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Diffusion in zeolites—a continuing saga

Extended abstract note

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1 Introduction

Following a brief discussion of zeolite structures and pore systems the mechanism of diffusion of guest molecules within the intracrystalline pores is discussed and the general pattern of the observed behavior is discussed. The relationship between tracer and transport diffusivity is considered and the experimental techniques that have been applied, over a period of several decades, to the measurement of both of these parameters are briefly reviewed. Some systems show satisfactory agreement between different types of measurement but other systems show large discrepancies in both the magnitudes of the diffusivities and their trends with loading. In general, where there are substantial discrepancies between different measurement techniques, it is observed that the smaller the length (and therefore time) scale of the measurement the higher is the value of the measured diffusivity. It appears that these differences arise from the defect structure of real zeolite crystals. Measurements over a short distance (a few unit cells) reflect the true transport resistance of an ideal crystal but over longer distances the diffusional resistance is increased by structural defects.

2 Pore structure and transport mechanism

Most commercial zeolite adsorbents have a well defined bimodal pore structure comprised of the intracrystalline pores (4–10 Å) interconnected through the intercrystalline network of macropores formed by the aggregation of the small crystals into macroscopic adsorbent particles. Transport within the intercrystalline pores occurs by a variety of different mechanisms (Knudsen diffusion, surface diffusion, molecular diffusion and viscous flow), depending on the nature of the diffusing species and the conditions. Although the behavior can be complex it is reasonably well understood and pore diffusivities can be predicted with some confidence from basic physical parameters. In contrast, intracrystalline diffusion, which is the focus of the present discussion, is much less well understood, especially when the diameter of the intracrystalline pores is comparable with the kinetic diameter of the guest molecule. Steric hindrance then becomes dominant and the diffusivity is largely controlled by the repulsive forces as shown in Fig. 1. This is the physical basis for size selective molecular sieve separations. Although intracrystalline diffusion has been studied over several decades by many different experimental techniques our understanding is still far from complete.

3 Transport diffusion—concentration dependence of diffusivity

The general pattern of variation of transport diffusivity with loading can be understood by considering the driving force to be the gradient of chemical potential (rather than the concentration as in Fick's equations). This leads to the relation:

$$D = D_0 \frac{d \ln P_A}{d \ln q} \tag{1}$$

which is sometimes called the Darken equation. For a system with a type 1 isotherm this leads to a strongly increasing diffusivity with loading, as illustrated for an ideal Langmuirian system in Fig. 2(a). As an example the experimentally observed behavior of benzene in faujasite is shown in Fig. 2(b).

