Prediction of Gas Adsorption in 5A Zeolites Using Monte Carlo Simulation

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Adsorption of air in 5A zeolites was studied using Monte Carlo simulations in the grand canonical ensemble (μ, V, T constant). Site-site potentials were used to model the adsorbate-zeolite and adsorbate-adsorbate interactions. The potential model contains one adjustable parameter that was fit to a single experimental isotherm data point. Adsorption isotherms and heats of adsorption were determined for pure argon, oxygen, and nitrogen at 203.15 K, 233.15 K, and 297.15 K from 0.1 bar to 4.0 bar. Multicomponent adsorption isotherms were determined for binary mixtures of oxygen and nitrogen at 203.15 K. The results for the pure-component isotherms are in excellent agreement with experimental data. The results for the heat of adsorption are in good agreement with experimental data for argon and oxygen, but not for nitrogen. The results for multicomponent adsorption isotherms are qualitatively correct; however, the simulation was not able to quantitatively predict mixture data.

Introduction

Since their introduction in the 1950's, synthetic zeolites have received increasing attention from the chemical and petroleum industries for use in a wide range of processes. The unique structure and chemistry of these microporous materials have led to their application in such areas as ion-exchange, drying, purification, catalysis, and separation by selective adsorption. Despite the widespread use of zeolites, there is no complete understanding of the behavior of adsorbate/zeolite systems. In addition, there is no universal equation for the adsorption isotherm for gases in zeolites. Therefore, a study which seeks to gain a clearer picture of adsorption would be of fundamental and practical importance to industry.

Since adsorption is a molecular phenomenon, it is natural to model the process on the molecular level. To compare a model with experimental data and to use it in the design of adsorption processes, the molecular model must predict macroscopic properties such as the adsorption isotherm and the heat of adsorption. Statistical thermodynamics provides the link between the microscopic and macroscopic worlds; however, it introduces mathematic complexities as well. One way of circumventing these complications is the Monte Carlo simulation technique (Binder, 1986). Monte Carlo simulations have been used to study many systems including bulk fluids, fluids at interfaces and phase transitions, and there have been several simulation studies of adsorption in zeolites (Soto, 1979; Soto et al., 1981; Soto and Myers, 1981; Woods et al., 1988; Woods and Rowlinson, 1989). These simulations have provided valuable insight into adsorption phenomena and demonstrated that the Monte Carlo technique is a promising tool in the study of adsorption in zeolites. These studies have been limited in some respects, however, because they have considered only spherical, nonpolar adsorbates such as methane and the noble gases; and all, but Soto et al., have ignored the polar nature of the zeolite surface. Furthermore, there have been no simulations of mixed gas adsorption in zeolites to date. It is evident that more work is needed to extend the scope of simulations to include nonspherical adsorbates and more complex molecular interactions.

The goal of this work is to determine whether we can use simulation to get good quantitative predictions of the adsorption characteristics of gases in zeolites. To achieve this goal we perform a detailed study on a model system, air in 5A zeolites, for which extensive experimental data exist so that we can compare the simulation results to experimental data. This system is also interesting because it is a good example of the ability of zeolites to separate a strongly quadrupolar species, nitrogen, from a weakly quadrupolar species, oxygen. Furthermore, it is an important system in industry as there are

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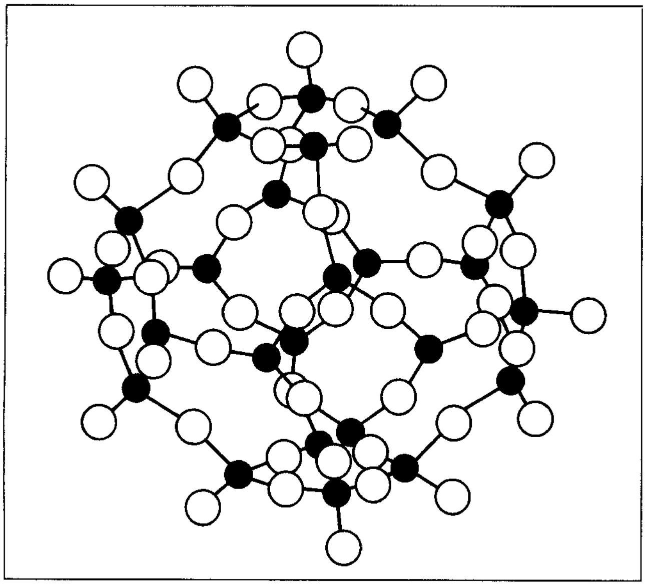

Figure 1. Truncated octahedron formed by joining AlO_4 and SiO_4 tetrahedra via shared oxygen atoms.

Here the black circles represent aluminum and silicon atoms and the open circles represent oxygen atoms.

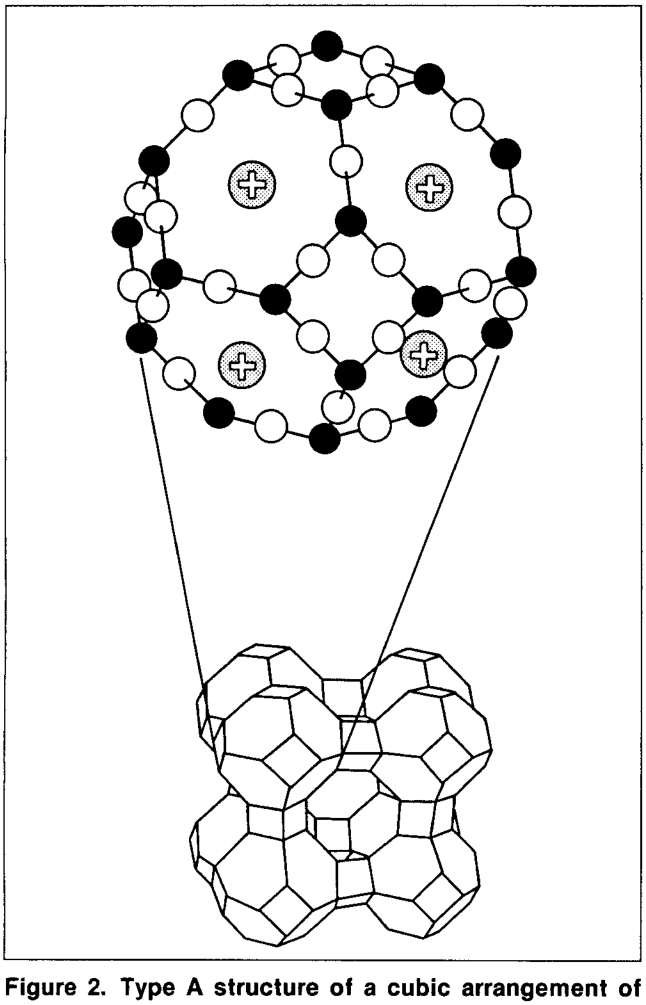

Figure 2. Type A structure of a cubic arrangement of sodalite units.

In the 5A zeolite, the cations sit near the centers of the six-membered oxygen rings.

