

Types of Dependence of Self-Diffusivity on Sorbate Concentration in Parameter Space: A Two-Dimensional Lattice Gas Study[†]

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The various factors that influence the dependence of self-diffusivity D on sorbate concentration c has been investigated by means of lattice gas model. Among the parameters varied are the activation energy, the temperature, the number of adsorption sites, and the pattern of adsorption sites. It is shown that the five types of D vs c dependence observed by Kärger and Pfeifer based on the PFG-NMR experiments on a variety of guest–zeolite systems can be understood in terms of the variation of just a few parameters. A self-diffusivity type diagram showing under what conditions a given type is found has been constructed. It is shown that even the approximate lattice gas treatment can reasonably predict the D vs c behavior of a number of guest–zeolite systems besides giving insight into why a particular behavior is observed.

1. Introduction

During the past few years several aspects of diffusion in zeolites have been investigated by a number of groups. Theodorou and co-workers^{1,2} have investigated the anisotropic diffusion of both monatomic and polyatomic systems through silicalite. Demontis and co-workers^{3,4} as well as Brickmann and co-workers^{5,6} have investigated the role of framework motion on the diffusion of simple monatomic species. Kärger and co-workers⁷ have studied several aspects of diffusion in zeolites. More recently Auerbach and co-workers^{8,9} have attempted to understand diffusion, in particular, of benzene in faujasite as a series of hops between different adsorption sites. They have used Kinetic Monte Carlo to study diffusion. van Santen and co-workers¹⁰ have attempted to understand the catalytic nature of zeolites by studying the intermediates that are formed during a reaction. Sauer and co-workers^{11,12} have investigated the possible reaction mechanisms that take place within a zeolite.

Normally the products formed within the zeolitic cavities have to diffuse through the void network. The product concentration within a cavity can vary from dilute limit to saturation. Even when a zeolite is used for separation of mixtures, the concentration of the different components can vary depending on the external conditions. In both these situations, self-diffusivity is an important property. It strongly influences the product profile in a reaction as well as the degree of separation of mixtures. Since the self-diffusivity depends on the sorbate concentration, it is necessary to understand the nature of the D vs c dependence as well as the factors that influence or alter the dependence. We attempt to do this in the present work.

Pulsed field gradient NMR (PFG–NMR) study by Kärger and Pfeifer¹³ of the different molecules adsorbed in various types of zeolites suggests that there exist at least five different types of dependence of the self-diffusivity D of the sorbate on its

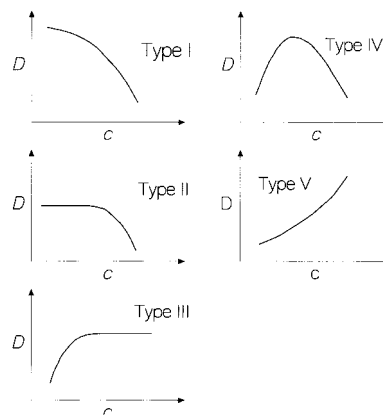


Figure 1. Different types of dependence observed by Kärger and Pfeifer¹³ in the PFG-NMR measurements of intracrystalline self diffusion coefficient D on sorbate concentration c .

concentration c . These are shown in Figure 1. The guest–host systems based on which the five distinct types of D vs c have been obtained comprise a widely differing set of guests as well as hosts. The guests include nonpolar molecules such as methane, ethane, etc., as well as highly polar species such as ammonia and water. The sizes of the guests also differ from small sized guests like water and methane to larger guests such as xylene. The host zeolites are quite different structurally, topologically and in their Si/Al ratio as well as the number of extra-framework cations: NaX, silicalite, and NaCaA.