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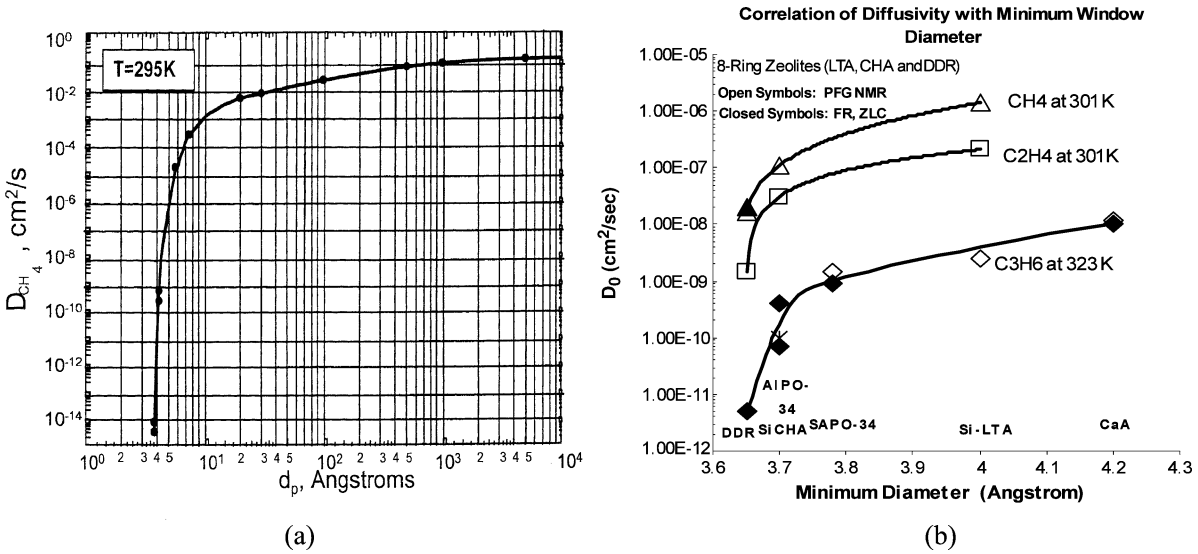
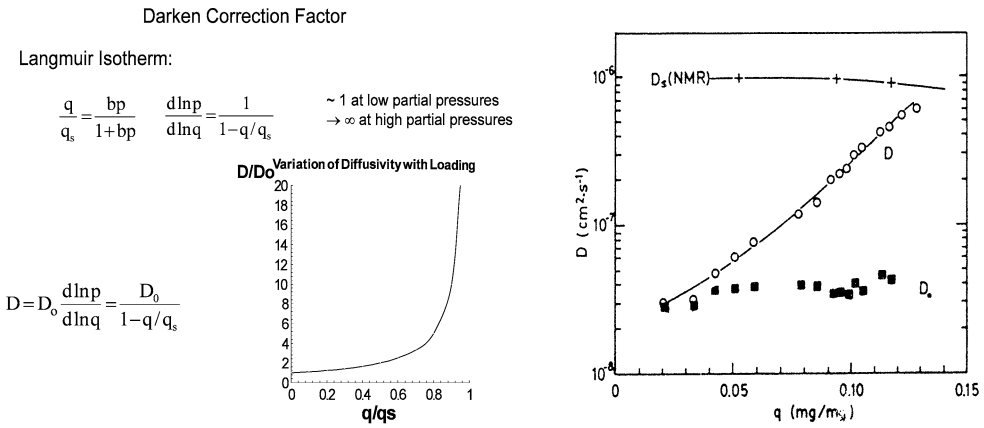


(a) (b)

Fig. 1 Effect of pore diameter on intracrystalline diffusivity. (**a**) Theoretical calculation for CH_4 at 295 K in cylindrical pores (Rao and Sircar 1993). (**b**) Experimental data for CH_4, C_2H_6 and C_3H_8 in several 8-ring zeolites (Ruthven and Reyes 2007)

Fig. 2 (**a**) Variation of diffusivity with loading for an ideal Langmuirian system with D_0 constant. (**b**) Experimentally observed variation of D with loading for benzene in faujasite at 403 K showing constancy of D_0 (Goddard and Ruthven 1986)



(a) (b)

4 Transport and self (tracer) diffusivities

The relation between the transport and tracer diffusivities can be derived from the Maxwell—Stefan model (Paschek and Krishna 2001) as shown in Fig. 3. For diffusion of D_2 in NaX at low temperature Jobic et al. (1999) was able to measure both self and transport diffusivities by neutron scattering. His data are shown in the insert. It is clear that the values fall in the expected sequence and the predicted convergence at low loadings is indeed observed.

5 Experimental techniques: comparison of diffusivities from different measurements

A wide variety of different experimental techniques have been applied to the measurement of intracrystalline diffusion in zeolites. A historical summary is given in Fig. 4.

The techniques may be divided into equilibrium (self-diffusion) and non-equilibrium (transport) measurements. They may also be classified according to the length (or time) scale over which the measurements are made. The diffusivities measured under equilibrium and non-equilibrium conditions are not identical but the relation between them is well understood, as noted above.

During the late 1970s and early 1980s a series of experiments were carried out in which the self-diffusivities, measured by PFGNMR, were compared with the macroscopically measured transport diffusivities. For some systems, notably Xe and CO_2 in 4A (Ruthven 1993), butane and propane in 5A (Kärger and Ruthven 1981) and methanol in 13X (Brandani et al. 1995) there was good agreement (see Fig. 5).

