MONTE CARLO SIMULATIONS OF TRACER DIFFUSION IN ZEOLITES

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ABSTRACT

Monte Carlo simulation was earlier shown to be a very useful approach for investigating diffusion behaviour in zeolites. In the present study tracer diffusion in zeolites is investigated by this approach. Traeer diffusion has been simulated in zeolites with three different types of channel structures which include non-intersecting cylindrical channels (one-dimensional channel system), intersecting cylindrical channels (two-dimensional channel system) and channels consisting of interconnected cages. The simulations in all the cases show that 'mean square displacement' versus 'time' relationship is nonlinear which implies a non-constant diffusivity. The effect has been observed to be more significant at higher sorbate concentration. The implication of these observations to the measurement of diffusivities by various experimental techniques is discussed.

INTRODUCTION

MONTE CARLO simulation has been shown to be a very potent approach to investigate diffusion behaviour of zeolites[1-3]. The physical phenomena in the experiments carried out to measure diffusivity by gravimetry have been previously simulated[1,2]. The simulated behaviour was in agreement with several experimentally observed trends. The most significant agreement was in respect of the variation of diffusivity with sorbate concentration. The approach was subsequently extended to simultaneous sorption of two sorbates. The analysis revealed relationship between the rates of diffusion of the two sorbates and their individual intrinsic diffusivities. The results are of particular importance since experimental investigation of the above relationship presents significant difficulties.

Besides the gravimetry technique, diffusivities in zeolites are also measured by tracer diffusion and the pulsed field gradient NMR technique. The inter-relationship between the diffusivities measured by these techniques has been a subject of considerable interest in recent years[4-8]. The gravimetric technique involves transport of sorbate molecules under a gradient of total sorbate concentration while the other two methods investigate the transport at constant total sorbate concentration of

similar molecules. In the light of the success achieved in simulating the gravimetry experiments by the Monte Carlo approach, it was considered worthwhile to investigate tracer diffusion and behaviour in the NMR experiments by this approach. Besides providing an insight into the general trends of behaviour, the analysis could be expected to provide useful clues regarding the inter-relationship between the diffusivities obtained by various techniques.

With this objective, the transport of tagged (tracer) molecules in zeolite cavities at constant total sorbate concentration is simulated in the present work. All the previous simulations[1-3] were carried out in zeolites with parallel and nonintersecting cylindrical channels. Tracer diffusion in such zeolites is first considered in the present work. Several zeolites commonly employed in practice (like mordenite and ZSM-5) have parallel and intersecting channels. Tracer diffusion in such channel systems is also considered subsequently.

The approach is further extended to diffusion in zeolites with cage-type channel structure (e.g. zeolite *A*, *X*, *Y*). A simple molecular model is proposed to describe transport in the zeolite channel structures consisting of interconnected cages. Diffusion under a gradient of

total sorbate concentration (gravimetry experiment) is first considered. The variation of diffusivity with sorbate concentration depicted by the simulations agrees with the reported trends observed experimentally. Tracer diffusion is then simulated using the above molecular model.

A significant finding of the analysis is that, for all the channel structures mentioned above, tracer diffusion could not be described by a single value of diffusivity. The implications of this finding are discussed.

Zeolites with non-intersecting cylindrical channels

The molecular model for zeolites with non-intersecting channels has been previously described[1-2]. The model assumes the adsorption sites to be uniformly distributed along the channel. The sorbate molecules are assumed to be subjected to a periodic potential field, the sorption sites represent the minima and are separated by an energy barrier equal to the activation energy of sorption process. The sorbate molecules are activated γ' times per second to overcome the energy barrier i.e. γ is the jump frequency. The jump frequency is assumed to be independent of sorbate concentration.

To simulate the tracer diffusion process, the appropriate number of sorbate molecules was distributed randomly in the pore to give the desired sorbate concentration θ_t. A few molecules in the middle region of the pore were tagged. The molecules were then activated randomly. An activated molecule can find itself in one of the following situations:
(i) both the adjacent sites are vacant,
(ii) only one of the adjacent sites is vacant, or
(iii) both the adjacent sites are occupied.
In case (i) the movement in either direction was considered equally probable, in case (ii) the molecule was assumed to move to the available vacant site, and in case (iii) the molecule was considered unable to move. To simulate the end of the pore, similar to the previous simulation[1,2], the pore was assumed to have fictitious extended region and the concentration in the extended portion was held

constant and equal to θ_t. Such a procedure permits free movement of molecules across the end, but the molecules moving in and out of the pore are equal in number (on the average) and hence the concentration within the pore remains constant.

Simulated movement of molecules by the procedure described above results in net displacement of molecules. The mean square displacement ($\overline{\Delta}^2$) at a given time was evaluated by the following formula:

$$\overline{\Delta}^2 = \Sigma\, i\delta^2_i \,/\, \Sigma\, i, \tag{1}$$

where i is the number of tagged molecules having a displacement δ_t at that time. Several pores had to be simulated before the mean square displacement reached a converged value. Such converged values of ($\overline{\Delta}^2$) were determined for several values of time. The diffusivity is then given by

$$D = \frac{1}{2}\,(\overline{\Delta}^2_s/t). \tag{2}$$

Figure 1 shows the plots of mean square displacement vs reduced time (t') at different sorbate concentrations obtained by the above procedure. These results were obtained by simulating a pore with 100 sites. All the molecules in the middle 60 sites were tagged. To obtain converged average value of ($\overline{\Delta}^2$), 20 to 40 pores had to be simulated. Contrary to what may be expected, the ($\overline{\Delta}^2$) vs t' plots show a distinct curvature. Application of (2) to these results would give a varying diffusivity with

