
Chapter 5

Computer simulation of zeolitic systems

5.1 Principles of the Monte Carlo method

The Monte Carlo method was invented by Nicholas Metropolis and Stanislaw Ulam in the mid-1940s at Los Alamos during the Manhattan Project to build the first nuclear bomb. The basic idea underlying the method is to obtain an estimate of a particular mathematical or physical value by applying a set of stochastic rules (hence the name ‘Monte Carlo’) to some system of interest. A simple example is Monte Carlo integration. Consider some arbitrary function $f(x)$ for which $0 \leq f(x) \leq 1$ for $0 \leq x \leq 1$. Two random deviates are selected in the range 0 to 1 inclusive. The first number is taken as the value of the x coordinate of a point and the second as the value of the y coordinate of that point. It is then determined whether or not the second value is less than, equal to or greater than $f(x)$. This procedure is repeated a very large number of times. The fraction of pairs of random numbers for which the second number is less than or equal to $f(x)$ is an estimate of the area under the curve. The estimate becomes more accurate as the number of pairs chosen increases. It can be shown that the difference, which can be thought of as the error in the estimate, between the estimate and the true value of the area is proportional to $N^{-1/2}$ where N is the number of points chosen.

The original use of the Monte Carlo method was for calculating the trajectory of a neutron as it was scattered by nuclei and other neutrons in a nu-

lear reactor or explosion. This was a difficult problem to tackle analytically because of the very large number of possible paths available to the neutron. Typical trajectories could be generated using the Monte Carlo method by making certain assumptions about the distance the neutron travelled between each scattering event and the manner in which the neutron was scattered. Initially, the procedure had to be carried out laboriously by hand. The development of electronic computers from the late 1940s, enormously increased the range of possible uses for the Monte Carlo method.

The most important early application of the Monte Carlo method to statistical mechanics was made by Metropolis *et al* (1953). They were interested in determining the equation of state for a system of rigid spheres in two and three dimensions. In their scheme, the spheres are originally arranged on a regular lattice. A particle is chosen from the ensemble and is displaced through a random distance and direction. If the total energy of the system would be decreased by the displacement of the particle then the move is allowed. If the energy would be increased, the probability P of the move being allowed is given by

$$P = \exp\left(-\frac{\Delta E}{kT}\right) \quad (5.1)$$

where ΔE is the difference in the energy of the system for the particle in its current position and its putative new position. After a large number of moves, the system will have relaxed to a state of dynamic equilibrium. The energy of the system will have reached a minimum (fluctuations dependent on the temperature and step size used for the displacement of the particle will occur about this minimum). An important facet of the Metropolis *et al* algorithm is that it automatically ensures that when the system reaches equilibrium, the particles will be correctly distributed with respect to energy according to Maxwell-Boltzmann statistics.

In their original investigation, Metropolis *et al* considered a canonical system in which the number of particles is fixed. The algorithm can be exten-

ded simply to grand canonical systems in which the number of particles in the system is allowed to change. A constant chemical potential bath is considered to surround the system. Particles can enter the system from this bath or leave to it. Each Monte Carlo cycle, one of three possible events can occur. Either an existing particle is moved through a random displacement vector, the particle is deleted (desorbed or leaves the system to the external bath) or a new particle is inserted (adsorbed or enters the system from the external bath). In the criterion for whether or not a move is allowed ΔE is replaced by $\Delta\mu$, the change in chemical potential of the system for the particular change in the position of the particle chosen from the ensemble. At equilibrium, the chemical potential of the system will be equal to that of the bath. Since the chemical potential of a system is a function of its state variables (pressure and temperature for the bath), it is thus possible to use the Metropolis *et al* algorithm to predict pressure v. loading isotherms.

5.2 Zeolitic systems and the Monte Carlo method

A large number of investigations of zeolitic systems using the Metropolis *et al* algorithm have been reported. A great deal of information about the structure of zeolites (location of cations and framework atoms), as well as the energetics, equilibrium locations and loadings of sorbed molecules has been obtained. Stroud *et al* (1976) used a canonical Metropolis *et al* algorithm to predict isotherms, isosteric heats of adsorption and heat capacities for methane in CaNa zeolite A. They neglected the polarisation energy that arises because of the interaction between the Ca^{2+} and Na^+ ions and the methane molecule and replaced the discrete network of framework atoms with a uniform, continuous distribution of force centres spread over the cage walls. The interactions between these force centres and the methane molecules and between the methane molecules themselves were described by a Lennard-Jones 6–12 potential. Kiselev and his collaborators (Bezus *et al* 1977, Kiselev and Du 1981) calcu-

lated various thermodynamic quantities for the adsorption of methane, argon, krypton, xenon, oxygen, nitrogen, carbon monoxide, carbon dioxide on X and Y zeolites in the low loading limit. The interactions of the sorbed species with the cations and the individual framework oxygens were considered (the silicon and aluminium atoms can be thought of as being buried in the electron clouds of the oxygen atoms and their interaction with the sorbed species is always neglected in computer simulations of zeolitic systems). The necessary integrals were evaluated by means of a ‘coordinate net,’ rather than by the Monte Carlo method. This involved evaluating the energy of a methane molecule for an array of cells at conditions of different pressure and temperature. Soto and his collaborators (Soto *et al* 1981, Soto and Myers 1981) were the first to undertake a grand canonical Metropolis *et al* algorithm study of the adsorption of gases on zeolites. They examined noble gases on CaNa zeolite A and Na zeolite X for both hard sphere and Lennard-Jones molecules and found reasonable agreement with experimental results. Woods and Rowlinson (1989) continued this work by studying the adsorption of xenon and methane on X and Y zeolites. Van Tassel and his collaborators at the University of Minnesota have made extensive studies using the grand canonical Metropolis *et al* algorithm of the adsorption of xenon, argon and methane on Na zeolite A (Van Tassel *et al* 1992, Van Tassel, Davis and McCormick 1993, 1994a, 1994b) and more recently xenon on mordenite (Nivarthi *et al* 1995a, 1995b). Their work is particularly interesting because of the light they have shed on adsorption sites in Na zeolite A. They have shown that for methane, there are thirteen adsorption sites. Twelve sites are arranged on a dodecahedral lattice symmetric about the centre of the α -cage plus a site at the centre of the α -cage.

5.3 Molecular Dynamics

Metropolis *et al* algorithm Monte Carlo simulations only provide information

about the equilibrium properties of the system. They do not provide any information about the time evolution of the system. However, an extension of some of the ideas of the method leads to molecular dynamics. If the potential energy of a particle as a function of space is known, it can be differentiated to find the force acting on the particle. Integrating Newton's second law of motion

$$\begin{aligned}\int \mathbf{F} dt &= \int m \frac{dv}{dt} dt \\ &= \int m dv\end{aligned}\quad (5.2)$$

where \mathbf{F} is the net force acting on a molecule of mass m and velocity v at time t , it is thus possible to determine the time evolution of the particle's velocity and position from which the tracer diffusion coefficient can be determined. Zeolitic systems are particularly amenable to investigation by molecular dynamics. A very large number of studies have been reported in the literature. It has been found that, in general, there is reasonable agreement between values of D_t obtained by molecular dynamics simulations and those obtained by PFG NMR and incoherent QENS. Yashonath and his collaborators at the Indian Institute of Science in Bangalore have been particularly active in this area. Yashonath *et al* (1988) and Yashonath, Demontis and Klein (1988) examined the diffusion of methane in Na zeolite Y. They concluded that at room temperature, methane molecules reside mainly close to the walls of the supercage. Reasonable agreement was obtained between the simulations and measurements of the equilibrium and dynamic properties of the system. The work was extended to benzene (Demontis, Yashonath and Klein 1989) and xenon (Yashonath 1991a,b, Santikary, Yashonath and Ananthakrishna 1992, Yashonath and Santikary 1992, 1993a). Yashonath and Santikary (1994a,b) examined a range of noble gases diffusing in both CaNa zeolite A and Na zeolite Y and found that the diffusion coefficient did not necessarily decrease with increasing size of the atom and, in fact, a max-

imum value for the diffusion coefficient was observed for atoms with diameters close to the diameter of the cage windows (the so-called diffusion anomaly). The diffusion of argon in CaNa zeolite A and Na zeolite A was studied and the diffusion anomaly noted in all cases (Santikary and Yashonath 1992, 1994, Yashonath and Santikary 1993b). Xenon and argon are particularly suitable atoms for molecular dynamics simulations because they are virtually spherical and have simple electronic structures. Consequently, their interactions with other species can be modelled satisfactorily with a Lennard-Jones 6–12 potential. Silicalite has been a favoured system for molecular dynamics investigations (June, Bell and Theodorou 1990, Catlow *et al* 1991, Goodbody *et al* 1991, Hufton 1991, June, Bell and Theodorou 1991, Kawano, Vessal and Catlow 1992, Demontis *et al* 1992, El Amrani, Vigné-Maeder and Bigot 1992, Nicholas *et al* 1993, Maginn, Bell and Theodorou 1993, El Amrani and Kolb 1993, Dumont and Bougeard 1995). Other simulations of diffusion in Na zeolite Y have been reported by Schrimpf *et al* (1992, 1995), Mosell *et al* (1996) and Mosell, Schrimpf and Brickmann (1996). Lee *et al* (1994) is unusual in that it deals with the diffusion of water, a polar molecule, and Na⁺ ions in Na zeolite A.

5.4 Monte Carlo simulations of kinetic and equilibrium properties

The main disadvantage of molecular dynamics is that because it is so computationally expensive it can only be used to study the evolution of systems over short periods of time (10^{-12} – 10^{-9} s). In many empirical situations, it is of interest to examine a system for much longer periods of time. For example, even for a very small crystallite ($\sim 10^{-8}$ m diameter), the characteristic time scale for the system to reach equilibrium during sorption processes is of the order of 10^{-6} s and in practical systems such as the IGA or a zeolite bed in a pressure or thermal swing process, the time scale can be many hours. The Metropolis *et al* algorithm can be adapted to study such systems. Much of the

early work on studying diffusion using this method was done on metal hydride systems. Here, a particle (proton) occupies a discrete site on a regular lattice. For a system at equilibrium, each particle has an equal probability of attempting a jump in a given time period. In such a simulation, each Monte Carlo cycle a particle is selected at random from the ensemble. A target site for the molecule is then chosen at random. Usually, this will be one of the nearest neighbours to the particle's current site. If the target site is already occupied by another particle the probability of the particle making the jump is zero. Otherwise, the probability of the the jump is given by the usual Metropolis *et al* algorithm expression that depends on the energy difference between the sites. In both cases, one Monte Carlo cycle is said to have taken place and the time that has elapsed for the system is incremented by one time period. This time period will be equal to the mean residence time of the particle on a site. The tracer diffusion coefficient D_t is given by

$$D_t = \frac{\langle r^2 \rangle}{2nt} \quad (5.3)$$

where $\langle r^2 \rangle$ is the mean square distance moved by the particles, n is the dimensionality of the system and t is the time elapsed, which will be proportional to the number of Monte Carlo cycles. The tracer correlation factor f_t is then given by

$$f_t = D_t \frac{6\tau}{\langle \ell^2 \rangle} \quad (5.4)$$

where $\langle \ell^2 \rangle$ is the mean square length of the jumps available to the particle.

Ruthven (1974) used such a scheme to study the diffusion of molecules in Na and CaNa zeolite A at low loading. He made the assumption that there was no multiple occupancy of cages. The molecules could then be considered to move on a simple cubic lattice. Each Monte Carlo cycle, a randomly selected molecule attempted to jump through one of its cages six windows into a neighbouring cage. The windows could be blocked by Na^+ ions with a reduced probability of a molecule successfully making a jump through it. It was found

that as the $\text{Ca}^{2+}:\text{Na}^+$ ratio was varied, a sudden increase in the value of D_t occurred for at a ratio of $\sim 1 : 1$. This is in agreement with experiment. Above this ratio, sufficient windows are free of cations that the molecule can percolate freely through the crystallite.

It is also possible to determine the chemical diffusion coefficient D_c using a similar method. By definition (see section 2.5)

$$D_c = \frac{-J}{\left(\frac{\partial c}{\partial x}\right)_T} \quad (5.5)$$

where J is the matter current density and $(\frac{\partial c}{\partial x})_T$ the concentration gradient at some point. In the simulation, a chemical potential gradient is imposed in a particular direction in the lattice. The probability of a particle making a jump down the chemical potential gradient is greater than it making it up the gradient and there will therefore be a net flux of particles down gradient. By measuring the number of particles that pass through a surface normal to the gradient in a given number of Monte Carlo cycles, it is possible to determine J and thus D_c . The mobility correlation factor f_M can then be found using the expression

$$f_M = \frac{D_c}{\langle \ell^2 \rangle / 6\tau}. \quad (5.6)$$

This method was used by Aust, Dahlke and Emig (1989). They determined concentration dependent chemical and tracer diffusion coefficients for an idealised two-dimensional zeolite network and claimed agreement with experimental results.

