**Subscripts**

| | |
|---|---|
| $c$ | = cylinder |
| $f$ | = fluid |
| $o$ | = background value |
| $p$ | = particle |
| $r$ | = radial direction |
| $\theta$ | = angular direction |
| $\infty$ | = value at infinity |

**Superscripts**

| | |
|---|---|
| ' (prime) | = dimensionless value |

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# Sorption Kinetics of *n*-Decane on 5A Zeolites from a Nonadsorbing Liquid Solvent


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With the increasing application of synthetic zeolites both in catalysis and selective sorption processes, the investigation of sorption kinetics has become a subject of intensive research. In view of this, new experimental techniques, for example, the NMR pulsed field gradient technique, have been developed and applied to sorption systems (Pfeifer, 1972, 1977). The comparison of the intracrystalline self-diffusion coefficients obtained by the method mentioned above with the sorption diffusion coefficients calculated for the intracrystalline region reveals serious differences (Kärger and Caro, 1975, 1977; Ruthven, 1977; Gelbin, 1979). The results obtained by NMR pulsed field gradient technique were proved to be true in a number of experiments, whereas sorption diffusion coefficients of several *n*-paraffins on 5A zeolites with different crystal sizes show an unreasonable crystal size dependence (Kärger et al., 1976, 1977; Bülow et al., 1980).

Having excluded the rather improbable possibility that the zeolite structure is correlated with the crystal size in such a pronounced way, it must be concluded that sorption is controlled by processes different from intracrystalline diffusion. Proportionality between the sorption diffusion coefficient and the crystal size which could be observed in some experiments (Kärger et al., 1976, 1977; Bülow, 1978) would suggest that the sorption is rather affected by surface effects than influenced by intracrystalline diffusion.

As a model system which allows us to control or to avoid different factors and processes influencing uptake rate in a defined way, we have chosen the sorption of *n*-decane from a nonadsorbing liquid solvent (that is, from a solvent the molecules of which are too large to enter the zeolitic micropores). Thus it should be possible to simulate barriers of different efficiency at the outer crystal surface.

The sorption of *n*-decane from a nonadsorbing liquid solvent is characterized by the following:

1. Generally, owing to the heat of sorption, the temperature of the sorbent changes significantly during the sorption process. In liquid sorption experiments, the rapid heat transfer between the zeolite crystal and the surrounding liquid solvent ensures isothermal conditions and excludes the possibility that the heat transfer may be rate limiting.

2. Using different solvents with comparable viscosities, intercrystalline transport behavior of the sorbate molecules should be expected to be unchanged.

3. Therefore, the sorption rate of the sorbate molecules should be influenced only by the nature of mutual interactions between solvent molecules and outer crystal surface.

4. Differences in the uptake rates for different nonadsorbing solvents would give direct evidence that sorption is controlled by processes different from intracrystalline ones. In this case, the sorption has to be interpreted by assuming a surface barrier transport mechanism.


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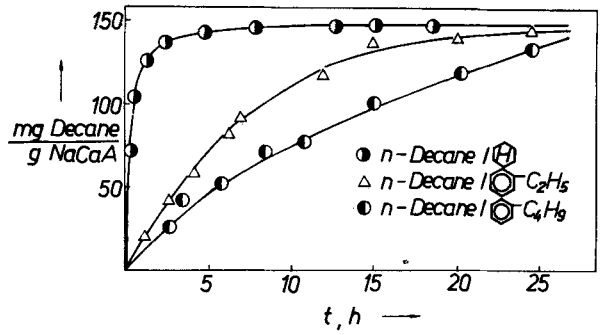


Figure 1. Uptake curves for the sorption of *n*-decane on NaCaA ( ≈ 70% Ca) zeolite with a diameter of about 6.5 μm at 23°C from different liquid solvents.

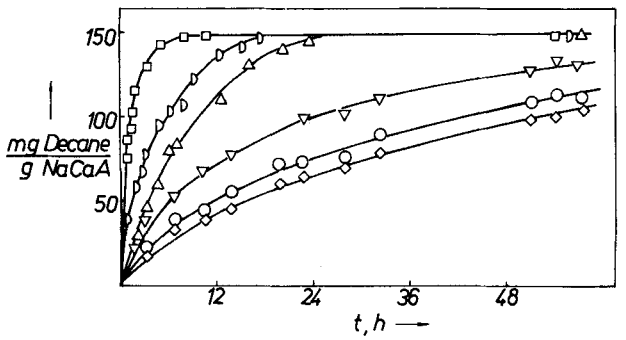


Figure 2. Uptake curves for the sorption of *n*-decane on NaCaA ( ≈ 70% Ca) at 23°C from ethylbenzene varying the crystal size of the zeolites applied. The following zeolites have been used:

| | | |
|---|---|---|
| ○, D | synthesized by | Shdanov |
| ◇ | synthesized by | Schmitz |
| △, ▽ | synthesized by | Finger |
| □ | placed at our disposal by | Ruthven. |

