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The structure and dynamics of adsorbed molecules in microporous solids; a comparison between experiments and computer simulations

Anthony K. Cheetham and Lucy M. Bull

Materials Department, University of California, Santa Barbara, CA 93106, U.S.A.

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A critical evaluation is made of the results of computer simulations of adsorbed molecules in microporous inorganic materials. Structural, thermochemical and dynamic data are compared with the corresponding experimental findings. The systems examined include inert gases and simple alkanes in zeolites Na-Y and silicalite, benzene and pyridine in Na-Y and K-L, respectively, and *p*-xylene in silicalite. Future developments in the area are also discussed.

Keywords: Zeolites; microporous solids; adsorbed molecules; computer simulations; molecular dynamics; Monte Carlo

1. Introduction

Recent applications of computer simulation methods to the modelling of adsorbed species in zeolites and other microporous solids have apparently met with considerable success. For example, it is now possible to predict a range of structural, thermochemical and dynamical properties, such as (i) the location of sorbate molecules, (ii) heats of adsorption as a function of temperature and sorbate concentration, (iii) diffusion coefficients, and (iv) activation energies for diffusion and other motions. Indeed, some of these properties are more difficult to measure than they are to calculate! A range of simulation techniques has been applied to sorbate-zeolite systems. Initial efforts focused mainly on the use of simple molecular mechanics (MM) procedures to predict structural and thermodynamic properties [1–9], and Monte Carlo (MC) methods [10–16], which probe the conformational energy space more efficiently. These are now giving way to molecular dynamics (MD) simulations [17–25], which yield not only the structural and thermodynamic properties, but also provide time-dependent information. Most of the calculations have assumed that the host framework is rigid and unperturbed by the presence of the guest molecule, but some recent simulations have allowed the lattice to relax [23]. In all cases, the atom-atom approximation has been used with a simple Lennard-Jones or Buckingham potential to describe the short range interactions. For some calculations, longer range Coulombic forces have also been considered.

In view of the widespread interest in computer modelling, it is both timely and desirable to examine critically the reliability of such simulations. This paper examines a number of systems for which both experimental and calculated properties are available. Experimental data will be taken from a number of techniques. X-ray and neutron diffraction studies, with both powders and single crystals, furnish information concerning the siting of sorbate molecules, particularly at low temperatures. Calorimetric and adsorption measurements provide data on the thermodymanics of sorbate-host interactions and the rates of sorbate diffusion, and NMR studies, particularly with ^{1}H, ^{2}H, ^{13}C and ^{15}N, yield both structural and dynamical information pertaining to guest molecules. As a result of such studies, in particular on zeolite-Y and silicalite, there is now a substantial body of reliable data against which the simulation results can be assessed.

2. Xe and simple alkanes in Na-Y and silicalite

The initial efforts to model adsorbed molecules in zeolites focused largely on treatments of inert gases and simple alkanes in Na-Y. For example, the early work of Kiselev and co-workers [1,2] was based upon the use of a Lennard-Jones potential that was parameterised to give a good fit to the heat of adsorption of methane in zeolite Na-Y. The agreement between the observed and calculated heats (internal energies) of adsorption for other alkanes in Na-Y, and those with the inert gases [4], gives a measure of the success of these earlier studies (see table 1). A subsequent molecular dynamics study of the CH_4/Na-Y system [17] underlined some of the advantages of the MD approach. In systems of this nature, where the mobility is high, the MD calculation yields both the thermochemical data that is otherwise obtained by MM or MC methods, plus the

Table 1
Internal energies of adsorption ($-\Delta U_{ads}$) of hydrocarbons in zeolite-Y (kJ mol^{-1}) [4]

	temp. (K)	calcd.	exptl.
Ar	173	10.2	9.7
Kr	173	14.8	15.3
Xe	213	19.6	17.1
CH_4	373	14.7	15.2
C_2H_6	323	23.5	23.3
C_3H_8	296	32.5	32.3

Table 2
Internal energies of adsorption and diffusion coefficients for Xe in silicalite at 298 K and 4 molecules per unit cell

