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Short communication

The predictive power of classical transition state theory revealed in diffusion studies with MOF ZIF-8



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ABSTRACT

Knowledge of the adsorption isotherm is demonstrated to be sufficient for predicting the concentration dependence of the diffusivity of light hydrocarbons in MOF ZIF-8. Guest molecules considered include saturated and unsaturated hydrocarbons and alcohols. Calculations are based on the application of the classical transition state theory (TST). The predictions cover concentration dependences of up to two orders of magnitude in transport diffusion and of one order in self-diffusion. In agreement with TST, self- and corrected (Maxwell–Stefan) diffusivities are seen to coincide.

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1. Introduction

Progress in science benefits from theoretical concepts in twofold respect. They first offer the framework for classifying and rationalizing the observed phenomena. Secondly, they may serve as the basis for predictions in such cases where experimental observation is still excluded or, at least, complicated and time-expensive. In both these functions, theoretical concepts are in immediate interaction with the results of experimental measurement, with the accuracy of the latter one as a prerequisite of their viability.

First applications of the transition state theory (TST) [1,2] to diffusion in nanoporous materials, notably zeolites [3,4], were accompanied by vivid discussions dedicated to the origin of the discrepancies [5–10] often observed in these days on comparing the results of the newly introduced technique of microscopic self-diffusion measurement by pulsed field gradient (PFG) NMR [11–15]. Comparison of theory and experiment was thus subject to substantial uncertainty. Simultaneously, owing to a remarkable progress in their efficiency, evidence of molecular dynamic simulations [16–21] was more and more exploited as a standard for comparison with TST and, in many cases, for attaining agreement between the two sets of prediction, TST had to be subject to – in general slight – “dynamic corrections” [22–25].

As a result of an in-depth study of molecular diffusion in nanoporous materials by the combined application of both macro- and microscopic measuring techniques [26–29] mass transfer in nanoporous materials was found to be quite commonly influenced and, in many cases, even controlled by transport resistances different from the diffusional resistance of the genuine pore network. Depending on the system under study and the pretreatment conditions, such transport resistances were found to occur on the external surface [30–32] just as within the bulk phase of the material as either extended layers such as stacking faults [33–38] or by ample blockage of the “windows” between adjacent cavities (notably of the “eight-ring” ones [39]) as a function of the initial dehydration conditions, the degree of hydration and the structural integrity of the framework [40].

Eventually, with the advent of the techniques of microimaging [41,42], notably of interference microscopy (IFM) [43] and IR microscopy (IRM) [44–47], also microscopic measurement of intracrystalline diffusivities under non-equilibrium conditions, i.e. of so-called transport diffusivities, has become possible. Moreover, the potentials of IRM to record both transient uptake and release and tracer exchange, did allow measurements under both equilibrium and non-equilibrium conditions. Application of one and the same measuring technique minimizes the risk of artefacts on comparing the experimental data obtained under these physically quite different situations. Most importantly, microimaging is able to record the evolution of the concentration profiles of the guest

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molecules within the host material under study which, via Fick's first and second laws, represents the most direct way to the diffusivities. Misinterpretation of the primary data of measurement, as a common problem with diffusion studies quite in general, are thus essentially completely excluded.

The present communication deals with the diffusivities, determined in several recent studies by means of microimaging [48,49] with guest molecules in MOFs of type ZIF-8 [50–57]. Being composed of large cavities separated by “windows” with diameters comparable with the sizes of the molecules considered, the host-guest systems under study are potential candidates for the application of TST for diffusivity prediction. We are going to exploit these possibilities.

2. Transition state theory adopted to diffusion in nanopores

In the following we are briefly recollecting the essentials of transition state theory (TST) in its classical form, which we shall use on discussing and correlating the literature data on guest diffusion in MOF ZIF-8 as determined by microimaging and recently communicated [48,49]. On doing so, we benefit from the pore space character which allows us to base our analysis on the assumption that molecular propagation is exclusively controlled by jumps through the windows between adjacent cages. All types of mass transfer, including transport and self-diffusion, may thus be represented in terms of jump rates.

