diffusivity and surface permeability to the overall mass transport. The accuracy of the evidence of the correlation plots between boundary concentration and overall uptake as derived in [4] is examined for one-dimensional transport processes simulated with concentration-dependent transport parameters. Furthermore, we show that three-dimensional mass transport in an isotrope cube yields similar correlation pattern between boundary concentration and overall uptake, so that also in this case the influence of the surface resistance can be quantified using such correlation plots.

2. Correlating Molecular Uptake with the Actual Boundary Concentration for One-Dimensional, Concentration-Independent Mass Transport

Relative molecular uptake (or release) up to a certain observation time follows by simple integration over the concentration profiles for the given instant of time. This provides the option to plot the boundary concentration as a function of the molecular uptake.

Assuming a constant transport diffusivity D and a constant surface permeability α, the normalized concentration profile within a host particle of length $2l$ during molecular uptake is given by the relation [5]

$$c(y,t) = 1 - \sum_{n=1}^{\infty} \frac{2L \cos\left(\beta_n y / l\right) \exp\left(-\beta_n^2 Dt / l^2\right)}{\left(\beta_n^2 + L^2 + L\right)\cos\beta_n} \tag{1}$$

where the β_n's are the positive roots of

$$L = \frac{l\alpha}{D} = \beta_n \tan \beta_n. \tag{2}$$

Integration over the system in diffusion (i.e. y-) direction from $-l$ to l yields

$$m(t) = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp\left(-\beta_n^2 Dt / l^2\right)}{\left(\beta_n^2 + L^2 + L\right)\beta_n^2} \tag{3}$$

for the relative uptake at time t. The implied constancy of D and α effects, that eqs.(1) and (3) hold for uptake from concentration zero as well as for any subsequent step, where then eq. (1) denotes the change in concentration rather than the concentration itself. Equivalently, the corresponding expressions for molecular release are just the sums in eqs.(1) and (3). This may be easily rationalized by realizing that, as a consequence of the implied constancy of D and α, the underlying diffusion equation is linear. Hence, the simultaneous occurrence of adsorption and desorption has to leave the system unchanged.

Figure 1: Correlation between the actual boundary concentration (c_{surf}) and the relative uptake (m) at the corresponding instant of time. Three different cases are shown: the mass transport is essentially limited by intracrystalline diffusion ($l\alpha / D = 100$), by surface barriers ($l\alpha / D = 0.01$) and both by intracrystalline diffusion and surface resistance ($l\alpha / D = 1$).
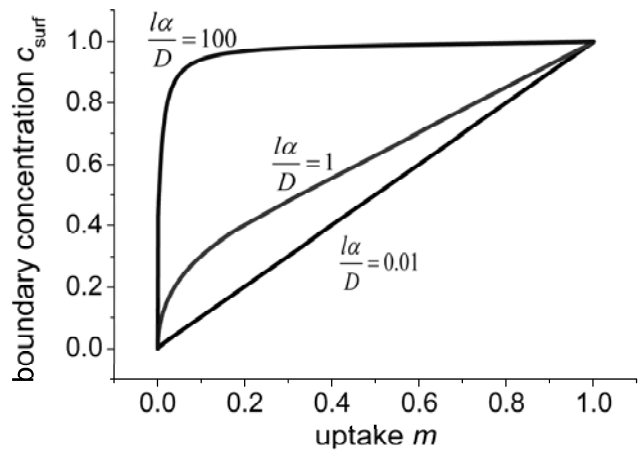
As already derived in [4], there exists a correlation between the actual boundary concentration (c_{surf}) and the relative uptake (m) at the corresponding instant of time, following from eqs.(1) for $y = -l$ or l and eq.(3) (fig. 1). The ratio $l\alpha/D$ has been chosen as the parameter of this representation. It represents nothing else than the ratio $\tau_{diff} / \tau_{surf}$ of the exchange times ("first moments" of the tracer-exchange, sorption or desorption curves which, owing to the

implied constancy of D and α, have to coincide). Thus it turns out that with increasing uptake the correlation plot very soon becomes a straight line. Its intercept with the ordinate (in the following referred to as w) vary strongly with the prevailing mechanism of transport resistance. For dominating surface barriers (e.g. for $4/\pi^2 \cdot l\alpha/D = 10^{-2}$), the total plot appears as a straight line with no perceptible intercept with the ordinate. With increasing influence of diffusion, this intercept becomes more and more extended. For completely diffusion controlled processes, w equals 1.