There have been a few attempts to understand the observed D vs c behavior in terms of the microscopic details of certain models. These studies have been discussed briefly by Kärger and Ruthven.⁷ Germanus¹⁴ has carried out a detailed investigation of the effect of adsorption site (termed active site), window barrier, etc., on the D vs c behavior and was partially successful in reproducing some of the types of D vs c behavior that were observed by Kärger and Pfeifer¹³ in their PFG-NMR studies. Aust et al.¹⁵ computed the transport as well self-diffusivity within zeolite by means of two-dimensional lattice models. Their aim was to assess the influence of different model assumptions

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on the concentration dependence of the diffusivity. Theodorou and Wei studied the diffusion and reaction in zeolites such as ZSM-5 with and without blocking of pores.¹⁶

In a preliminary Monte Carlo study reported recently,¹⁷ we looked at the self-diffusivity dependence on the sorbate concentration of a two-dimensional lattice gas model with and without confinement. We investigated the role of hop length, nature, and strength of sorbate–sorbate interaction and the degree of confinement on the D vs c behavior. It was found that more than one type of D vs c behavior could be obtained by varying one or more of these factors. It was also found that (a) introduction of adsorption sites on a plain square lattice changes the pattern of D vs c at a given temperature (type I goes over to type IV), (b) the increase in hop length does not affect the type of D vs c , and finally (c) confinement when introduced does not seem to alter the D vs c behavior. However, we believe that this point needs further investigation.

Several questions still remain unanswered: (i) what are the parameters that may influence the D vs c behavior? (ii) what is the precise nature of the influence of each of these factors on D vs c behavior? (iii) After obtaining the answers to these two questions one would naturally like to know under what conditions does one obtain a particular type of D vs c behavior? In other words, the range of each of the different factors over which one would obtain a particular type of D vs c behavior.

2. Lattice Gas Model

The model consists of a two-dimensional lattice of 50×50 sites. Of the $n_{\text{total}} = 2500$ sites, some were designated “adsorption sites” with an energy of ϵ_a and others were the “normal sites” with energy ϵ_n . Note that the on-site energies for the adsorption sites are lower than the normal sites, i.e., $\epsilon_a < \epsilon_n$.

The number of adsorption sites n_{ads} used in the present study are, 50, 144, 150, 256, 313, 625, 834. A section of total lattice, viz., a 10×10 array of sites is shown in Figure 2 for all except the lattice with 150 adsorption sites which has a random arrangement of the adsorption sites. Of the remaining, lattices with 144, 256, and 625 have what may be termed as a square arrangement of adsorption sites while the others have a diagonal array of sites (see Figure 2). Except for the case of random arrangement of adsorption sites, the pattern of adsorption sites is such that no two adsorption sites are nearest neighbors on the lattice.

Calculations have been carried out at different concentrations c . Double occupation of a site is forbidden which leads to a decrease in diffusivity with c whenever the number of sorbates exceeds 1250, that is, 50% of the total number of available sites. Therefore, no calculations for concentrations higher than 50% occupancy are reported in the present study.

Nearest-neighbor (nn) sites are defined as those lattice sites nearest to a given site along the x - or the y -direction. Only interactions between particles on nearest neighbor (nn) sites have been considered. These interactions are attractive. Hopping of sorbates between nn sites only is considered.

3. Computational Details

All simulations have been carried out on a (50×50) lattice. Normal site energies were taken to be $\epsilon_n = -10$ kJ/mol and for adsorption sites the energy ϵ_a was assigned values of either -20 or -25 kJ/mol. The interaction ϵ_{ss} between particles located on nn sites is taken to be -0.5 kJ/mol. The total number of adsorbates is in the range 50–1250.

All simulations have been carried out in the canonical (NVT) ensemble using the standard Metropolis Monte Carlo importance