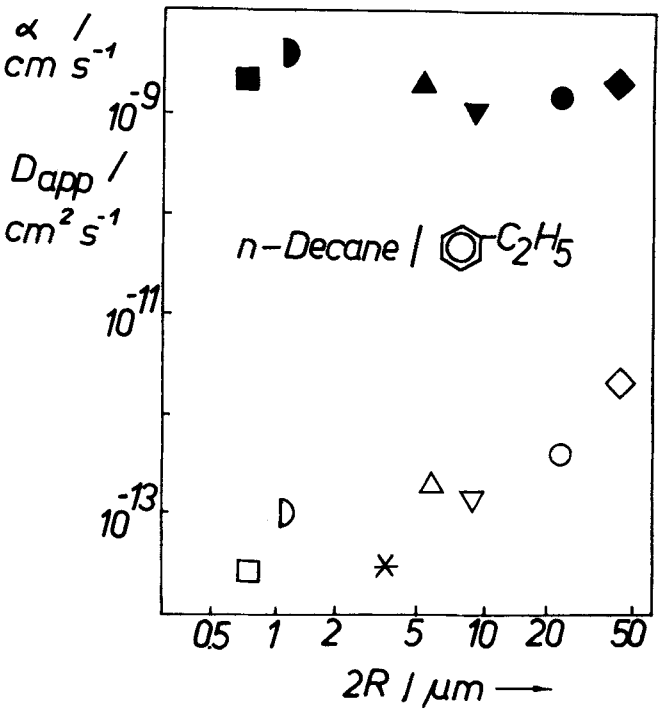


Figure 3. Crystal size dependence of the apparent diffusion coefficient $D_{app}$ (open symbols) according to Equation (2) and the values of the barrier parameter $\alpha$ (full symbols) calculated according to Equation (3) for the sorption of *n*-decane on NaCaA ( ≈ 70% Ca) at 23°C from ethylbenzene. The symbols for the different zeolites are the same as in Figure 2.
* Zeosorb 5A (data of Pilchowski 1972, given for comparison).

## EXPERIMENTAL ARRANGEMENT

The A types of zeolites of varying crystal sizes were from different provenance (marked by different symbols in Figures 2 and 3) and represent NaCaA ( ≈ 70% Ca) in every case. Prior to the start of the uptake process considered, the zeolite was outgassed at 400°C and $10^{-3}$ Pa during ≥5 h. After the activated zeolite was cooled under vacuum to room temperature, the sorption flasks were filled with purified and dried nitrogen up to atmospheric pressure. The amount of the liquid bulk solution (solvent and *n*-decane) added to the zeolite powder (about 0.5 g) was to ensure in every run a concentration decrease due to sorption from initial 7 down to 3.5 mass% *n*-decane in the solvent. The experiments were carried out under magnetic stirring. The uptake curves were deduced from the concentration changes of the liquid bulk phase indicated by gas chromatographic analysis of repeatedly taken liquid samples. Owing to the rectangular sorption isotherm of the system considered for *n*-decane concentrations > 1 . . . 2 mass%, the saturation values of sorption (that is, 147 ± 7 mg *n*-decane/g zeolite) is reached in any case. Therefore, working in the concentration region > 1 . . . 2 mass% *n*-decane, we use mathematical transport models with constant boundary conditions, although the concentration of the adsorbed compound in the liquid bulk phase is decreasing (batch method). On the other hand, owing to the strong slope of the isotherm, there are large difficulties in realizing differential uptake measurements. For this reason, the activated zeolite sample is usually saturated by one step up to the saturation value, so that by simple fitting of the uptake curves to solutions of the diffusion equation no quantitative data concerning the concentration dependence of the transport coefficients can be obtained. Therefore, the values given here are integral transport coefficients.