In the long-time limit (only considering the first summand), eq. (3) may be easily combined with eq. (1) at $y = -l$ or l yielding

$$c_{surf}(t) = c(y = l, t) = 1 - \frac{\beta_1^2}{L} + \frac{\beta_1^2}{L} \cdot m(t) . \tag{4}$$

Thus, the intercept w of the asymptote of the c_{surf} - m - correlation plot to the ordinate is found to be given by the relation

$$w = 1 - \frac{\beta_1^2}{L} . \tag{5}$$

In a qualitative way, the reciprocal value of this intercept, w^{-1}, is expected to indicate the relevance of surface barriers for the overall process of molecular exchange. The ratio of the quotient of the exchange times and the reciprocal value of w can be reformulated to

$$\frac{\tau_{surf+diff} / \tau_{diff}}{w^{-1}} = \frac{\pi^2}{4} \left(\frac{1 - \beta_1 / \tan \beta_1}{\beta_1^2} \right) \tag{6}$$

which results to be between $\pi^2/12 \approx 0.82$ and 1 for β_1 varying in the range of 0 and $\pi/2$ (corresponding to a variation of $L = l\alpha/D = \beta_1 \cdot \tan \beta_1$ between 0 and ∞, i.e. over all possible values). Therefore, the reciprocal value of the intercept of the extrapolated linear part of the c_{surf} - m - correlation plot with the ordinate may be taken as an estimate of the factor, by which the presence of the surface barrier leads to a prolongation of molecular uptake and release.

The equivalence of the ratio of the exchange times $\tau_{surf+diff} / \tau_{diff}$ and the reciprocal value of the intercept w^{-1} (eq.(6)) implies concentration-independent transport parameters. In real systems, however, the transport diffusivity, as well as the surface permeability, may depend on concentration. The aim of the 4th section is to study the relation between $\tau_{surf+diff} / \tau_{diff}$ and w^{-1} for one-dimensional, concentration-dependent transport diffusion and surface permeation.

3. c_{surf} - m - Correlation for Mass Transport in an Isotrope Cube

The concentration profiles during uptake by a cuboid with a three-dimensional channel system may be calculated by [5, 6]

$$c(x,y,z;t) = 1 - 8L_x L_y L_z \cdot$$

$$\sum_{n,m,k=1}^{\infty} \frac{\cos\left(\beta_{x,n} x / l_x\right)\cos\left(\beta_{y,m} y / l_y\right)\cos\left(\beta_{z,k} z / l_z\right)\exp\left(-\beta_{x,n}^2 D_x t / l_x^2 - \beta_{y,m}^2 D_y t / l_y^2 - \beta_{z,k}^2 D_z t / l_z^2\right)}{\left(\beta_{x,n}^2 + L_x^2 + L_x\right)\left(\beta_{y,m}^2 + L_y^2 + L_y\right)\left(\beta_{z,k}^2 + L_z^2 + L_z\right)\cos\beta_{x,n}\cos\beta_{y,m}\cos\beta_{z,k}}$$

(6)

where the β_n's are the positive roots of

$$\beta_{x,n}\tan\beta_{x,n} = L_x = \frac{l_x \alpha_x}{D_x}, \quad \beta_{y,m}\tan\beta_{y,m} = L_y = \frac{l_y \alpha_y}{D_y} \quad \text{and} \quad \beta_{z,k}\tan\beta_{z,k} = L_z = \frac{l_z \alpha_z}{D_z}. \tag{7}$$

In the following, we restrict our consideration to homogeneous and isotropic diffusion ($D_x = D_y = D_z = D$) and surface permeation ($\alpha_x = \alpha_y = \alpha_z = \alpha$) in a cube with edge length $2l$.