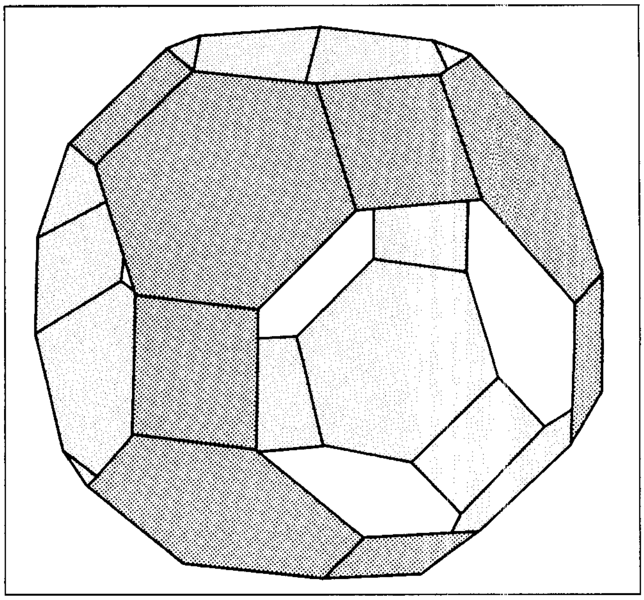

Figure 3. Nearly spherical 5A zeolite cavity.

It contains six windows that connect it to adjacent cavities.

already processes to separate air via adsorption on the small scale, and there is a continuing effort to develop adsorption as a viable alternative to cryogenic distillation (Ruthven, 1988). Our study goes beyond those of Soto et al., Woods et al., and Woods and Rowlinson in that we explicitly account for the nonspherical nature of diatomic molecules using the site-site approach and include quadrupolar interactions between adsorbate molecules and between adsorbate molecules and zeolite molecules. Simulation makes it possible to determine the effects of structure, number and type of cations, sorbate chemistry, and operating temperature and pressure on the amount of gas adsorbed and the selectivity. If successful, this valuable method will help develop and test adsorption theories, and design new commercial zeolites.

5A Zeolite Structure

The 5A zeolite framework is composed of silica and alumina tetrahedra, in which the silicon and aluminum atoms are surrounded by four oxygen atoms. These tetrahedra are joined together through shared oxygen atoms to form the truncated octahedral, or sodalite, structure shown in Figure 1. The zeolite also contains exchangeable cations, most commonly Na^+ and Ca^{2+}, which serve to offset the negative charge introduced by the $(AlO_2)^-$ groups. The cations are not part of the framework, and instead sit near the six membered oxygen rings as indicated in Figure 2. The type A zeolite structure is a simple cubic arrangement of sodalite units with lattice constant $a_0 = 12.29$ Å (1.23 nm) (Seff and Shoemaker, 1966). The sodalite units are connected by the four oxygen atoms at the square faces of the truncated octahedra. A simplified diagram of this structure is shown in Figure 2. This arrangement forms a nearly spherical cavity, which is surrounded by eight sodalite units. The shape of the type A cavity is shown in Figure 3. All of the aluminum and silicon atoms are buried in tetrahedra of oxygen atoms and are not exposed to the surface. Therefore, the surface is composed of oxygen atoms and the cations. The cavity-free diameter is 11.4 Å (1.14 nm) and the cavity volume is reported to be 775 Å^3 (0.775 nm^3) (Breck, 1974). The pore structure is a lattice of interconnected cavities. In the type A zeolite, the cavities lie on a cubic lattice, in which each cavity is connected to the six adjacent cavities. The window between the cavities is an eight-membered oxygen ring with a free diameter of about 4.3 Å (0.43 nm) (Barrer, 1978).

The composition of the dehydrated 5A zeolite is (Seff and Shoemaker, 1966):

$$Ca_4^{2+}Na_4^{+}[(AlO_2)_{12}(SiO_2)_{12}]$$

Aluminum and silicon are present in a 1:1 ratio, and there are eight cations in each cavity. The positions of the framework atoms have been determined by crystallographic methods (Seff and Shoemaker, 1966).

Potential Energy Model

The accuracy of the computer simulation results depends largely on the accuracy of the potential energy model. As has been shown in previous investigations (Soto, 1979) in the modeling of adsorption in zeolites, it is important to account for the interactions between adsorbate molecules and the interactions between the adsorbate molecules and the zeolite cavity wall. The total potential is the sum of the total adsorbate-adsorbate potential, U_{AA}, and the total adsorbate-zeolite potential, U_{AZ}:

$$U_{\text{total}} = U_{AA} + U_{AZ} \tag{1}$$

Most simulation studies of adsorption in zeolites have neglected electrostatic effects and used simple smoothed potentials to calculate the adsorbate-zeolite energy, although some investigators have used more complex potential models to estimate the heat of adsorption and Henry's Law constants (Kiselev and Du, 1981; Derrah and Ruthven, 1975). These more complex models are based on the site-site potential model, in which the surface is treated as a collection of overlapping spheres or sites. Sites can correspond to individual atoms or to groups of atoms. In this study, both adsorbate-adsorbate and adsorbate-zeolite interactions are modeled using the site-site approach. The interaction of a molecule with a surface, for example, is the sum of the interactions of all the sites of the molecule with all the sites of the surface. The advantage of the site-site model is that it gives a realistic representation of the shape and orientation of the molecules and of the surface; yet, it retains the computational simplicity of each interaction being spherically symmetric.

Adsorbate-adsorbate potential

The absorbate-adsorbate potential energy includes terms for the dispersion, repulsion and quadrupole-quadrupole interactions. The adsorbate-adsorbate interactions are assumed to be pairwise-additive: that is, the total adsorbate-adsorbate energy, U_{AA}, is the sum of the energy of all the adsorbate pairs, u_{ij}:

$$U_{AA} = \sum_{i}^{N} \sum_{j>i}^{N} u_{ij} \tag{2}$$

Table 1. Parameters Used in Calculating the Adsorbate-Adsorbate Potential

Atom	ϵ/k (K)	σ (nm)	ℓ (nm)	$Q \times 10^{26}$ (e.s.u.)
Ar	119.8	0.3405	–	–
N(N$_2$)	35.3	0.3314	0.1102	1.50
O(O$_2$)	44.5	0.3090	0.1017	0.40

where N is the total number of adsorbate molecules.

The adsorbate-adsorbate pair potential, u_{ij}, includes a site-site Lennard-Jones potential for the dispersion and repulsion energy, and a quadrupole-quadrupole term:

$$u_{ij} = u_{ij}^{LJ} + u_{ij}^{QQ} \tag{3}$$

The site-site Lennard-Jones potential is the sum of the potential energies of each pair of adsorbate sites on different molecules (Binder, 1986):

$$u_{ij}^{LJ} = \sum_{\alpha\gamma} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}^{\alpha\gamma}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}^{\alpha\gamma}} \right)^{6} \right] \tag{4}$$

where i and j refer to molecules, and α and γ refer to sites on the molecule. The site-site parameters, σ and ϵ, are the site diameter and the energy well depth, and $r_{ij}^{\alpha\gamma}$ is the distance between sites. The potential energy of sites on the same molecular is not included. In the site-site potential, oxygen and nitrogen are modeled as rigid diatomics. The sites correspond to the oxygen and nitrogen atoms, and are separated by a distance ℓ, which is equal to the experimental bondlength. In the case of argon, there is only one site per molecular, and the site-site Lennard-Jones potential reduces to the standard Lennard-Jones potential.

