

## Simulation of Transport and Self-Diffusion in Zeolites with the Monte Carlo Method

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In this paper new models for theoretical investigations of zeolite diffusion by Monte Carlo methods are presented. The goal was to assess the influence of different model assumptions on the concentration dependence of transport and self-diffusion in a two-dimensional zeolite network. Experimentally determined diffusivities are in qualitative agreement with the simulation results. © 1989 Academic Press, Inc.

### INTRODUCTION

During the last 10 to 15 years the application of zeolites as catalysts and sorbents in industrial processes has become more and more important (1-3). With the ratio of zeolite pore diameter to molecular diameters being close to unity, most of the catalytic reactions in zeolites are limited by diffusion (4). The specific adsorption interaction of molecular sieves has rendered these compounds superior in the application to the separation of fluid mixtures. Despite the widespread use of zeolites, however, no complete understanding of transport processes in zeolites has yet been established. Some of the major problems still awaiting resolution are concentration dependence of the diffusivity, multicomponent transport, and large discrepancies between experimental diffusion coefficients. The peculiar pore structure of zeolites and the rather limited number of sorbed molecules per cage may justify raising doubts as to whether zeolite diffusion can be adequately described by means of continuum state variables. It was probably this idea that inspired a number of researchers to draw on the help of the Monte Carlo method, and to study idealized model systems with discrete concentration distributions.

Some of the theoretical investigations on the problem of diffusion in zeolites and the concentration dependence of the diffusion coefficient were carried out previously by the Monte Carlo method (4-6). Due to the rigid geometric structure of zeolites and the existence of small independent subunits (cages), a random-walk of particles in an abstracted zeolite should be a reasonable approximation of zeolite diffusion.

Previous simulations with the Monte Carlo method were either conducted for a one-dimensional pore model (6) or for effects of pore blocking in a two-dimensional lattice (4, 5). Ruthven (7) presented a Monte Carlo simulation for a three-dimensional zeolite model to estimate the effects of ion exchange on diffusion in zeolites. Because of the ion exchange the pore diameter varies and thus, the difference in the diffusion characteristics between exchanged and unexchanged zeolites is the same as for diffusion through blocked and unblocked pore networks. In this paper we present some more extended and complex models for diffusion in a two-dimensional array.

One of the goals of this study was to assess the validity of Darken's equation (8), a thermodynamic relationship for correlating the concentration dependence of the diffusivity. The other objective was to deter-

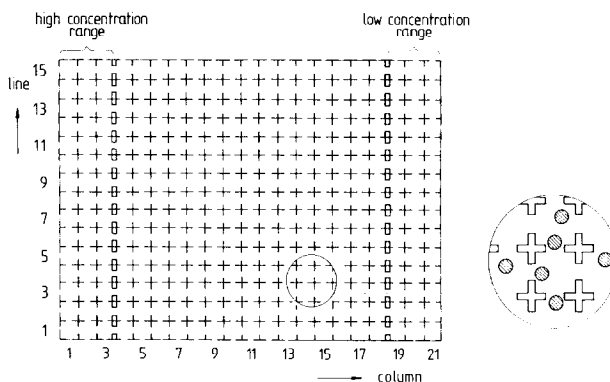


FIG. 1. Simulation array.

mine the transport properties of an abstracted zeolite network, with respect to alterations of the microdynamic assumptions in the random-walk of diffusing species. Finally, it was examined how self-diffusion of tracer molecules relates to transport diffusion under the force of a concentration gradient. All results were to be reviewed critically as to the capabilities of random-walk simulations in modeling zeolite diffusion.

Inside the network of channels and cages of a zeolite no "free gas phase" exists, due to the strong force field of the adsorbent surface (8). Since the diffusion of molecules in the zeolite channel network is commonly viewed and observed as an activated process, it is reasonable to assume for simplicity that a molecule inside this network can only be found in two different energy states. One of these we will call the adsorbed state; i.e., the molecule is adsorbed at a distinct site in a cage of the zeolite. The second state will be referred to as the transition state, and characterizes a molecule of increased energy content with the ability of moving from one adsorption site to the next, i.e., migrating to the next neighboring cage.

In the description of the different models, two different types of concentration appear. First of all, there is the concentration with respect to a single cage. For each cage an integer number of particles is permitted.

Often the concentration can be put in dimensionless form called occupation, by dividing the concentration by the maximum allowed number of molecules per cage. The occupation thus varies between 0 and 1. In other instances, concentration will be referred to as an average value within a particular domain of the simulated network. Such a domain would be, for instance, a limited range of the zeolite in equilibrium with an external fluid phase. This latter definition of occupation corresponds to the well-known pore filling factor  $\theta$ .

#### (1) TRANSPORT DIFFUSION UNDER A CONSTANT CONCENTRATION GRADIENT

In this model the case of steady-state diffusion was simulated. Here, the following situation was assumed: A two-dimensional zeolite crystal is exposed to gas phases of pressure  $p_H$  on the left side and  $p_L$  on the right side, where  $p_H$  is greater than  $p_L$ . The lateral boundaries of the zeolite are impermeable to mass transfer. Thus, the mass flow will only occur from left to right. The simulated zeolite array is depicted in Fig. 1.