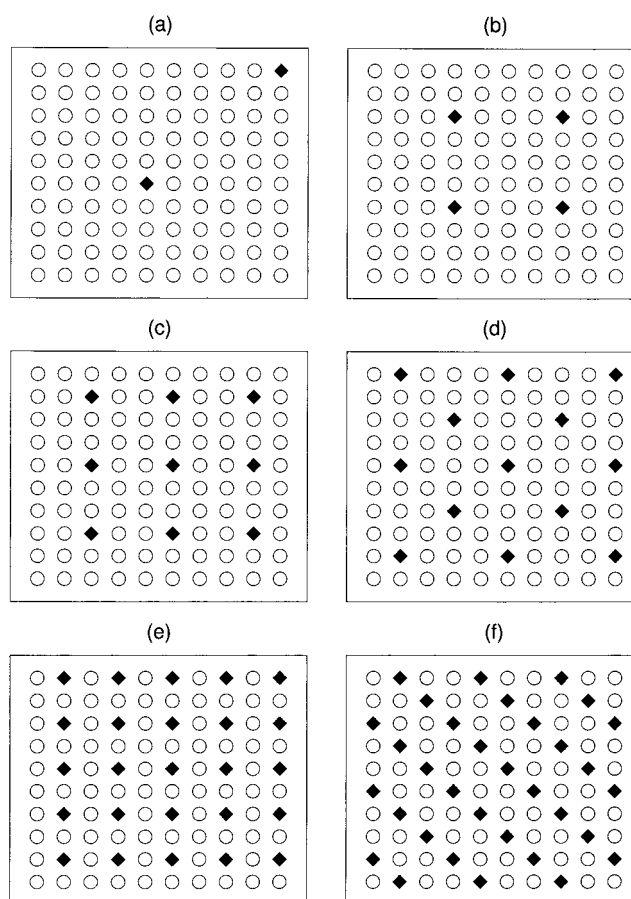


Figure 2. Five different arrangements of the adsorption sites on a 10×10 section of the lattice are shown: (a) $n_{\text{ads}} = 50$, (b) $n_{\text{ads}} = 144$, (c) $n_{\text{ads}} = 256$, (d) $n_{\text{ads}} = 313$, (e) $n_{\text{ads}} = 625$, (f) $n_{\text{ads}} = 834$. The lattice with $n_{\text{ads}} = 150$ has random arrangement of adsorption sites. Note that lattices with 144, 256, and 625 have what may be termed as square arrangement of adsorption sites while the rest have a diagonal array of adsorption sites. Open circles represent normal sites and filled diamonds represent adsorption sites.

sampling algorithm¹⁸ employing periodic boundary conditions. In the lattice gas model, the volume V is replaced by the total number of sites on the lattice. Each Monte Carlo step consists of an attempt to move each of the particles once by choosing them cyclically, in one of the four directions. The direction is chosen randomly. Probability for the hop is calculated taking into account the on-site and sorbate–sorbate interaction energies at the new and the old sites.

Whenever simulations were carried out with $\epsilon_a = -20$ kJ/mol, an equilibration phase consisting of 3000 MC steps and a production phase of 60000 MC steps was carried out. An exception is the case for $n_{\text{ads}} = 50$, $\epsilon_a = -20$ kJ/mol, where an equilibration phase of 6000 MC steps and a production phase of 120000 MC steps was carried out. For all the cases with $\epsilon_a = -25$ kJ/mol, the equilibration phase and production phases consisted of 6000 MC steps and 120000 MC steps, respectively.

The self-diffusion coefficient for the two-dimensional lattice gas model was calculated from

$$D = \frac{\langle (r(t_0 + \tau) - r(t_0))^2 \rangle}{4\tau} = \frac{\langle u^2(\tau) \rangle}{4\tau}$$

where $r(t_0)$ and $r(t_0 + \tau)$ are two positions, separated by τ MC steps. The $\langle \dots \rangle$ implies that averaging has been done over a number of time origins t_0 as well as over all the particles. The definition of the unit of time is arbitrary. We take one MC step

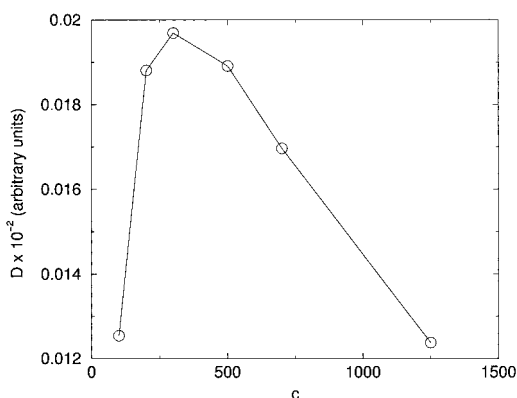


Figure 3. D vs c dependence for $n_{\text{ads}} = 144$ square arranged adsorption sites.

as representing the unit of time. MC configurations were stored every 10th MC step for a run of 60000 MC steps while MC configurations were stored every 20th MC step for a run 120000 MC steps. The mean square displacement curve was computed from these stored steps. The error in the calculated self-diffusivities were 19% and 3% for systems with $\epsilon_a = -20$ and -25 kJ/mol respectively. These estimates were obtained from MC runs of the duration same as above and for a lattice with 50 adsorption sites.