The potential energy between two linear quadrupoles, u_{ij}^{QQ}, can be written (Barrer, 1978):

$$u_{ij}^{QQ} = \frac{3Q_iQ_j}{4r_{ij}^5} \left[1 - 5(b_{ij}^2 + b_{ji}^2) - 15 b_{ij}^2 b_{ji}^2 + 2(c_{ij} + 5 b_{ij} b_{ji})^2 \right] \tag{5}$$

where Q is the quadrupole moment, r is the distance between the centers of mass of the molecules, and b_{ij}, b_{ji} and c_{ij} are the functions of the relative orientation of the molecules:

$$b_{ij} = \mathbf{\Omega}_i \cdot \mathbf{R}_{ij} / r_{ij} \tag{6}$$

$$c_{ij} = \mathbf{\Omega}_i \cdot \mathbf{\Omega}_j \tag{7}$$

Here $\boldsymbol{R}_{ij}$ is the vector $\boldsymbol{R}_j - \boldsymbol{R}_i$ joining the center of mass vectors $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$ of molecules i and j, and $\mathbf{\Omega}_i$ and $\mathbf{\Omega}_j$ are the unit axial vectors of molecules i and j.

The parameters used in the calculation of the adsorbate-adsorbate potential are given in Table 1. The site-site Lennard-Jones parameters and the bondlength for nitrogen and oxygen were determined by Cheung and Powles (1976) by fitting their molecular dynamics simulation results to experimental density and internal energy data. Lennard-Jones parameters for argon are those recommended by Hirschfelder et al. (1954) and were determined from second virial coefficient data. In the simulation of mixed gas adsorption, it is necessary to determine the Lennard-Jones potential parameters for the interactions between unlike molecules. We used the standard mixing rules for ϵ_{ij} and σ_{ij}:

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{8}$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \tag{9}$$

No additional interaction parameters are used in calculating the mixture potential energy. It is difficult to measure quadrupole moments, and there is a wide range of values for most compounds. The values used here for oxygen and nitrogen are generally accepted as the most accurate values (Stogryn and Stogryn, 1966).

Adsorbate-zeolite potential

The total adsorbate-zeolite potential energy, U_{AZ}, includes terms for the dispersion, repulsion, induction, and ion-quadrupole interactions:

$$U_{AZ} = U_{\text{Disp}} + U_{\text{Rep}} + U_{\text{Ind}} + U_{IQ} \tag{10}$$

The dispersion and repulsion energies are calculated using site-site potentials. As in the adsorbate-adsorbate energy, the adsorbate sites correspond to the constituent atoms of the adsorbate molecules. The surface sites correspond to the surface oxygen atoms and to the sodium and calcium ions. Due to the tetrahedral structure of the alumina and silica groups, the aluminum and silicon atoms of the zeolite framework are obscured by the oxygen atoms. Consequently, the interactions of the adsorbate with the aluminum and silicon atoms are shielded and are therefore neglected (Barrer, 1978). The dispersion and repulsion energies are calculated as the sum of the interactions of each adsorbate site with each surface site, assuming pairwise additivity:

$$U_{\text{Disp}} = \sum_{i=1}^{S} \sum_{k=1}^{Z} u_{ik}^{\text{Disp}} \tag{11}$$

$$U_{\text{Rep}} = \sum_{i=1}^{S} \sum_{k=1}^{Z} u_{ik}^{\text{Rep}} \tag{12}$$

where S is the number of adsorbate sites and Z is the number of surface sites. To a first approximation, the dispersion energy varies inversely as the sixth power of the distance:

$$u_{ik}^{\text{Disp}} = -\frac{B_{ik}}{r_{ik}^{6}} \tag{13}$$

where B_{ik} is the dispersion constant, and r_{ik} is the distance between adsorbate site i and surface site k. An inverse twelfth power expression is used to model the repulsive energy:

$$u_{ik}^{\text{Rep}} = \frac{A_{ik}}{r_{ik}^{12}} \tag{14}$$

Table 2. Dispersion and Repulsion Constants used in Calculating the Adsorbate-Zeolite Potential

Atom Pair	A_{ik} (J•nm^{12}/mol)	B_{ik} (J•nm^{6}/mol)
Ar – O	0.004638	4.708
Ar – Na$^+$	0.002010	0.576
Ar – Ca^{2+}	0.008020	1.506
N – O	0.002850	3.319
N – Na$^+$	0.000967	0.406
N – Ca^{2+}	0.003770	1.061
O – O	0.001410	1.962
O – Na$^+$	0.000577	0.240
O – Ca^{2+}	0.002311	0.629

where A_{ik} is the repulsion constant. The calculation of the dispersion and repulsion constants will be discussed in a separate section.

The induction energy, U_{Ind}, results from the interaction of the electric field produced by the zeolite ions with the dipole moment that the field induces in the polarizable adsorbate molecules. From electrostatics, the potential of a group of induced dipoles in an electric field is given by (Jackson, 1967):

$$U_{\text{Ind}} = \sum_{i=1}^{S} -\frac{\alpha_i}{2}\, \mathbf{E}(\mathbf{r}_i) \cdot \mathbf{E}(\mathbf{r}_i) \tag{15}$$

where S is the number of induced dipoles (i.e., adsorbate sites), α_i is the polarizability of site i and $E(r_i)$ is the electric field at r_i, the position of site i. The electric field is equal to the vector sum of the fields produced by the individual zeolite ions:

$$\mathbf{E}(\mathbf{r}_i) = \sum_{k=1}^{Z} q_k \frac{(\mathbf{r}_i - \mathbf{r}_k)}{r_{ik}^{2}} \tag{16}$$

where Z is the number of zeolite ions, q_k is the charge of ion k, $\mathbf{r}_i$ and $\mathbf{r}_k$ are the position vectors of adsorbate site i and zeolite ion k respectively and r_{ik} is the distance between site i and ion k. All ions within one lattice constant of the cavity center are included in this sum.

The final term in the adsorbate-zeolite potential is the energy of the interaction of the adsorbate quadrupole moment and the zeolite ions. For a linear quadrupole, the potential is given as (Barrer, 1978):

$$U_{IQ} = -\frac{1}{4} \sum_{i}^{N} \sum_{k}^{Z} q_k Q_i \frac{(3\cos^2\theta - 1)}{r_{ik}^{3}} \tag{17}$$

where N is the number of adsorbate molecules, Z is the number of ions, q_k is the charge of ion k and Q_i is the quadrupole moment of adsorbate molecule i. θ is the angle between the vector joining the center of mass of the adsorbate molecule with the zeolite ion and the axial vector of the adsorbate molecule, and r_{ik} is the distance between the center of mass of molecule i and ion k. The ion-quadrupole potential can be either attractive or repulsive, depending on the orientation of the adsorbate molecule.