In order to account for sorption equilibrium at the fluid/zeolite interfaces, three columns of zeolite grid points at the phase boundaries were maintained at constant mean concentration throughout the simulations. If a molecule jumped out from the equilibrium domain into the zeolite grid, the mean occupation in the boundary region

was held constant by adding another molecule at a random position in this region. At all times it was taken care to ensure that the maximum occupation of a single cage was not exceeded. Similarly, if a molecule jumped from the center of the grid into an equilibrium region, another molecule was removed from this region.

For the steady-state conditions, the net fluxes of particles through the phase boundaries on the left and right sides of the zeolite were equal, when averaged over a long time. We arbitrarily chose the net flux through the left boundary in comparing the simulation results with Fick's Law:

$$\dot{n} = -D * A * (dc/dx). \quad (1)$$

The concentration gradient ( $dc/dx$ ) is approximated by the difference ratio  $\Delta c/\Delta x$ , where  $\Delta c$  represents the concentration difference between the two equilibrium regions.  $\Delta x$ , in arbitrary units, is the distance between these regions and is equal to the length of the zeolite crystal.  $A$  is the cross section for diffusion. Solving Eq. (1) for the diffusion coefficient  $D$  one obtains

$$D = -\dot{n} * \Delta x / (A * \Delta c). \quad (2)$$

Allowing a single cubic cage to have the spatial lengths  $L_x = L_y = L_z = L$  and with  $X$  and  $Y$  as the numbers of cages in the respective direction, one obtains

$$\Delta x = X * L$$

$$A = Y * L^2$$

$\Delta c$  = concentration difference between equilibrium regions on left and right side of the zeolite

$\dot{n}$  = net flux of particles per single jump interval

So  $D$  is found as

$$D = -(X/(Y * L)) * \dot{n} / \Delta c \quad (3)$$

and in units of [ $L^2 * \text{jump frequency}$ ].

For all simulations  $X$  and  $Y$  were set to 15. Thus, each equilibrium domain contained 45 cages each. The concentration

difference across the zeolite was chosen as 5 molecules per 45 cages, i.e.,  $\Delta c = 5/45 = \frac{1}{9}$  particles per cage.

At the beginning of each simulation, predetermined numbers of particles were placed in the high- and low-pressure equilibrium regions. Second, the square zeolite array between the equilibrium regions was assigned a random distribution of molecules, so that the same average occupation per cage as in the high concentration range was attained.

The elements of the array, i.e., the molecules, were activated for migration in a random sequence, so no ordering or directional influence of the activation could distort the results. In contrast we found a significant difference if instead of a random activation one starts with the first element in the first column, proceeds to the second element in the first column, and so on, or vice versa. With such an ordered activation of the molecules the fluxes could be altered significantly, particularly at high concentrations of diffusing molecules.

In order to facilitate the simulation of the simultaneous random walk of a large number of molecules in the zeolite network, two arrays were defined which contained the distribution of molecules before and after each jump event. Thus, it was possible to satisfy conditions for successful jumps and still guarantee to a large extent the randomness of the diffusion process. Such jump conditions were clearly defined prior to each simulation run. They included microdynamic considerations such as the number of molecules per cage that may be activated per event; whether molecules can pass each other in a channel between neighboring cages; and the maximum number of molecules per cage permitted at any time.

The first 5000 jumps during each run were ignored in order to eliminate the influence of the initial distribution. The number of 5000 was found to be sufficiently large in preliminary tests of the simulation program. After this start-up period, for the following 10,000 jumps, the flux of molecules

was counted that passed from columns three to four and vice versa (see Fig. 1).

The net flux which is proportional to the diffusion coefficient was calculated as the difference between these two fluxes divided by 10,000. Thus, one obtained the net number of particles transmitted per jump interval through the zeolite.

For repeated runs the standard deviation of  $D(\theta)$  was found to be less than one percent. It was therefore determined sufficient to carry out each simulation only once. Only at some sensitive points, e.g., extremely high or low concentrations, a simulation was carried out for three to five times. When going through the simulation results of this work, the reader might note the pronounced fluctuations of  $D$  over the concentration range. These fluctuations were not the result of excessive scattering and, therefore, low statistical significance of the simulation results. Reproducibility of the results was always very high.

The average computation time (CPU – time) for the system described above (i.e., array of  $15 \times 21$  cages and 15,000 jumps) on a MicroVax II required about 120 min.

#### *Model Assumptions and Observed Concentration Dependence*

Palekar and Rajadhyaksha (6) used a Monte Carlo simulation to find the concentration dependence of the diffusion coefficient in a simplified one-dimensional zeolite pore. They simulated an uptake rate experiment and found a concentration dependence that agreed to some extent with the predictions of Darken's equation (8):

$$D = D_0 \frac{d \ln p}{d \ln c}. \quad (4)$$

They assumed the following restrictions:

- A single adsorption site (i.e., cage) can be occupied by no more than one particle at any time.
- Particles cannot pass each other in a window.
- Each particle is activated for jumping at every time step.