4. Results and Discussion

Fairly large number of runs were made under different conditions. Usually, a particular parameter was varied over a range of values. The parameters that were so varied are (i) the temperature T , (ii) the adsorption site energy ϵ_a , and (iii) the number of adsorption sites n_{ads} . Along with these the pattern of adsorption sites was also varied in order to see its effect on D vs c behavior.

4.1. Variation of the Pattern of Adsorption Sites. In the previous study¹⁷ we found that the introduction of adsorption sites on a plain lattice with only normal sites, resulted in type I behavior going over to type IV behavior. It is, however, possible to arrange the adsorption sites in different patterns. The D vs c behavior of at least three different patterns were specifically examined in the previous study¹⁷: square, clustered, and chessboard. The D vs c behavior for these three patterns of adsorption sites were, however, obtained under differing conditions and no conclusions of the effect of these patterns on the D vs c behavior could be made. Here we report D at different sorbate concentrations for square as well as random arrangement of adsorption sites at $T = 300$ K. The number of adsorption sites are 144 and 150 for square and random arrangement, respectively. Figures 3 and 4 show the D vs c curves for square and random pattern of sites. It is seen that both are of type IV. In the previous work¹⁷ the D vs c curve for 150 adsorption sites with clustered arrangement of adsorption sites also showed type IV behavior. We do not discuss the chessboard pattern since in this case when double hops are introduced, (see ref 17) the sorbate can diffuse without occupation of normal sites. *It therefore seems that the nature of D vs c , in general, remains the same for different arrangements of adsorption sites.*

4.2. Variation of Temperature. Figure 5 shows the effect of variation of temperature on a lattice consisting of 256 square arranged adsorption sites with $\epsilon_a = -20$ kJ/mol. It is seen that, at 2500 K, the D vs c behavior is of type I. Lowering the temperature to 460 K leads to a type II behavior. It can also be seen that, at $T = 600$ K, an intermediate behavior is seen. Thus, the behavior seen seems to continuously vary between one type

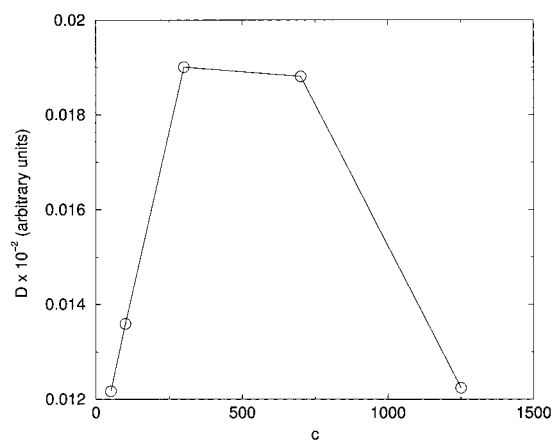


Figure 4. D vs c dependence for $n_{\text{ads}} = 150$ random arranged adsorption sites.

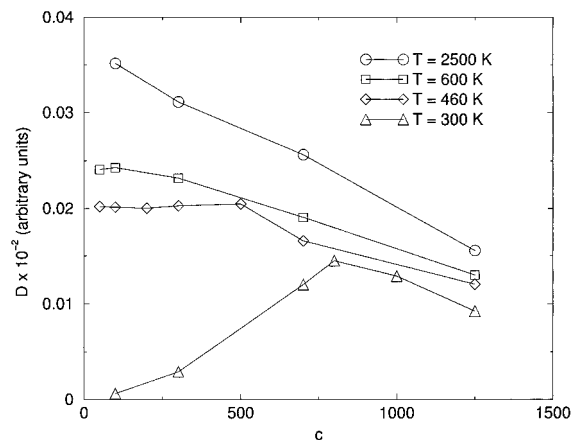


Figure 5. D vs c dependence for $n_{\text{ads}} = 256$ square arranged adsorption sites at temperatures $T = 300, 460, 600, 2500$ K.