## SURFACE BLOCKING EFFECTS CAUSED BY SOLVENT MOLECULES

From investigations of the influence of the solvent on uptake behavior, it has been shown that the rate of sorption significantly depends on the nature of the solvent as well as on traces of impurities. In general, molecules with sufficiently large cross sections (thus prohibiting penetration into the micropores and providing a strong interaction with the outer crystal surface) cause a considerable decrease of sorption rate (Aleksandrov et al., 1967; Wolf and Pilchowski, 1971, 1972; Satterfield and Cheng, 1972). As typical examples for the different uptake behavior, the kinetic curves for molecular uptake of *n*-decane on 5A zeolite from solutions in cyclohexane, ethyl- and butylbenzene are shown in Figure 1. It follows from these uptake curves that sorption rate depends rather strongly on the nature of the solvent (Aleksandrov et al., 1967). With respect to the peculiarities described previously, it may be pointed out that at least the sorption of *n*-decane from the solvents ethyl- and butylbenzene must be affected by blocking effects caused by solvent molecules strongly interacting with the outer crystal surface. Figure 3 represents the unreasonable crystal size dependence of the apparent diffusion coefficient calculated by best fitting the uptake curves of *n*-decane sorption from ethylbenzene (Figure 2) to appropriate solutions of the diffusion equation [for example, to Equation (2) as well as to complete solutions]. In addition to the information resulting from uptake behavior by using different solvents,* the striking crystal size dependence of the apparent diffusion coefficient $D_{app}$ represents the most conclusive indication that in the given case the sorption is not determined by intracrystalline diffusion. In accordance with this statement, uptake kinetics can be better interpreted in terms of a barrier limited sorption model. In contrast to the apparent diffusion coefficients $D_{app}$ which are not invariant to crystal size, the analysis of the experimental data according to a barrier-model leads to a rather independent of crystal size value of the surface parameter $\alpha$ [full symbols in Figure 3 calculated according to Equation (1)]. The reciprocal of this parameter characterizes the efficiency of the zeolite surface blocking.

* In order to distinguish between diffusion and barrier limited sorption by uptake curve analysis, a more refined treatment of the time dependences of uptake was impossible because of the low accuracy of gas chromatographic technique applied.

## EVALUATION OF BLOCKING EFFICIENCY

In the following, an estimation of the influence of this blocking effect on the probability of penetration of sorbate molecules through the crystal surface will be given. Comparing the equation for barrier limited sorption

$$\gamma = 1 - \exp(-3\alpha t/R) \tag{1}$$

with the approximation formula for intracrystalline diffusion

$$\gamma \approx 1 - (6/\pi^2)\exp(-\pi^2 Dt/R^2) \tag{2}$$

and neglecting the slight difference in the pre-exponential factors, we get

$$\alpha \approx \pi^2 D_{app}/3R \tag{3}$$

On the other hand, the ratio between the flux density $j$ through the crystal surface and the barrier parameter $\alpha$ is given by

$$\alpha = j/[a_s - a_{s,(eq)}] \tag{4}$$

The comparison of Equations (3) and (4) leads immediately to the proportionality

$$D_{app}/R \propto \alpha \propto j \tag{5}$$

Taking into account this approximate result and comparing the diffusion coefficients derived from uptake curves (Figure 1), one can show that by using cyclohexane instead of ethylbenzene as a solvent the probability of $n$-decane entrance into the zeolite micropores through the crystal surface is at least three orders of magnitude higher than by using ethylbenzene. This should be caused by a more weak interaction of the cyclohexane molecules with the outer crystal surface due to the differences in the molecular structure between cyclohexane and ethylbenzene.


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## NOTATION

$D$ = Fickian diffusion coefficient

$D_{app}$ = apparent diffusion coefficient obtained by best fitting of uptake curves of sorption processes different from intracrystalline ones to appropriate diffusion equations

$R$ = zeolite crystal 'radius' (the half of the edge length of the cubic A type crystals used)

$a_{s,(eq)}$ = sorbate concentration at the crystal surface (in equilibrium with the surrounding liquid phase)

$j$ = flux density of sorbate through the outer crystal surface

$\alpha$ = barrier parameter

$\gamma$ = relative amount of adsorbed compound

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# Binary Diffusion in Liquid Systems


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Diffusion in liquid systems plays an important role as far as industries and fundamental research are concerned. Mass transfer in absorption, solvent extraction, distillation and other diffusional operations need basic data.

No completely theoretical equations for estimating the diffusion coefficients for all the systems encountered in chemical engineering operations are available in the literature. Thus, empirical and semitheoretical methods of estimating physical properties play an important role in design calculations and for many other purposes in engineering and applied science. A number of workers have developed some correlations for calculating diffusion coefficients. Sometimes the predictions based on these expressions may differ from the true values by as much as 50%. Each expression holds for a certain set of systems. The Wilke and Chang (1955) system fails for highly viscous solvents. For such systems, the correlation given by


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