The data accessible by interference microscopy are the concentrations integrated over the observation direction (x)

$$\frac{1}{2l}\int_{-l}^{l} c(x,y,z)\mathrm{d}x = 1 - \sum_{n,m,k=1}^{\infty} \frac{8L^4 \cos\left(\beta_m y / l\right)\cos\left(\beta_k z / l\right)\exp\left(-\left(\beta_n^2 + \beta_m^2 + \beta_k^2\right)Dt / l^2\right)}{\left(\beta_n^2 + L^2 + L\right)\beta_n^2\left(\beta_m^2 + L^2 + L\right)\cos\beta_m\left(\beta_k^2 + L^2 + L\right)\cos\beta_k}. \tag{8}$$

Integrating the concentration over the entire system, i.e. over x, y and z from $-l$ to l yields

$$m(t) = 1 - \sum_{n,m,k=1}^{\infty} \frac{8L^6 \exp\left(-\left(\beta_n^2 + \beta_m^2 + \beta_k^2\right)Dt / l^2\right)}{\left(\beta_n^2 + L^2 + L\right)\left(\beta_m^2 + L^2 + L\right)\left(\beta_k^2 + L^2 + L\right)\beta_n^2 \beta_m^2 \beta_k^2} \tag{9}$$

for the relative uptake at time t. In the long-time limit we may combine the integrated concentration at the surface ($y=l$) with the overall uptake to

$$\frac{1}{2l}\int_{-l}^{l} c(x,y=l,z;t)\mathrm{d}x = 1 - \frac{\beta_1^4}{L^2}\frac{\cos(\beta_1 z / l)}{\cos(\beta_1)}\left(1 - m(t)\right). \tag{10}$$

Hence, in the centre of the crystal ($z=0$), the intercept w of the asymptote of the $\int c_{\mathrm{surf}}\mathrm{d}x$ - m - correlation plot to the ordinate is found to be given by the relation

$$w = 1 - \frac{\beta_1^4}{L^2 \cos(\beta_1)}. \tag{11}$$

Consequently, the reciprocal value of this intersect, w^{-1}, indicates the relevance of surface barriers for the overall process of molecular exchange. The ratio of the quotient of the exchange times and the reciprocal value of w can be reformulated to

$$\frac{\tau_{\mathrm{surf+diff}}/\tau_{\mathrm{diff}}}{w^{-1}} = \frac{\pi^2}{4}\left(\frac{1}{\beta_1^2} - \frac{1}{\tan\beta_1 \cdot \sin\beta_1}\right) \tag{12}$$

which results to be between $\pi^2/24 \approx 0.41$ and 1 for β_1 varying in the range of 0 and $\pi/2$ (corresponding to a variation of $L = l\alpha/D = \beta_1 \cdot \tan\beta_1$ between 0 and ∞, i.e. over all possible values). Therefore, even for three-dimensional mass transport in an isotropic cube, the

reciprocal value of the intercept of the extrapolated linear part of the $\int c_{surf} dx$ - m - correlation plot with the ordinate may be taken as a reasonable estimate of the factor, by which the presence of the surface barrier leads to a prolongation of molecular uptake and release.

4. c_{surf} - m - Correlation for Concentration-Dependent Transport Parameters

The analysis of the c_{surf} - m - correlation for concentration-dependent transport diffusivities and surface permeabilities is complicated by the fact that there is no analytic solution of the diffusion equation with these boundary conditions. Therefore, we use a *finite difference solution* algorithm of Fick's 2nd law [5, 7] to calculate the concentration profiles. In this algorithm the transport parameter can have any dependency. From the thus calculated concentration profiles the boundary concentration c_{surf}, the overall uptake m and the exchange time τ for a particular uptake can be easily determined.