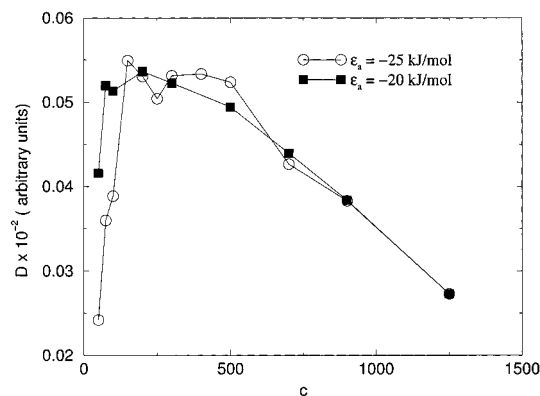


Figure 6. D vs c dependence for $n_{\text{ads}} = 50$ adsorption sites at temperature $T = 300$ K with $\epsilon_a = -20, -25$ kJ/mol.

of behavior to another depending on the temperature. Further lowering the temperature to 300 K leads to a type IV behavior (see Figure 5). Thus, variation in temperature can lead to at least three different types of behavior: I, II, and IV.

4.3. Variation of Adsorption Site Energy. Calculations were carried out with two different energies for the adsorption site, viz., -20 and -25 kJ/mol. The D vs c curves for these are presented in Figure 6 for 50 adsorption sites. It is seen that for 50 adsorption sites at 300 K, a type IV behavior is seen for both $\epsilon_a = -20$ and -25 kJ/mol. However, the range over which the magnitude of D increases is much larger for $\epsilon_a = -25$ kJ/mol. $D \times 10^{-2}$ is seen to increase between 0.04 and 0.055 for $\epsilon_a = -20$ kJ/mol while it increases between 0.025 and 0.055

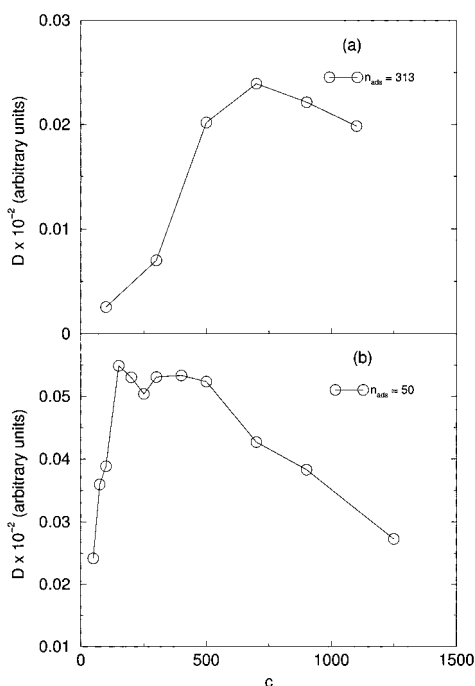


Figure 7. D vs c dependence with $\epsilon_a = -25$ kJ/mol $T = 300$ K for (a) $n_{\text{ads}} = 313$, (b) $n_{\text{ads}} = 50$.

for $\epsilon_a = -25$ kJ/mol. This suggests that a larger variation in magnitude of D is possible when ϵ_a is lower or $|\epsilon_a|$ is larger.

We would like to point out that D vs c curve for the lattice with $n_{\text{ads}} = 50$ and $\epsilon_a = -25$ kJ/mol has an extended region ($200 < c < 500$) over which D is nearly constant. In the case when the data on D is available only up to $c = 500$, the resulting D vs c curve would be one with an initial increase followed by a plateau. This would be then type III behavior according to classification by Kärger and Pfeifer.¹³ Thus, it appears that a type III dependence can be obtained when ϵ_a is significantly lower and c is varied considerably beyond n_{ads} but much below the value when the mean free path of the sorbate decreases due to increased c . The decrease in mean free path would lead to a decrease in D with c .

4.4. Dependence on Number of Adsorption Sites. Figure 5 has shown that at low temperatures, type IV behavior will be seen in the presence of adsorption sites. Figure 7a shows the D vs c curve for a system with $n_{\text{ads}} = 313$ and $\epsilon_a = -25$ kJ/mol at 300 K. It is seen that the D peaks around $c = 700$. Figure 7b shows a plot of the D vs c curve for a system with $n_{\text{ads}} = 50$ and $\epsilon_a = -25$ kJ/mol at 300 K. It is seen that the maximum occurs at a much lower value of c , viz., $c = 200$. The maximum in D in type IV behavior shifts toward higher values of c with increase in the number of adsorption sites. This is further confirmed by Figures 8a–c which show the variation of D with c for lattices with three different number of adsorption sites, viz., $n_{\text{ads}} = 50$, 256, and 625 with $\epsilon_a = -20$ kJ/mol. It is seen that the maximum shifts from $c = 200$ to 750 to 900.