In our simulations we attempted to use a wider variety of geometric and microdynamic factors that simulated the zeolite network and the diffusion process within the same. Unlike Palekar and Rajadhyaksha (6), we used a two-dimensional zeolite and tested the following influences on the concentration dependence of the diffusivity:

- (a) maximum number of particles per cage (value varied from 1 through 10);
- (b) particles can/cannot pass each other in the windows between cages;
- (c) number of particles that can leave the cage per jump event;
- (d) the particle(s) has (have) to leave the cage if the adjacent sites are not completely occupied and the windows are unblocked.

(a) *Varying the maximum number of particles per cage.* This parameter seems to have a reasonable physical justification since for many zeolite-sorbate systems the maximum number of molecules per cage is well known, and their values are almost always greater than one. For example, Kärger and Ruthven (9) measured an occupation of up to 3.3 molecules per cage for the system benzene in zeolite 13X, a system which we have also studied experimentally in our laboratory (10). Most hydrocarbons are known to be sorbed in common zeolites with more than one molecule per cage at saturation (1, 11).

Under the following restrictions of

- one particle leaves the cage per step,
- only one particle can migrate through a window per step,
- the particle has to leave the cage if one neighboring cage is vacant,

the following dependence was found (Fig. 2):

For a maximum of one particle per cage the diffusion coefficient was found to depend exponentially on the occupation

$$D = D_0 * \exp(k * \theta). \quad (5a)$$

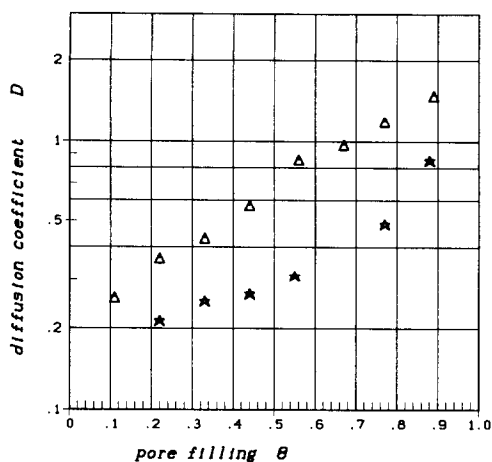


FIG. 2. Concentration dependence of diffusion coefficient; one molecule per cage and event allowed to jump; no passing in windows; ( $\Delta$ ) max. 1 particle/cage; ( $\star$ ) max. 2 particles/cage.

In contrast, for two molecules the dependence was observed to obey a relationship of the form

$$D = D_0/(1 - \theta)^k. \quad (5b)$$

The values of  $D$  decreased when increasing the maximum number of particles per cage.

For maximum occupations higher than two, no simple relationship between  $D$  and  $\theta$  could be found. The diffusion coefficient started to oscillate for increasing concentration. Here the simulation technique seemed to have reached its limits, and it would be necessary to extend the simulation to larger arrays.

(b) *The particles can pass each other in a window.* A characteristic parameter for diffusion in zeolites is the so-called "key factor" which is the ratio of the sizes of the diffusing molecule and the zeolite window (12). For a key factor much less than unity the pore diameter is much greater than the molecule's diameter. Now if one proceeds on the assumption that the pore diameter is wide enough and the repulsive forces between two molecules are negligible, a bypassing of two molecules inside an orifice of the zeolite lattice might be possible.

Allowing only one particle per cage, the

curve  $D = D(\theta)$  is the same as under the previous conditions (see case (a)). For two of these molecules per cage,  $D$  was no longer proportional to  $\exp(k * \theta)$ . In a  $\log D$  vs  $\log(1 - \theta)$  plot a slope close to minus one was found up to three particles per cage. The higher the number of particles per cage the smaller became the simulated diffusion coefficient. For  $\theta$  close to one, the diffusion coefficients did not differ from each other (Fig. 3). Comparing Figs. 2 and 3, a slightly higher diffusion coefficient for the case of bypassing can be observed.

For the Langmuir-isotherm the term  $d \ln p/d \ln c$  in Eq. (4) is equivalent to  $1/(1 - \theta)$  and Eq. (4) now becomes  $D = D_0/(1 - \theta)$ . In a  $\log D$  vs  $\log(1 - \theta)$  plot the slope is minus one.

(c) *More than one particle may leave the cage at a time.* With similar assumptions as in case (b) the cage of a zeolite may be big enough to contain more than one particle in the transition state. Thus, at least one molecule is able to migrate through a window. In each simulation step a random integer number was assigned to each adsorption site. The random integer represented the number of molecules which were permitted to leave the cage at the current step. The number was always greater or equal to one.