The parameters used in calculating the adsorbate-zeolite potential are summarized in Tables 2 and 3. Table 2 lists the dispersion and repulsion constants, B_{ik} and A_{ik}, which are determined for each adsorbate site-zeolite site pair. Table 3 lists the polarizabilities, α_i, the ionic charges, q_k and the van

Table 3. Site Parameters Used in Calculating the Adsorbate-Zeolite Potential

Atom	$\alpha \times 10^{24}$ (cm^3)	q (e)	r (nm)
Ar	1.64	-	0.3820
N(N$_2$)	0.87	-	0.3718
O(O$_2$)	0.79	-	0.3467
O(5A)	0.147	$-1/3,0$	0.3040
Na$^+$	0.18	$+1$	0.1960
Ca^{2+}	0.471	$+2$	0.1980

Table 4. Theoretical vs. Empirical Values of the Dispersion Constant*

Atom Pair	London	Slater-Kirkwood	Kirkwood-Muller	Empirically Determined
Ar – O	2.481	4.141	5.252	4.708
Ar – Na$^+$	0.165	1.107	0.741	0.576
Ar – Ca^{2+}	0.492	1.682	3.071	1.506
N – O	1.268	2.553	2.480	3.319
N – Na$^+$	0.086	0.484	0.494	0.406
N – Ca^{2+}	0.255	1.084	1.329	1.061
O – O	1.116	2.366	1.992	1.962
O – Na$^+$	0.076	0.464	0.364	0.240
O – Ca^{2+}	0.227	0.991	1.012	0.629

*All B_{ik}s are in J•nm/mol.

der Waals radii, r_i.

The dispersion constant, B_{ik}, may be calculated using one of several theoretical equations. The most widely used equations are the London equation, the Slater-Kirkwood equation, and the Kirkwood-Muller equation (Hirschfelder, 1967):

$$B_{ik}^{\text{London}} = 1.5\alpha_i\alpha_k \frac{I_i I_k}{(I_i + I_k)} \tag{18}$$

$$B_{ik}^{S-K} = \frac{3eh\alpha_i\alpha_j}{4\pi\sqrt{m}(\sqrt{\alpha_i/n_i} + \sqrt{\alpha_k/n_k})} \tag{19}$$

$$B_{ik}^{K-M} = 6mc^2 \frac{\alpha_i\alpha_k}{(\alpha_i/\chi_i + \alpha_k/\chi_k)} \tag{20}$$

where I is the ionization potential, n is the number of outer shell electrons, χ is the diamagnetic susceptibility, m and e are the mass and charge of an electron, c is the velocity of light and h is Planck's constant. Values of B_{ik} calculated using these equations are shown in Table 4. The equations yield values which may differ by as much as a factor of six. Since the theoretical approach can give only an estimate of the dispersion constant, we have taken an empirical approach. All three theoretical equations agree that the dispersion constant is a function of the product of the polarizabilities; therefore, in our empirical approach, B_{ik} is determined by:

$$B_{ik} = \beta_i\alpha_i\alpha_k \tag{21}$$

where β_i is an adjustable parameter. Kiselev and Du (1981) used a similar approach to fit the dispersion constant. β_i for each adsorbate is fit at a single low-pressure adsorption data point, to the data of Miller et al. (1987) using a trial-and-error method until the simulation result agrees with the experimental data. A low-pressure point is used so that there is not more than one adsorbate molecule in the cavity. If there were more, then fitting β_i might also be correcting for any errors in the adsorbate-adsorbate potential. The parameters obtained via the empirical approach are considered reasonable because, as shown in Table 4, the empirical values are in the approximate range defined by the calculated values.

The repulsion constant is determined by setting the equilibrium separation, r_{eq}, of an adsorbate-zeolite pair equal to the average of the van der Waals radii (Derrah and Ruthven, 1975):

$$\left(\frac{\partial u_{ik}}{\partial r_{ik}}\right)_{r=r_{\text{eq}}} = 0 \tag{22}$$

$$r_{\text{eq}} = \frac{1}{2}(r_i + r_k) \tag{23}$$

where u_{ik} is the pair interaction energy. The radii of the oxygen, sodium and calcium of the zeolite are those used by Derrah and Ruthven (1975). The van der Waals radii of the adsorbates are determined from the Lennard-Jones potential parameters:

$$r_i = 2^{1/6}\sigma_i \tag{24}$$

The pair interaction energy, u_{ik}, is taken as the sum of the repulsion, dispersion and induction energies of an isolated adsorbate-ion pair:

$$u_{ik} = \frac{A_{ik}}{r_{ik}^{12}} - \frac{B_{ik}}{r_{ik}^6} - \frac{\alpha_i q_k^2}{2r_{ik}^4} \tag{25}$$

where the last term on the right is the result of applying Eq. 15 to an isolated adsorbate-ion pair. Combining Eq. 22 and 25, the repulsion constant is given by:

$$A_{ik} = \frac{1}{2} B_{ik} r_{\text{eq}}^6 + \frac{1}{6} \alpha_i q_k^2 r_{\text{eq}}^8 \tag{26}$$

The polarizabilities of the adsorbate molecules and of the cations have been determined experimentally from the measurements of dielectric constants and refractivities, and quite accurate values are available (Weast, 1986). In the site-site model, however, the polarizability of the adsorbate site is needed. It may be assumed that the molecule polarizability is the sum of the polarizabilities of the constituent atoms (Pauling, 1970). For homonuclear diatomic molecules such as oxygen and nitrogen, the site polarizability is simply one half of the molecular polarizability. The site-site treatment of the polarizability was necessary to enable us to fit the repulsion constant A_{ik} in Eq. 26. There is no experimentally determined value for the polarizability of the zeolite framework oxygen atoms. The value used was estimated by Barrer (1978) from the refractivity of feldspar, which is structurally similar to the zeolites.

Since the zeolite is electroneutral, the total negative charge of the framework must balance the positive charge of the cations. To model the electrostatic interactions, the way in which the negative charge is distributed on the oxygen atoms in the framework must be estimated. Several previous investigators have suggested distributing the negative charge evenly over all of the framework oxygen atoms (Derrah and Ruthven, 1975; Barrer, 1978). In the 5A structure, this even distribution leads to a $-1/4$ charge on each oxygen atom. In our test simulations, however, this arrangement results in heats of adsorption that are unrealistically high when compared to experimental data. Based on the suggestion of Kiselev that the negative charge may be concentrated near the cations (Kiselev, 1981), we have assumed a different charge distribution, in which the negative charge is distributed only on the oxygen atoms adjacent to the cations. In this arrangement, the oxygen atoms in the hexagonal faces of the sodalite unit are given a $-1/3$ charge, and the other oxygen atoms are assumed to be neutral. We did not differentiate between oxygen atoms surrounding the Na^+ or the Ca^{++} cations. Increasing the negative charge near the cations decreases the magnitude of the electric field in the region and therefore decreases the magnitude of the induction energy.

