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On Comparing NMR and Adsorption Rate Diffusion Coefficients

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In a recent publication, (Ruthven and Doetsch, 1976), and in a further study (Ruthven, 1977), it has been mentioned that large discrepancies are observed between diffusion coefficients in identical systems measured by NMR and by adsorption rate experiments. Although he did not support the view, Ruthven commented in detail on one proposal to explain the observed differences. Kärger et al. (1976) assume that NMR determines the true mobility of adsorbed molecules within the body of adsorbent, whereas for certain types of zeolites, the limiting resistance in the adsorption rate experiment is a barrier resistance at the outer crystal surface.

With the NMR method, the average displacement of magnetically tabbed molecules is measured during a known period of time under equilibrium conditions, and from these data the diffusivity is calculated according to Einstein's law.

In several publications (Kärger and Walter, 1974; Pfeifer, 1972; Caro, 1977) Arrhenius plots of NMR diffusivities have been presented as in Figure 1. The solid line represents the measured results and may be divided into three regions: at lower temperatures intracrystalline diffusion coefficients D_z are measured with low activation energy, at intermediate temperatures there is a plateau, and at higher temperatures effective intercrystalline diffusivities D_a/K_A are measured with higher apparent activation energy. With increasing temperature, the plateau is reached when the average displacement of an adsorbed molecule during the NMR experiment is about equal to the crystal radius; this is documented for several systems and for different crystal radius in the literature cited. It is evident that the adsorbed molecules are not able to leave the crystals to enter the intercrystalline space over a range of temperatures, and some authors interpret this as meaning that a special barrier resistance exists at the outer crystal surface. However, we extrapolate the measured intercrystalline diffusivity (the dashed line, Figure 1). Adsorbed molecules moving within the crystals reach the outer surface (the low temperature end of the plateau) at a temperature where the intercrystalline diffusivity is an order of magnitude lower than the intracrystalline diffusivity; the system is macropore limited. Average molecular displacement increases only when the effective macropore diffusion coefficient becomes larger than the coefficient calculated from displacement equal to the crystal radius. Results are thus readily interpreted in terms of the common macropore-micropore model, and there is no need for introducing a third resistance. If such a third resistance exists and is greater than the macropore resistance, one should expect the measurements to follow the dotted line, lying below the effective intercrystalline diffusivity for some range of temperatures. No system in the literature to our knowledge shows this behavior; the plateau always ends near the intersection with the intercrystalline diffusion line. NMR measurements therefore prove conclusively that any barrier resistance is appreciably lower than the intercrystalline resistance. The barrier can by no means explain the three to four orders of magnitude by which NMR and adsorption rate results differ in the intracrystalline region.

Kärger et al. (1976) have attempted to prove the existence of the barrier by varying crystal size in adsorption rate experiments. Since the time parameter for the diffusion model is D_z/R^2 and for the barrier model $\mathcal{B}/R$, apparent diffusion coefficients should increase directly proportional to R if the barrier resistance theory applies. Figure 2 shows data presented by Kärger et al. (1976) for three systems with crystal sizes varying from 1 to 50 μ. The ordinate axis has been adjusted to permit representation of all systems in one figure, so that the D_z values are not given. All systems show an initial rise in D_z at a rate much faster than proportional to R and a gradual transition to a constant value at crystal sizes around 50 μ. Evaluation of the experiments according to the barrier model as done by Caro (1977) leads to barrier transfer coefficients varying with crystal size. It is evident that the diffusion coefficients measured by Kärger et al. (1976) and Caro (1977) are not invariant to size, but replacing them with size dependent barrier transfer coefficients is no solution to the problem.

As has been pointed out by Ruthven (1977), both NMR and adsorption rate diffusivities show similar trends with respect to increasing hydrocarbon chain length in

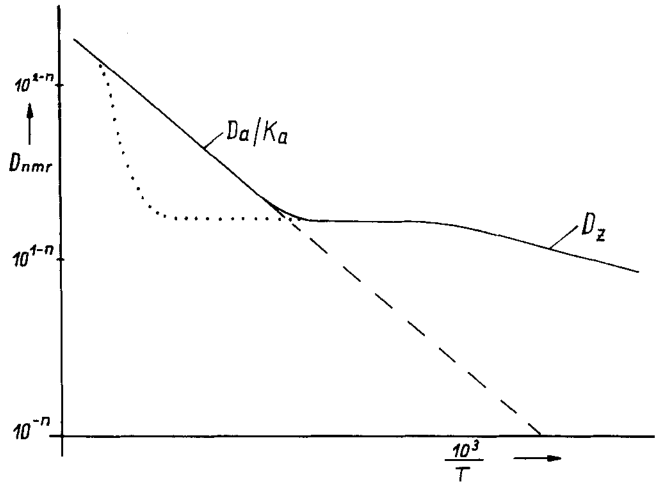

Fig. 1. Sketch of Arrhenius plot of NMR diffusivities.