This shows that when type IV behavior is seen, the maximum in the D vs c curve can be indicative of the number of adsorption sites in the system. This also suggests that if the system consists of a large number of adsorption sites, greater than the highest concentration at which D has been obtained (but below the concentration at which D decreases with c due to crowding)—either from experiment or theory or calculation—then one would observe a type V behavior: that of monotonic increase in D with c .

4.5. Other Factors and Types of D vs c Behavior. The D vs c curve for simulations with $\epsilon_a = -25$ kJ/mol at $T = 300$ K

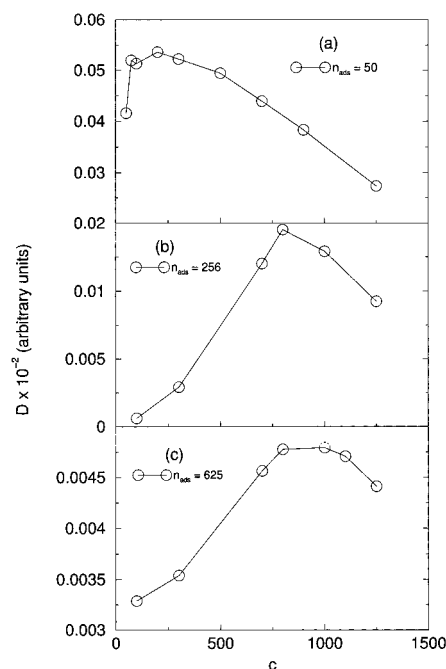


Figure 8. D vs c dependence with $\epsilon_a = -20$ kJ/mol $T = 300$ K for (a) $n_{\text{ads}} = 50$, (b) $n_{\text{ads}} = 256$, (c) $n_{\text{ads}} = 625$.

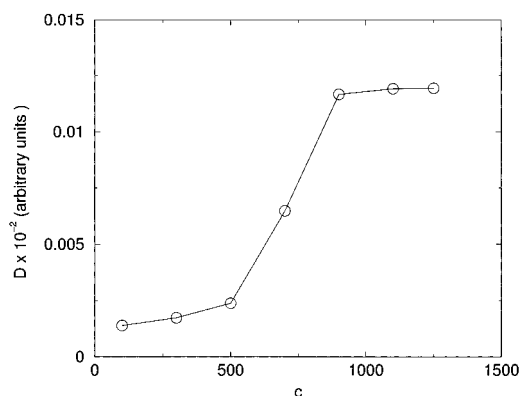


Figure 9. D vs c dependence with $\epsilon_a = -25$ kJ/mol $T = 300$ K for $n_{\text{ads}} = 625$.

and $n_{\text{ads}} = 625$ is shown in Figure 9. It is seen that the curve is initially flat and then D is seen to increase with c , but later again is flat. This type of behavior has not been observed in the PFG-NMR experiments on any of the systems Kärger and Pfeifer¹³ have studied. This new type of behavior, which we term as type VI, is observed when the range over which c is varied extends to either side of the number of adsorption sites and the adsorption site energy is significant; here c is varied between 100 and 1200 whereas $n_{\text{ads}} = 625$. This yields another important insight into the relationship between the D vs c curve and the number of adsorption sites n_{ads} : an increase in D with c occurs when c is in the vicinity of n_{ads} or when $|\epsilon_a|/RT$ is large.

5. Conclusions

The above results are summarized in Table 1. We have seen that the type of D vs c behavior is altered when the temperature is varied. Similar changes in the D vs c behavior may be seen when we vary the activation energy which is the difference between the energy of the normal site and the adsorption site: $\Delta E_a = \epsilon_n - \epsilon_a$. The dimensionless quantity that is of relevance here is $\Delta E_a/RT$ where R is the gas constant and ΔE_a is expressed

TABLE 1: Summary of Results from Two-Dimensional Lattice Gas Model with $\epsilon_n = -10$ kJ/mol, $\epsilon_{ss} = -0.5$ kJ/mol, $n_{\text{total}} = 2500$