Grand Canonical Monte Carlo Method

In the grand canonical ensemble, the independent variables are the chemical potential, the temperature, and the volume. At equilibrium, the chemical potential of the adsorbed phase equals the chemical potential of the bulk gas, which can be written as a function of the temperature and the bulk gas pressure (McQuarrie, 1976):

$$\mu_{\text{ads}} = \mu_{\text{bulk}}(T,P) \tag{27}$$

Consequently, the independent variables in the grand canonical Monte Carlo simulation are the temperature, the pressure of the bulk gas, and the volume of the zeolite cavity. This set of variables is convenient because the temperature and pressure are the independent variables in the adsorption isotherm. Therefore, the adsorption isotherm can be obtained directly from the simulation by evaluating the ensemble average of the number of adsorbate molecules whose chemical potential equals that of a bulk gas at a given temperature and pressure.

The simulation algorithm is based on the algorithms proposed by Adams (1975) and by Soto (1979). Before the simulation begins, an initial configuration of adsorbate molecules is placed in the zeolite cavity. Each adsorbate molecule has a position vector associated with it, defined with respect to a cartesian coordinate system. The diatomic molecules have an orientation vector as well, which determines the direction of the site-site axis. The probabilities used in the simulation are the same as those given by Soto (1979). To simplify the probabilities, the bulk gases are assumed to obey the ideal gas law. The PVT data for these gases (Vargaftik, 1975) indicate that this assumption is valid for the conditions considered here; however, it is not a necessary assumption in the use of the grand canonical Monte Carlo method.

In the first step of the simulation cycle, a molecule is picked at random and is moved. For argon, this move is always a translation, while for oxygen and nitrogen, moves can be translations or re-orientations. The decision whether to translate or re-orient is made at random and with equal probability. In a translation, the new components of the position vector, $\boldsymbol{R}$, are determined by:

$$\begin{aligned} R_x^{\text{new}} &= R_x^{\text{old}} + \delta u \\ R_y^{\text{new}} &= R_y^{\text{0ld}} + \delta v \\ R_z^{\text{new}} &= R_z^{\text{old}} + \delta w \end{aligned} \tag{28}$$

where u, v and w are random numbers between -1 and 1, and δ is a constant. The new orientation vector, $\boldsymbol{O}$, is determined by:

$$\begin{aligned} O_x^{\text{new}} &= \frac{\ell}{2}\frac{u}{r} \\ O_y^{\text{new}} &= \frac{\ell}{2}\frac{v}{r} \\ O_z^{\text{new}} &= \frac{\ell}{2}\frac{w}{r} \end{aligned} \tag{29}$$

where

$$r = \sqrt{u^2 + v^2 + w^2} \tag{30}$$

where u, v and w are random numbers between -1 and 1, and ℓ is the bondlength. In this notation, $\boldsymbol{R}$ is the position of the center of mass of the molecule, and the orientation vector, $\boldsymbol{O}$, has a magnitude equal to half of the bondlength. Therefore, the positions of the adsorbate sites are given by $\boldsymbol{R}+\boldsymbol{O}$ and $\boldsymbol{R}-\boldsymbol{O}$. Equation 30 does not give a completely random distribution of orientations, since orientation vectors are distributed uniformly on the surface of a cube rather than a sphere; however, it has been determined that this does not affect the simulation results. The potential energy of the new configuration is calculated. A decision is then made whether to accept the move or to return to the old configuration based on the probability, p_{move}:

$$p_{\text{move}} = \min[\exp(-\Delta U/kT);\ 1] \tag{31}$$

where

$$\Delta U = U_{\text{new}} - U_{\text{old}} \tag{32}$$

To make the decision, a random number between 0 and 1 is generated and is compared to the calculated probability, p_{move}. If the random number is less than the probability, the new configuration is accepted. If the random number is greater than the probability, the system is returned to the old configuration.

The second step in the simulation cycle is the decision whether to attempt to add a molecule or to subtract a molecule. This decision is made at random with equal probability. If an addition is attempted, then the third step begins with the random generation of a position and an orientation vector for the new molecule. The potential of the new configuration is calculated, and the addition is accepted or rejected based on the probability, p_{add}:

$$p_{\text{add}} = \min\left[\frac{1}{(N+1)}\frac{PV}{kT}\exp(-\Delta U/kT);\ 1\right] \tag{33}$$

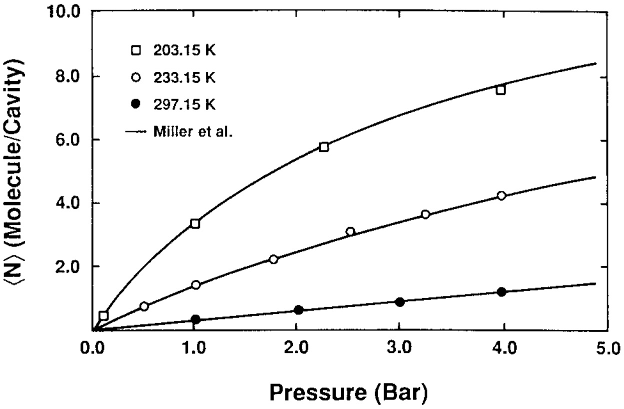

Figure 4. Adsorption isotherms for argon in a 5A zeolite.

The simulation results are compared to the experimental results of Miller et al.

where N is the number of molecules before the addition, P is the pressure of the bulk gas, and V is the volume of the zeolite cavity. If the addition is accepted, the new molecule is kept. If the addition is rejected, the new molecule is deleted, and the system returns to the old configuration.

If a subtraction is attempted, then the third step begins with the deletion of a randomly chosen adsorbate molecule. The potential of the new configuration is calculated, and the subtraction is accepted or rejected based on the probability, p_{sub}:

$$p_{\text{sub}} = \min\left[\frac{NkT}{PV}\exp(-\Delta U/kT);\ 1\right] \tag{34}$$

where N is the number of molecules before the subtraction. If the subtraction is accepted, then the deletion is made permanent. If the subtraction is rejected, then the deleted molecule is returned to its old position.

To simulate mixtures, a few minor changes are made. The pressure in the probability expressions is replaced by the partial pressure of the species being added or subtracted. In addition to the change in the probability, an additional decision must be made at each simulation step to determine which type of adsorbate molecule to move, add, or subtract. This decision is made randomly with equal probability.

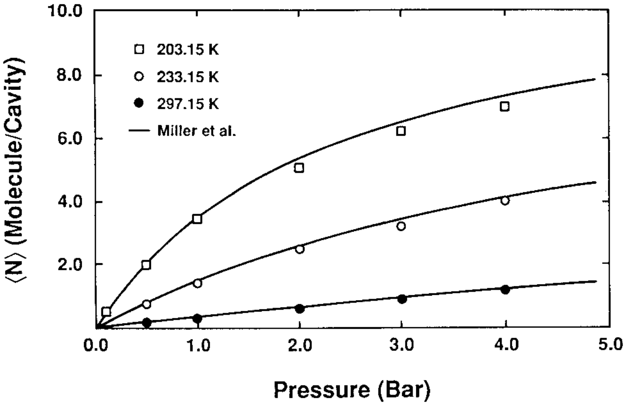

Figure 5. Adsorption isotherms for oxygen in a 5A zeolite.