However, for other systems such as the linear alkanes in silicalite and single ring aromatics in 13X, the PFGNMR

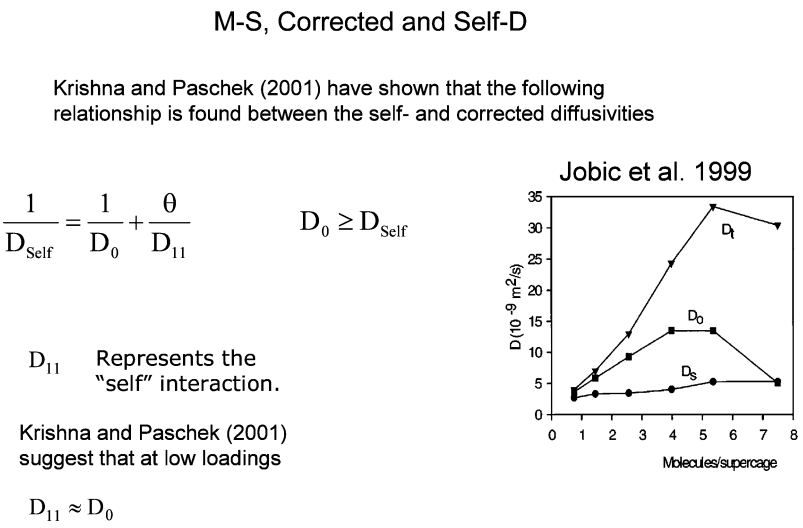


Fig. 3 Relationship between self and transport diffusivities form the Stefan Maxwell model and the experimental data of Jobic et al. (1999) showing $D > D_0 > D_s$ and at zero loading $D \rightarrow D_0 \rightarrow D_s$

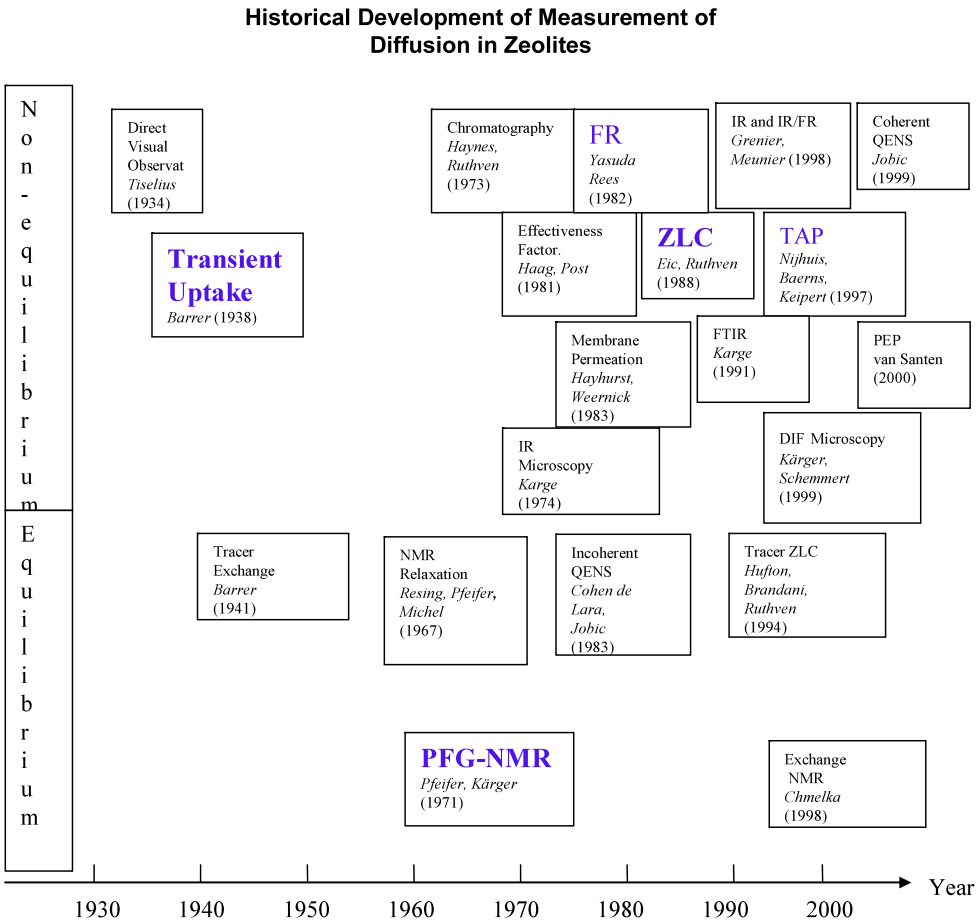


Fig. 4 Historical summary of experimental techniques for measurement of intracrystalline diffusion in zeolites (Courtesy of Prof. S. Brandani)

self-diffusivities were larger by several orders of magnitude (see for example Figs. 5(b) and 2). In some cases the discrepancy was evidently due to the intrusion of extracrystalline heat and mass transfer resistances in the macroscopic measurements. However, for several systems, the macroscopic measurements, with large zeolite crystals of several different size fractions, were shown to yield consistent diffusivity values that were still much smaller than the PFGNMR self-diffusivities.