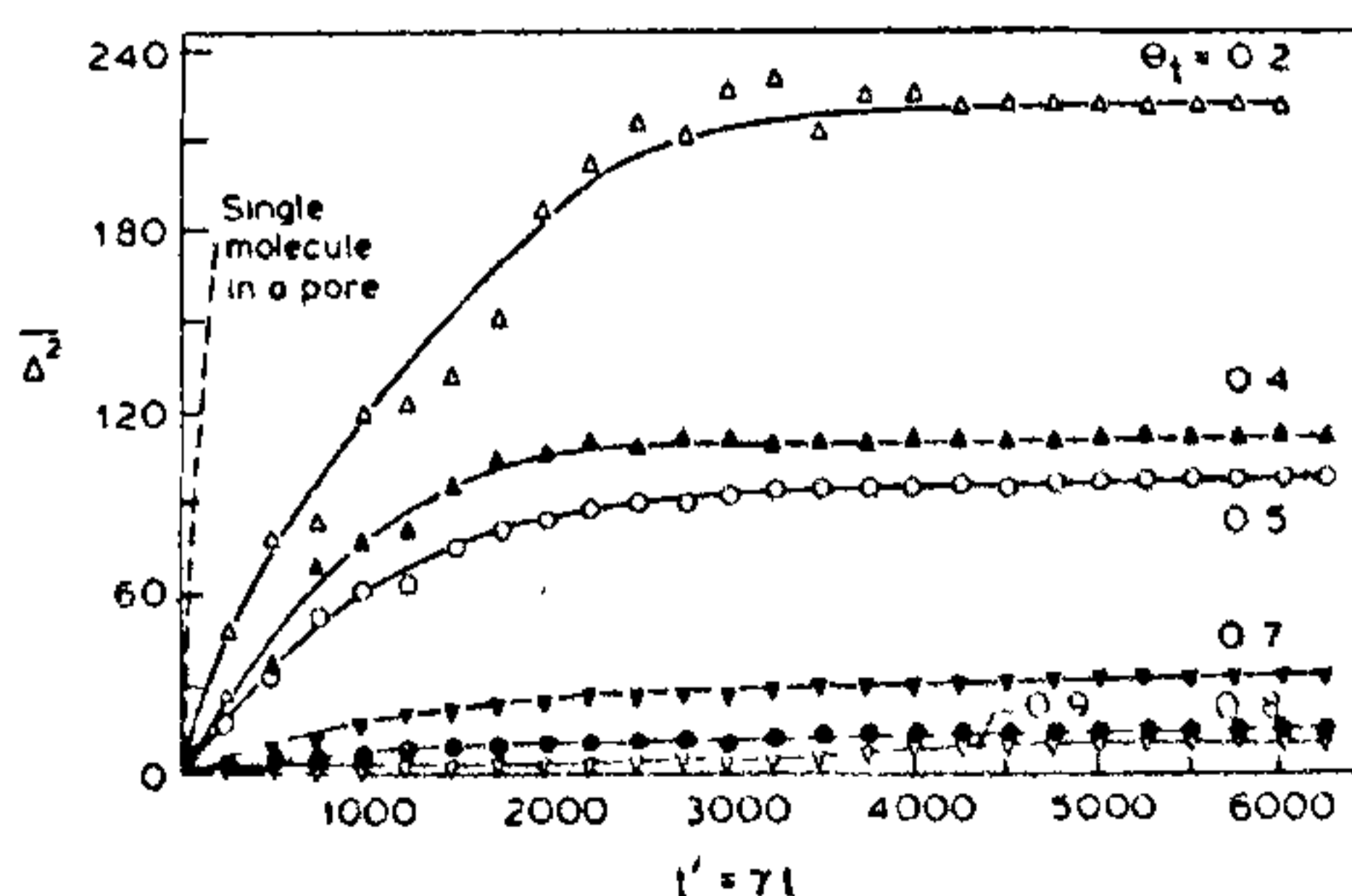**Figure 1.** $\overline{\Delta}^2$ vs t' plots at different occupancies: tracer diffusion in one dimensional channel structure.

time. To investigate whether this is an intrinsic feature of transport in the one-dimensional channel system or whether it is the result of finite occupancy, the movement of a single molecule in a vacant pore was simulated. As shown in figure 1, the plot of $(\overline{\Delta}^2)$ vs t' for this situation was found to be a straight line indicating that the curvature in the other plots probably arises out of finite occupancy. To investigate the possible role of end effects simulations were repeated for pores with 200 and 1000 sites. The results were found to be invariant with the length of the pores. Moreover the maximum displacement was less than half the length of the pore in all the cases. Since the evaluation of converged value $(\overline{\Delta}^2)$ involves simulation of several pores, the results are independent of the initial distribution of molecules. The computations were also repeated with different computer programs for generation of random numbers. These investigations suggest that the curvature observed in the simulation is probably representative of its true behaviour.