The simulation results are compared to the experimental results of Miller et al.

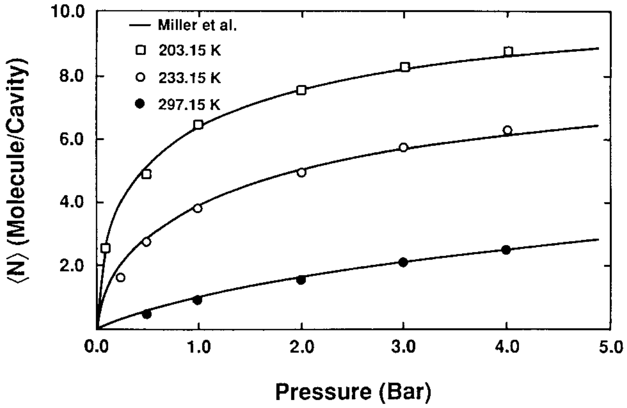

Figure 6. Adsorption isotherms for nitrogen in a 5A zeolite.

The simulation results are compared to the experimental results of Miller et al.

In the last step of the cycle, the number of adsorbate molecules and the total potential energy are recorded. In addition, the density profile is recorded by dividing the cavity volume into a number of concentric spheres, and recording the number of molecules in each spherical shell. From these data, a histogram showing the density as a function of the distance from the cavity center is constructed. Once the pertinent data are recorded, the simulation returns to step one. When the simulation is complete, ensemble averages of the number of adsorbate molecules per cavity, $\langle N\rangle$ and the total potential energy, $\langle U\rangle$, are calculated:

$$\langle N\rangle = \frac{1}{M}\sum_{i=1}^{M} N_i \tag{35}$$

$$\langle U\rangle = \frac{1}{M}\sum_{i=1}^{M} U_i \tag{36}$$

where M is the number of cycles, and N_i and U_i are the number of molecules and potential energy recorded after cycle i. Because the ensemble averages are determined by sampling a set of randomly generated configurations, there is some uncertainty associated with the results. After a certain number of cycles, the averages tend to fluctuate about a steady value, rather than converging to their final values and remaining constant. The uncertainty of "experimental" error of the simulation results can be roughly estimated as the magnitude of fluctuations in the computed property about its final value once equilibrium is obtained. The errors in the results of the simulations performed in this work are estimated to be ±3%.

A typical simulation runs for approximately 10^5 cycles. To eliminate any effect of the initial configuration on the simulation results, 5×10^4 cycles are run before any data are recorded. On average, a simulation at one set of T, μ and V requires 10-20 hours of CPU time on a MicroVax II. Simulation times increase nearly linearly with the number of molecules adsorbed in the cavity.

Simulation Results and Discussion

Grand canonical ensemble Monte Carlo simulations were carried out to determine the adsorption characteristics of pure

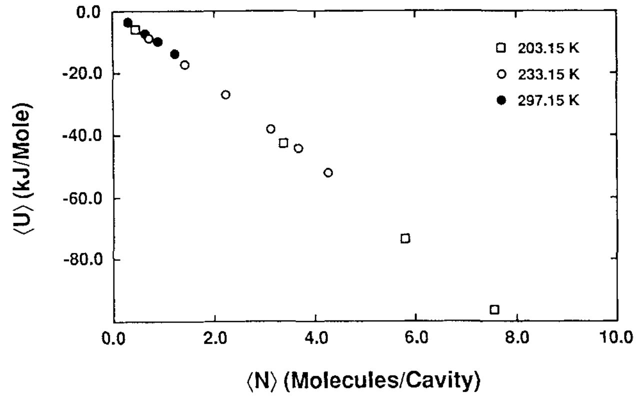

Figure 7. Total potential energy as a function of the amount adsorbed for argon in a 5A zeolite

and mixed gases in a 5A zeolite cavity. Pure-gas simulations were performed for argon, oxygen, and nitrogen at 203.15 K, 233.15 K, and 297.15 K over a pressure range from 0.1 bar to 4.0 bar. Multicomponent simulations were performed for binary mixtures of oxygen and nitrogen at 203.15 K. The mole fraction of nitrogen in the gas phase ranged from 0.25 to 0.6. In each simulation, the ensemble averages of the number of adsorbate molecules per cavity, $\langle N \rangle$, the total potential energy, $\langle U \rangle$ and the density of the adsorbed molecules as a function of radial position in the cavity were determined.

Pure component isotherms, $\langle N \rangle$ vs. P, for argon, oxygen and nitrogen in the 5A zeolite are shown in Figure 4 through Figure 6. The points are the simulation results, and they are compared to the experimental data of Miller (Miller et al., 1987). The experimental data are represented by curves that are calculated using modified Langmuir equations that Miller fit to his measured data. For each gas, the adsorbate-zeolite dispersion constant, B_{ik}, was fit to the experimental isotherm at 203.15 K and 0.1 bar. At this pressure, the number of molecules per cavity is close to one, and therefore, there are no adsorbate-adsorbate interactions. Consequently, using a low-pressure data point to determine the dispersion constant assures that only the adsorbate-zeolite interactions are fit. There is good agreement between the predicted and experimental isotherms, and the predicted isotherms show no loss in accuracy as the pressure increases, which indicates that the adsorbate-adsorbate potential model is of sufficient accuracy for this application.

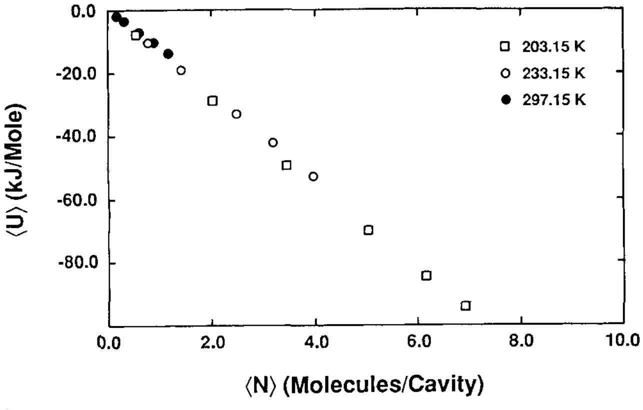

Figure 8. Total potential energy as a function of the amount adsorbed for oxygen in a 5A zeolite.