The transient concentration profiles are calculated for a huge variety of concentration dependencies (see fig. 3) which should ensure a general statement for the transport process. Hence, in some simulations the diffusivity as well as the surface permeability changes by more than two orders of magnitude whereas in other simulations these parameters have opposed concentration dependencies or pass a maximum or minimum value. In all calculations, mass transport into a one-dimensional channel system of length 2 l with an initial concentration of 0 and a final, equilibrium concentration of 1 is considered. The adsorption process with a transport parameter depending on c corresponds to a desorption process with a transport parameter depending on (1-c).

As an example, figure 2a shows the concentration profiles calculated with one selected diffusivity and surface permeability for several instants of time. In figure 2b, the boundary concentration is plotted as a function of the uptake by the crystal. As a typical feature of this plot, with increasing uptake the mutual dependence is found to become a straight line. Prolongation of this straight line to the ordinate leads to an intercept of $w = 0.32$.

The aim of this work is to investigate the accuracy of the statements so far rigorously derived only for constant transport parameters [4] if these transport parameters change with concentration. In particular, we want to study the relation between the reciprocal value of the intercept, w^{-1}, and the ratio of the exchange times $\tau_{surf+diff}$ / τ_{diff}. This means, we are ongoing to investigate whether w^{-1} remains to be a reasonable estimate of the factor by which the transport process is prolongated because of the surface resistance, even if the transport diffusivity and surface permeability vary significantly with concentration.
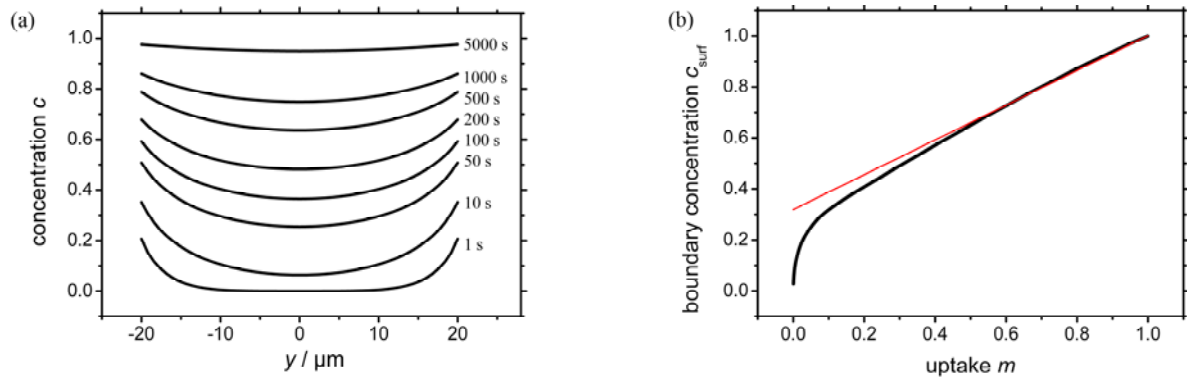
Figure 2: (a) Concentration profiles calculated with $D = \exp(5(1-c))\ 10^{-13}\ \text{m}^2\ \text{s}^{-1}$, $\alpha = 2\exp(5(1-c))\ 10^{-8}\ \text{m s}^{-1}$ (fig. 2i) for several instant of time. (b) Boundary concentration as a function of the overall uptake (black line). The extrapolation of the long-time range is also displayed (red line). The value of $L = l \cdot \int_0^1 \alpha(c)\mathrm{d}c \Big/ \int_0^1 D(c)\mathrm{d}c$ equals 2.

