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Effect of Sorbate–Zeolite Interaction on Cluster Lifetime and Size of Sorbates: Xe in NaY*

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

Molecular dynamics calculations are reported for Xe in sodium Y zeolite with varying strengths of sorbate–zeolite dispersion interaction. In the absence of any dispersion interaction between the sorbate and the zeolite, the presence of the zeolite has a purely geometrical role. Increase in the strength of the sorbate–zeolite interaction increases the monomer population and decreases the population of dimers and higher sized clusters. The lifetime of the monomers as well as dimers increases with the strength of the dispersion interaction. The observed variations in the lifetime and the population of the different sized clusters is explained in terms of the changes in the potential energy surface caused by the increase in the strength of the dispersion interaction.

Introduction

Properties of small atoms and molecules sorbed in host structures have attracted much interest in recent times (*1*). Examples of such systems in nature are clathrates, intercalation compounds, clays, and zeolites (*2, 3*). In all these systems, it is not clear what influence the presence of host has on the structure of the guest species. A number of factors, such as the structure of the host, nature of guest–host interaction, etc, are expected to influence the structure of the guest species. If the voids are strictly one dimensional, e.g., narrow channels, then the sorbates are confined to one dimension. In clays, the sorbate atoms have a two-dimensional character, since they are confined to the region between the silicate planes. In zeolites such as faujasites, the voids extend in three dimensions. The structure of guest species sorbed in faujasite has been investigated by computer simulation studies earlier by Rowlinson and co-workers (*4, 5*) and several other workers including ourselves (*6–9*). It has been found that an α-cage of faujasite can accomodate a maximum of about ten xenon atoms (*5*). What is, however, not clear from the above studies is the influence of the zeolite on the structure of the sorbate. We address this question in this work. Here we have investigated the effect of the sorbate–zeolite interaction on the lifetime and average population of the monomers, dimers, trimers, and tetramers for Xe sorbed in NaY. A molecular dynamics calculation of Xe in NaY is reported with varying strengths of xenon–zeolite dispersion interactions.

Structure of Sodium Y Zeolite

The structure of zeolite Y recently obtained from neutron diffraction by Fitch

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et al. (*9*) have been used in this study. The structure is similar to that reported by Olson (*10*). The lattice parameter of the bare zeolite at room temperature with $a = 25.8536$ Å has been employed. The space group is $Fd\bar{3}m$. One unit cell has 48 Na, 48 Al, 144 Si, and 384 O atoms for a Si/Al ratio of 3.0. For this particular ratio the extraframework sodium atoms occupy the SI and SII sites completely. The zeolite Y structure consists of sodalite and α-cages, also known as supercages. Earlier studies show that the guest species are adsorbed in the α-cages. The diameter of xenon (4.6 Å) is too large to be accommodated in the sodalite cage. Each α-cage is interconnected tetrahedrally to four other α-cages through 12-membered rings. The approximate diameter of the α-cage is about 11.4 Å and that of the interconnecting 12-ring window 8 Å. There are eight α-cages in one unit cell of zeolite Y. Below we refer to an α-cage simply as cage.

Intermolecular Potential Functions

Guest–zeolite interaction potential. All sorbate–zeolite interactions were modeled in terms of short range interactions. The potential employed by us in the present study is the one proposed by Kiselev and Du (*11*). In this, the xenon–zeolite Y interactions are modeled in terms of atom–atom pair potential functions. The interactions between the silicon or aluminium and xenon are taken to be zero as the close approach of xenons to these atoms is prevented by the surrounding oxygens. The interactions are of the modified Lennard–Jones (*6–12*) form

$$\phi_{az}(r_{az}) = -\frac{fA_{az}}{r_{az}^6} + \frac{B_{az}}{r_{az}^{12}} \quad a = \text{Xe}; z = \text{O, Na}, \quad (1)$$

where $f = 0$, 0.5, or 1.0. When $f = 0$, there is no dispersion interaction between the sorbate and the zeolite. If, however, $f = 1$, the potential parameters reduce to those given by Kiselev and Du (*11*).