Zeolites with intersecting cylindrical channels

A schematic representation of the two-dimensional channel structure considered in the simulation is shown in figure 2(a). The channel intersections were assumed to be the sorption sites. To simulate tracer diffusion, an appropriate number of sorbate molecules was randomly distributed in the two-dimensional grid (typically 38 × 38 sites) to give the desired concentration. The molecules were randomly activated for movement. The movement of
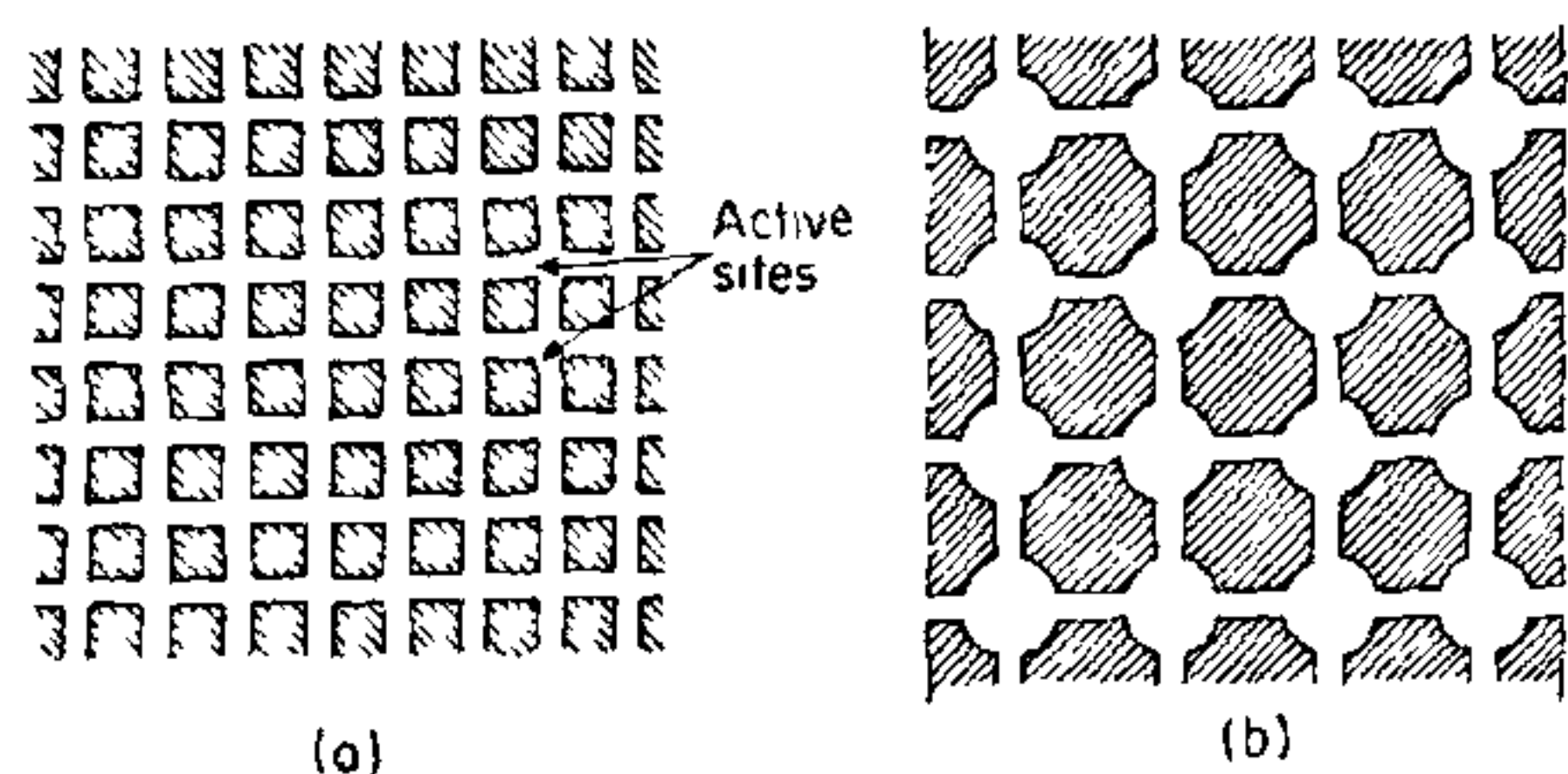
molecule to any one of the available adjacent vacant sites was considered to be equally probable. The displacement of a given molecule at a given time was evaluated as $\delta = (\delta_x^2 + \delta_y^2)^{1/2}$, where δ_x and δ_y are its displacement in the x and y directions respectively. The mean square displacement of tagged molecules was evaluated by a procedure similar to that described above. The results are shown in figure 3. A clear curvature is evident in this case as well. However, the linear portion is increased and the deviation from linearity occurred at a larger value of the mean square displacement.

Sorption in zeolites with cage type channel structure

A channel structure consisting of two-dimensional array of interconnected cages was considered [figure 2(b)]. The cages were considered capable of accommodating more than one sorbate molecule. The sorption capacity of the cages was set equal to m (molecules). The energy barrier for the movement of molecules within a cage was assumed to be much smaller as compared to that for the transport between the cages. Thus molecules could rapidly exchange sites within a cage but jumps between the cages will be significantly less frequent. The energy barrier for the jumps of molecules between the cages represents the characteristic activation energy for the diffusion process. It was assumed that every sorbate molecule is activated γ times per second to overcome this barrier.
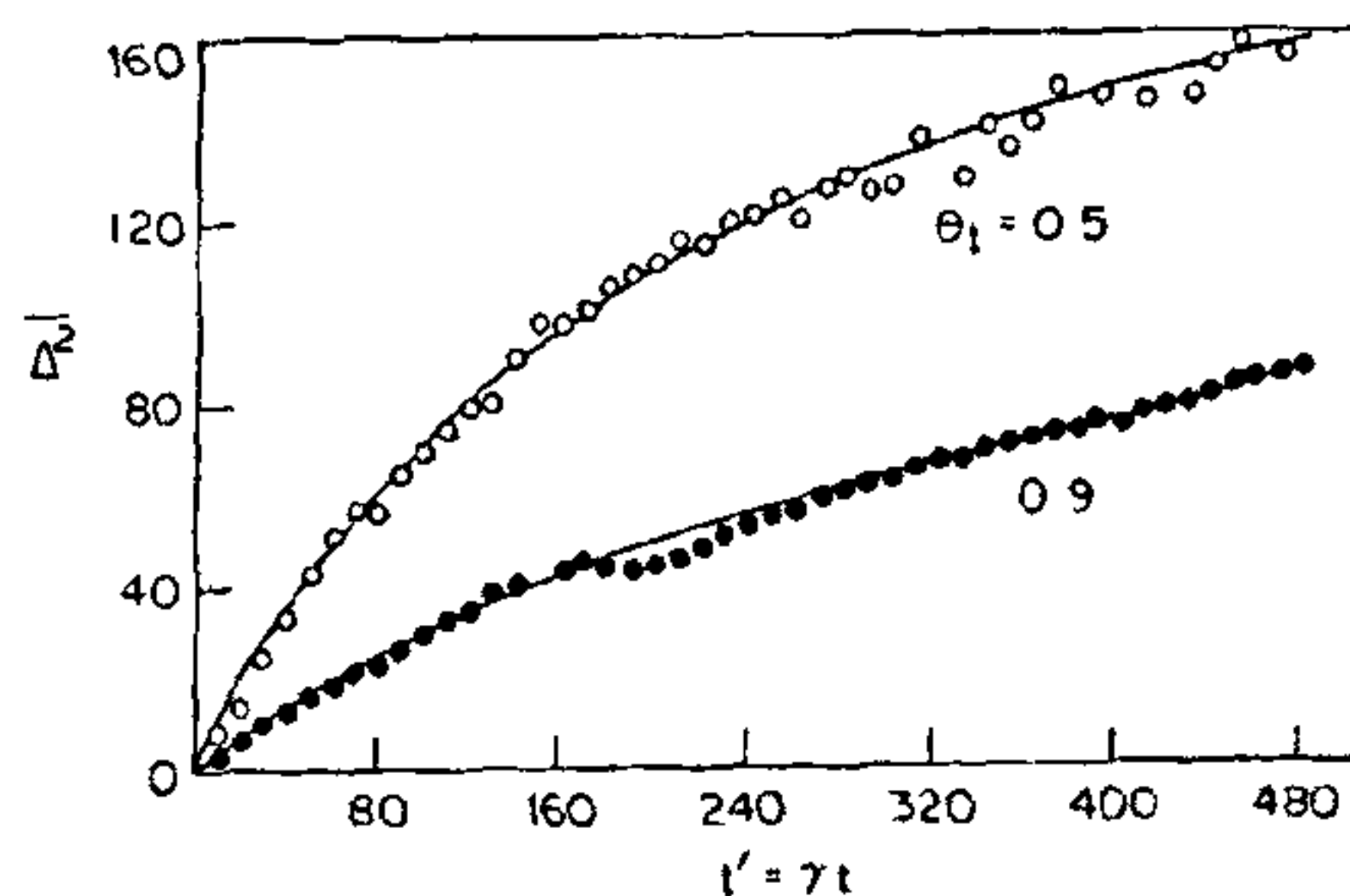