In order to study the behaviour of systems away from equilibrium and, in particular, the evolution of systems as they relax towards equilibrium after some change to their environment such as a step increase or decrease in pressure, a slightly different approach must be taken. Over the years a number of investigations of the kinetics of adsorption (and desorption) on surfaces have been reported beginning with the work of Young and Schubert (1964),

who examined the condensation of tungsten on tungsten. The papers of Gordon (1968) and Abraham and White (1970) were seminal in the development of this field. However, it is only recently that this particular application of the Metropolis *et al* algorithm Monte Carlo method, known as the dynamic (or kinetic) Monte Carlo method, has been placed on a sound theoretical footing. Fichthorn and Weinberg (1992) extended the ideas of Limoge and Bocquet (1988, 1990). Kang and Weinberg (1989) and Ray and Baetzold (1990) applied similar ideas to sorption and diffusion on metal surfaces. Care must be taken in its utilisation and some caution exercised when interpreting the results presented in earlier papers. In the dynamic Monte Carlo method, the period of time by which the system 'clock' is incremented after a change in the microstate of the system depends upon factors related to the rates of the various processes that can occur to the system, a fact not always taken into account by early researchers, who often (implicitly) assumed that the rate of the system 'clock' was constant. This can be shown to be the case by considering a simple example. Imagine a finite area of some surface on which there is a simple square lattice of adsorption sites. At any instant, each site is either empty or occupied by a molecule. For an empty site, a molecule can be adsorbed from the gaseous phase above the surface or, if one or more of the neighbouring sites is occupied, a molecule can jump from such a site to the previously empty site. For an occupied site, the molecule can be desorbed into the gaseous phase or, if one or more of the neighbouring sites is unoccupied, the molecule can jump to such a site from the previously occupied site. The different processes will occur with (possibly very widely) differing characteristic timescales. If the system is examined, the relative probability of a particular process being observed to occur in a particular instant will depend upon the ratio of rate of that process to the sum of the rates of all the possible processes for the system. If there are N sites in the system for each of which there are j possible processes (the rate of some processes might

be zero), then the relative probability $P_{n,i}$ of the i th process occurring to the n th site is given by

$$P_{n,i} = \frac{k_{n,i}}{\sum_{n=1}^N \sum_{i=1}^j k_{n,i}} \quad (5.7)$$

where $k_{n,i}$ is the rate of the i th process for the n th site. As the system approaches equilibrium, $P_{n,i}$ will change as the number of empty and filled sites changes since the rate of the different processes depends upon whether or not neighbouring sites are occupied. For the n th site, the probability P_n of some process occurring to that site in a small time period Δt is given by

$$P_n = \sum_{i=1}^j k_{n,i} \Delta t. \quad (5.8)$$

The probability of some process occurring to the site is thus governed by Poisson statistics. The probability P of some process occurring to any site is thus given by

$$P = \sum_{n=1}^N \sum_{i=1}^j k_{n,i} \Delta t. \quad (5.9)$$

This is also governed by Poisson statistics. Therefore, the mean time τ between events for the system is given by

$$\tau = \frac{1}{\sum_{n=1}^N \sum_{i=1}^j k_{n,i}}. \quad (5.10)$$

For a site in a system at equilibrium, the mean number of occupied and empty neighbouring sites will be constant (neglecting fluctuations). Consequently, the mean time between events occurring to a site will be constant. For simulations of such systems, the elapsed time is proportional to the number of Monte Carlo cycles. This will not be the case for a system that is not at equilibrium. The mean time between events occurring to the system will change as the site occupation probability changes.

Perhaps because of the success of Metropolis *et al* algorithm grand canonical Monte Carlo simulations in predicting the equilibrium properties of zeolitic systems and molecular dynamics in predicting the dynamic properties, only

one series of simulations of the kinetics of sorption processes in zeolites has been reported (Palekar and Rajadyaksha 1985a, 1986, Pitale and Rajadhyaksha 1988). The initial work considered one-dimensional and two-dimensional networks of pores. A somewhat artificial setup was used. The gas phase exterior to the crystallite was modelled as a continuation of the interior of the crystallite, but was already at equilibrium at the beginning of each step change in loading. Chemical and tracer diffusion coefficients were calculated. The sorption of binary mixtures of gases was considered. Although mention is made of work extending the model to three dimensions for A and Y zeolite-type structures, the results do not appear to have been published.

Auerbach and Metiu (1996) have used the Dynamic Monte Carlo Method to study the diffusion of benzene in Na zeolite Y. They make the simplifying assumption that the particular types of sites occupied by the benzene molecules can be taken as an internal characteristics and that for long range diffusion, the molecules are thought of as hopping from cage to cage. They derive mean residence times and jump lengths (and hence tracer diffusion coefficients), but not chemical diffusion coefficients or isotherms.

Wei and his collaborators at the Massachusetts Institute of Technology undertook Monte Carlo simulations of diffusion in zeolites (Theodorou and Wei 1983, Mo and Wei 1986, Tsikoyiannis and Wei 1991a,b). Their interest has been in diffusion and reaction in a simplified two-dimensional model of ZSM-5, an aluminous form of silicalite that contains some cations at high loadings. The blockage of channels by cations and molecules was taken into account. Similar ideas were used by van den Broeke, Nijhuis and Krishna (1992). Faux, Hall and Sundaresan (1991) looked at the directional bias for diffusion for large molecules in the zig-zag channels of ZSM-5 and found that this occurs to a certain extent at low loading, but becomes less important at higher loading.

In a dynamic Monte Carlo simulation, a site is chosen at random from the system each cycle. For each site, there will be a number of possible pro-

cesses that can occur depending on the environment of the site (e.g. the type of neighbouring sites and whether or not they are occupied). The relative probabilities of all the processes for each site in the system are normalised relative to the process for any site with the largest rate. For the chosen site, there is a certain probability that one of the possible events will occur for that Monte Carlo cycle. A test is made to determine whether or not an event does occur. If it does, the particular process that occurs is determined from the relative probabilities of all the processes possible for the site. Only if an event occurs is the time for the system incremented. A random deviate x between 0 and 1 inclusive is selected. The time for system is then incremented by an amount Δt given by

$$\Delta t = -\tau \ln x \quad (5.11)$$

where τ is defined by (5.10). Since τ will change as number and type of sites occupied changes, the time elapsed for the system is not proportional to the number of Monte Carlo cycles.

Dynamic Monte Carlo programs have been written that simulate the sorption and diffusion of small molecules such as methane and water on zeolites A and Y. This is the first time that an attempt has been made to develop a simulation of zeolitic systems that can be used to simultaneously predict both kinetic and equilibrium properties of zeolitic systems in a self-consistent manner. In particular, it differs from the recent study of Auerbach and Metiu (1996), which only considered the kinetic properties of such systems. Such simulations provide a useful bridge between traditional Metropolis *et al* algorithm simulations of the equilibrium properties of zeolitic systems and molecular dynamics simulations of the kinetic properties. In Metropolis *et al* algorithm simulations, there is a certain probability each Monte Carlo cycle that a particle will be inserted (adsorbed), deleted (desorbed) or translated from its original position to a new position. No account is taken of the differing rate of the various processes. A dynamic Monte Carlo simulation extends this idea by

ascribing a set of self-consistent rates to the different processes, allowing the kinetics of the system to be studied. However, the rates will not, in general, be known from first principles. They might be determined from experiment (quasielastic neutron scattering or pulsed field gradient nuclear magnetic resonance), molecular dynamics simulations or be treated as free parameters.

It is necessary to make a number of assumptions in order to make the problem tractable to the dynamic Monte Carlo technique. Ruthven's 1974 study was concerned with long-range self-diffusion (i.e. the motion of molecules over distances of many cage sizes) at loadings of less than one molecule per cage so that interactions between neighbouring molecules could be ignored. At such loadings, the distinction between a mobile fluid-like phase and a phase fixed on adsorption sites cannot be made. At higher loadings, however, the distinction becomes important. Although as mentioned above, Monte Carlo simulations have shown that there are thirteen adsorption sites for methane molecules in A zeolites, other simulations and neutron diffraction data (see chapter 8) suggest that for methane in both A and Y zeolites, the molecules are delocalised and a fluid-like phase exists. The magnitude of the interaction between the methane molecules is relatively small compared to their interaction with the zeolite framework and cations. Therefore, it is reasonable to replace the interaction between individual molecules with a mean field interaction. For a dynamic Monte Carlo simulation of a mobile phase, it is not possible to follow the motion of individual molecules within the cage as this would require a detailed model of the motion of the model (this could be provided by a molecular dynamics simulation). This corresponds to the analytical model used for predicting the form of the neutron scattering functions where a simple model for the motion of a molecule in a spherical potential is used. Instead the motion of molecules between cages is simulated.

These sites are not to be imagined as fixed in space, rather they are to be thought of as the (moving) volume of space that can contain a methane

molecule. The motion of molecules as they jump between sites in neighbouring cages. In A zeolites, the cages are arranged on a simple cubic lattice, whereas in Y zeolites, the cages are arranged on a tetrahedral lattice, which requires more care in handling. A tetrahedral lattice can be considered as two interpenetrating face centred cubic lattices. Each interior cage has four nearest neighbours, which are on the other lattice. Those cages with fewer than four nearest neighbours are on the surface on the crystallite, whereas for A zeolites, it is clear which cages are on the surface. Molecules can be adsorbed and desorbed from the crystallite into the gas phase. For each Monte Carlo cycle during the simulation, a cage and a site within that cage is chosen at random. The site will be either empty or filled. If the cage is on the surface of the crystallite, then a molecule can either be adsorbed or desorbed depending on whether or not the site is occupied. The rate r_a of adsorption through a window is given by the rate at which molecules strike an area equal to that of the window. This can be shown from simple kinetic theory (Tabor 1979) to be

$$r_a = \frac{2\pi r^2 P}{\sqrt{2mkT}} \quad (5.12)$$

where P is the pressure, r is the radius of the zeolite cage window, m is the mass of the molecule and k is Boltzmann's constant. r_a is dependent on both the pressure and temperature of the gas phase, i.e. on its chemical potential. Each possible process for an adsorbed molecule will have a different rate r_p given by

$$r_p = r_m \exp\left(-\frac{\Delta E}{kT}\right) \quad (5.13)$$

where r_m is the rate of the fastest process and ΔE is the change in energy of the molecule for the jump. For desorption rate, ΔE is the energy of adsorption of the molecule, which will be large compared to ΔE for jumps between changes, provided the loading of the cages is not near saturation. It is not possible to determine r_m from simple physical arguments, although it could

be determined in principle from a molecular dynamics simulation. In practice, this is an adjustable parameter that can be varied to provide the best fit to the experimental data. An idea of the value of r_m can be determined from QENS or PFG NMR experiments.

If the chosen site is empty then a molecule can jump into the site if there are molecules in the neighbouring cages or if it is on the surface of the crystallite, it can adsorb a molecule from the gaseous phase. If the site is occupied then the molecule can jump to a site in a neighbouring cage provided they are not all occupied or if the cage is on the surface of the crystallite, the molecule can be desorbed. The probability of each possible process for the molecule is normalised relative to the process with the fastest rate. If it is determined that an event does occur, the time for the system is incremented by the usual randomly determined amount from equation (5.11).

The evolution of the system towards equilibrium can thus be followed. After each cycle, the time and the change in loading of molecules per cage for that particular pressure step are recorded. When a suitable number of Monte Carlo cycles have taken place, a NAG routine is used to fit a curve for the suitable solution of the Fick's second law to the time v. change in loading curve. If it is determined that the system is close to equilibrium (the usual criterion for this being that the change in loading is $>99\%$ of the predicted equilibrium value), the system continues on to the next pressure step. The size of the next pressure step is determined by extrapolation from the points on the isotherm already determined in order to try and ensure that the change in loading for each pressure step are more or less the same. The value of D_c as a function of concentration can be determined from the fitted curve. Once the system is close to equilibrium, the system can be followed for a further number of Monte Carlo cycles. D_t and f_t as functions of concentration can be determined using the usual expressions. When a complete isotherm has been calculated, D_c/D_t can be determined from the gradient of the fitted curve.

Provided the simulation is correct, the values for the ratio obtained by the different methods should be in (reasonable) agreement. The model has only two free parameters, the rate of the fastest process and the form of the energy of interaction between the guest molecules. The simulations can provide self-consistent predictions of both the static (isotherm, entropy, enthalpy) and dynamic (D_c and D_t) properties of the system.

5.5 Results of dynamic Monte Carlo simulations

A number of runs of the dynamic Monte Carlo simulation of the sorption of idealised methane-like molecules in CaNa zeolite A have been made. The runs illustrate the effect of varying the different parameters on the kinetic and equilibrium properties of the system. The most important parameters are the pressure, temperature, the adsorption energy and the jump rate. The jump rate for a molecule is a complicated function of the molecular potential (a strong function of position within the zeolite) and the temperature and could, in principle, be found from a molecular dynamics simulation or a QENS experiment, but is treated as a free parameter in the simulations. A range of values for the different parameters were examined. Not all the values were necessarily those to be expected for methane in CaNa zeolite A, but they provide an idea of the range of different kinds of behaviour possible for this type of system. Higher values of the jump rate are representative of non-polar molecules such as hydrogen or methane, while lower jump rates are representative of polar molecules such as water that can be tightly bound on adsorption sites or heavier non-polar molecules such as argon.

The results of three representative runs are shown in figures 5.1–5.30. The parameters that differed between the runs are given in table 5.1. k_0 is the jump rate, Φ_1 and Φ_2 are the molar heats of adsorption of sites of the two different types of site. E_A^{11} , E_A^{12} and E_A^{22} are the activation energies for molecules jumping between two type I sites, between sites of different type

and two type II sites respectively. Each cage contained six sites of the two types, although for runs A and B, the sites were energetically identical.

Parameter	Run A	Run B	Run C
k_0/s^{-1}	2.4×10^{11}	2.4×10^9	2.4×10^9
Φ_1/Jmol^{-1}	1.2×10^4	0.6×10^4	0.6×10^4
Φ_2/Jmol^{-1}	1.2×10^4	0.6×10^4	0.9×10^4
$E_A^{11}/\text{Jmol}^{-1}$	1.6×10^3	1.6×10^3	0.8×10^3
$E_A^{12}/\text{Jmol}^{-1}$	1.6×10^3	1.6×10^3	1.6×10^3
$E_A^{22}/\text{Jmol}^{-1}$	1.6×10^3	1.6×10^3	0.8×10^3

Table 5.1 Parameters for dynamic Monte Carlo simulation runs

The DMC program is very CPU intensive, with each run of three adsorption and desorption isotherms taking several days on a Digital AlphaStation 600 Model 5/266 computer running Digital UNIX. Consequently, only a small crystallite could be treated ($11 \times 11 \times 11$ cages, 1.0×10^{-8} m along each edge of the crystallite). Zeolite crystallite can be formed of agglomerations of smaller units with dimensions of the order of a few hundredths of a micrometre, so such a situation is not necessarily physically unrealistic, but the crystallite size can have an effect on some of the results of the simulations. The isotherms were taken at 50, 75 and 100°C. All the isotherms (figures 5.1 and 5.2 for run A, 5.11 and 5.12 for run B, 5.21 and 5.22 for run C) are essentially reversible on desorption as would be expected for a system in which no changes to the internal structure are occurring and as found empirically for methane. This agreement strongly suggests that equilibrium has been reached on both adsorption and desorption. The loading decreases with temperature, again as expected and found empirically as is the form of the isotherms with the Henry's law region at low pressure. Run A had the largest jump rate and the equilibrium loading is correspondingly lower with a greater uncertainty to each point. Fickian diffusion can only occur if there is a well-defined con-

centration gradient in a region. If the jump rate of the molecules within the zeolite is very high then, for a small crystallite, there will not be such a concentration gradient. In such a case, because the probability per unit time of a molecule sorbed in the crystallite making a jump is greater than the probability of a molecule being adsorbed. A molecule arriving at the surface is very likely to move away from the surface and move through the crystallite before further molecules arrive at the surface. This prevents the formation of a concentration gradient. The situation is similar to adsorption onto a two dimensional surface and will be governed by a expression of the form

$$\Delta n = \Delta n_{\infty}(1 - \exp(-kt)), \quad (5.14)$$

where Δn is the change in loading, Δn_{∞} is the loading at equilibrium and k is the characteristic rate of the process. In such a case, it is not possible to estimate D_c from the time v. change in loading data. The quoted figures for D_c will be too low by up to two orders of magnitude as indicated by the difference in jump rate. This is the situation for run A (figures 5.3 and 5.4). Run B (figures 5.13 and 5.14) and run C (figures 5.23 and 5.24) were for a lower jump rate that was sufficiently slow for Fickian diffusion to take place. For run B, there is qualitative agreement on adsorption between the value of the ratio of D_c/D_t obtained from the measured values of the diffusion coefficients and the values obtained from differentiating the isotherm (figure 5.19). Also on adsorption, D_t is more or less constant below a loading of ~ 2 molecules per cage (figure 5.15). D_t then undergoes a sharp increase of $\sim 50\%$ and at higher loadings increases steadily. In the upper region, D_t is higher for higher temperatures, suggesting the process is activated. The same pattern is seen for D_c on adsorption (figure 5.13), although the increase above ~ 2 molecules is less marked and the activated nature of diffusion at higher loading is more clearly observed. The tracer correlation factor (figure 5.17) increases steadily from a value of ~ 0.25 at a loading of ~ 0.5 molecules per cage to a value of ~ 0.325 at a loading of ~ 4 molecules per cage.