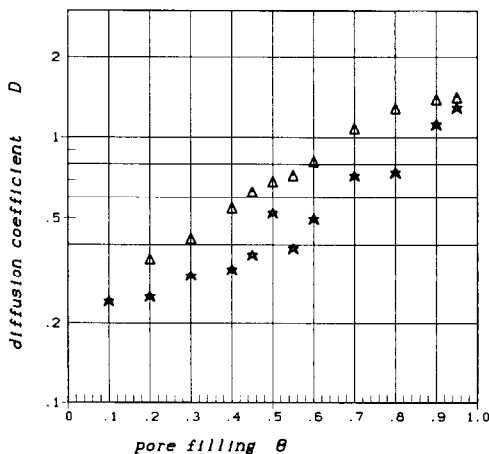


FIG. 3. Concentration dependence of diffusion coefficient; particles can pass each other in windows; ( $\Delta$ ) max. 1 particle/cage; ( $\star$ ) max. 2 particles/cage.

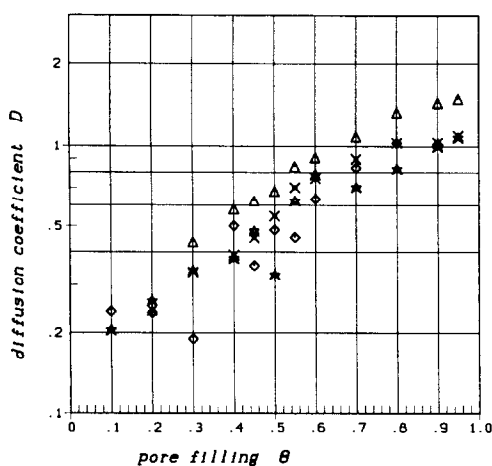


FIG. 4. Concentration dependence of diffusion coefficient; more than one particle per time step may leave cage; ( $\Delta$ ) max. 1 particle/cage; ( $\times$ ) max. 2 particles/cage; ( $\star$ ) max. 3 particles/cage; ( $\diamond$ ) max. 4 particles/cage.

However, only one particle could migrate through a window per event.

Simulating the steady-state diffusion for a maximum cage occupation between one and four particles per cage, the diffusion coefficient seemed to be independent of the maximum occupation and only depend on average occupation of the zeolite lattice. The diffusion coefficients fall together in a narrow band when plotted as  $\log D$  vs.  $\theta$  (Fig. 4). Remarkable is the higher diffusion coefficient for  $\theta$  approaching unity in case of a maximum cage occupation of one.

(d) *The molecules need not leave the cage in a single step.* In previous works in the literature, two different concepts of jumping of a single particle were presented. Palekar and Rajadhyaksha (6) simulated the jump event in the same way as proposed in this paper: The particle must leave the cage if an adjacent site is vacant and the windows are unblocked. In contrast, Theodorou and Wei (5) as well as Ruthven (7) assumed that a particle stayed in its present cage if the first jump attempt was unsuccessful; i.e., either the site in the assigned direction is fully occupied or the window in this direction is blocked.

We now modified our initial assumption in that way, that only once for every time step a random jump direction was assigned to the particle. In case the adsorption sites in the jump direction were completely filled, or the window was blocked by another particle, the molecule had to remain in the cage. The jump conditions are now similar to those of Theodorou and Wei (5) and Ruthven (7).

From comparison of Figs. 2 and 5, one can conclude that the assumption "the particle has to leave the cage" leads to a simulated concentration dependence of  $D$  which is more consistent with the majority of experimentally observed increases of  $D$  with  $\theta$ . This is quite surprising since one may object that the particles are unlikely to go through more than one transition state in a single jump interval. The problem in determining the proper simulation conditions in a random walk, however, is the fact that the nature of the diffusion transition state in zeolites is not generally known. We prefer to view the adsorbed molecules in the cages as subject to considerable oscillatory movement rather than being static or slowly creeping entities. With this idea in mind it might be more comprehensible to admit

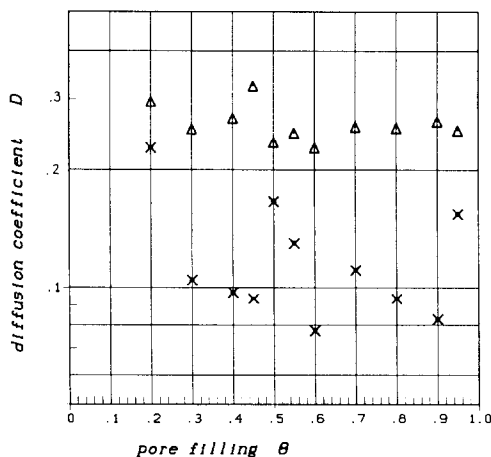


FIG. 5. Concentration dependence of diffusion coefficient; particles may not leave cage if first assigned direction leads to unsuccessful jump; ( $\Delta$ ) max. 1 particle/cage; ( $\times$ ) max. 2 particles/cage.

molecules for repeated activations per jump interval.