Figure 2. Channel structure of zeolites: (a) two-dimensional cylindrical channels, (b) two-dimensional cage type channels.

Figure 3. $\overline{\Delta}^2$ vs t' plots : tracer diffusion in two-dimensional system.

When a molecule is activated for a jump it was assumed that it would attempt to leave the cage through a window nearest to it at that instant since the molecules were considered to be in continuous movement within a cage and movement in any direction was considered equally probable. Hence the direction of movement was determined randomly. Whether the molecule would succeed in executing a jump would also depend on the occupancy of the adjacent cage in that direction. The probability of success was set equal to $(1 - \theta_c^n)$ where θ_c is the occupancy in the adjacent cage at that instant. Thus if the adjacent cage is fully occupied the jump would not take place, if it is vacant the jump is a certainty and the probability has an intermediate value at fractional occupancy.

Diffusion under a gradient of sorbate concentration (gravimetry)

To simulate diffusion under a gradient of total sorbate concentration an one-dimensional array of interconnected cages had to be considered since the computer time required for the two-dimensional structure was prohibitive. An appropriate number of molecules was randomly distributed in the predecided number of cages to give the desired initial concentration θ_o. The pore was considered closed at one end and open to the gas phase at the other end. The concentration θ_o represents the occupancy in equilibrium with the initial gas pressure. Sorption would commence when the gas pressure is increased. It was assumed that the interface would instantaneously attain the new equilibrium sorbate concentration θ^* which would then remain constant. To simulate this behaviour the pore was assumed to extend beyond the interface and the sorbate concentration in the extended region was held constant and equal to θ^*. To simulate the diffusion process, molecules were randomly activated and allowed to reallocate themselves by the procedure described above. The simulated diffusion resulted in a net increase in sorbate concentration which could be monitored as a function of time.

Simulations were carried out tor a pore consisting of 200 cages. The sorption capacity of the cages was set equal to four. Several pores had to be simulated before converged values of sorption uptake at a given time could be determined. Figure 4 shows fractional uptake vs $\sqrt{t'}$ curve for $\theta_o = 0.9$, $\theta^* = 0.95$ based on the average of simulation of 80 pores. The diffusivity is proportional to the square of slope of this line.

To investigate the variation of diffusivity with sorbate concentration simulations were carried out for $\theta_o = 0.1, 0.2, 0.3, 0.5, 0.7, 0.8,$ and 0.9. The increment $\theta^* - \theta_o$ was set equal to 0.05 in all the cases. To obtain converged values of sorption an uptake 80 to 120 pores had to be simulated. When the sorption uptake vs $\sqrt{t'}$ was plotted, a linear relationship at lower uptake values was observed in all the cases. The square of the slope of this line (m_1^2) was considered a measure of diffusivity. Simulations were carried out for $n = 1, 2$ and 3. Figure 5 shows the variation of m_1^2 with sorbate concentration obtained by simulations. The apparent diffusivity decreases and then increases with an increase in sorbate concentration. The trend is unaffected by the value of n, which seems to suggest that this is an intrinsic feature of the behaviour.