The D_c values for desorption (figure 5.14) are lower than the adsorption values by about an order of magnitude, whereas the D_t values (figures 5.15 and 5.16) are comparable. This suggests that diffusion during desorption is non-Fickian. This may be because of the surface barrier created by the required heat of desorption. Interestingly, both the D_t and D_c values have similar forms as a function of loading. The value is fairly constant at higher loading (~ 3.0 molecules per cage, but dependent upon temperature), then a jump to a higher value followed by a gradual decrease towards lower loading. As might be expected the magnitude of the D_t values and the form of the tracer correlation factor (figure 5.18) is similar to the adsorption case.

For run A, the tracer diffusion coefficients (figures 5.5 and 5.6) are about two orders of magnitude greater than for run C (figures 5.25 and 5.26) as is to be expected from the increased jump rate. The form of each of the diffusion coefficients as a function of loading is similar for both adsorption and desorption with an increase in the rate of change towards higher loadings. In this case, loadings are low, < 1 molecule per cage. This increase may be accounted for if the finite size of the crystallite is considered. At high loadings (several molecules per cage), during the phase after the system has reached equilibrium that is used for determining D_t , each molecule only makes a small number of jumps and the presence of the surface will not seriously skew D_t towards a lower value. However, this will not be the case at low loading. As the loading increases, the mean number of jumps per molecule will reduce, the surface effect will become less severe and the D_t will tend more towards its true value. The program could be improved by the introduction of cyclic boundary conditions during this phase, although this would mean fixing the number of molecule in the system at some point and so some of the physicality of the system would be lost. The D_c values on desorption (figure 5.4) show the same type of surface barrier effect as for run C (figure 5.24).

As is to be expected from the parameters, runs B and C have more in

common with one another than with run A. The form of D_t for run B (figure 5.15) is similar in some ways to run C (figure 5.16) for adsorption with a step change at a loading of ~ 2.5 molecules per cage with more suggestion of the diffusion being activated. The f_t values are also similar indicating that the effect of the presence of the surface is not severe (figures 5.17 and 5.27). The adsorption D_c values (figure 5.13) have a similar form to those of run A (figure 5.3). It seems probable that the diffusion is non-Fickian. The desorption D_c values (figure 5.14) again show evidence of retardation by required heat of desorption. It is interesting to note that the diffusion can be non-Fickian and thus for it not to be possible to determine D_c from the kinetics data, but reasonable estimates of D_t and f_t can still be obtained. Significantly, the trend of both the f_t and D_c values is that of the type V concentration dependence of intercrystalline self-diffusion (Kärger and Pfeiffer 1991). For n-alkanes such as methane in CaNa zeolite A, it is found experimentally that the self-diffusion coefficient increases with concentration. This is an encouraging result as it suggests that the simulation predicts the empirically observed behaviour.