	Calculated	Experimental	
		PFG-NMR	Rate uptake
ΔU_{ads}, kJ mol^{-1}	-26.9 (0.2)	n.a.	-24.5
D, 10^{-9} m^2 sec^{-1}	1.86 (0.44)	4.00	0.10
ref.	[22]	[27]	[28]

diffusion coefficients. Furthermore, if the simulations are performed as a function of temperature, activation energies for diffusion and other dynamical processes can also be computed from Arrhenius plots. For CH_4/Na-Y, the estimated diffusion coefficient at 300 K, 2.0×10^{-8} m^2 s^{-1}, agrees well with the value of 1.5×10^{-8} m^2 s^{-1} determined by pulsed field gradient NMR [26], although, in a subsequent paper, it has been shown that the diffusion coefficient is 20% larger if the dynamics of the lattice are taken into account [23]. In most of the systems examined to date it has not been necessary to consider intramolecular motion of the sorbate, though clearly this will become an important consideration as the size and complexity of the sorbate molecules being studied increases (see below).

Other recent MD studies [22–25] have simulated the behavior of alkanes and inert gases in silicalite, the siliceous analogue of ZSM-5. In the Xe/silicalite system, for example, good agreement was found with both thermochemical and diffusion coefficient data (table 2), although the calculated diffusion coefficient showed better agreement with the pulsed field gradient experiment than the rate-uptake value, a finding that appears to generally the case. Note that the heat of adsorption of Xe in silicalite is much greater than that in Na-Y. This arises primarily because of the narrower channel in the former host, a feature that is also apparent in a recent computational study of Xe diffusion in 1-dimensional channel systems (table 3); ferrierite and ZSM-5 have 10-ring channels, whereas zeolite-L, like faujasite, is based upon a 12-ring channel. The activation energy for diffusion of Xe is calculated to be 5.5 kJ mol^{-1}, in good agreement with the value of ~ 4 kJ mol^{-1} recently determined by PFG-NMR

Table 3
Comparison of dynamical simulations of Xe in various zeolites [29]

	D	ΔU_{ads}	E_a	D_0
Ferrierite	12	-25.4	3.8	41
Zeolite-L	1.8	-20.0	4.9	7.6
Silicalite	1.8	-26.9	5.5	15

Diffusion coefficients, D, and pre-exponential factors, D_0, are given in 10^{-9} m^2 s^{-1}; heats of adsorption, ΔU_{ads}, and activation energies, E_a, are in kJ mol^{-1}.

Table 4
Anisotropy of diffusion of Xe in silicalite at 298 K, 4 molecules per unit cell [22]

	D	E_a	D_0
x	1.26	4.7	10
y	4.03	6.2	34
z	0.28	5.5	3

Diffusion coefficients, D, and pre-exponential factors, D_0, are given in 10^{-9} m^2 s^{-1}; heats of adsorption, ΔU_{ads}, and activation energies, E_a, are in kJ mol^{-1}.

[30], but in poor agreement with a rate-uptake value of 20 kJ mol^{-1} [28]. A further aspect of the Xe/silicalite study that is worthy of note is that the simulations were able to reveal the full anisotropy of the diffusivity, a feature that has so far been beyond the scope of the available experimental methods (largely because of the absence of single crystals large enough for diffusion studies). The results, shown in table 4, show some interesting features. As expected, the diffusivity is most facile along the y direction and least along z. However, the origin of this difference is seen to lie in the pre-exponential terms rather than the activation energies; indeed, the activation energy is apparently greatest along y. Thus, the slower diffusion along z stems primarily from the tortuosity of the pathway, which involves diffusion along both the linear and sinusoidal channels of the silicalite structure, rather than from energetic considerations.

The overall picture in studies on small molecules appears to be that good agreement is generally obtained between experiments and simulations, both for heats of adsorption and diffusion coefficients, although a recent computational study of methane, ethane and propane in silicalite found that the diffusion coefficients diverged from the experimental (PFG-NMR) values as the C_n number increased [25]. This was ascribed to the neglect of intramolecular motion with ethane and, especially, propane. We now consider the status of simulations involving simple aromatic sorbates.