Simulations were also carried out for a pore consisting of 400 cages. Figure 6 compares the fractional uptake vs $\sqrt{t'}$ plots for pores with 200 and 400 cages for $n = 2$. In agreement with
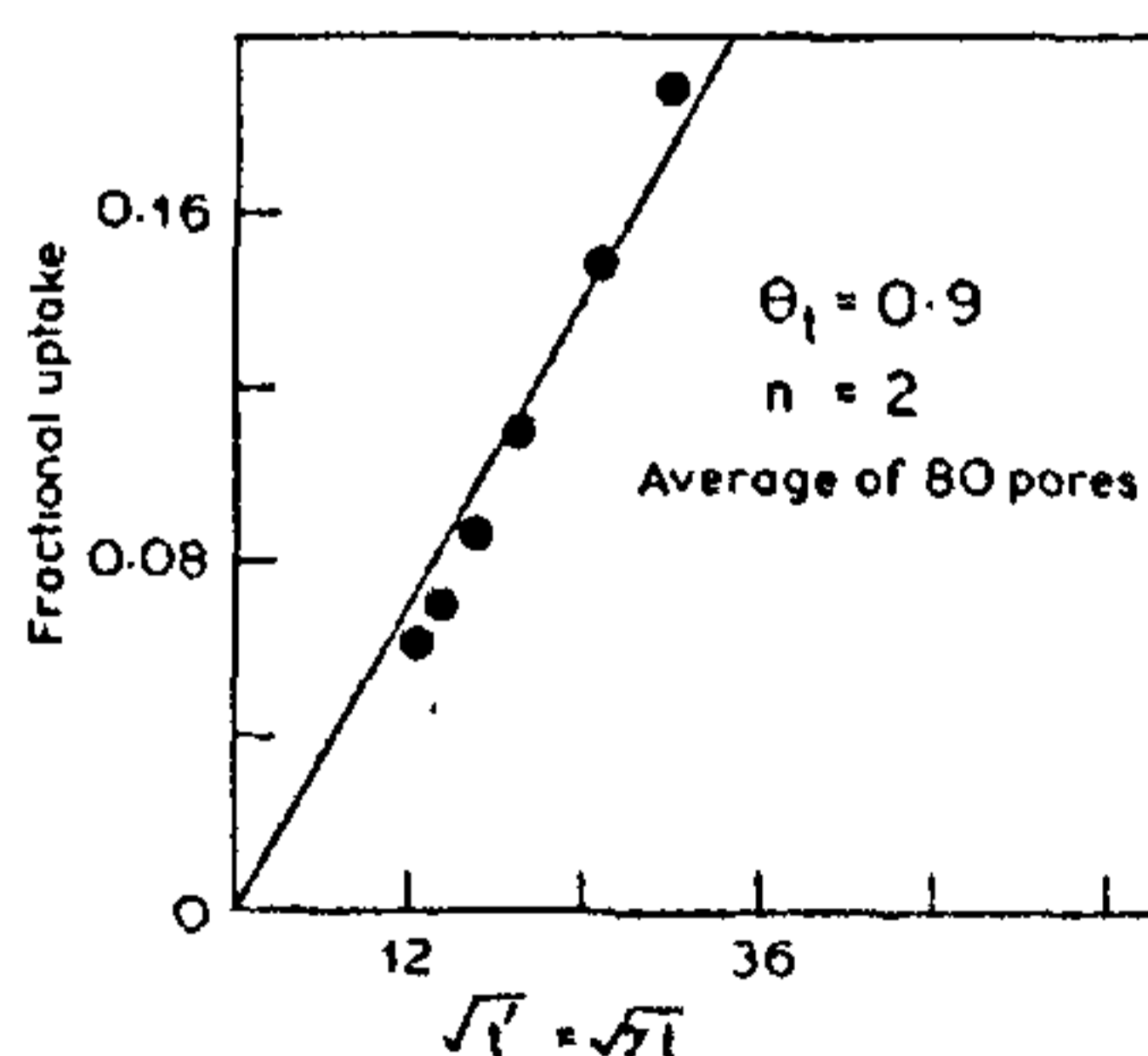
Figure 4. Variation of fractional uptake as a function of time:single sorbate sorption· in cage type channel structure.
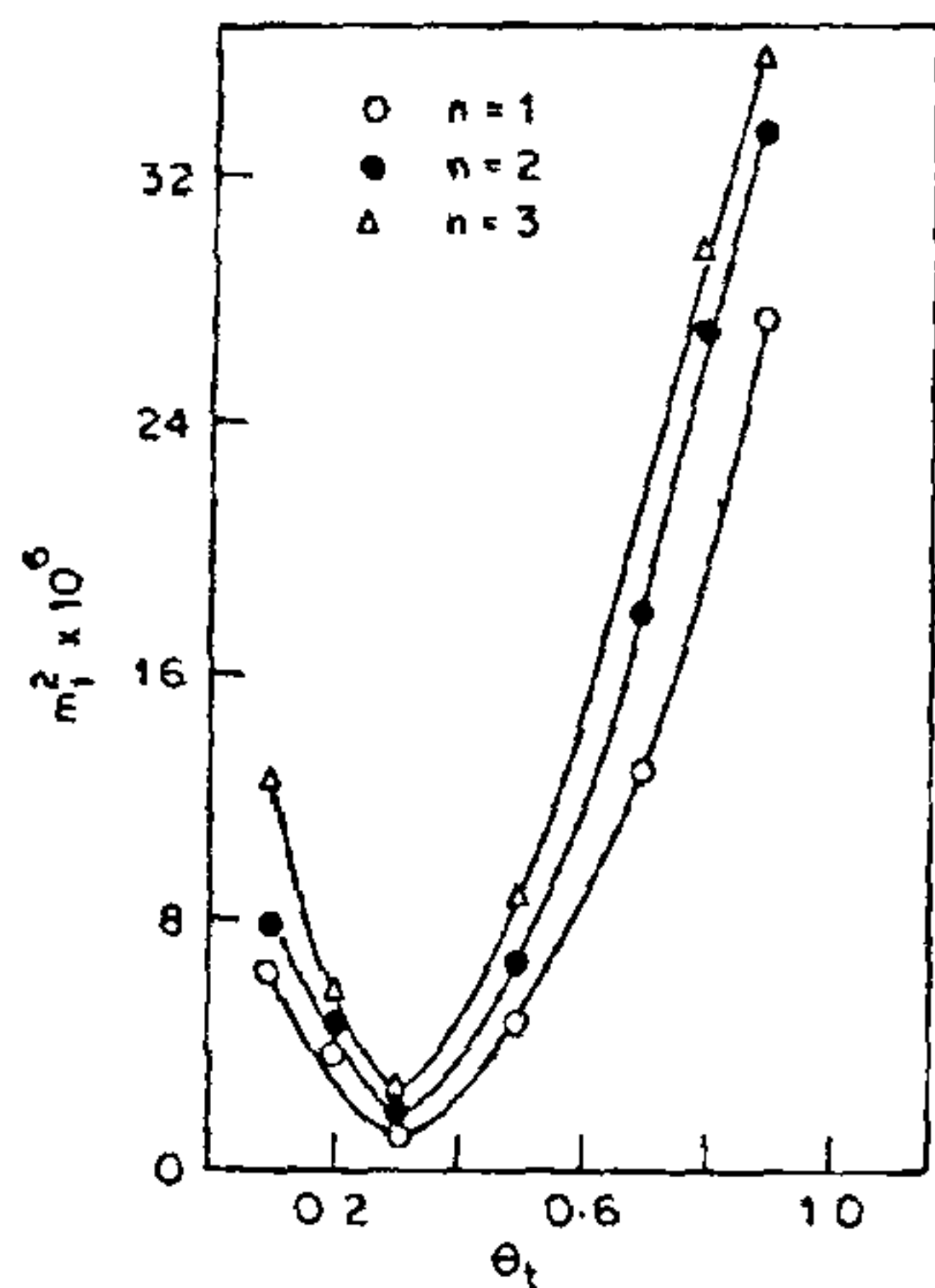
Figure 5. Variation of diffusivity with sorbate concentration obtained by simulation:single sorbate sorption in cage type channel structure.