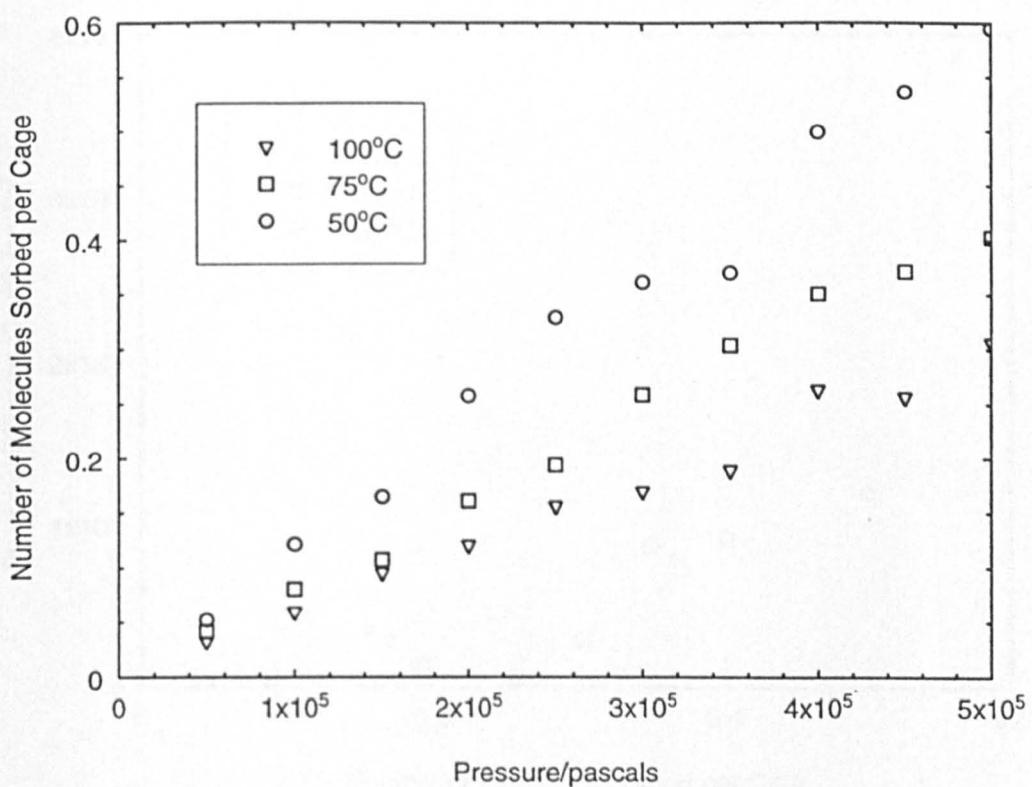


Figure 5.1 Simulated adsorption isotherm: run A

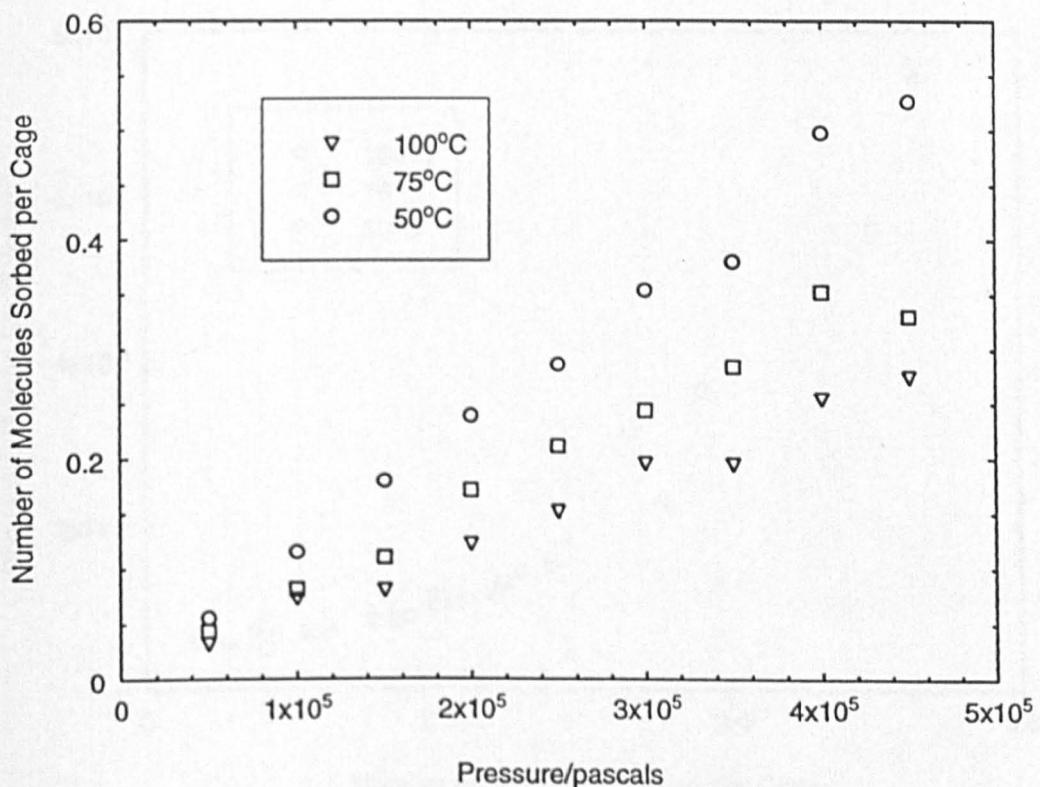


Figure 5.2 Simulated desorption isotherm: run A

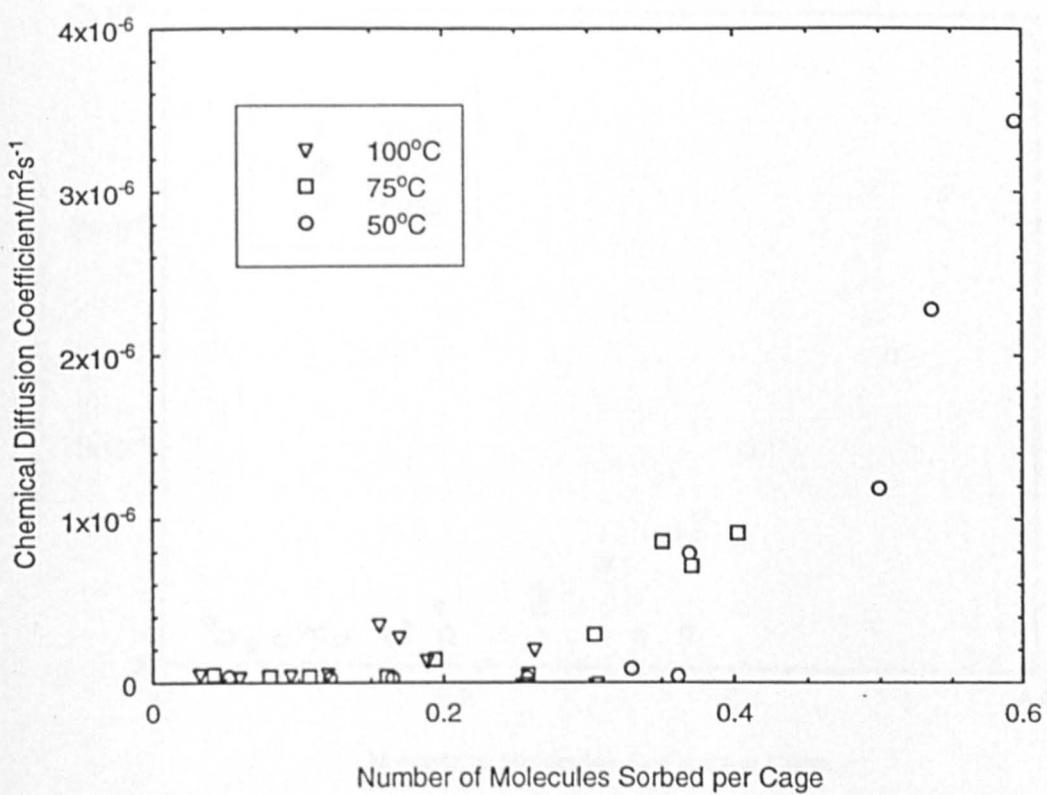


Figure 5.3 Simulated adsorption chemical diffusion coefficient: run A

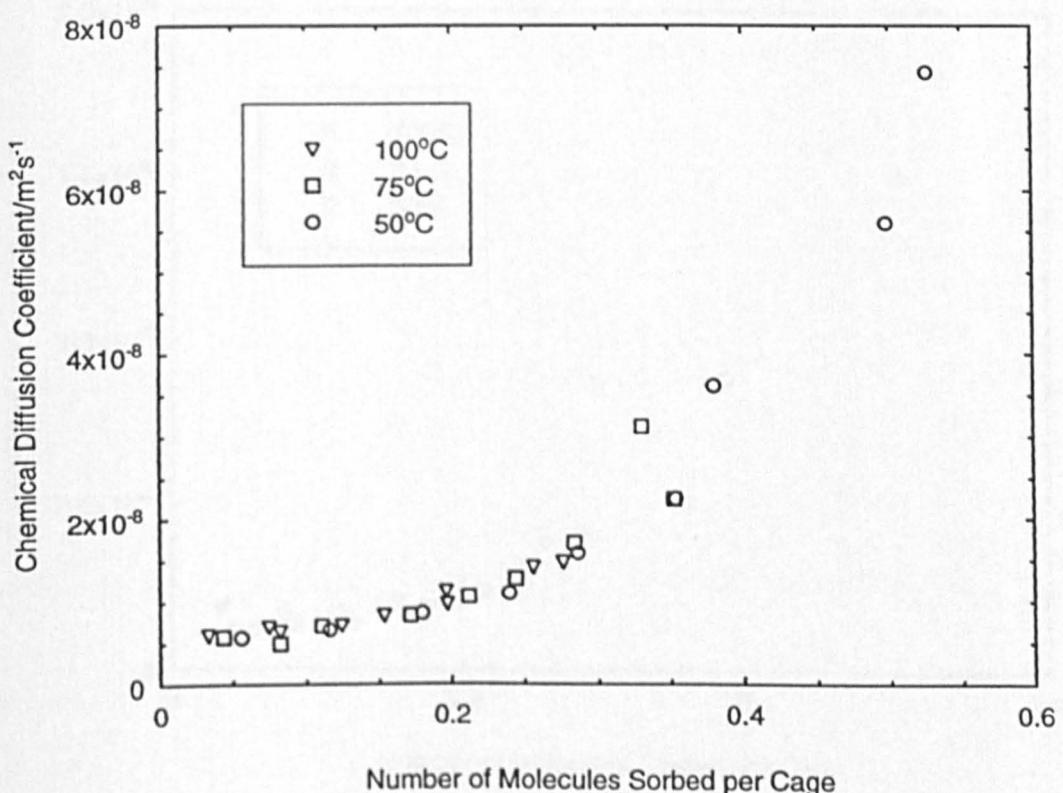


Figure 5.4 Simulated desorption chemical diffusion coefficient: run A

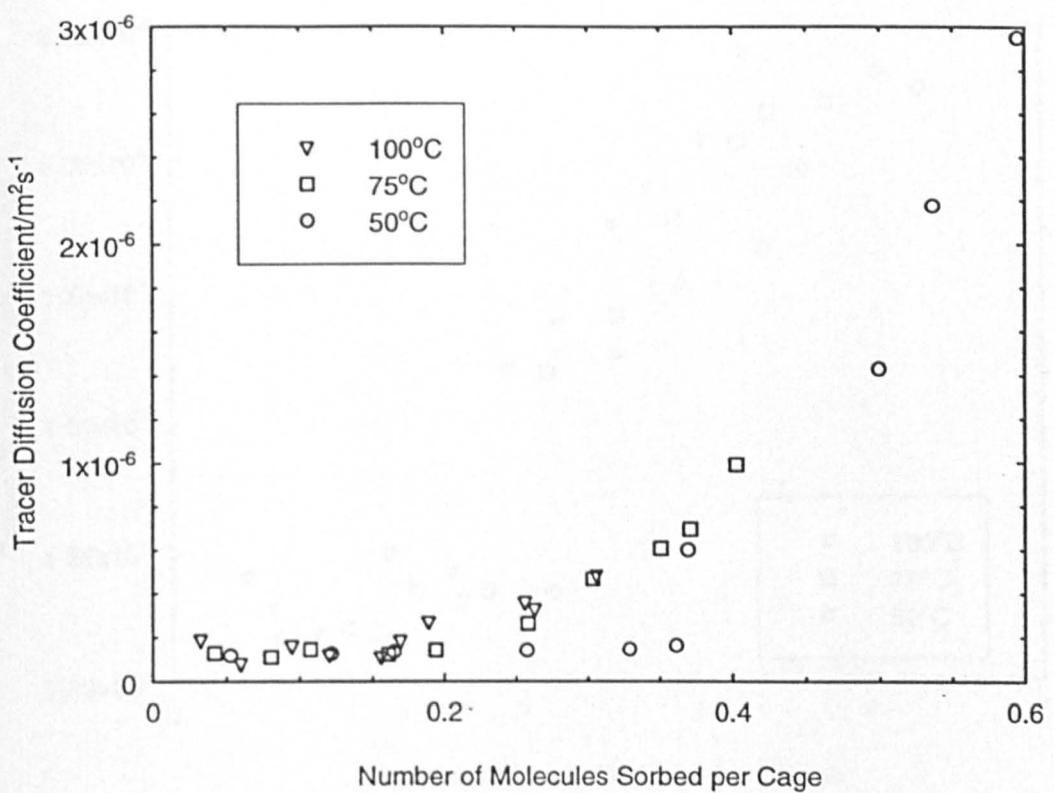


Figure 5.5 Simulated adsorption tracer diffusion coefficient: run A

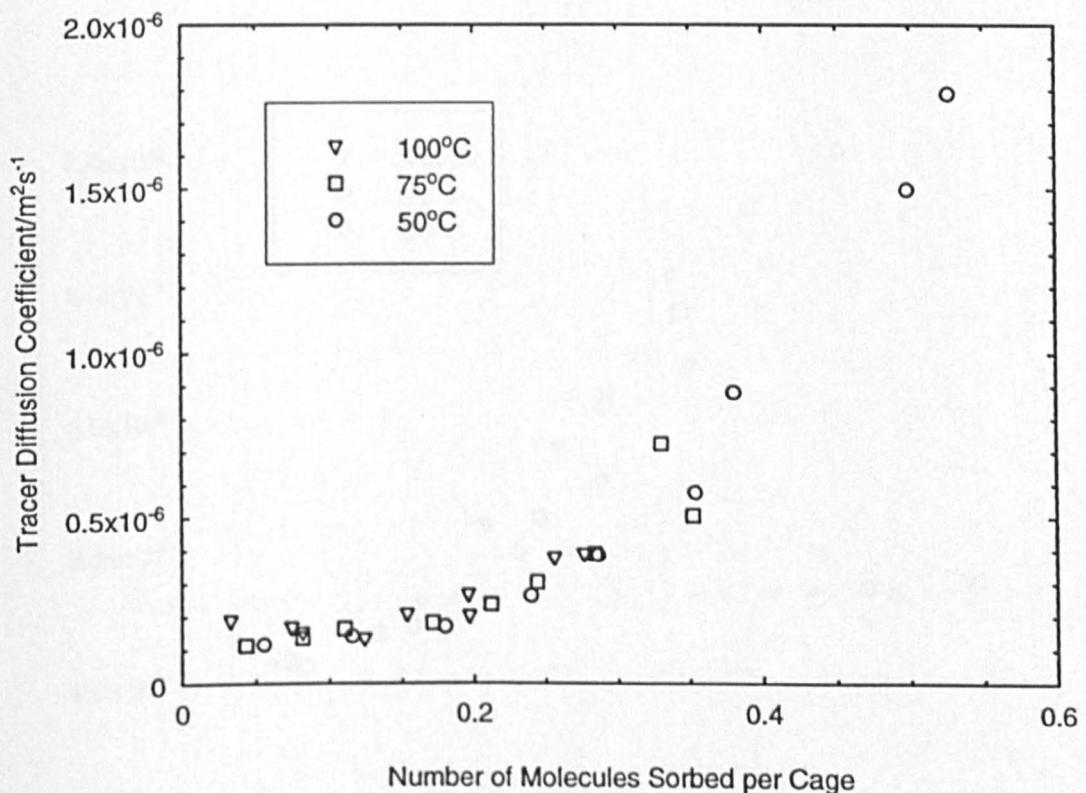


Figure 5.6 Simulated desorption tracer diffusion coefficient: run A

