The Options of Interference Microscopy to Explore the Significance of Intracrystalline Diffusion and Surface Permeation for Overall Mass Transfer on Nanoporous Materials

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1. Introduction

Interference microscopy (IFM) [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 during molecular uptake or release. As a most remarkable finding of the first measurements by this technique, for many host-guest systems under transient conditions the boundary concentration close to the particle surfaces was 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 [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 this work.

2. Correlating Molecular Uptake with the Actual Boundary Concentrations

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. Therefore, IFM provides the option to plot the boundary concentration as a function of the corresponding molecular uptake.

For constant diffusivity and surface permeability, one may derive a correlation between the actual boundary concentration (c_{surf}) and the relative uptake (m) at the corresponding instant of time (fig. 1a) [4]. 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) varies strongly with the prevailing mechanism of transport resistance. For dominating surface barriers (e.g. for $l\alpha/D=10^{-2}$), 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.
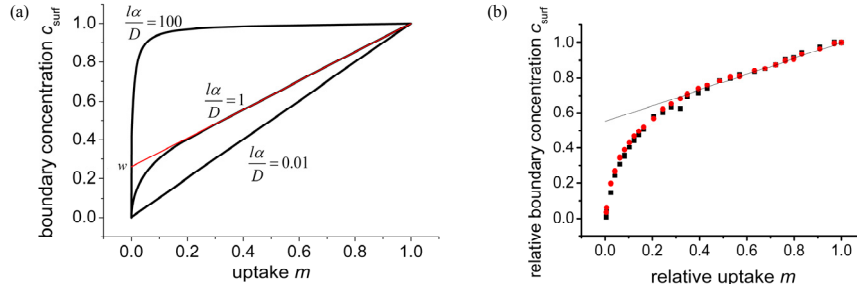
Figure 1: (a) Correlation between the actual boundary concentration (c_{surf}) and the relative uptake (m) for constant transport parameters at the corresponding instant of time. Three different cases are shown: the mass transport is essentially limited by intracrystalline diffusion ($l\alpha/D=100$), by surface barriers ($l\alpha/D=0.01$) and both by intracrystalline diffusion and surface resistance ($l\alpha/D=1$).
(b) Correlation between the actual boundary concentration (c_{surf}) and the relative uptake (m) at the corresponding instants of time for the uptake of methanol by ferrierite for a pressure step from 0 to 10 mbar. One may find that the surface barrier prolongates the transport process by a factor of about 1.8 ($w=0.55$). [4]

Assuming a constant transport diffusivity D and a constant surface permeability α, one may derive that the reciprocal value of the intercept w of the asymptote of the c_{surf} - m - correlation plot equals the quotient of the exchange times $\tau_{surf+diff}$ / τ_{diff} [4]. Therefore, w^{-1} 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 $\tau_{surf+diff}$ / τ_{diff} and the reciprocal value of the intercept, w^{-1}, implies concentration-independent transport parameters. In real systems, however, the transport diffusivity, as well as the surface permeability, may depend on concentration. It is shown in [5] that this $c_{surf} - m$ - correlation and the equivalence of w^{-1} and $\tau_{surf+diff}$ / τ_{diff} even holds for concentration-dependent transport parameters.

Therefore, applying this method to intracrystalline concentration profiles obtained by IFM yields an easy method to quantify the influence of the surface barrier on the overall mass transport (see fig. 1b) [4].

3. Conclusion

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. It may be shown that the c_{surf} - m – correlation plot allows an estimate of the factor by which the uptake process is prolongated by the surface barrier. This correlation yields therefore an easy estimate of the influence of the surface barrier on overall mass transport.

References
[1] U. Schemmert *et al.*, Europhys. Lett. 46 (1999) 204.
[2] L. Heinke *et al.*, Microporous Mesoporous Mat. (in press).
[3] L.K. Lee, D.M. Ruthven, J. Chem. Soc. Faraday Trans I 75 (1979) 2406.
[4] L. Heinke *et al.*, Adsorption (submitted).
[5] L. Heinke, Diffusion Fundamentals 4 (2007) 12.1.