TABLE I

INTERMOLECULAR POTENTIAL PARAMETERS: GUEST–GUEST AND GUEST–ZEOLITE

Atom	$A(10^3$kJ/mole, Å$^6)$	$B(10^6$kJ/mole, Å$^{12})$
Guest–guest		
Xe–Xe	34.913	165.84
Guest–zeolite		
Xe–O	8.2793	11.1345
Xe–Na	2.9143	7.9079

Induction interactions have not been taken into account as it is computationally prohibitive due to the many-body nature of the interactions. The parameter values for A_{az} and B_{az}, a = Xe and z = 0, Na were taken from the work of Kiselev and Du (*11*). These parameters have been found to yield results in reasonable agreement (*12*) with available experimental data. The potential parameters are listed in Table I. The atomic mass of the xenon was taken to be 131 amu.

Guest–Guest interaction potential. The xenon–xenon interactions were taken to be of the Lennard–Jones (*6–12*) form

$$v(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}, \quad (2)$$

where the parameter $A = 4\varepsilon\sigma^6$ and $B = 4\varepsilon\sigma^{12}$. The values of $\varepsilon_{\text{Xe}} = 221$ K and $\sigma_{\text{Xe}} = 4.1$ Å were taken from literature. Rowlinson and co-workers (*4, 5*) have obtained reasonable agreement with experimental data over a range of pressures with these parameters.

Molecular Dynamics Calculations

All calculations were carried out in the microcanonical ensemble at fixed (N, V, E) (*13*). Cubic periodic boundary conditions were employed. The zeolite atoms were assumed to be rigid and were not included in the integration. All calculations were performed at a loading of $c = 1$ Xe/cage and 282 K. One unit cell of the zeolite was employed in all calculations.

All runs were carried out with a starting configuration with the xenons placed at the cage centers. A time step of 40 fsec was

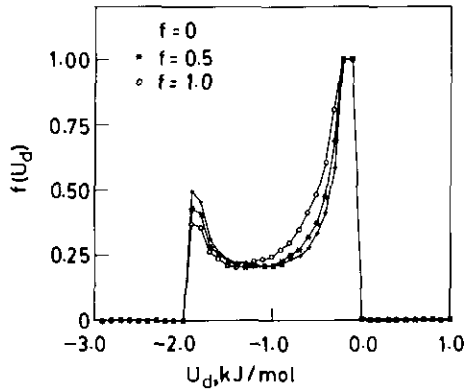

FIG. 1. Dimerization energy distribution function, $f(U_d)$ is shown for $f = 0, 0.5, 1$. The function was calculated by averaging, over 2.6 nsec, the length of the molecular dynamics run.

employed which yielded good energy conservation. Properties were calculated from configurations stored at intervals of 0.2 psec. Equilibration was performed over a duration of 250 psec during which velocities were scaled to obtain the desired temperature. Long production runs of 2600 psec have been carried out at each of the temperatures and loadings.

Results and Discussion

Figure 1 shows the dimerization energy distribution function, $f(U_d)$, for $f = 0, 0.5$, and 1.0. Here U_d is the interaction energy of a pair of xenon atoms. The distribution function $f(U_d)$ has been averaged over all molecular dynamics steps and also all xenon atoms. In Fig. 1, the neighbors which are far apart and consequently have negligible interaction, contribute to the peak at zero energy. The peak near -2.0 kJ/mole arises from dimers with an interaction energy equal to ϵ_{Xe}. An increase in the strength of the dispersion interaction leads to a decrease in the population of dimers, as shown by a decrease in the intensity of the peak at $U_d = -2.0$ kJ/mole. A decrease in the dimer population should be accompanied by an increase in the population of either monomer or higher sized clusters such as trimer, tetramer, etc. In order to obtain this information we show a plot of the bonding energy distribution function, $f(U_b)$ (Fig. 2). The energy required to take a xenon atom to infinity in the absence of the zeolite is termed U_b. The distribution is averaged over all xenon atoms and time steps (*14*). Here, the peak near $U_b = 0.0$ kJ/mole arises from isolated sorbate particle, that is, monomers. The peak at -2.0 kJ/mole may be attributed to dimers and the tail beyond it extending up to -4.0 kJ/mole to higher sized clusters. We note that the peak height near zero energy corresponding to the monomers has decreased in intensity with the increase in the strength of the dispersion interaction. This is also evident from Table II where we list the fraction of xenons that are present as monomers, dimers, etc. for the three different dispersion strengths $f = 0, 0.5$, and 1.0. The estimated errors are indicated in parenthesis. The monomer population has increased from 63.5% for $f = 0$ to 67.5% for $f = 0.5$ and 72.5% for $f = 1.0$. The dimer population has decreased from 25.5% for $f = 0$ to 19.2% for $f = 1$. It is also seen that the population of higher sized clusters has also decreased with increase in the strength of the sorbate–zeolite dispersion interaction.