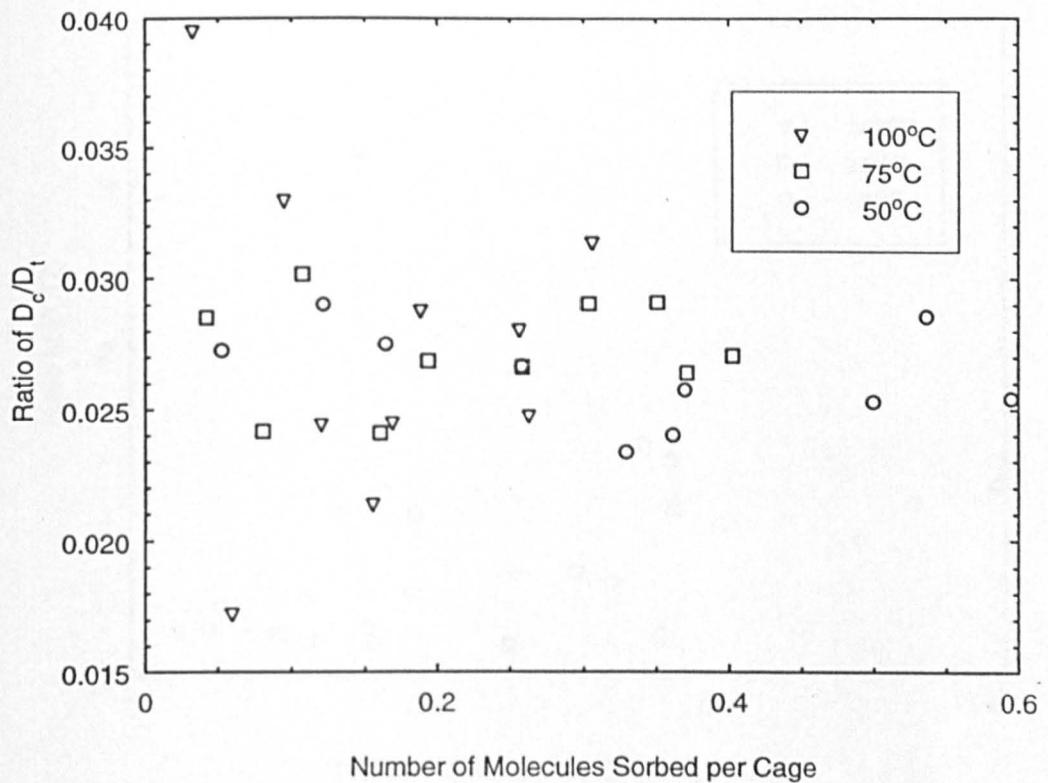


Figure 5.7 Simulated adsorption tracer correlation factor: run A

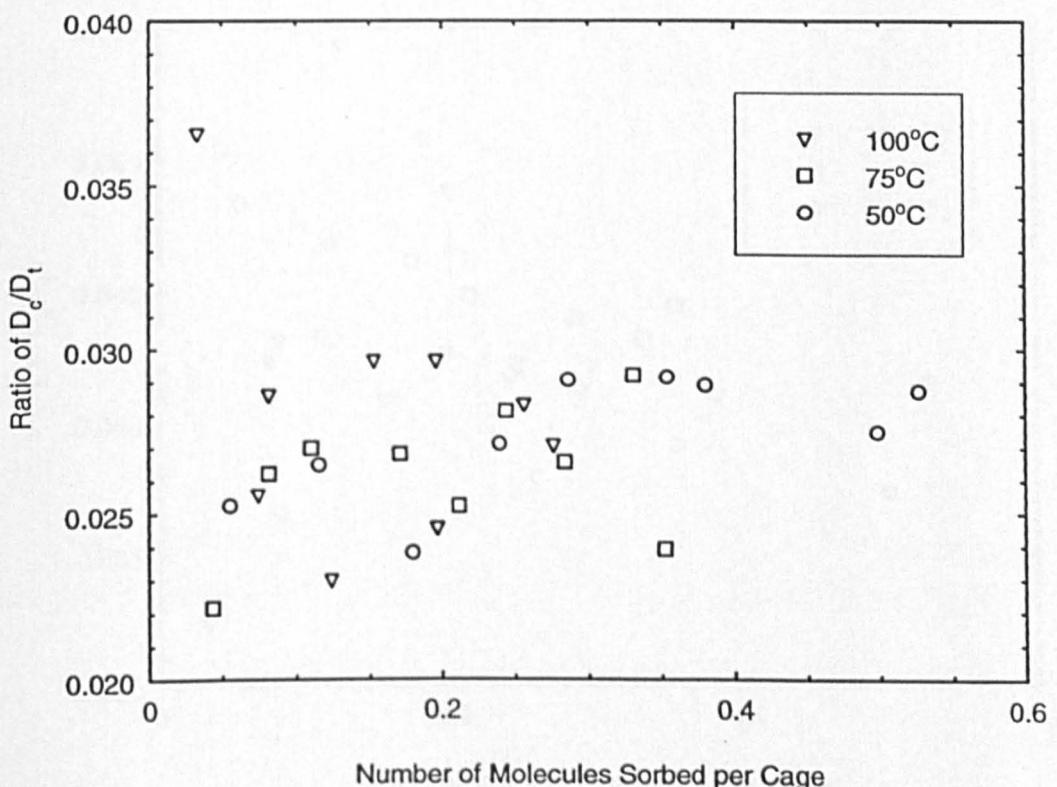


Figure 5.8 Simulated desorption tracer correlation factor: run A

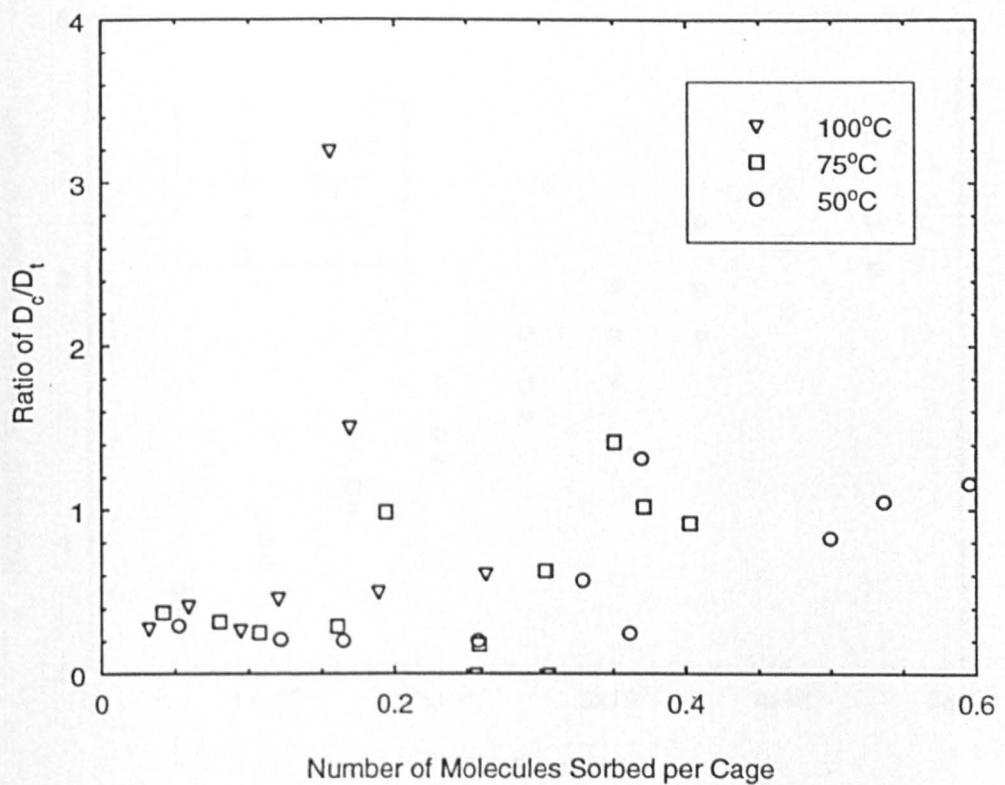


Figure 5.9 Simulated adsorption D_c/D_t ratio: run A

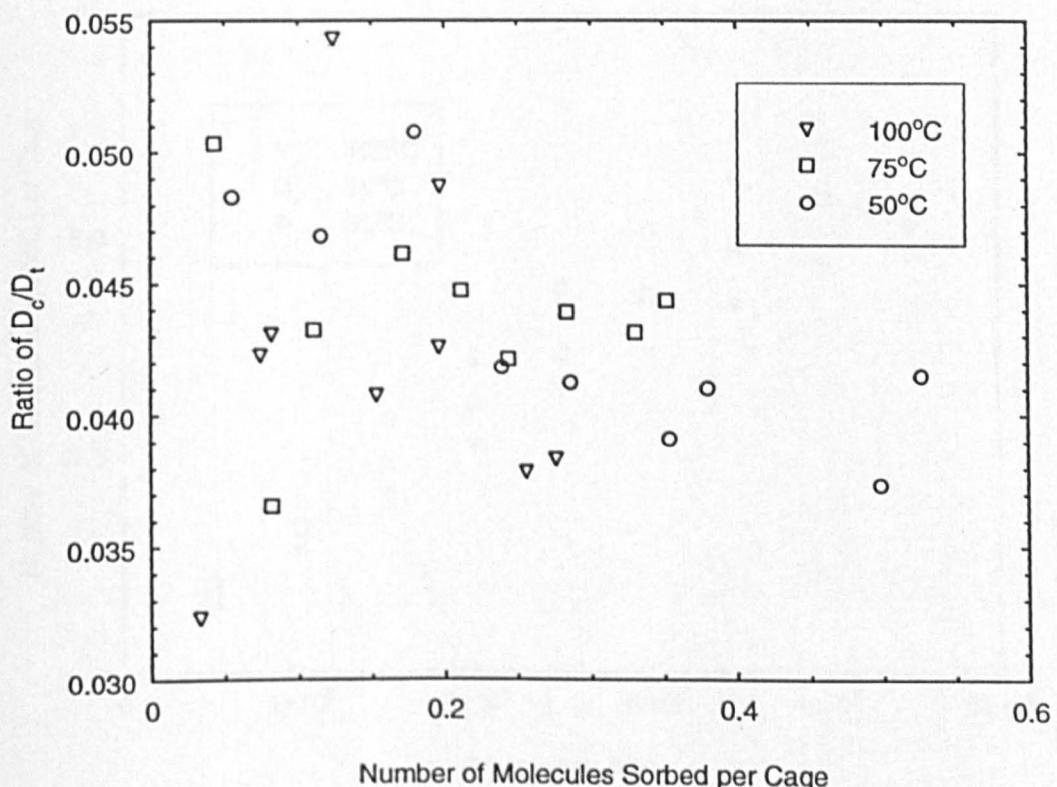


Figure 5.10 Simulated desorption D_c/D_t ratio: run A

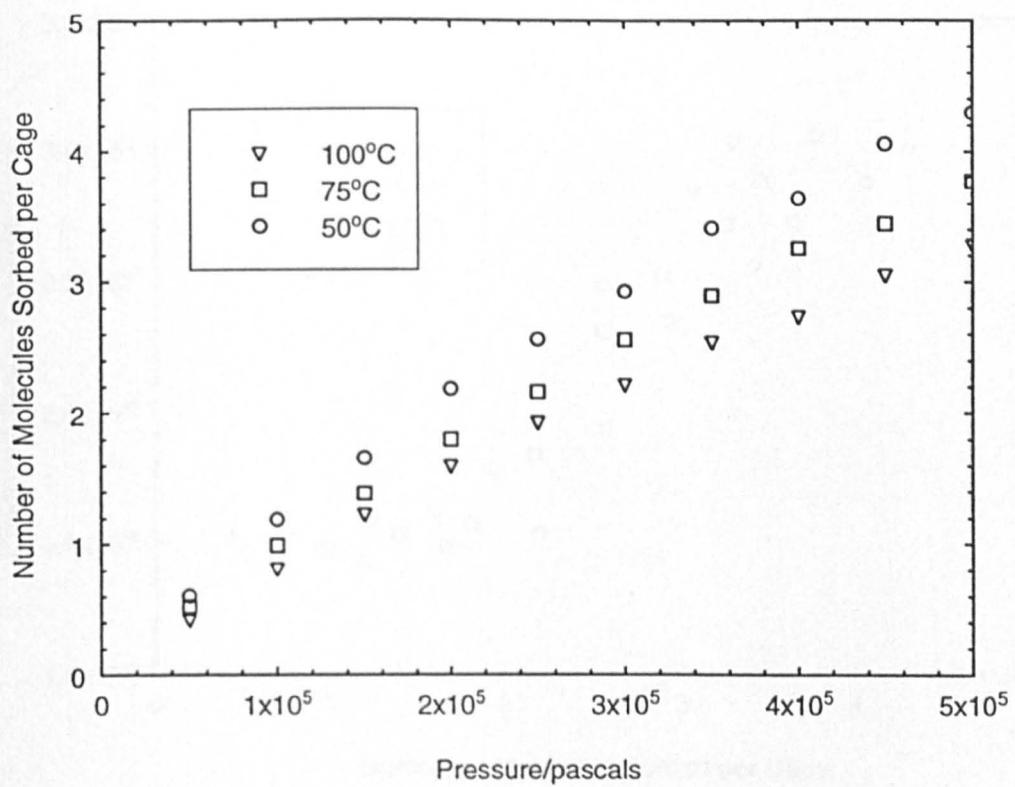


Figure 5.11 Simulated adsorption isotherm: run B

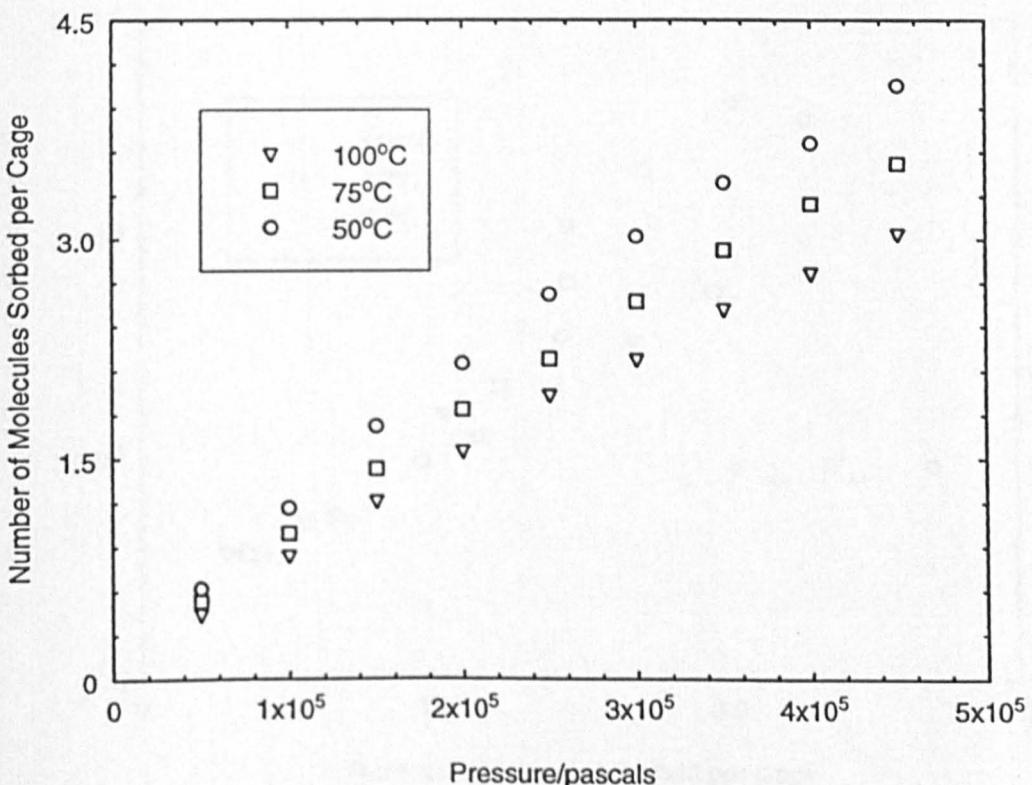


Figure 5.12 Simulated desorption isotherm: run B

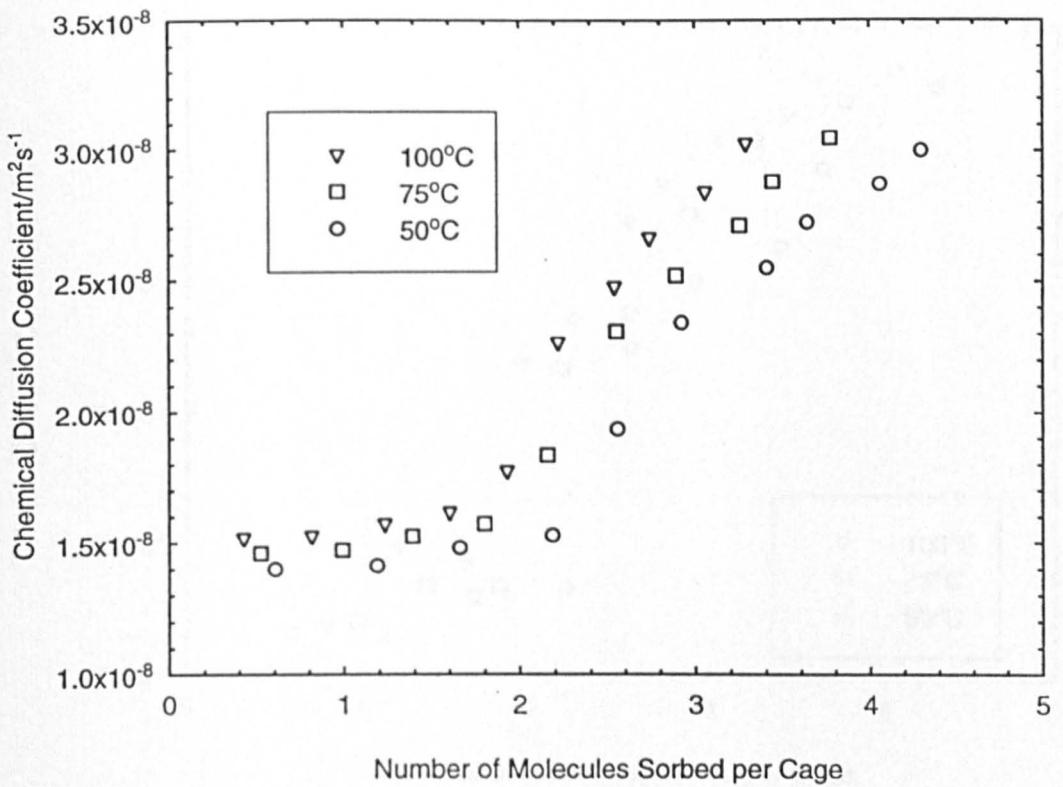