For this purpose, we calculate the transient concentration profiles for a plethora of concentration dependencies of the transport parameters with $L = l \cdot \int_0^1 \alpha(c)\mathrm{d}c \Big/ \int_0^1 D(c)\mathrm{d}c$ varying between 0.002 and 500. The huge range of L is realised by changing the magnitude, not the functional dependence, of the surface permeability. The exchange times are calculated for transport processes controlled by both intracrystalline diffusion and surface resistance ($\tau_{\text{surf+diff}}$) and by diffusion alone (τ_{diff}), i.e. for diffusivities kept constant while the surface permeability is increased to infinity.

Figure 3 compares the ratio $\tau_{\text{surf+diff}} / \tau_{\text{diff}}$ of the exchange times with the reciprocal value of the intercept (w^{-1}) plotted as a function of L. In general, the agreement between w^{-1} and the ratio of the exchange times is satisfactory. If the transport parameters do not change by more than one order of magnitude, the deviation of w^{-1} from the ratio of the exchange times is even negligible small in comparison with $\tau_{\text{surf+diff}} / \tau_{\text{diff}}$, i.e. with the factor by which the uptake process is prolongated by the surface resistance. For transport parameters varying over several orders of magnitude in the considered concentration range, w^{-1} may notably deviate from $\tau_{\text{surf+diff}} / \tau_{\text{diff}}$. However, the reciprocal value of the intercept w^{-1} is still a valuable estimate of the factor by which the surface resistance prolongates the uptake process. It is also visible that a strong concentration dependence of the surface permeability causes a somewhat larger deviation of w^{-1} from $\tau_{\text{surf+diff}} / \tau_{\text{diff}}$ than a strong concentration dependence of the diffusivity (see fig. 3 d and e, j and k, m and n). Transport parameters, especially surface permeabilities, decreasing with increasing concentration result smaller deviations of w^{-1} from $\tau_{\text{surf+diff}} / \tau_{\text{diff}}$ than increasing permeabilities (see fig. 3 c and i, d and j, e and k, s and t).

Figure 3: Reciprocal value of the intercept w^{-1} (black squares) and ratio of the exchange times $\tau_{surf+diff}$ / τ_{diff} (red spheres) as a function of $L = l \cdot \int_0^1 \alpha(c)dc \Big/ \int_0^1 D(c)dc$ for the concentration dependencies of the diffusivity and the surface permeability shown above (transport diffusivity (black) and the surface permeability (red)).