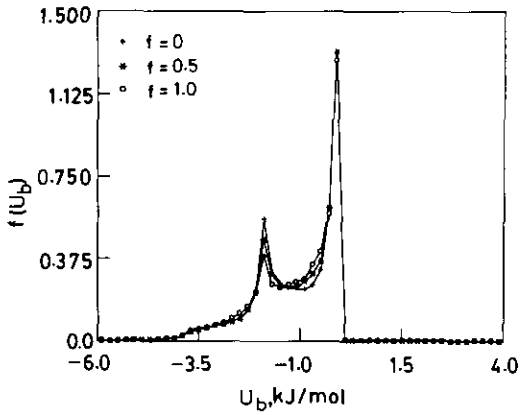

FIG. 2. Bonding energy distribution function, $f(U_b)$ is shown for $f = 0, 0.5, 1$.

TABLE II

AVERAGE FRACTION OF XENON ATOMS CONTRIBUTING TO THE FORMATION OF MONOMER AND HIGHER SIZED XENON CLUSTERS

	f		
Cluster	0.0	0.5	1.0
Monomer	63.5 (± 1.2)	67.5 (± 0.6)	72.5 (± 0.8)
Dimer	25.5 (± 0.6)	22.7 (± 0.3)	19.2 (± 0.4)
Trimer	8.2 (± 0.8)	7.2 (± 0.4)	6.10 (± 0.4)
Tetramer	2.4 (± 0.3)	2.1 (± 0.3)	1.6 (± 0.2)

The average lifetime of different sized clusters are listed in Table III. It is seen that the lifetime of the monomer shows an increase from 3 psec for $f = 0$ to about 3.4 psec for $f = 1$. The standard deviations are given in parenthesis. The increase in the average lifetime with f is consistent with the observed increase in the average number of xenons existing as monomers. Average lifetime of the trimer and tetramer has decreased with an increase in f. This is also consistent with the decrease in the average number of xenons participating in the formation of trimer and tetramers (see Table II). The situation in the case of dimers is, however, different. Even though the dimer population decreased with an increase in the strength of the dispersion interaction, the average lifetime shows an increase from $\langle\tau\rangle = 0.306$ for $f = 0$ to $\langle\tau\rangle = 0.40$ for $f = 1$. The observed increases are significantly larger than the statistical errors in the calculation.

The distribution of lifetimes for the clusters of different sizes is shown in Fig. 3. It is seen that an increase in the lifetime of monomers, when the strength of the dispersion interaction is increased, occurs near 4 psec, with a corresponding fall near 1 psec. Similarly, for dimers an increase in the intensity of the distribution is observed at large values of τ. For trimers and tetramers, there is generally an increase in the intensity of the distribution for higher values of τ.

The above results can be understood if we look at the potential energy surface provided by the host. The guest atoms, in this case, xenons feel strongly the potential of the host. When $f = 0$, there is no dispersion interaction between the sorbate and the zeolite. The potential energy contours for the region inside the α-cage for this situation shows no sorption sites. The potential energy surface due to the host does not show any deep potential wells. In other words, the potential energy surface has no "valleys and hills" and is structureless. For $f = 1$, when the dispersion interaction is fully switched on, there exist potential wells inside the α-cage (*12*) the potential energy surface being highly structured. This is one of the important changes that occurs with increase in the value of f. There is another important change when the value of f is increased. From earlier work (*14*), it is known that when $f = 1$, the sorbates preferentially occupy regions close to the inner surface of the cage. This is, however, not true when $f = 0$ since the strong attraction due to the inner walls of the cage is absent.