Figure 5.13 Simulated adsorption chemical diffusion coefficient: run B

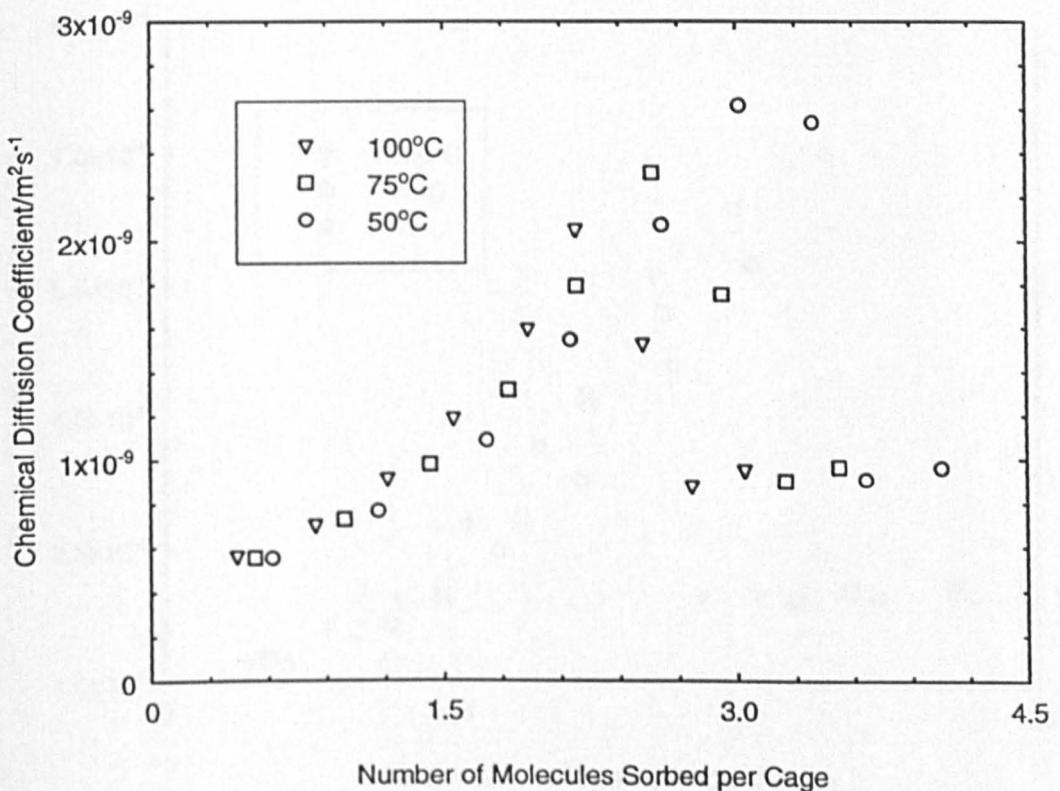


Figure 5.14 Simulated desorption chemical diffusion coefficient: run B

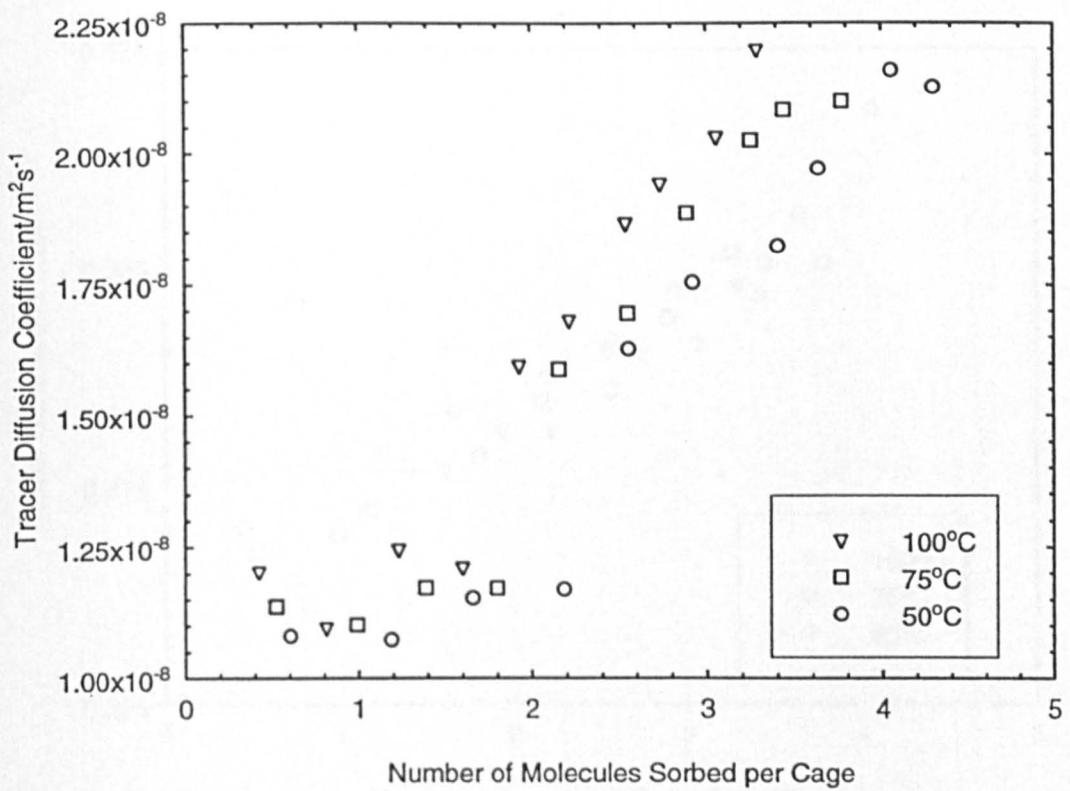


Figure 5.15 Simulated adsorption tracer diffusion coefficient: run B

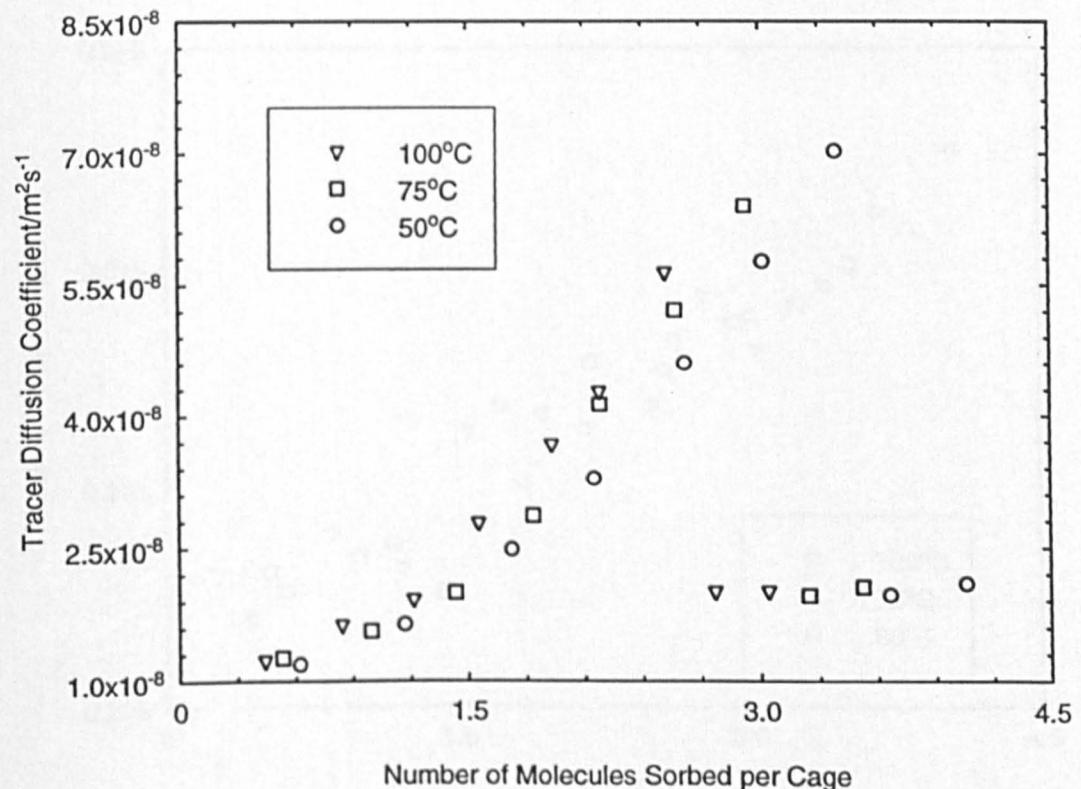


Figure 5.16 Simulated desorption tracer diffusion coefficient: run B

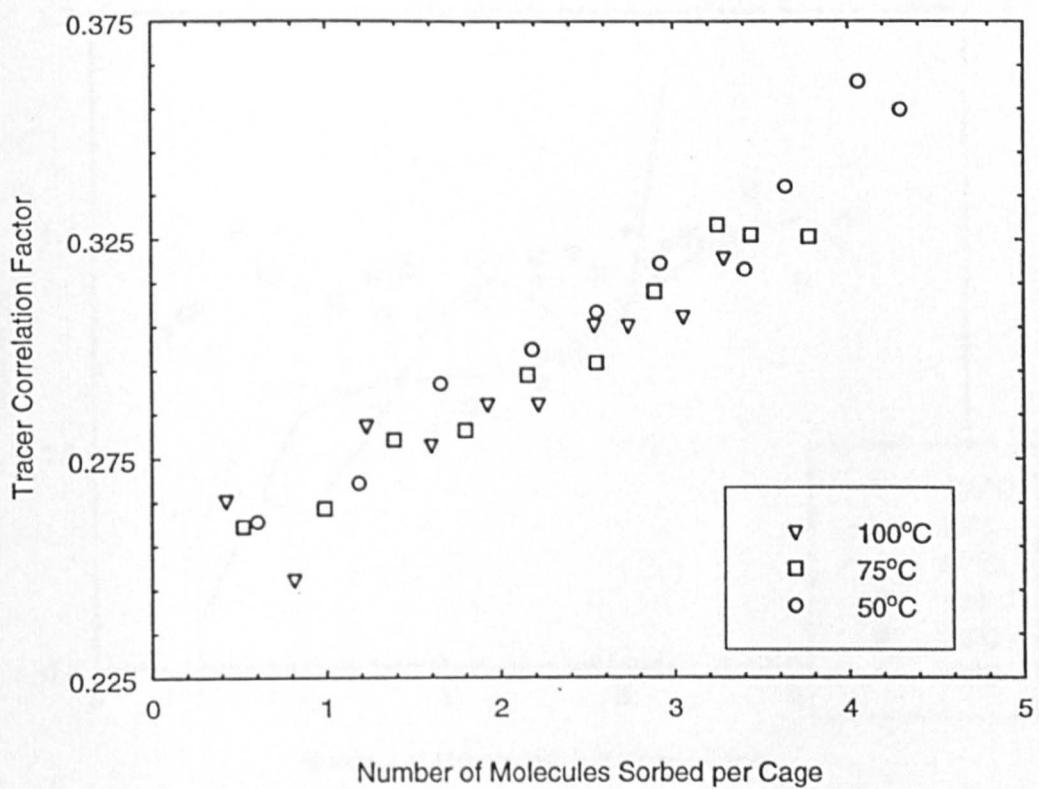


Figure 5.17 Simulated adsorption tracer correlation factor: run B

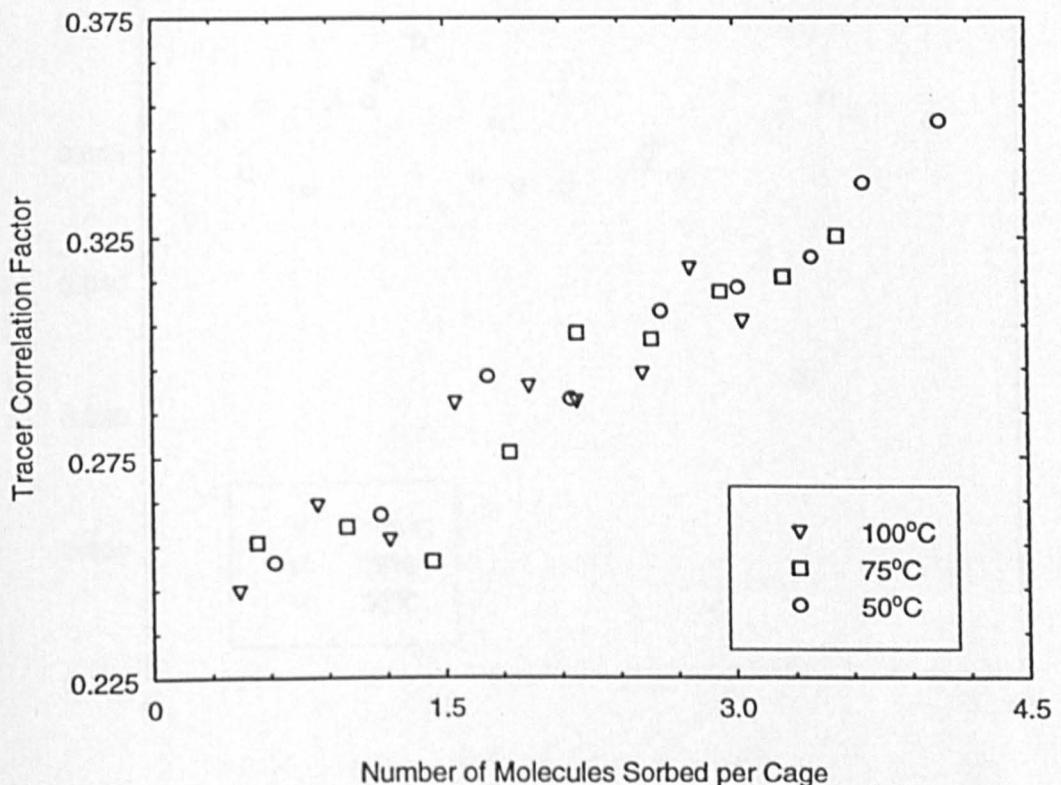


Figure 5.18 Simulated desorption tracer correlation factor: run B

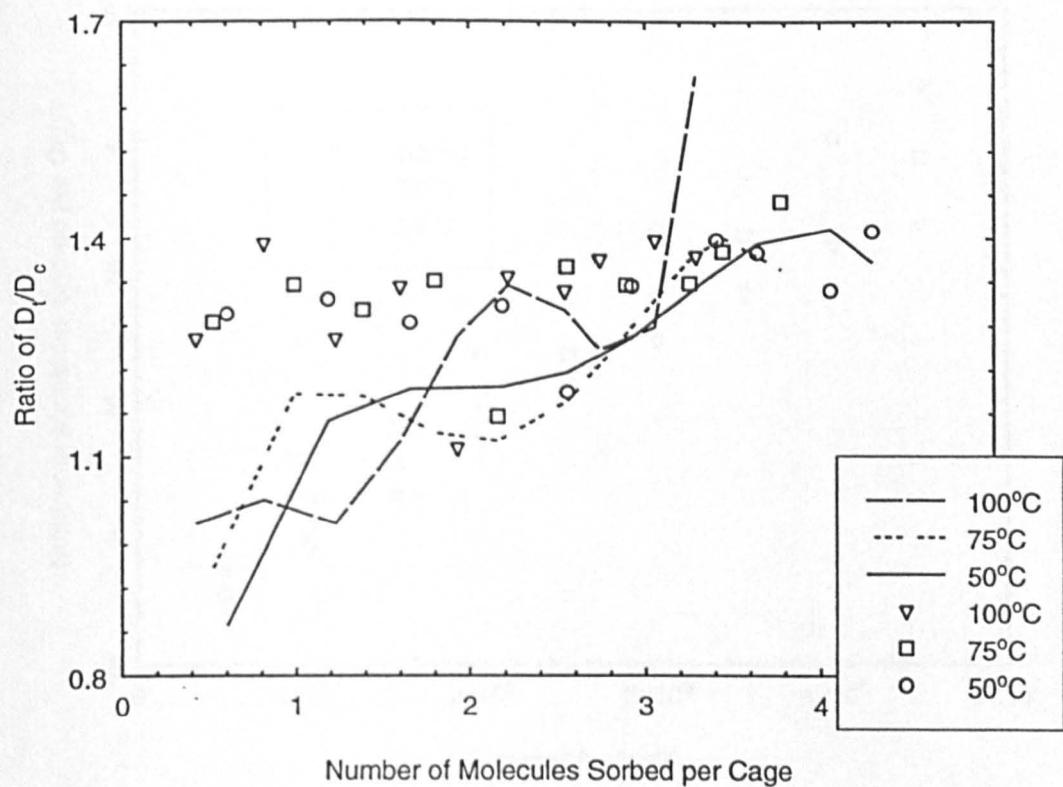