### Discussion of Transport Diffusion Results

A number of variations of a random-walk process for the steady-state diffusion in a two-dimensional lattice have been presented. The goal was to assess the influence of model alterations on the concentration dependence of the observed diffusivity, and to compare this dependence against the prediction of Darken's equation.

There is no question that some of the model assumptions presented above are somewhat crude, and would never enable the user of this random-walk program to eventually predict an accurate diffusion coefficient for a real physical system. However, a number of conclusions can be drawn from our results that bear some physical significance for real systems.

In almost all of the above model simulations we altered the mobility of sorbed molecules by different assumptions. Yet we treated the sorption system as ideal, in the respect that no interaction energy between sorbed molecules was present and that the distribution of molecules in the grid was random. Therefore, the sorption characteristic of these systems can be expected to be similar in all cases, that is the thermodynamic correction of the diffusion coefficient with Darken's equation becomes very similar in all these cases. As is seen from the concentration dependence of the different simulations, however, in hardly any case can Darken's equation be considered adequate in describing the rise in the diffusivity with increasing pore filling. It is therefore advisable to have a closer look at the rigorous equation for mass transport in zeolites as given by Ruthven (8, Eq. (5.6)), which is another form of Eq. (4):

$$D = BRT \frac{d \ln p}{d \ln c}. \quad (6)$$

Clearly, there are two parts to the right-hand side of this equation that describe contributions from thermodynamics and

mobility or microdynamics to the concentration dependence of  $D$ . With a known sorption isotherm, the thermodynamic effect in Eq. (6) can be eliminated, and the microdynamic contribution determined. The latter is represented by the quantity  $B$  (mobility).

In our case, for ideal nonlocalized sorption the isotherm can be derived from statistical thermodynamics and is given by Ruthven (8, p. 81). One parameter in this isotherm is the maximum number of particles per cage,  $m$ . In case  $m$  is equal to unity, one obtains the Langmuir isotherm. For  $m$  approaching infinity, the isotherm takes the form of the Volmer equation.

Applying the numerically obtained correction factors to some of our simulation results gave the mobility  $B$  as a function of the concentration  $\theta$ . The results are represented graphically in Figs. 6–8. The quantity  $BRT$  in Eq. (6) corresponds to the corrected diffusivity  $D_0$  that is usually found in the literature, when the concentration dependence of zeolite diffusion is reported.

The results in Figs. 6–8 make clear how the mobility of the diffusing species is affected by the model assumptions in the present case studies. One general trend in

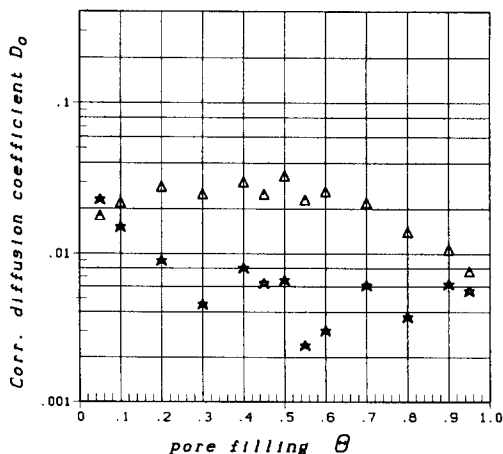


FIG. 6. Concentration dependence of corrected diffusion coefficient; 4 molecules per cage; no passing in windows; ( $\Delta$ ) all 4 particles can jump; ( $\star$ ) only 1 particle can jump.

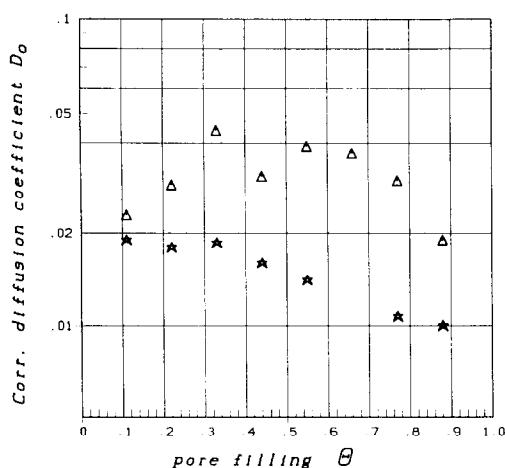


FIG. 7. Concentration dependence of corrected diffusion coefficient; 1 molecule per cage and event permitted to jump; no passing in windows; ( $\Delta$ ) max. 1 particle/cage; ( $\star$ ) max. 2 particles/cage.

most simulations is the decrease of the corrected diffusivities with increasing pore filling. As in Fig. 6, the decrease was very pronounced where the number of particles leaving the cage was restricted. This result was expected intuitively, since with the first data set of Fig. 6 the migration of particles is only obstructed when an increasing number of neighboring cages has reached its saturation capacity or the jumping of particles is hindered by the counterflux of particles. In Figs. 7 and 8, examples are represented for a maximum pore filling of 1 or 2 particles per cage. Considering the large variation of  $D$  with concentration, the dependence of  $D_0$  on  $\theta$  in Fig. 7 is rather small. In Fig. 8 the case of two molecules/cage is simulated and differentiation is made by allowing or not allowing counterdiffusion of molecules in windows. It is obvious from the data in Fig. 8 that the addition of this condition has very marginal if any effect on the mobility of the diffusing species. Again, the dependence of  $D_0$  in Fig. 8 is rather weak over a wide concentration range, and showing a marked drop at  $\theta$  approaching unity.