These changes seem to influence the cluster size distribution and their lifetimes. When $f = 0$, the sorbate population near

TABLE III

AVERAGE LIFETIME FOR CLUSTERS OF DIFFERENT SIZES

	f		
Cluster	0.0	0.5	1.0
Monomer	3.0 (± 1.0)	3.1 (± 0.05)	3.4 (± 0.1)
Dimer	0.3 (± 0.04)	0.3 (± 0.03)	0.4 (± 0.01)
Trimer	0.7 (± 0.02)	0.6 (± 0.02)	0.6 (± 0.01)
Tetramer	0.4 (± 0.01)	0.5 (± 0.03)	0.5 (± 0.02)

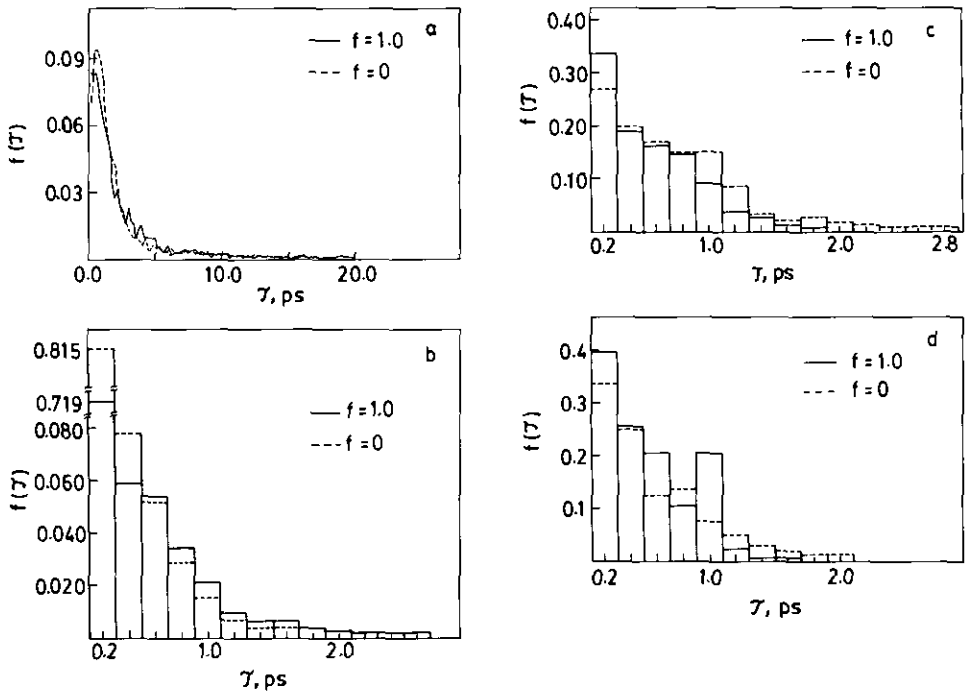

FIG. 3. Distribution of lifetimes of clusters of the sorbate xenon atoms for (a) monomer, (b) dimer, (c) trimer, and (d) tetramer for $f = 0$ and 1. The distribution was calculated by averaging over all molecular dynamics steps of duration 2.6 nsec.

the cage center is significant. A sorbate near the cage center can more easily be surrounded by several sorbates than a sorbate located near one of the inner walls of the cage. Hence, dimer, trimer, as well as tetramer, population is higher for $f = 0$. Increase in the strength of dispersion interaction not only results in a confinement of the sorbates mostly near the inner wall of the cage away from the cage center but also the presence of sorption sites trap some of the sorbates for a sufficiently long period of time. This results in an increase in the lifetime of monomer and dimer only, since trimers and higher sized clusters can not be formed easily near the surface due to geometrical constraints. This is because it is difficult for a trimer to be in the most favorable arrangement with respect to each of the other two xenons if the trimer is located near an inner surface; the concave surface of the zeolite prevents it from being in the best possible trimer configuration. The situation is worse for tetramer and higher sized clusters. It is probable that for $f = 1$, out of the two xenons forming a dimer, one of the xenons is actually located in an adsorption site which explains the increase in the dimer lifetime.

Conclusion

An increase in the strength of the dispersion interaction is accompanied by a decrease in the population of the clusters of sizes greater than or equal to 2, with a corresponding increase in the monomer population. The lifetime of monomers and dimers increases whereas the lifetime of trimers and tetramers decreases. These have been explained in terms of the changes in the density profile inside the α-cage and the potential energy surface provided by the zeolite.

The field of zeolites was first introduced to one of us (S.Y.) by Sir John Thomas in

1986 at the University of Cambridge. It was a pleasure working with him. He has shown continued interest in our work on zeolites. We are extremely happy to dedicate this work to Sir John Thomas on the occasion of his sixtieth birthday.

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