((a) $D = D_0$, $\alpha = \alpha_0$, (b) $D = D_0 \exp(c)$, $\alpha = \alpha_0 \exp(c)$, (c) $D = D_0 \exp(5c)$, $\alpha = \alpha_0 \exp(5c)$, (d) $D = D_0 \exp(5c)$, $\alpha = \alpha_0$, (e) $D = D_0$, $\alpha = \alpha_0 \exp(5c)$, (f) $D = D_0(1+10\,c)$, $\alpha = \alpha_0(11-10\,c)$, (g) $D = D_0(11-10\,c)$, $\alpha = \alpha_0(1+10\,c)$, (h) $D = D_0 \exp(1-c)$, $\alpha = \alpha_0 \exp(1-c)$, (i) $D = D_0 \exp(5(1-c))$, $\alpha = \alpha_0 \exp(5(1-c))$, (j) $D = D_0 \exp(5(1-c))$, $\alpha = \alpha_0$, (k) $D = D_0$, $\alpha = \alpha_0 \exp(5(1-c))$, (l) $D = D_0(1+10 \sin(\pi c))$, $\alpha = \alpha_0(1+10 \sin(\pi c))$, (m) $D = D_0(1+10 \sin(\pi c))$, $\alpha = \alpha_0$, (n) $D = D_0$, $\alpha = \alpha_0(1+10 \sin(\pi c))$, (o) $D = D_0(11-10 \sin(\pi c))$, $\alpha = \alpha_0(11-10 \sin(\pi c))$, (p) $D = D_0(11-10 \sin(\pi c))$, $\alpha = \alpha_0$, (q) $D = D_0$, $\alpha = \alpha_0(11-10 \sin(\pi c))$, (r) $D = D_0/(1-0.99c)$, $\alpha = \alpha_0/(1-0.99c)$, (s) $D = D_0 \exp(5(1-c))$, $\alpha = \alpha_0 \exp(5c)$, (t) $D = D_0 \exp(5c)$, $\alpha = \alpha_0 \exp(5(1-c))$.