If one is to summarize the trends of the concentration dependence of  $D_0$  in Figs. 6–

8, a few common features are apparent. The region of  $\theta$  between 0 and approximately 0.7 is characterized by relatively constant values of  $D_0$ . In almost all cases, the mobility then decreases with a further increase of  $\theta$ . Some of the model variations for jumping of particles had a marked effect on the mobility: maximum number of particles per cage; number of particles that were allowed to leave the cage at a given jump interval. On the other hand, the discrimination between cases where the encounter of particles in a cage window was allowed or not showed no significant effect on the mobility at all. In general, the overall tendency of  $D_0$  in Fig. 6–8 is the more or less pronounced decline with increasing values of  $\theta$ .

It is illustrative to compare some experimentally observed values of  $D_0$  to the concentration dependent mobilities  $B$  of our simulations. Depending on the experimental system and conditions, all possible concentration dependencies of corrected diffusivity can be found in the literature. As an example,  $D_0$  for benzene in ZSM-5 and silicalite was found to decrease (12), Bülow *et al.* (14) found an almost constant  $D_0$  for benzene in NaX zeolite, and finally Kärger

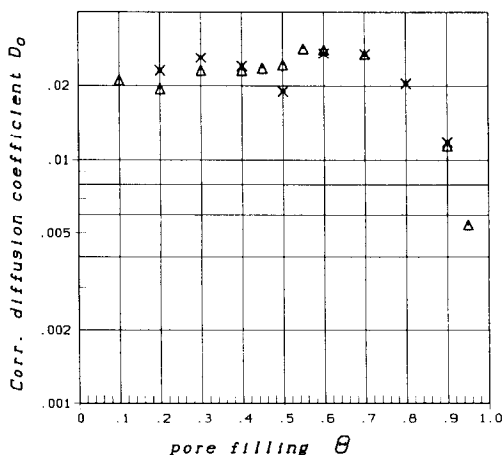


FIG. 8. Concentration dependence of corrected diffusion coefficient; 2 molecules per cage; 2 molecules can leave cage at a time; ( $\Delta$ ) passing in windows; ( $\times$ ) no passing in windows.



and Ruthven (9) observed an oscillatory concentration dependence of  $D_0$  with an increase toward high concentrations for benzene in large 13X crystals. All of these data have been collected with the sorption uptake method. Despite the similarity of the systems with regard to the geometric proportions of diffusing species and zeolite cages, one may raise doubts as to whether some of the data were falsified by unaccounted effects during measurements. One of these unaccounted effects could be the commonly quoted limiting sorption heat removal.

Despite the crudeness of some of the model assumptions in our simulations, we suggest that an observed concentration dependence of the corrected diffusivity could serve as a means to test the consistency of the data. This is possible when simulation results are available which can be expected to compare reasonably with the experimental system. From the results of our simulation, for instance, we would expect for diffusion in a sorbate/zeolite system with a maximum pore filling of about 5 molecules per cage to show a decline of corrected diffusivity with increasing concentration after an initial region of almost constant  $D_0$ . This statement is, of course, invalid when our simulation assumptions sharply contrast the behavior of a real physical system. Such exceptions would be the diffusion of long, stretched molecules (such as paraffins), or polar molecules with strong sorbate-sorbate interaction. There the simplified model assumptions break down, and require a more sophisticated description in the random-walk simulation.

We are aware that more refined models need to be studied, with a closer resemblance to the physical process of zeolite diffusion, before a final judgement regarding such a consistency test can be drawn.

## (2) THE SELF-DIFFUSION COEFFICIENT

One of the current, important topics in the literature of zeolite diffusion, is the large discrepancy between parameters de-

termined by different experimental methods. An abundance of experimental data have been published for self-diffusion measurements with the NMR pulsed-field-gradient Technique (15). When comparing the results of this method to those of sorption uptake measurements or the chromatographic method, there are a number of considerable deviations regarding the magnitude of zeolite diffusivities (1, 8, 9), the magnitude of observable activation energies (9, 16), and concentration dependence of the diffusion coefficient (1, 9, 17). We therefore attempted to simulate the self-diffusion of tracer particles in the simulation grid of Section (1) and compared the results of self- and transport diffusion.