- (i) We introduce the notation $1/\tau(c)$ for the jump rate out of a cage of population (concentration) c . We thus imply that the jump probability is independent of the concentration of the cage to which the jump is directed. This is a consequence of the basic assumption of TST that the probability of finding a molecule in the transition state (i.e. in the “windows”) is an “infrequent event” (see also chapter 9 in Ref. [15]) and hence small enough so that jumps out of a given cage get essentially unhampered into that adjacent one to which they have been directed.
- (ii) Introducing the jump rates from the ground state (cage) into the activated state (window), $\frac{1}{\tau_c}$ and, vice versa, from the window into the cage, $\frac{1}{\tau_w}$, detailed balance requires

$$\frac{n_c}{\tau_c} = \frac{n_w}{\tau_w} \quad (1)$$

with n_c and n_w denoting the number of molecules within the cages and the windows, respectively.

- (iii) The jump through a window is considered as a rare event. Therefore, mutual molecular interaction in the windows may be excluded. We may hence imply that the mean life time in the windows is independent of concentration:

$$\tau_w = \tau_w(c) \quad (2)$$

and that the amount of molecules in the windows increases with the external pressure:

$$n_w \propto p \quad (3)$$

- (iv) Since the jump rate $\frac{1}{\tau_c}$ from cage to window is clearly proportional to the jump rate $1/\tau$ between adjacent cages and the number n_c of molecules per cage proportional to concentration c , relations (1) to (3) can be rearranged leading to the following relation for the dependence of the jump rate between adjacent cages on the local concentration c :

$$1/\tau(c) \propto \frac{p(c)}{c} \quad (4)$$

With the well-known random walk relation for statistically independent jumps [15,58–60] of mean squared jump length l^2 , the concentration dependence of the self-diffusivity may immediately be noted as

$$D \propto \frac{l^2}{\tau} \propto \frac{p(c)}{c} \quad (5)$$

with p denoting the guest pressure in the surrounding atmosphere in equilibrium with the guest concentration c in the microporous host system.

The corresponding relation for the coefficient D_T of transport diffusion follows in a straightforward way with the net flux, calculated with a concentration gradient and concentration-dependent jump rates (see, e.g. Refs. [61,62] for two-component diffusion or Section 2.5 in Ref. [63]) yielding

$$D_T = \frac{d}{dc}(Dc) \propto \frac{dp(c)}{dc} \quad (6)$$

A relation between the transport and self-diffusivity may be attained by combining Eqs. (5) and (6), yielding

$$D_T = D \frac{d \ln p}{d \ln c} \quad (7)$$

It is exactly this equation which is commonly used for splitting the transport diffusivity D_T into the reciprocal value of the logarithmic derivative of the adsorption isotherm $c(p)$, recognized as the thermodynamic factor (which in the range of linearity, $c \propto p$, degenerates to unity) and a quantity D_0 referred to as the corrected or Stefan–Maxwell diffusivity [6,15,59,64,65]. With Eq. (7), this quantity is now seen to be – within the frame of TST – identical with the self-diffusivity D . Within the frame of irreversible thermodynamics [66,67], this coincidence appears as an immediate consequence of TST since it excludes the occurrence of cross-correlation between different fluxes. However, this exclusion of cross-correlation – notably between differently labeled fluxes – has been identified as a prerequisite for a correct prediction of self-diffusivities using Eq. (7). In this context, this relation was also referred to as the Darken equation [6,68–70].

We illustrate the message of Eqs. (5)–(7) on the concentration dependences of the respective diffusivities by implying a Langmuir-type isotherm

$$c(p) = \frac{kp}{1 + kp/c_\infty} \quad (8)$$

with k and c_∞ denoting the Henry constant and the saturation capacity, respectively. Calculating the relevant derivatives we attain (via Eq. (5))

$$D \propto \frac{1}{1 - c/c_\infty} \quad (9)$$

and (via Eq. (6))

$$D_T \propto \frac{1}{(1 - c/c_\infty)^2} \quad (10)$$

For Langmuir-type isotherms and within the frame of TST, the corrected diffusivity (now coinciding with the self-diffusivity) is thus seen to contribute to exactly the same extent as the thermodynamic factor to the concentration dependence of the transport

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