The relative transport diffusivity and the relative surface permeability are related to the values at a concentration of 0 and a surface concentration of 0, respectively.)
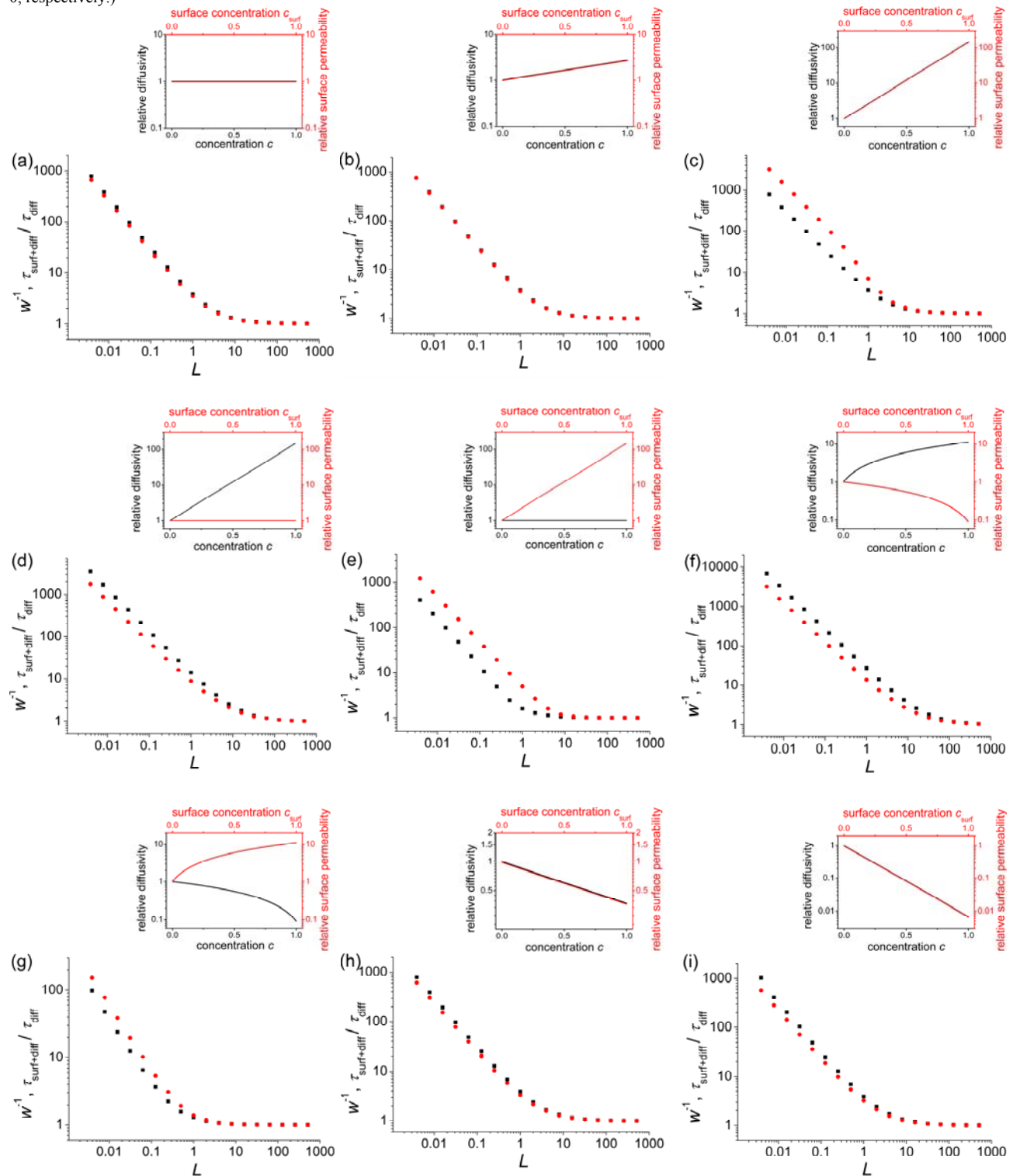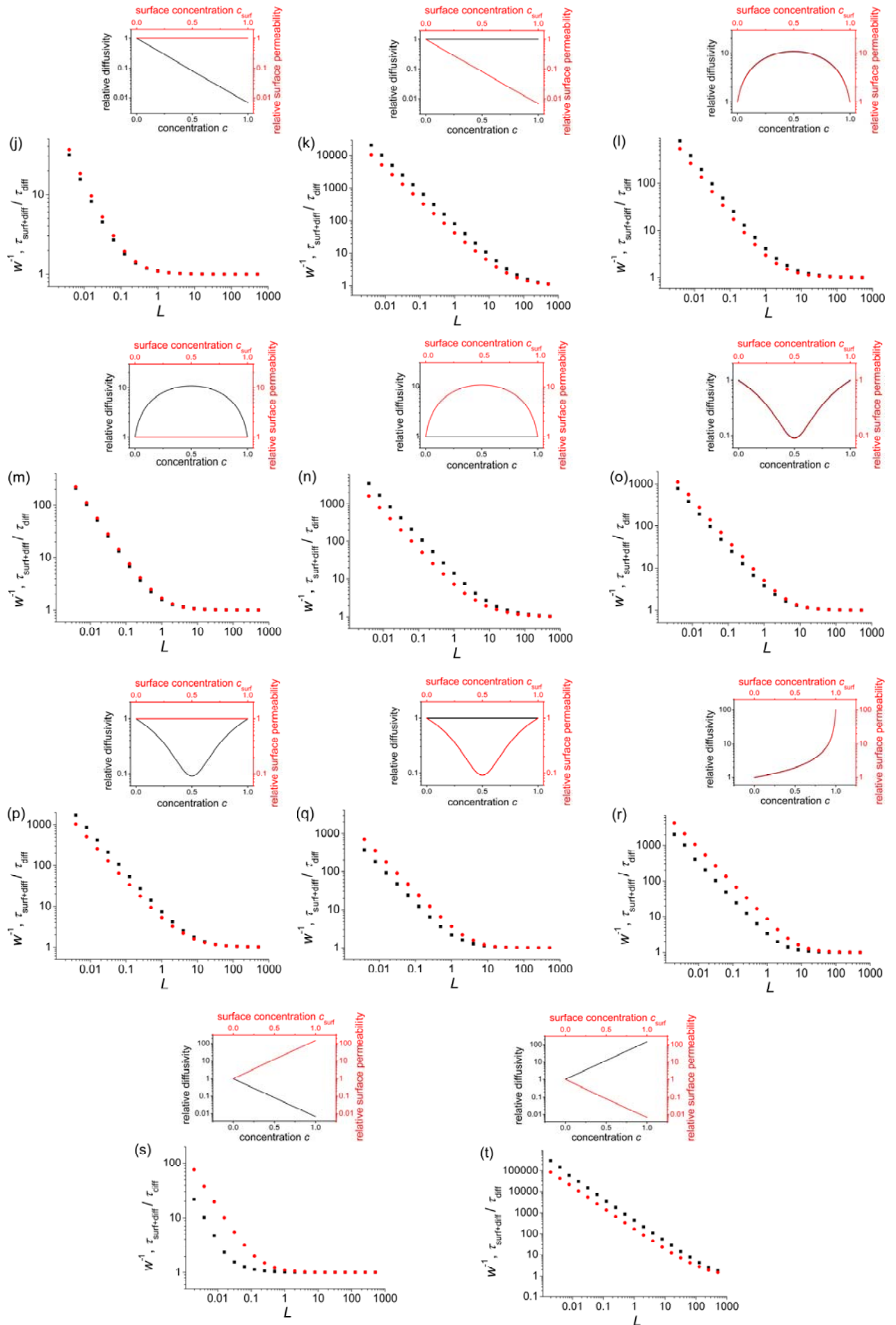
It is noteworthy that the concentration dependence of the transport parameters may result in quite different influences on the significance of the surface resistance. For instance, the uptake process with $L = l \cdot \int_0^1 \alpha(c)\mathrm{d}c \Big/ \int_0^1 D(c)\mathrm{d}c = 1$ is prolongated by a factor of more than 10 for $D = D_0$ and $\alpha = \alpha_0 \exp(5(1-c))$ (fig. 3k) whereas the influence of the surface resistance is very small ($\tau_{\mathrm{surf+diff}} / \tau_{\mathrm{diff}} \approx 1$) for $D = D_0 \exp(5(1-c))$ and $\alpha = \alpha_0$ (fig. 3j). In the first case, at high concentration the surface permeability is very low so that the surface limits mass transfer at high concentration. In the latter case, it is the diffusivity, which is very low at high concentrations so that diffusion becomes the limiting process in the overall uptake (see fig. 3 s and t).