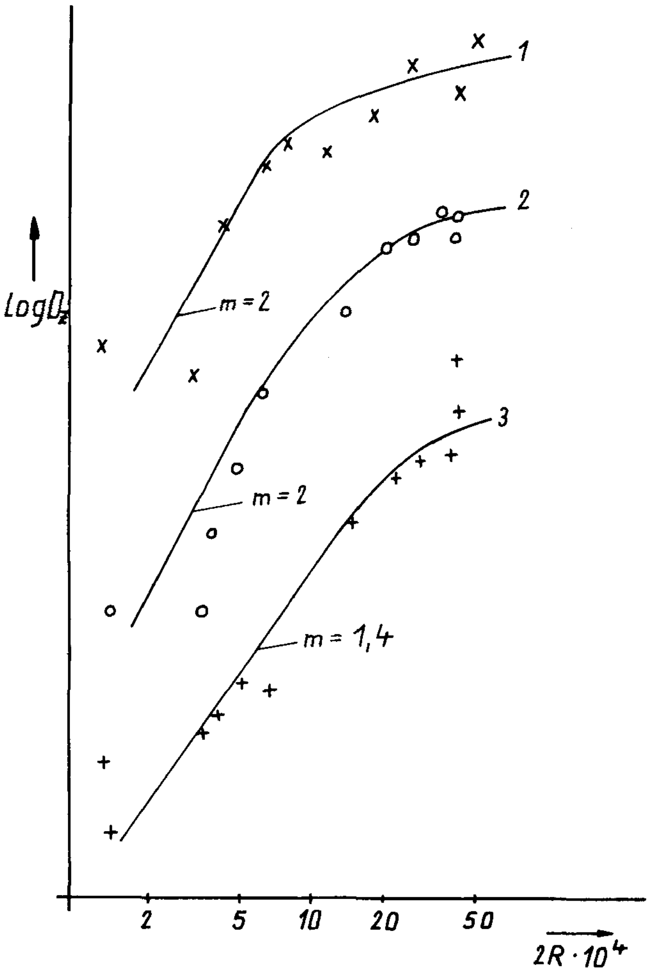

Fig. 2. Intracrystalline diffusion coefficients as a function of crystal size. Data from Kärger et al. (1976) and Caro (1977). 1. Ethane/NaCaA/−80°C; 2. propane/NaCaA/+23°C; 3. *n*-butane/NaCaA/+23°C.

5A zeolites, with respect to varying degree and type of cation introduced into the lattice, and with respect to increasing adsorbate concentration. From this point of view, they do not appear to be measuring completely different phenomena. Finally, the adsorption rate experiments are adequately described during an extended initial phase by the $\sqrt{t}$ law valid for diffusion; initial uptakes are not directly proportional to t as should be expected from the barrier resistance model.

In conclusion, there are differences of some orders of magnitude between NMR and adsorption rate diffusivities, and diffusion coefficients reported on the basis of adsorption rate experiments increase with crystal size. However, the barrier resistance theory does not give a satisfactory explanation of the observed phenomena.

NOTATION

D_a = intercrystalline diffusion coefficient, cm^2/s
D_{NMR} = diffusion coefficient measured by NMR, cm^2/s
D_z = intracrystalline diffusion coefficient, cm^2/s
K_A = adsorption equilibrium constant
m = slope of log-log plot
R = crystal radius, cm
t = time, s
$\mathcal{B}$ = barrier transfer coefficient, cm/s

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Nonisothermal Fouling of Catalyst Pellets Using Langmuir-Hinshelwood Fouling Kinetics

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Catalyst deactivation by fouling is often an unavoidable process, since it is linked with the chemical reactions employed. Its effect may be minimized, however, and this has led to a number of theoretical linvestigations. An early analysis of the problem of poisoning and fouling coupled with intraparticle temperature gradients was made by Wheeler (1955). Most subsequent analytical studies of catalyst fouling have assumed integral or zero order rate expressions for both the main and fouling reactions. Thus, Masamune and Smith (1966) assumed both reactions to be first order and isothermal; subsequently, an extension to nonisothermal fouling using the same first-order expressions was made by Sagara et al. (1967). Greco et al. (1973) also assumed first-order fouling in a study of the dehydration of alcohols. Kam et al. (1975, 1977*a*, *b*, *c*) have given a number of analyses for catalyst fouling under isothermal and nonisothermal conditions accompanied by interphase and intraparticle resistances; in every case, however, the models were developed on the assumption of the fouling kinetics being first order.

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