ϵ_a (kJ/mol)	n_{ads}	temperature (K)	type of D vs c
-20	144	300	IV
-20	150	300	IV
-20	256	300	IV
-20	256	460	II
-20	256	600	I
-20	256	2500	I
-20	625	300	V
-20	625	460	I
-20	625	600	I
-20	50	300	IV
-20	50	460	I
-20	50	600	I
-25	50	300	III
-25	313	300	IV
-25	625	300	VI
-25	834	300	V

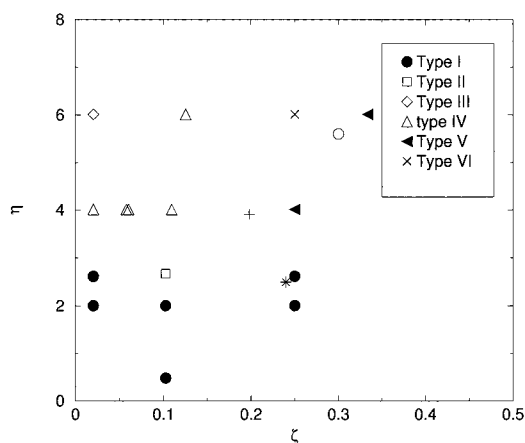


Figure 10. Diffusivity type diagram. Here the * denotes the parameters for methane in NaX. +, ○ denote parameters for ethane in NaX and NaCaA respectively.

in kJ/mol. The other dimensionless factor that alters the D vs c behavior is seen to be $n_{\text{ads}}/n_{\text{total}}$. It is possible to obtain a “diffusivity type diagram” akin to a phase diagram. Here different types of D vs c behavior (instead of different phases) is observed for different sets of values of these parameters. Figure 10 shows such a diagram where the axes are $\eta = \Delta E_a / RT$ and $\zeta = n_{\text{ads}}/n_{\text{total}}$. The various points are those obtained from simulations reported here. We also carried out several additional runs under different conditions to obtain a little more carefully the border regions in Figure 10. These results are also listed in Table 1, but are not discussed in the previous section.

From Figure 10, it is evident that for low values of η (and irrespective of ζ) which correspond to low activation energies (or weak adsorption sites) or high temperatures there is just one type of behavior: type I. At higher values of η different types of D vs c begin to appear for different values of ζ . Type IV is observed over a reasonably wide range of ζ . Type II is found for intermediate values of ζ and η . Type IV goes over to type V at high values of ζ when η is around 4. Still higher values of η lead to type III as well as type IV behavior at low and intermediate values of ζ . Type III behavior was discussed in section 4.3. Type III is expected when $|\epsilon_a|$ is significant and n_{ads} is small. Type VI is seen at still higher values of ζ as compared to type III behavior.

We would like to see now if the observed D vs c behavior obtained from PFG-NMR measurements can be explained from Figure 10. PFG-NMR results are available on a range of guests and hosts. We will have to first obtain the values of η and ζ

and locate the corresponding point in Figure 10. In these guest–host systems n_{total} can be approximately taken to be the maximum number of guests that can be accommodated in a cage or a unit cell of zeolite structure. Earlier MD simulations of methane in NaY¹⁹ have shown that the global minimum energy is around -18 kJ/mol and the potential energy is maximum near the window which is around -12 kJ/mol. The adsorption site is seen to be located near the central four membered ring of the three four membered rings that connect two six membered rings. The tetrahedral symmetry of the cage gives rise to six such sites. Also, the adsorption isotherm calculation of Woods and Rowlinson²⁰ has shown that a cage can take up to a maximum of 7.5 methane molecules. Hence, the values of η and ζ are respectively 2.4 and 0.8. The condition that no two adsorption sites are nn puts restriction on the range of ζ for a two dimensional square lattice. But for the case of three dimensional real space the range is larger. Therefore, in the context of the zeolite Y, 0.8 can be taken as maximum possible value. For two dimensional lattice gas the maximum value that has been investigated of ζ is 0.3. Therefore, 0.8 for the three-dimensional zeolite corresponds to $0.3 \times 0.8 = 0.24$ in the two-dimensional lattice gas model. So, the values of η and ζ for two dimensional lattice gas model may be said to correspond to 2.5 and 0.24, respectively. This point (0.24, 2.5) is indicated by the “*” in Figure 10. It is evident that the predicted behavior from the diagram is also of type I. This is in agreement with the PFG-NMR data for methane in NaX¹³ zeolite which suggests type I behavior at a temperature of 300 K.