The Monte Carlo method seems to be particularly suitable for the simulation of the self-diffusion. In the simulation a marked particle was placed at the center of the quadratic simulation field. After filling the grid to the desired concentration, the random walk of all particles was started. The number of time steps ( $n_s$ ) was preset in that way that the marked particle could at the most reach the boundary. The self-diffusion coefficient was then calculated from the squared distance between the initial and final positions of the marked particle  $\Delta x_s^2$ , divided by the number of migration steps:

$$D_s = \Delta x_s^2 / (4 * n_s). \quad (7)$$

This procedure was repeated at least one hundred times until a reliable average diffusion coefficient was arrived at.

Some of the results are represented in Fig. 9. It can be seen, that the self-diffusion coefficients at low concentrations agree with the values obtained by the results of the gradient transport simulations in Section (1) of this paper. In addition it is important to note that the concentration dependence of the self-diffusion coefficients in Fig. 9 is rather weak. Only at pore filling factors higher than  $\theta = 0.8$  is the mobility remarkably hindered and does a drop of the self-diffusion coefficient occur. The decline

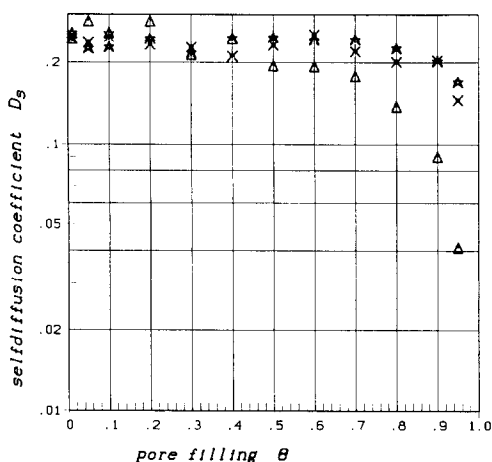


FIG. 9. Concentration dependence of self-diffusion coefficient; ( $\Delta$ ) max. 1 particle/cage; ( $\times$ ) max. 4 particles/cage; ( $\star$ ) max. 6 particles/cage.

is less marked for higher  $\theta$  numbers of particles per cage.

Observing the system zeolite/adsorbens at infinite dilution which is simulated by a single particle jumping in an empty zeolite grid the self-diffusion coefficient averaged over one million jumps is calculated to  $0.223L^2 * \text{jump frequency}$ .

The concentration dependence changes dramatically if the random walk is modified so that diffusing particles can cover a dis-

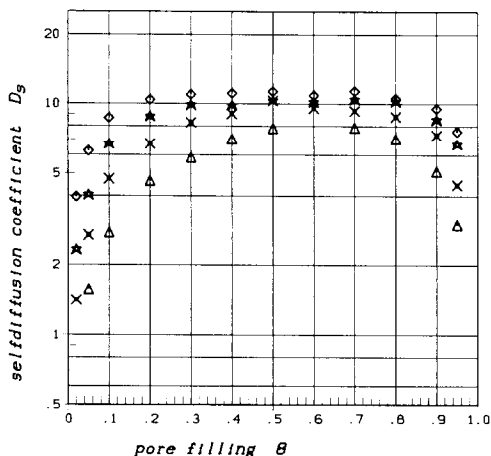


FIG. 10. Concentration dependence of self-diffusion coefficient; constant-jump-length model of Barrer ( $n = 3$ ); ( $\Delta$ ) max. 1 particle/cage; ( $\times$ ) max. 2 particles/cage; ( $\star$ ) max. 4 particles/cage; ( $\diamond$ ) max. 8 particles/cage.

tance of more than one cage length per activation. This is similar to the constant-jump-length model of Barrer (18). We arbitrarily chose a value of  $n = 3$  as jump distance per particle flight, and obtained the results in Fig. 10. Starting from a rather low value at high dilution, the self-diffusion coefficient reached a flat plateau before declining as concentration approached unity. It is remarkable that the plateau values are larger than the low concentration values by almost one order of magnitude and that the whole intermediate range is characterized by a very weak concentration dependence.

#### Discussion of Self-Diffusion Results

Kärger and Ruthven compared the corrected diffusion coefficient determined by uptake measurements,  $D_0$ , with the self-diffusion coefficients obtained by NMR pulsed-field-gradient measurements  $D_s$  (9). They found that this comparison is only feasible for small values of the pore filling factor and derived the relationship between  $D_0$  and  $D_s$ ,

$$D_0 = D_s / \{1 - g(c) * p\}, \quad (8)$$

where  $g(c) * p$  is a function describing the interaction between molecules on different adsorption sites. At low concentrations,  $D_0$  and  $D_s$  are expected to be identical. Even though Eq. (8) suggests that  $D_s$  is smaller than, and at the limit equal to,  $D_0$ , experimental results frequently show much larger values of  $D_s$  (1, 7, 9). Inspection of our simulation results in Fig. 9 indicates that, for the present Monte Carlo study, the prediction of identical transport and self-diffusion coefficients at very low concentration is indeed fulfilled. The very weak concentration dependence of  $D_s$  in Fig. 9 and in the intermediate range of Fig. 10 and the marked drop at high pore filling  $\theta$  of Figs. 9 and 10 are in fair agreement with NMR self-diffusion measurements in numerous experimental systems (1, 7, 9, 17). Quite remarkable is the fact that  $D_s$  values in Fig. 10 beyond concentration  $\theta = 0.2$  are about by one order of magnitude larger than the lim-