the Fickian model the slopes bear an inverse relationship with the length of the pore.

Simulation of tracer diffusion

To simulate tracer diffusion a 38 × 38 two-dimensional grid of cages was considered. The required number of molecules was randomly and uniformly distributed in the cages to give the desired sorbate concentration θ_t. The molecules in a few cages at the centre of the grid were tagged. The molecules were activated randomly and allowed to move by the procedure described earlier. The grid was extended in all the four directions to avoid end
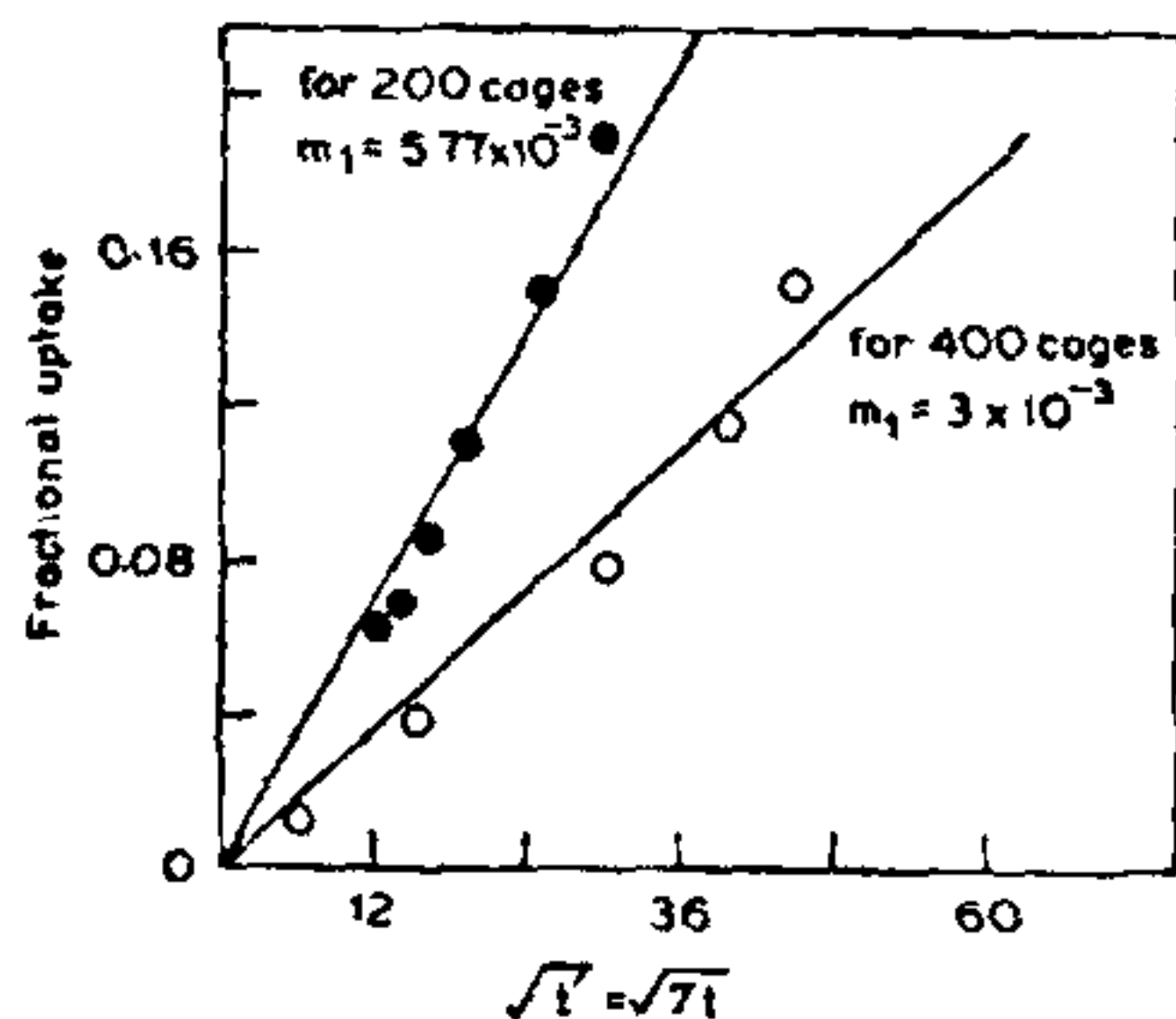
effects and the sorbate concentration in the extended region was set equal to θ_t. The displacement of molecules was evaluated as $\delta = (\delta_x^2 + \delta_y^2)^{1/2}$. The simulations were repeated until converged values of displacements could be obtained. In all the cases the displacement was well within the grid of 38 × 38 cages.

The variation of mean square displacement vs reduced time for various sorbate concentrations is shown in figure 7 for $n = 2$. A curvature can be seen in all the curves.

Figure 8 shows $\overline{\Delta}^2$ vs reduced time plots for a constant θ_t but different values of parameter n. The non-linear behaviour is seen at all values of n.