3. Simple aromatics in zeolites K-L and Na-Y

The simplest MM calculation is one that establishes the global energy minimum for the adsorbed molecule, and it is appropriate that this should be compared with a low temperature structural study since the sorbate is likely to become distributed over additional, higher energy sites as the temperature of the system is raised. The first hydrocarbon-zeolite system in which this question was addressed was the complex between pyridine and zeolite K-L [6]. The force field used was one in which the sorbate-host interaction was described in terms of a short range 6–12 (Lennard-Jones) potential (parameterised according to Kiselev and coworkers [1]), plus an electrostatic contribution based upon partial charges. The zeolite framework was assumed to be rigid. The global minimum, in which the nitrogen of the pyridine participated in a Lewis acid-base interaction with the potassium whilst the aromatic ring approaches the cavity wall, was found to be in excellent agreement (within 0.2 Å) with the results of a Rietveld analysis of powder neutron diffraction data collected at 4 K.

No thermochemical or dynamical data, experimental or simulated, are available for the pyridine/K-L system, but the adsorption of benzene in faujasite-type zeolites has been extensively investigated by a variety of techniques. Neutron diffraction studies [31] have revealed two adsorption sites for benzene at 4 K. The dominant site, which is occupied exclusively at low coverages (~ 1 mol/cav), lies in the supercage, coordinated to the SII cation. The second, which appears at higher concentrations, is centered in the 12-ring window. At room temperature the benzene molecules occupy sites close to those observed at 4 K, but are "performing vigorous molecular motion" [31]. The siting and dynamics of benzene in Na-Y at a loading of two molecules per supercage have been simulated by molecular dynamics [21]. The benzene-benzene interactions were described in terms of a Buckingham potential, and the benzene-host interactions were treated with a Lennard-Jones potential, plus a long range electrostatic term; the latter, which was required to describe the interaction of the quadrupolar benzene molecule with the charged framework and exchangeable cations, was modeled with partial charges (Si/Al = +1.2; O = −0.7; Na = +0.8). The host and guest were held rigid.

At low temperatures, an energy minimum of -90 kJ mol^{-1} was found at the SII site. Raising the temperature to 326 K, the behavior of the benzene became bimodal with approximately half the molecules occupying a position in the vicinity of the SII site with an average energy of -75 kJ mol^{-1}, and the remaining molecules delocalised around the walls of the supercage and in the 12-ring window with a mean energy of -60 kJ mol^{-1}. The dynamical behavior of the guest molecule was analysed from the MD trajectory and found to be highly anisotropic, the migration between sites occuring parallel to the walls of the cavities. The estimated heat of adsorption (77.8 kJ mol^{-1}) was found to be in reasonable accord with thermodynamic data [32], as was the diffusion coefficient (calculated 4×10^{-9} sec^{-1}; PFG-NMR value, 1×10^{-10} sec^{-1}) in Na-X [33]. The difference in energy (15 kJ mol^{-1}) between molecules in the vicinity of the SII cations and those in other parts of the supercage is in good agreement with an activation energy for diffusion of ~ 13 kJ mol^{-1}, obtained in a recent study of T_1 relaxation times by ^{2}H NMR [34].

4. Energetics of *p*-xylene in silicalite

Other studies involving aromatic systems lead one to believe that the results of modern simulations are not always as reliable as the above example would suggest. For instance, there have been at least three recent attempts to simulate the location of *p*-xylene in silicalite. In the work of Pickett et al. [35], the simple 6–12 potential was employed, with a rigid framework and no electrostatic contribution to the host-guest interaction. For low sorbate concentrations, two minima were located in the channel intersection, with energies of -80 and -82 kJ mol^{-1}, respectively; in each case the *p*-xylene molecule is oriented with its two-fold axis aligned along the linear channel direction. A third was found in the straight channel (-85 kJ mol^{-1}), and the minimum energy within the sinusoidal channel was found to be -77 kJ mol^{-1}. The corresponding work of Reischman et al. [36] employed a closely related potential of the Buckingham type; this requires 3 parameters rather than 2, one of which was adjusted so that the global minimum was in agreement with the experimental isosteric heat of adsorption of -75 kJ mol^{-1} [37]. The electrostatic interactions were again set to zero and the zeolite was held rigid. At a concentration of 4 sorbate molecules per unit cell (i.e. low loadings), a minimum of -82 kJ mol^{-1} was again found in the channel intersection, in broad agreement with the work of Pickett et al., but the minima in the straight and sinusoidal channels were strikingly different at only -48 and -30 kJ mol^{-1}, respectively.