Figure 5.19 Simulated adsorption D_c/D_t ratio: run B

Lines show D_c/D_t ratio derived from simulated isotherms

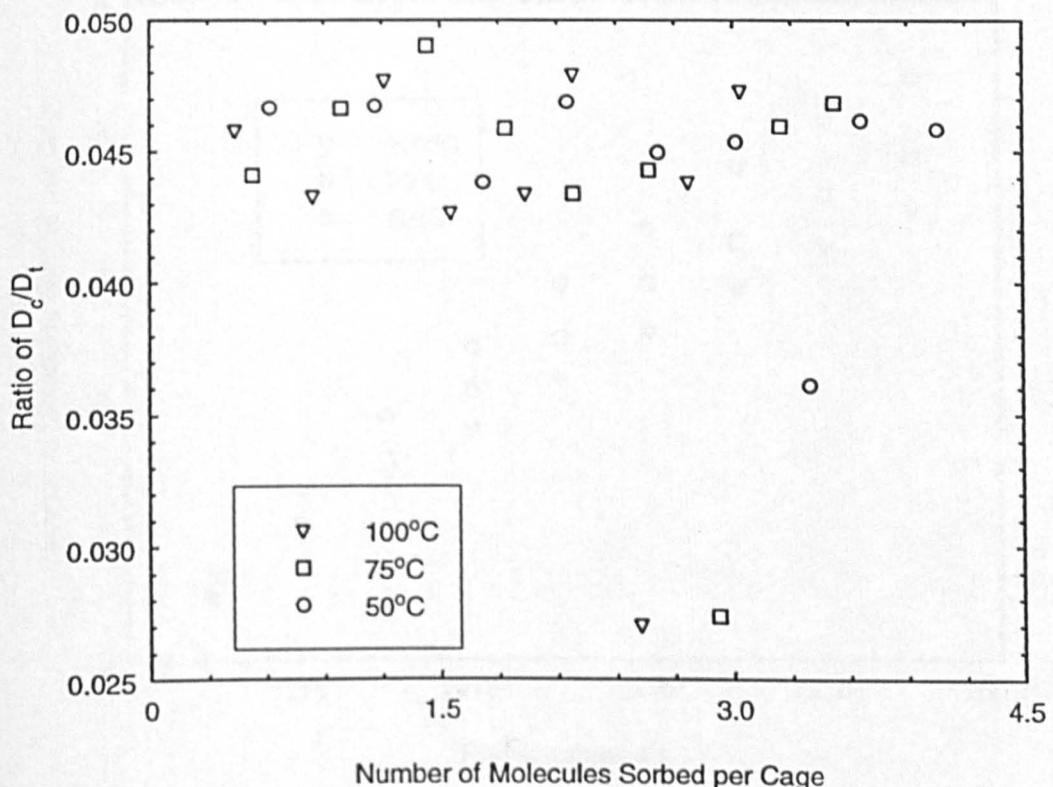


Figure 5.20 Simulated desorption D_c/D_t ratio: run B

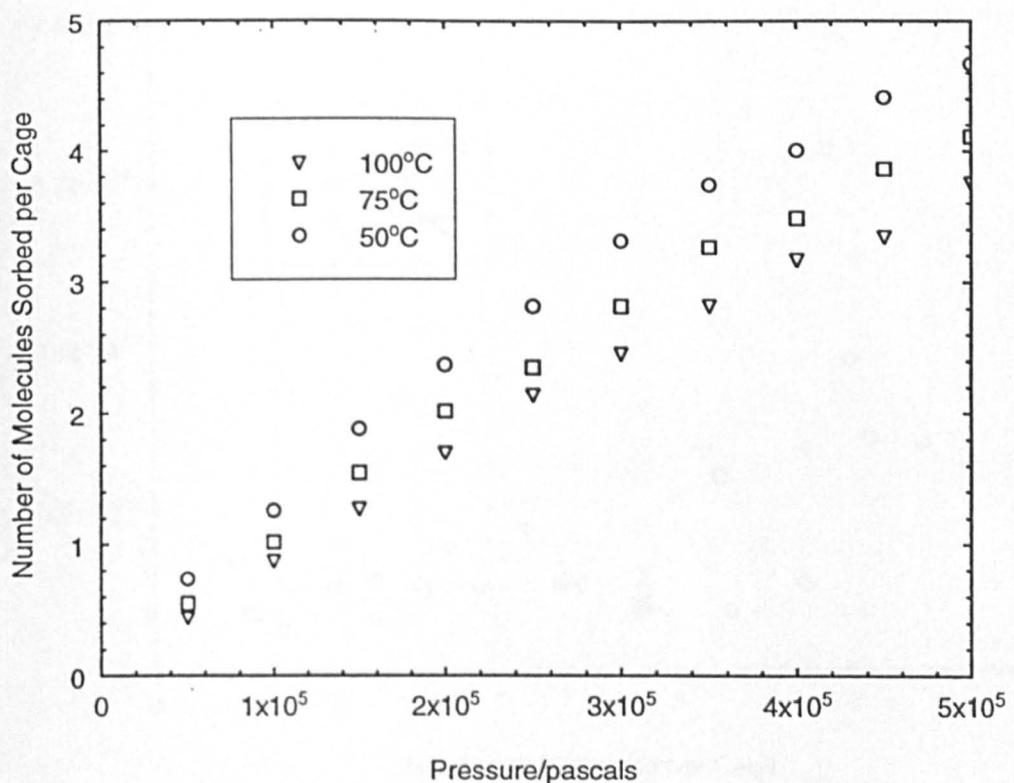


Figure 5.21 Simulated adsorption isotherm: run C

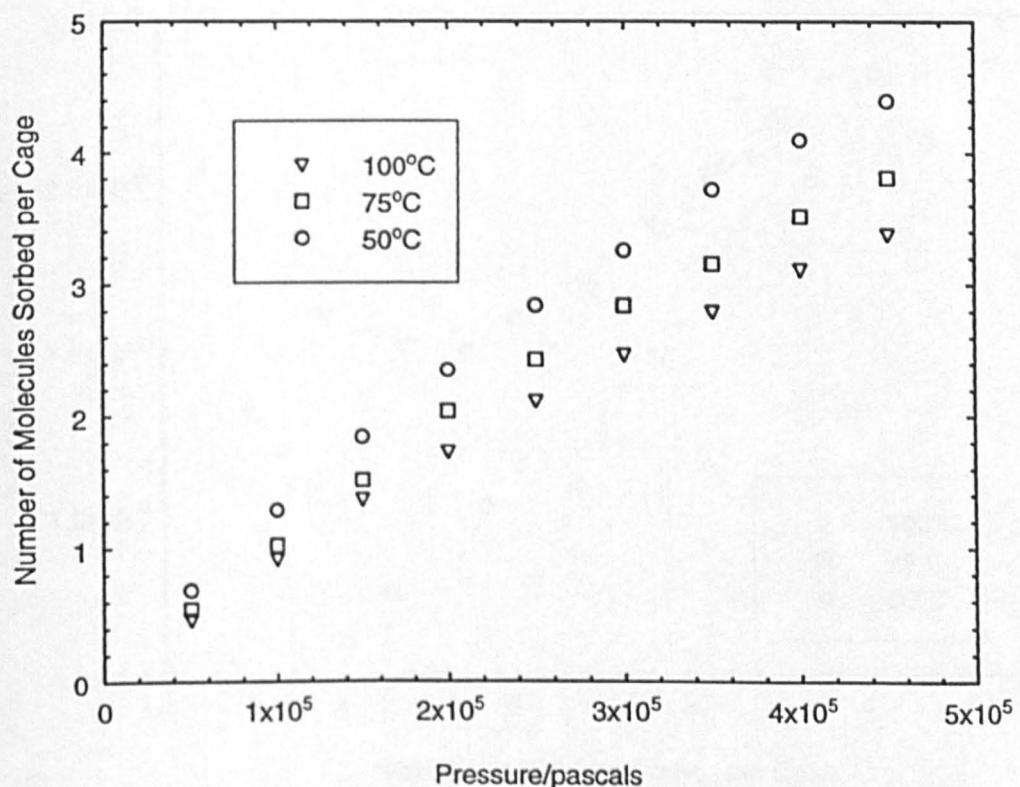


Figure 5.22 Simulated desorption isotherm: run C

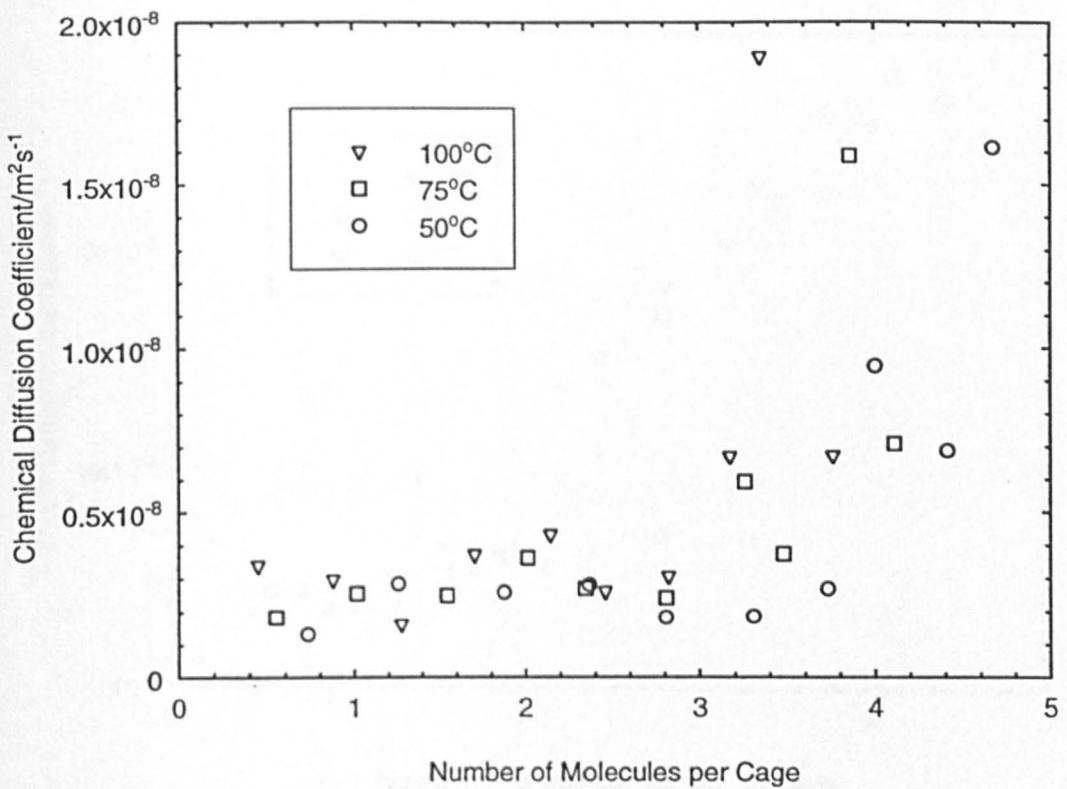


Figure 5.23 Simulated adsorption chemical diffusion coefficient: run C

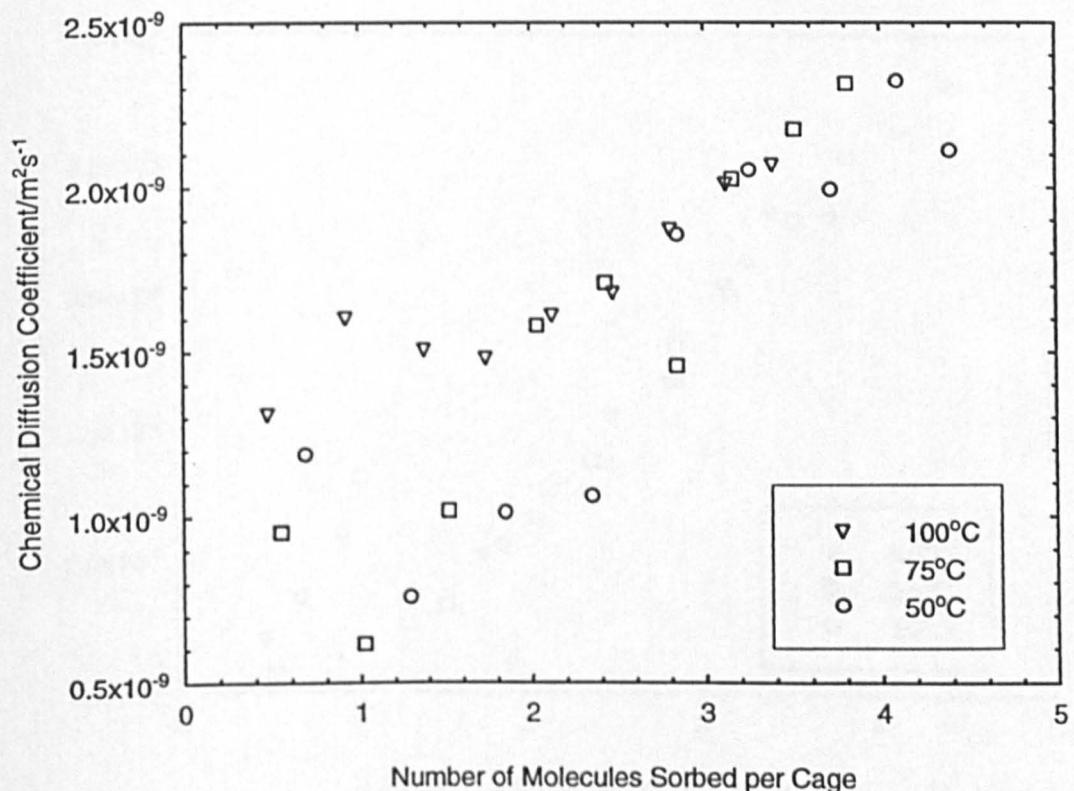


Figure 5.24 Simulated desorption chemical diffusion coefficient: run C