Conclusion

The transport properties of guest molecules are crucial features for technical application of nanoporous materials. Therefore, the surface permeability is among the key quantities for their practical performance. Application of interference microscopy to monitoring transient sorption on nanoporous host-guest systems allows a measurement of the evolving actual boundary concentration (c_{surf}), simultaneously with the total uptake (m) of guest molecules up to this instant of time. For constant transport parameter it may be shown analytically that the c_{surf} - m − correlation allows a calculation of the factor by which the uptake process is prolongated by the surface barrier. In this work, this correlation is under examination for concentration-dependent transport parameter. A numerical solution of Fick's 2nd law is used to calculate the concentration profiles for a large variety of concentration dependencies. It is shown that also for transport processes with concentration-dependent transport diffusivities and surface permeabilities, the c_{surf} - m − correlation plots yield a reasonable estimate of the ratio of the exchange times $\tau_{\mathrm{surf+diff}} / \tau_{\mathrm{diff}}$. It is found to be valid even in such extreme cases where the transport parameters vary by more than two orders of magnitude during the considered uptake process.

Acknowledgment

References

[1] U. Schemmert, J. Kärger, C. Krause, R. A. Rakoczy, J. Weitkamp, Monitoring the Evolution of Intracrystalline Concentration, Europhys. Lett. 46 (1999) 204-210.

[2] L. Heinke, C. Chmelik, P. Kortunov, D. B. Shah, S. Brandani, D. M. Ruthven, J. Kärger, Analysis of Thermal Effects in Infra-Red and Interference Microscopy: n-Butane-5A and Methanol-Ferrierite Systems, Microporous Mesoporous Mat. (in press).

[3] L. K. Lee, D. M. Ruthven, Analysis of Thermal Effects in Adsorption Rate Measurements, J. Chem. Soc. Faraday Trans I 75 (1979) 2406-2422.

[4] L. Heinke, P. Kortunov, D. Tzoulaki, J. Kärger, The Options of Interference Microscopy to Explore the Significance of Intracrystalline Diffusion and Surface Permeation for Overall Mass Transfer on Nanoporous Materials, Adsorption (submitted).

[5] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 1975.

[6] H. Tautz, Wärmeleitung und Temperaturausgleich, Akademieverlag, Berlin, 1971.

[7] L. Heinke, Analytische Betrachtungen und IR-Experimente zum Sorptionsverhalten nanoporöser Materialien, Diploma thesis (2006).