Some aspects of the two simulations are in good accord. Not only do they both reveal minima in the channel intersections, but in both cases the principal axis of the molecules is aligned with the linear channel direction. Nevertheless, it is disconcerting, to say the least, that the results of two simulations, with similar potentials but different parameterisations, give conflicting results concerning the energetics within the linear and sinusoidal channels. Nor is it clear whether either of the calculations is reliable. The simulation of Reischman et al. predicts an activation energy for diffusion along the linear channel of at least 37 kJ mol^{-1}, which is rather larger than the value of 30 kJ mol^{-1} determined from zero length column measurements [38]. On the other hand, since the interaction energies within the linear and sinusoidal channels are rather poor, the heat of adsorption is predicted to become significantly less favorable as the sorbate concentration increases beyond 4 molecules per unit cell, a result that contradicts the experimental findings [39].

A recent paper by Bosselet et al. [39] compared the relative merits of the Lennard-Jones and Buckingham potentials for simulations of the *p*-xylene/silicalite system and obtained results similar to those described in references [35] and [36]. They concluded that the sorbate siting was better predicted by the latter treatment, but that diffusion pathways were estimated more reliably with the Lennard-Jones potential. They also stressed the importance of using a correct structural model in computer simulations.

A single crystal X-ray study of *p*-xylene in H-ZSM-5 [40] at high loadings (8 molecules per cell) affords an interesting comparison with the simulations. The diffraction study reveals four molecules per cell in the intersections and four in the sinusoidal channels, in apparently good agreement with simulations by

Reischman et al. at this higher loading. However, it is found that the presence of the sorbate at high loadings (> 4 molecules per cell) induces a symmetry change from *Pnma* to $P2_12_12_1$, a result that could not be predicted a priori by the simulations. Unpredictable changes of this type clearly introduce a further element of uncertainty into the calculations.

5. Conclusions

It is difficult to draw general conclusions concerning the reliability of computer simulations of sorbate/zeolite systems on the basis of the comparisons presented above. On the one hand, the results obtained by several workers for hosts containing inert gases and small alkanes in a variety of zeolites, and simple aromatics in Na-Y and K-L, show good agreement with experiments; these systems have a common feature in that the sorbate is always much smaller than the host cavity. On the other hand, the conflicting results obtained for the *p*-xylene/silicalite system may give the impression that simulations of sorbate location and energetics in zeolites are fraught with difficulties. There is evidence to indicate that the *p*-xylene/silicalite presents some unusual, albeit not unique, problems. One is that aromatics such as *p*-xylene are quite tightly fitting in silicalite and, as a consequence, the estimated interaction energies are extremely sensitive to the parameterisation of the force field. For example, the repulsion parameter (B_{ij} in the term B_{ij}/r_{ij}^{12}) in the Lennard-Jones potential is calculated from the sum of the atomic radii of atoms i and j. For hydrocarbons in a zeolite the crucial contact is the O...H distance, and uncertainty in this quantity can have a marked effect on the magnitude of the short-range repulsion term. A second problem is that the host structure is quite flexible in this system, a fact that is reflected in the changes in symmetry that occur ($Pna2_1 \rightarrow Pnma \rightarrow P2_12_12_1$) when *p*-xylene is introduced into silicalite. Such a change does not occur in zeolites Y and L.

It is important to remember that the quality of the simulations rests heavily upon the reliability of the potentials and their parameterisations. Hitherto the latter have adjusted to fit appropriate experimental data, but it is now widely felt that a more rigorous approach is to obtain the parameters from fitting to the results of ab initio molecular orbital calculations. The other principal area of uncertainty concerns lattice relaxations and vibrations. Recent static simulations [42] have shown that relaxation effects account for several kJ mol^{-1} of the interaction energy, and can depend upon subtle changes in Si/Al ratios. The main obstacle to implementing these contributions to the calculations is the increased c.p.u. requirement. In spite of these problems, however, it is clear that computer modelling of adsorbed species in microporous solids is starting to make significant contributions in the areas of adsorption and catalysis.

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