DISCUSSION

Simulation of sorption uptake experiments for zeolites with channels consisting of interconnected cages, shows that the diffusivity decreases and then increases with an increase in the sorbate concentration. This trend was found to be unaffected by the value of the parameter n. A similar trend has been observed experimentally in variety of systems[9-11]. This behaviour is believed to be a result of decrease in the intrinsic diffusivity D_n and a simultaneous increase in the thermodynamic activity correction factor with increase in sorbed phase concentration[12]. The apparent diffusivity, which is a product of the two terms, exhibits a minimum. Simulation of gravimetry
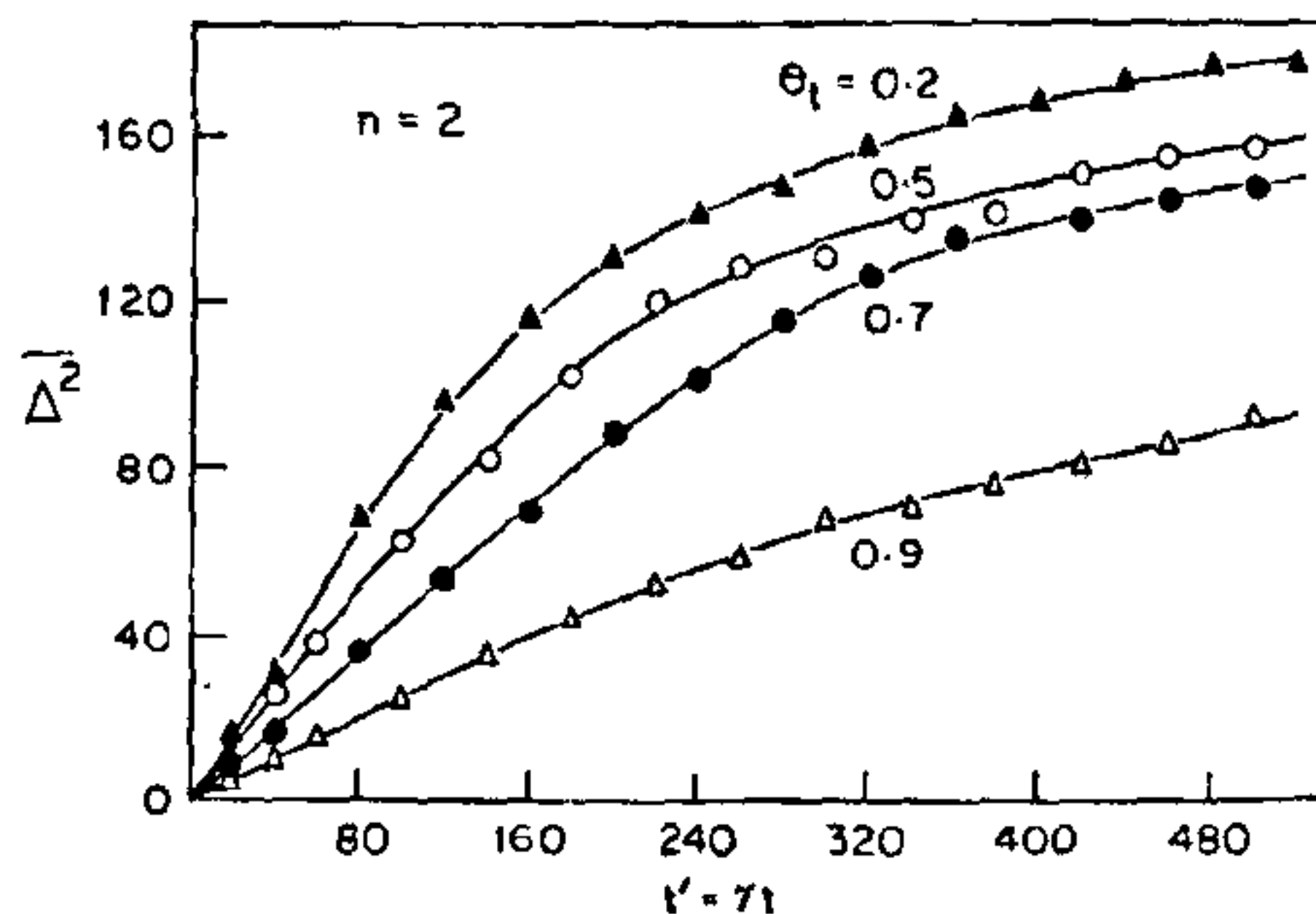

Figure 6. Analysis of effect of crystallite size by simulation:single sorbate sorption in cage type channel structure.