The properties of ethane in NaX and NaCaA, at temperatures of 300 and 173 K respectively, have been reported by Kärger and co-workers.¹³ PFG-NMR studies on ethane in NaX suggest an activation energy of 9.8 kJ/mol.²¹ The number of adsorption sites of ethane in NaY is found to be four from our calculations using the potential parameters of Jorgensen et al.²² The maximum number of ethane molecules a cage can accommodate is around six.¹³ Therefore, the ratio ζ is 0.66 which corresponds to $\zeta = 0.3 \times 0.66 = 0.198$ for two dimensional lattice gas. The ratio η is about 3.9. This point (0.198, 3.9) is shown in Figure 10. The point lies in the vicinity of region exhibiting type I but not exactly within it. In view of the approximations made in the lattice gas treatment the agreement obtained is not too bad. The D vs c behavior found by Kärger and Pfeifer¹³ is type I.

The PFG-NMR measurements²³ on ethane in NaCaA suggest an activation energy of 7.98 kJ/mol at low loading. Our calculations on ethane in NaCaA employing the potential parameters of Jorgensen et al.²² suggest there are six adsorption sites. The total number of ethane molecules that can be accommodated in the α -cages of NaCaA¹³ is expected to be around 6. This ratio thus is the maximum in ζ . Such a maximum in ζ really corresponds to 0.3 in the two dimensional lattice and $\eta = 5.6$. This point (0.3, 5.6) is shown in Figure 10 and is seen to be in a region with type V behavior. PFG-NMR studies¹³ also suggest a type V behavior. This behavior of ethane in NaCaA is in contrast to the type I behavior of ethane in NaX or NaY.

Benzene in faujasite has been studied in considerable detail experimentally⁷ and theoretically.^{8,24} As a result of the former we have knowledge of D vs c behavior and the latter provides the microscopic details such as ΔE_a and n_{ads} . Neutron diffraction work²⁵ as well as computer simulation studies^{8,24} suggest that there are two types of adsorption sites: the cation or C site and the window or W site. The adsorption energies in these sites are approximately -90 and -65 kJ/mol, respectively.²⁴ Eic et

al.²⁶ experimentally observed an activation energy of 25.2 kJ/mol. At $T = 373$ K,¹³ the corresponding η value is 8.12. This falls outside the range of η values studied in the present work for two dimensional lattice gas (see Figure 10). However, recently Saravanan and Auerbach⁸ have suggested that benzene in NaX and NaY can show type I, II, and IV behavior at different temperatures. This may be compared with the D vs c behavior shown in Figure 5. Here we find that for different values of η the D vs c behavior undergoes change from type I (T high) to type II to type IV (T low).

Here we have attempted to construct the diffusivity type diagram based on two-dimensional lattice gas model which is an approximation to the real guest–zeolite systems. Hence, it will not be surprising if some of the D vs c behavior obtained from PFG-NMR are not explained by diffusivity type diagram shown in Figure 10. In a real system, D is seen to decrease sharply with c when a molecule large in size such as toluene or xylene is introduced. An example of this is may be seen in Figure 4 by Kärger and Pfeifer.¹³ This is an example of type II behavior. D is seen to decrease with c even at somewhat low guest concentrations. In the two-dimensional lattice gas simulations reported here, we have not introduced any parameter which accounts for the effect of crowding arising out of large molecular size (as compared to the void volume) on the diffusivity. A dimensionless parameter such as the ratio of the molecular volume to the cavity volume should be introduced to account for this. When this is introduced within the lattice gas model, this would be a noncontinuous and discrete one in which the sorbate would occupy integral number of lattice sites. Thus, lattice gas model can account for this only in a crude way. Apart from this, there is also the possibility that there are differences in the prediction of the lattice gas model and the experimental observation simply because of the approximations involved in the lattice gas model itself.

By means of Figure 10, it is possible to predict the D vs c behavior for a given guest–host system under a given set of conditions. If the values of ΔE_a , n_{ads} and n_{total} are known either from experiment or theory, it is then possible to predict type of D vs c behavior with the help of the diffusivity type diagram provided the third parameter discussed in previous paragraph does not strongly influence the D vs c behavior.

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