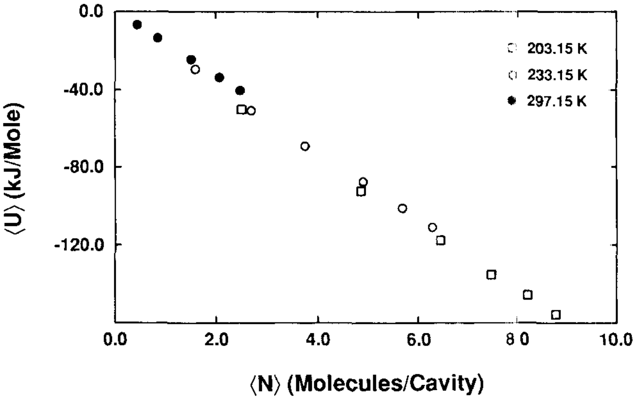

Figure 9. Total potential energy as a function of the amount adsorbed for nitrogen in a 5A zeolite.

Simulation results for the total potential energy, $\langle U \rangle$, as a function of the amount adsorbed, $\langle N \rangle$, are shown in Figure 7 through Figure 9. In the literature, the energy of adsorption generally is reported in terms of the isosteric heat of adsorption , H_{st}, which is defined by:

$$H_{st} = R\left(\frac{\partial \ln P}{\partial 1/T}\right)_N \tag{37}$$

This form is not convenient for the analysis of the simulation results; however, assuming that the gas is ideal and that the adsorbed phase is much denser than the gas, H_{st} can be related to the differential heat of adsorption, H_D, by (Myers and O'Brien, 1985; Myers, 1987),

$$H_{st} = H_D + RT \tag{38}$$

where (Soto, 1979)

$$H_D = -\left(\frac{\partial \langle U \rangle}{\partial \langle N \rangle}\right)_{T,V,A} \tag{39}$$

where A is the surface area of the zeolite. The simulation results for the energy, $\langle U \rangle$, vary linearly with $\langle N \rangle$ so the differential heat of adsorption is determined by calculating the slope of the plots of $\langle U \rangle$ vs. $\langle N \rangle$. Isosteric heats of adsorption calculated from the simulation results are given in Table 5. Heats of adsorption determined experimentally by Miller et al. are given for comparison. There is excellent agreement between simulation and experiment for argon and oxygen; however,

Table 5. Isosteric Heat of Adsorption*

System	H_{st} (kJ/mol) Simulation	H_{st} (kJ/mol) Experiment
Ar – 5A	14.11	14.02
O_2 – 5A	14.81	14.10
N_2 – 5A	18.79	31.3-19.9

*Heats of adsorption determined from simulation results are compared to the experimental results of Miller et al.

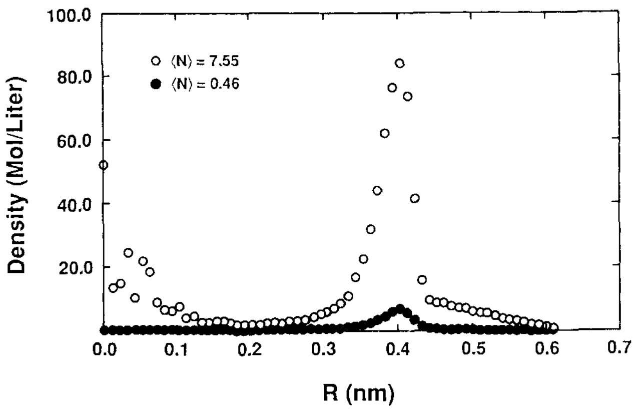

Figure 10. Density profile of argon in the 5A cavity as a function of the distance from the cavity center for two average densities.

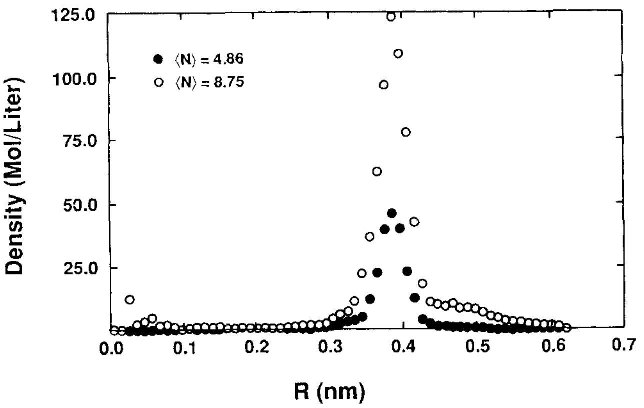

Figure 12. Density profile of nitrogen in the 5A cavity as a function of the distance from the cavity center for two average densities.

the results are not as good for nitrogen. The experimental heat of adsorption for nitrogen is given as a range because Miller reports that, while the heats of adsorption of argon and oxygen are independent of the amount adsorbed, this is not true for nitrogen. As the quantity of nitrogen adsorbed increases, the heat of adsorption determined from experimental data is observed to decrease and eventually reach a steady value. This behavior is expected, because at low coverage the nitrogen molecules are more likely to adsorb near the cations where the ion-quadrupole energy is greatest. As more molecules adsorb, they occupy sites away from the cations where the potential energy is lower. The constant heat of adsorption for argon and oxygen is also expected, because the energy in these systems is dominated by the dispersion-repulsion interaction, which is not site-specific.

A possible explanation for the failure of the simulation to predict the experimentally observed behavior of the heat of adsorption for nitrogen may be found by examining the absorbate-zeolite potential model. The total potential energy is dominated by the contribution of the adsorbate-zeolite potential (Soto, 1979). Therefore, inaccuracies in the heat of adsorption are due most likely to inaccuracies in the adsorbate-zeolite potential model. As was mentioned earlier, the dispersion constants that are fit to the isotherms are reasonable when compared to the approximate values calculated using the various theoretical equations. A closer look at the dispersion constants, Table 4, reveals that the empirical values of B_{ik} for argon and oxygen are within the range defined by the theoretical values, but the empirical value of the dispersion constant for the $N-O$ pair interaction is slightly higher than the theoretical values. This higher value could be compensating for an underestimation of the ion-quadrupole energy by lumping the effect of the ion-quadrupole energy in the empirical dispersion constant. Errors in calculating the ion-quadrupole energy are probably due to errors in the approximation for the charge distribution on the zeolite framework. Mortier has suggested methods for calculating the charge on each crystallographic position based on quantum mechanical calculations or electronegativity arguments (Mortier, 1984). Further investigation of these methods could prove useful in getting a better estimate of the charge distribution.

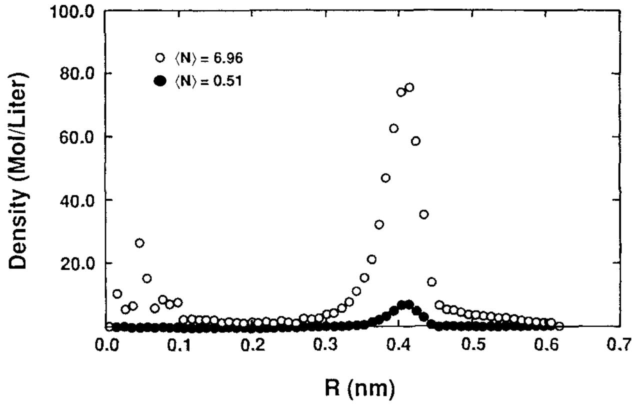

Figure 11. Density profile of oxygen in the 5A cavity as a function of the distance from the cavity center for two average densities.