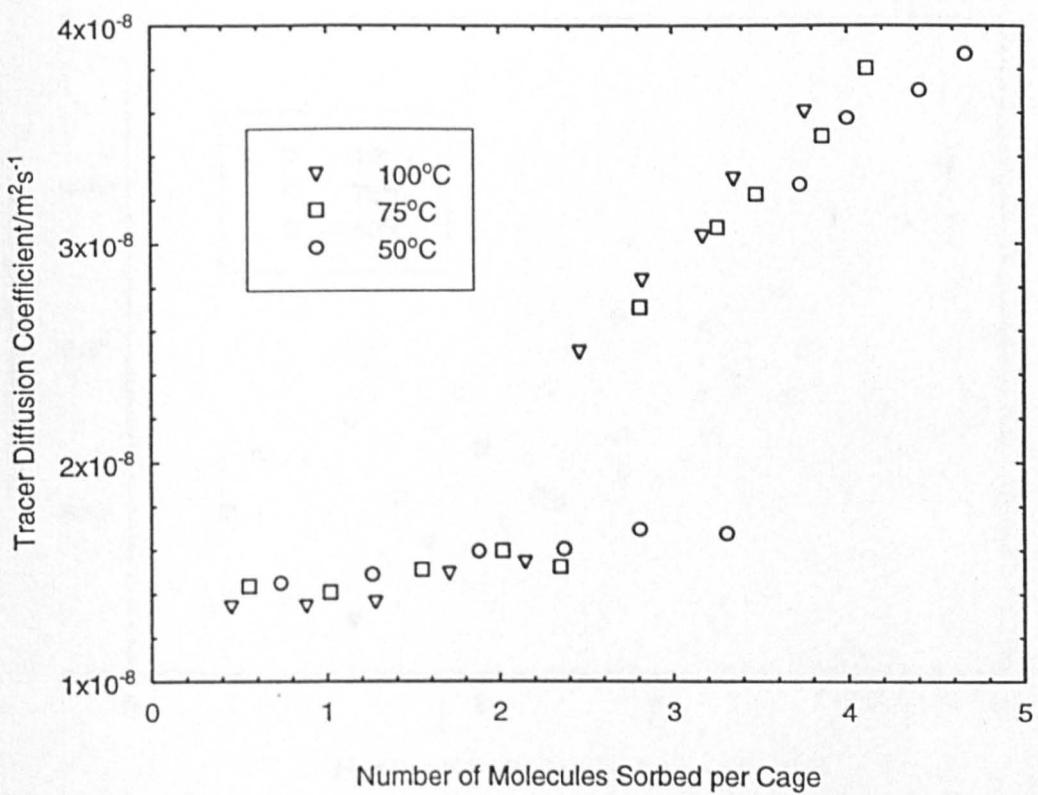


Figure 5.25 Simulated adsorption tracer diffusion coefficient: run C

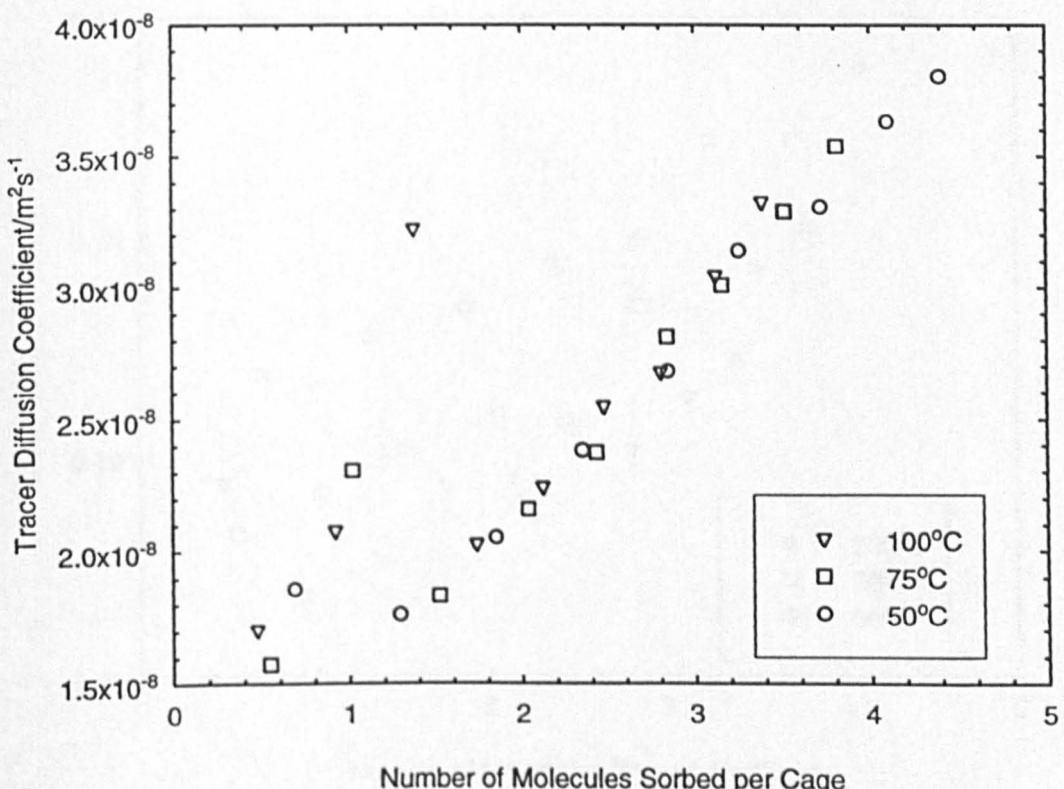


Figure 5.26 Simulated desorption tracer diffusion coefficient: run C

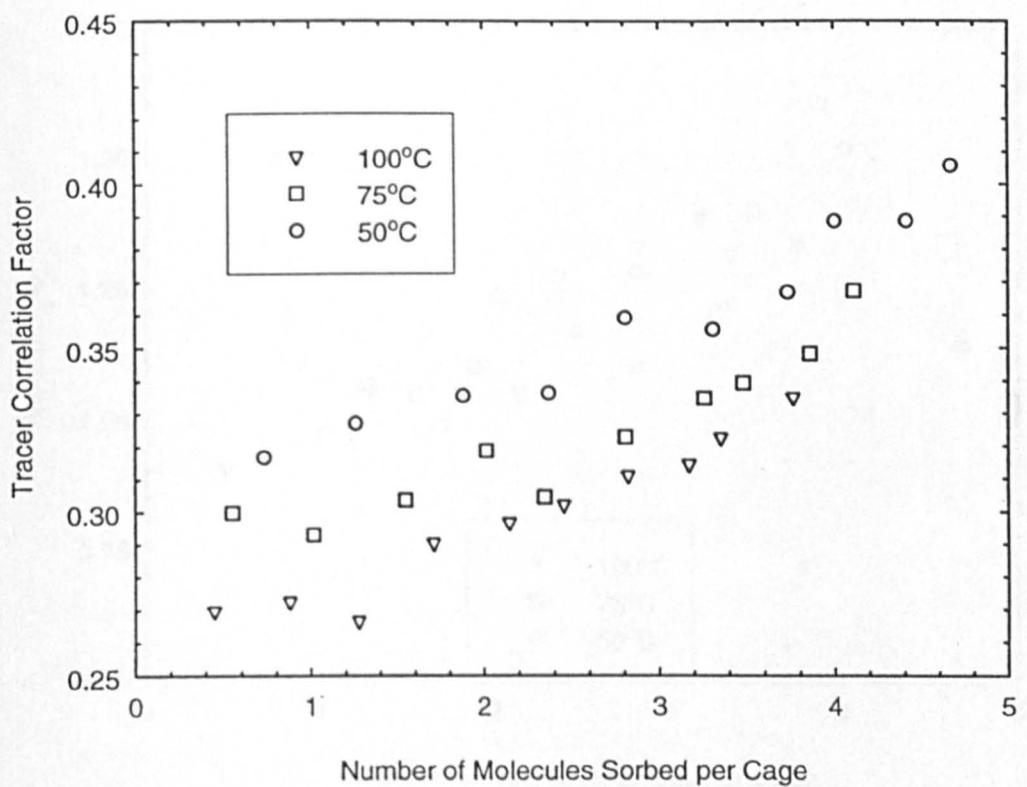


Figure 5.27 Simulated adsorption tracer correlation factor: run C

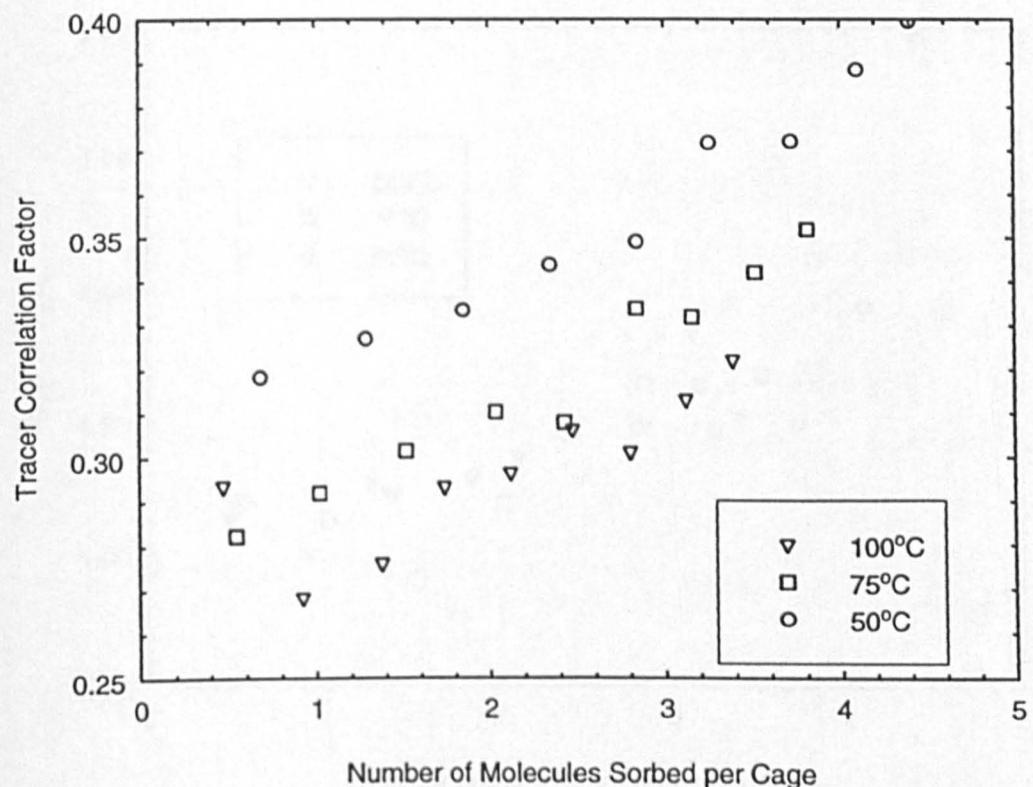


Figure 5.28 Simulated desorption tracer correlation factor: run C

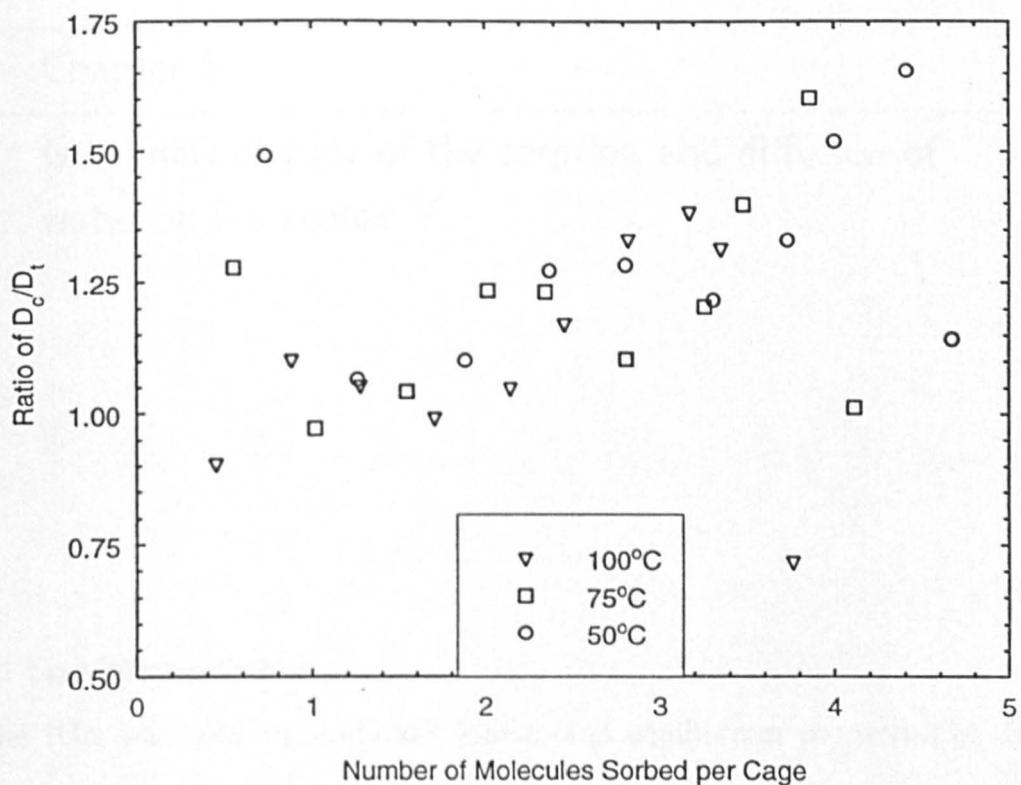


Figure 5.29 Simulated adsorption D_c/D_t ratio: run C

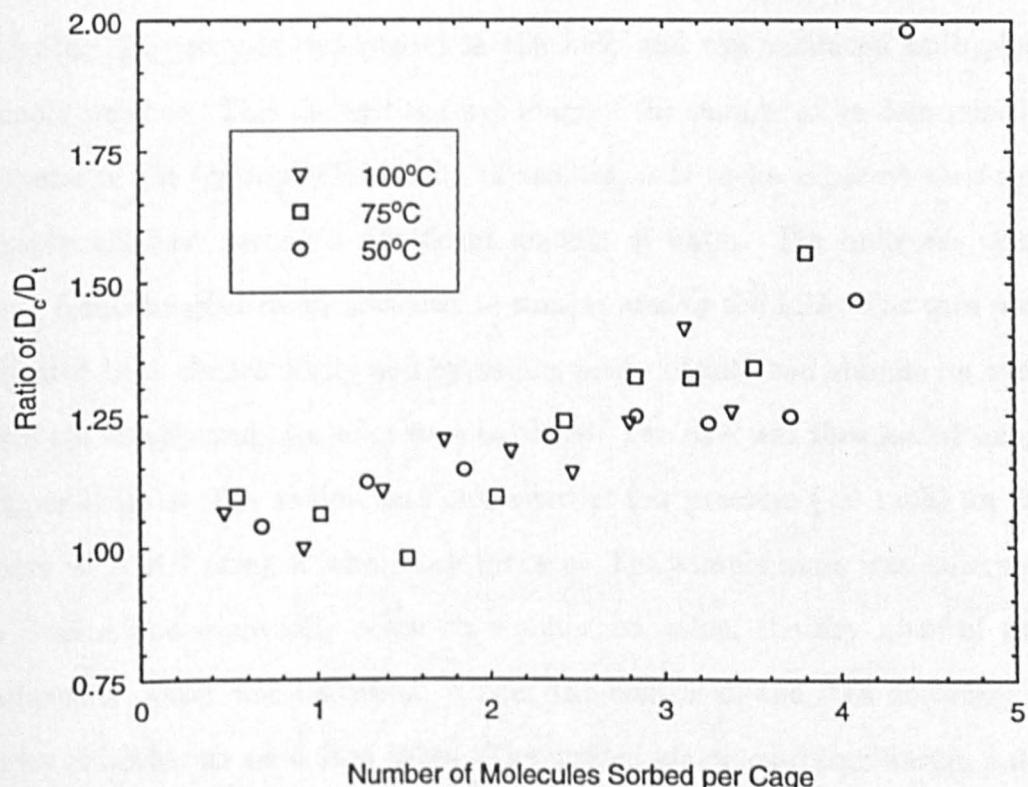


Figure 5.30 Simulated desorption D_c/D_t ratio: run C