Recent PFGNMR studies have shown that, for some systems, the measured diffusivity decreases with increasing length scale of the measurement, suggesting the influence of periodic barriers, probably associated with structural defects. An example (butane–silicalite) is shown in Fig. 6. This

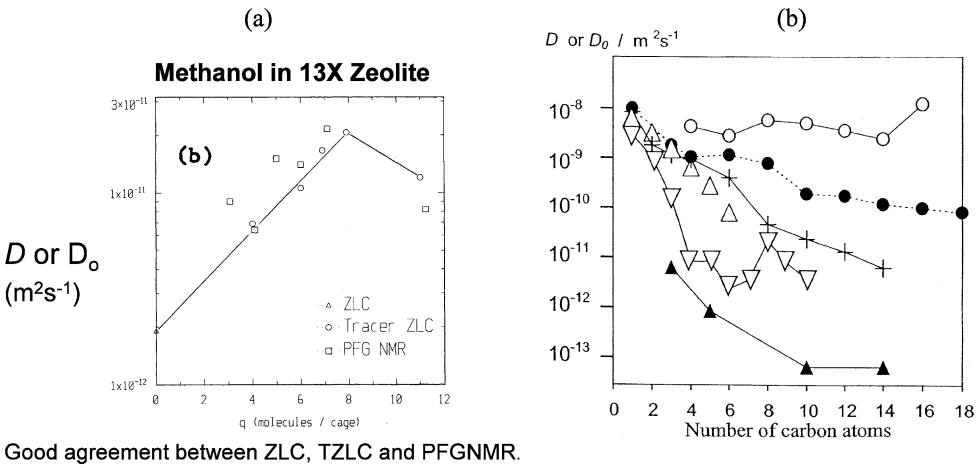


Fig. 5 (**a**) Comparison of self-diffusivities (measured by PFGNMR) and corrected transport diffusivities (measured by ZLC) for methanol in NaX (Brandani et al. 1995); (**b**) Diffusivities for n-alkanes in silicalite at 300 K measured by different techniques. ●, ○ MD simulations; +, QENS; ▽, single crystal membrane; △, PFG NMR; ▲, ZLC. From Jobic (2000)

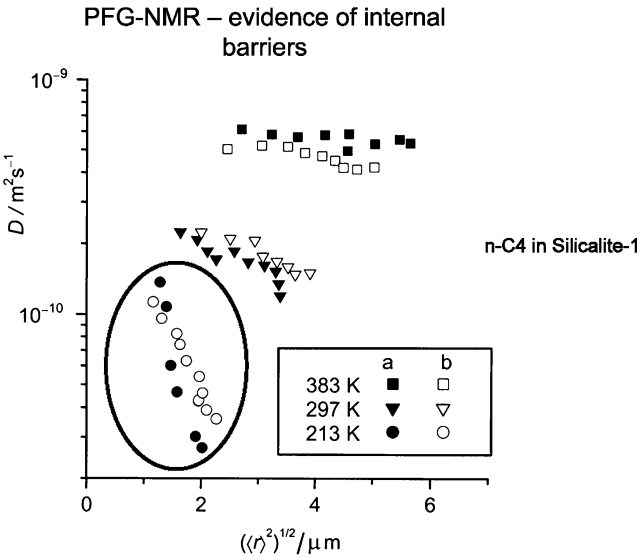


Fig. 6 Self-diffusion of butane in silicalite showing effect of structural barriers (at low temperatures). From Vasenkov and Kärger (2002)

would explain the observation that when measurements by different techniques are compared (Fig. 5(b)) we often see that the measured diffusivity decreases in the sequence:

QENS > PFGNMR > ZLC ≈ Single Crystal Membrane

which is the sequence of the length scales.

Recent measurements by infra-red and interference microscopy, discussed in Professor Kärger's lecture, have revealed many additional details and surprises in the behavior of "real" zeolite crystals including anisotropy, surface resistance and, in ferrierite, the preferential transport through the 8-ring channels rather than through the larger diameter 10-ring channels!

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