iting value at zero concentration. The interpretation of the data in Fig. 10 initiated our search for similar experimental observations in the literature. In all the experimental work on self-diffusion that we are aware of, we have not been able to find measurements at extremely high dilution. Typically reported data start at concentration values of about  $\theta = 0.2$  (9, 15, 17). Some recent work on the self-diffusion of toluene and xylenes in NaX zeolites (17) suggests a decline of  $D_s$  toward lower concentrations, similar to the simulation results in Fig. 10, but unfortunately, no experimental data are given below  $\theta = 0.25$ .

### (3) CONCLUSION

Diffusion in a two-dimensional zeolite pore network has been simulated by a random walk of particles under a constant concentration gradient. The objective of this work was to obtain the concentration dependence of the apparent diffusion coefficient for a variety of model cases. Model alterations were achieved by allowing for different maximum cage concentrations, and by redefining the rules for successful jumps of the particles between cages. Special care was taken to assure the randomness of the diffusion process. The results are in qualitative agreement with the predictions of Darken's equation, and show larger diffusion coefficients with increasing concentration. The rate of increase, however, is dependent on the assumptions of the individual models. The model differences become clearer when the diffusion coefficients are corrected for the thermodynamic contribution, as described by Darken's equation. The so obtained corrected diffusivities, or mobilities, show, without any exception, a decrease with increasing pore filling factors  $\theta$ .

Even though the presented Monte Carlo simulations are based on partly simplistic model assumptions, we suggest that some general trends of the simulation results could be utilized to evaluate the consistency of experimental diffusion data in zeo-

lites. Such consistency tests could be of use in precluding influences of unaccounted physical effects during measurements, or the improper evaluation of diffusion parameters from experimental data. From our own simulation results, we tentatively propose that sorbate-zeolite systems with similar cage capacity and no strong sorbate-sorbate interaction should exhibit decreasing corrected diffusivities with increasing concentration. We are aware that such predictions will become more credible with the use of more sophisticated random walk models, where an increased knowledge of the physical system of interest is incorporated.

In the second part of this work we have presented simulation results on the self-diffusion of marked tracer particles in the two-dimensional zeolite network of the previous section. Since identical random walk assumptions were chosen, we were able to compare the results to the transport diffusion coefficients of part (1) of this paper. The important results were identical self- and transport diffusivities at low concentration, and a weak concentration dependence of the self-diffusion coefficient, as is often reported from experimental measurements with the NMR technique. Thus, the presented simulations give no explanation of the large discrepancies between experimental self- and transport diffusion results in the literature.

Finally, the model of the self-diffusion process was modified in order to test the constant-jump-length model of Barrer (18). We found a very peculiar concentration dependence of the tracer diffusivity, with an extended plateau in the intermediate concentration range and sharp decreases toward the limits of zero and unity pore filling factors  $\theta$ . Again we observed identical self- and transport diffusion coefficients at infinite dilution. These limiting values were approximately one order of magnitude smaller than the plateau in the intermediate concentration range. To our knowledge, this kind of concentration dependence has not been

reported in the literature, possibly due to the lack of self-diffusion data at high sorbate dilution.

$\theta$  Dimensionless concentration (pore filling factor)

## APPENDIX: NOMENCLATURE

$A$	Cross section for diffusion, $L^2$
$b$	Constant in Vollmer equation, $\text{bar}^{-1}$
$B$	Mobility, $L^2 * \text{jump frequency}$
$c$	Concentration, molecules per cage
$D$	Diffusion coefficient, $L^2 * \text{jump frequency}$
$D_0$	Corrected diffusion coefficient, $L^2 * \text{jump frequency}$
$D_s$	Self-diffusion coefficient, $L^2 * \text{jump frequency}$
$g(c)$	Concentration dependent quantity in Eq. (8), $\text{bar}^{-1}$
$k$	Parameter in Eq. (5a)
$k'$	Parameter in Eq. (5b)
$L_x$	Spatial length in $x$ -direction of a single cubic cage
$L_y$	Spatial length in $y$ -direction of a single cubic cage
$L_z$	Spatial length in $z$ -direction of a single cubic cage
$m$	Parameter in sorption isotherm
$n$	Parameter of constant-jump-length model of Barrer (18)
$\dot{n}$	Particle flux, particles * jump frequency
$p$	Pressure, bar
$R$	Gas constant, $\text{Nm}/(\text{mole} * \text{K})$
$T$	Temperature, K
$\Delta x$	Length of diffusion path, $L$
$\Delta x_s$	Length of self-diffusion path, $L$
$X$	Number of cages in flux direction
$Y$	Number of cages in direction perpendicular to flux direction

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