Figure 7. $\overline{\Delta}^2$ vs t' plots for different sorbate concentrations:tracer diffusion in cage type channel structure.
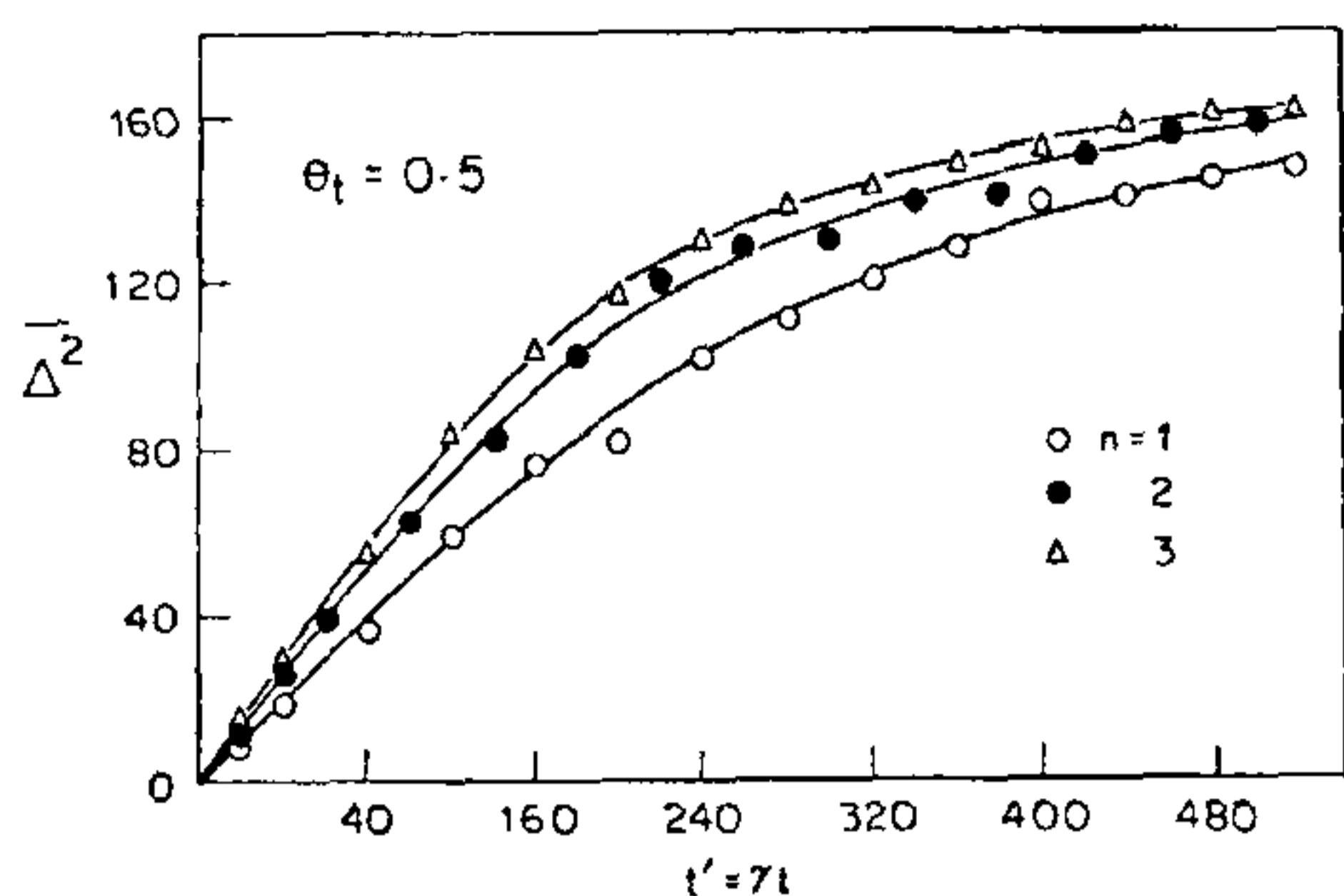
Figure 8. Variation of $\overline{\Delta}^2$ vs t' plot with n:tracer diffusion in cage type channel structure.

experiments for zeolites with cylindrical channels[1] on the contrary depicts a monotonous increase in apparent diffusivity with increase in sorbate concentration. This is also in agreement with the experimentally observed trend for this type of zeolites. These observations lend credibility to the physical basis of the molecular models employed in this analysis.

When transport of tracer molecules at a constant total sorbate concentration was simulated using these models the mean square displacement of tracer molecules was observed to be a nonlinear function of time for all the channel structures which implies that tracer diffusion cannot be represented by a single value of diffusivity. The nonlinearity is observed to be markedly dependent on sorbate concentration. Transport of a single molecule in the zeolite does not show any nonlinearity whereas the effect is very significant at high sorbate concentration. These observations clearly indicate that the non-Fickian movement of tracer molecules is due to the presence of other molecules. No simple explanation for this behaviour seems obvious at this stage. No such non-Fickian behaviour could be noticed in the simulation of gravimetry experiments.

The above observation, however, has significant implications to the diffusion measurement in zeolites. The results of simulation indicate that the value of diffusivity will be dependent on the magnitude of the displacement involved in the measurement. In a conventional tracer diffusion experiment, the tracer molecules

have to undergo progressively increasing displacement from their initial position as the tracer diffusion progresses. The present results would imply that in such an experiment, the diffusion coefficient should decrease with the extent of tracer diffusion. The effect will be more significant at higher sorbate concentration. In the NMR technique, however, the displacement of molecules over a very short interval of time (micro-seconds) is measured. The displacement involved would be much smaller than that in tracer diffusion experiments and would probably lie in the initial linear portion of $\overline{\Delta}^2$ vs t plots shown in figures 1, 3 and 7. The diffusivity obtained by this technique is, therefore, likely to be much greater than that obtained by the tracer technique. The relevance of these conclusions to the experimental findings is discussed in the next paper.

CONCLUSION

In the present paper Monte Carlo simulation of tracer diffusion in zeolites with three different channel structures is presented. The types of channel structures considered in the analysis cover most of the zeolites employed in practice. The analysis, for the first time, demonstrates that the mean square displacement of tagged molecules in zeolite channels has nonlinear dependence on time. An important implication of the above finding is that different experimental techniques which involve measurements over widely different time scale can give significantly different values of diffusivity.

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ANNOUNCEMENTS

ROCKY MOUNTAIN BIOLOGICAL LABORATORY, CRESTED BUTTE, COLORADO, 61ST SUMMER SESSION

The summer session of the Rocky Mountain Biological Laboratory (RMBL) will be held from 12 June to 6 August 1988. For more than sixty years the RMBL of Gothic, Colorado has offered summer courses in biology to college students Many renowned researchers have taught a variety of subjects over the years. The RMBL now accepts applications for future summer courses of eight week's duration. Room, board, travel reimbursement and a stipend are provided..

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This symposium to be held at New Delhi from 14 to 17 April 1988 is aimed at starting a process of interaction amongst the scientists and technologists engaged in underground engineering for various sectors of economy and socio-economic development. Mining and hydropower are two important sectors where underground engineering is practised. There are other fields where underground construction technology may find its rightful place. Metropolitan underground railways, underground storages for industrial and petrochemical products, water management through underground structures, defence installations in strategic areas and underground nuclear waste repositories are some of the applications which may find wider applicability in the years to come.

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