In addition to the adsorption isotherms and the heat of adsorption, the structure of the adsorbed fluid was also determined. Typical data on the density of the adsorbed gas as a function of radial position in the cavity are shown in Figures 10 through 12. The cavity center corresponds to $R=0$ and the cavity wall atoms are approximately 0.72 nm from the cavity center. For each gas, the density is plotted for a low average number of molecules and a high average number of molecules. Figure 10 shows the density of argon in the cavity. At both low and high $\langle N\rangle$, the plots show a peak at about 0.4 nm, which corresponds to a layer of molecules in contact with the cavity wall. At the higher $\langle N\rangle$, there is a second peak near the cavity center. This peak is separated from the larger peak by a distance approximately equal to the equilibrium separation of argon and corresponds to a second layer of adsorption. In addition, there is a region of nonzero density between the major peak and the wall. This part of the plot indicates that as more molecules adsorb, they begin to fill the windows between the cavities. Figure 11 shows the density of oxygen in the cavity; it is similar to the argon results. At low $\langle N\rangle$ the molecules form a layer at the wall, and at higher $\langle N\rangle$ the molecules form a second layer and occupy the space in the windows. Figure 12 shows the density of nitrogen in the cavity, and it too exhibits a large peak corresponding to a layer of molecules at the wall. In contrast to the argon and oxygen results, there is not a large second layer of molecules in the cavity center at high $\langle N\rangle$. The nitrogen molecule is bigger than the argon and oxygen

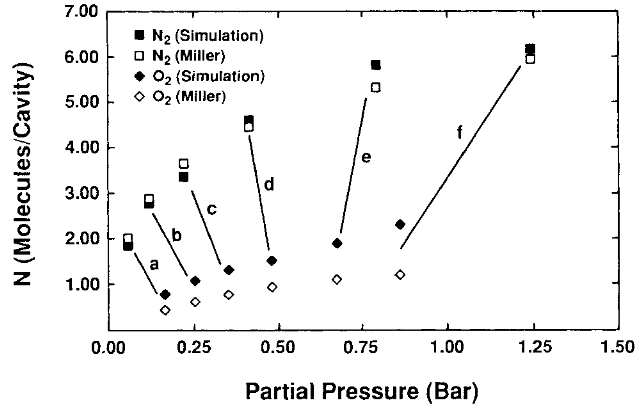

Figure 13. Adsorption isotherms for mixtures of oxygen and nitrogen in a 5A zeolite at 203.15 K.

Mixed gas data points are connected by lines a-f. Simulation results are compared to the experimental results of Miller et al.

molecules, and so there is simply not enough room in the cavity for a second layer to fit.

Multicomponent results

Adsorption isotherms for binary mixtures of oxygen and nitrogen in a 5A zeolite at 203.15 K are shown in Figure 13. In this figure, the pressure axis indicates the partial pressure of each component in the bulk gas. The simulation results are compared to the experimental results of Miller et al. The simulation shows the correct qualitative behavior, yet it fails to predict the mixture equilibria quantitatively. The separation factor, α_{12}, can be defined as:

$$\alpha_{12}=\frac{x_1/y_1}{x_2/y_2} \tag{40}$$

where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk gas phase. Separation factors calculated from the simulation results and the experimental results are compared in Table 6. At each mixed gas data point, the simulation underpredicts the separation factor by about a factor of two. Since no additional interaction parameters were introduced in the mixture simulations, the inaccuracy of the mixture results could indicate that the mixing rules used in the determination of the mixture site-site Lennard-Jones parameters are incorrect. It is always difficult to predict mixture behavior from pure component parameters, and in many cases an empirical binary interaction parameter, k_{ij}, is used in the mixing rule for the energy parameter ϵ:

$$\epsilon_{ij}=(\epsilon_{ii}\epsilon_{jj})^{1/2}(1-k_{ij}) \tag{41}$$

The binary interaction parameter for the oxygen/nitrogen system could be determined by fitting simulations of bulk mixtures of oxygen and nitrogen to experimental mixture data. Another possible source for the error in the mixture results is the failure of the adsorbate-zeolite potential model to account for the ion-quadrupole energy correctly as discussed in the previous section.

Table 6. Separation Factors*

Point	α_{N-O} Simulation	α_{N-O} Experiment
a	7.09	13.5
b	5.48	9.78
c	4.11	7.51
d	3.52	5.49
e	2.64	4.13
f	1.87	3.43

*Separation factors calculated from simulation results are compared to separation factors calculated from the experimental results of Miller et al.

Conclusions

Monte Carlo simulation has been shown to be a useful technique for the determination of the adsorption characteristics of gases in zeolites. Using knowledge of the structure and composition of the zeolite and a model of the potential energy of the gas/zeolite system, the adsorption isotherms, heat of adsorption and structure of the adsorbed fluid have been determined for argon, oxygen and nitrogen in a 5A zeolite. In addition, adsorption isotherms for mixtures of oxygen and nitrogen have also been determined. Excellent agreement between simulation and experimental results is achieved by fitting a single parameter, the dispersion constant, to a single experimental isotherm point. The ability of the simulation to predict the adsorption isotherms over a broad range of temperature and pressure using only one empirical parameter indicates that the potential energy model captures the essential features of the adsorbate-adsorbate and adsorbate-zeolite potential energy. Heats of adsorption determined from the simulation results are in good agreement with experimentally determined heats of adsorption for argon, a nonpolar molecule, and oxygen, a slightly polar molecule. The simulation fails to predict the correct behavior of the heat of adsorption for nitrogen, which is a more strongly polar molecule. This failure indicates that the adsorbate-zeolite potential model does a good job in modeling the nonpolar interactions, but the calculation of the ion-quadrupole interaction may be in error. This error can be attributed to errors in the estimation of the charge distribution on the zeolite framework.

The structure of the simulated fluid indicates that the adsorbed molecules form a layer on the cavity surface, and then as more molecules are adsorbed, a second layer begins to form in the cavity center and molecules begin to occupy the windows between the cavities as well. No second layer of adsorption is observed for nitrogen because the molecules are too big.

Simulations of mixed gas adsorption are able to predict the correct qualitative behavior of the adsorption isotherms, however the probable errors in the mixing rules used in the adsorbate-adsorbate potential energy and errors in the ion-quadrupole interaction make the simulation unable to predict the mixed gas isotherms quantitatively.

The work presented here demonstrates that the grand canonical Monte Carlo simulation method is capable of generating accurate adsorption data for simple gases in zeolites. Improving the potential model so that it models the ion-quadrupole and other more complex interactions accurately could make the simulation method a useful tool in studying the mechanism of adsorption and in designing better commercial adsorbents for a wide variety of systems.

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Notation

A = repulsive energy constant
a_o = lattice constant
B = dispersion energy constant
b,c = orientation functions
c = speed of light
e = elementary charge
E = electric field
h = Plank's constant
H_D = differential heat of adsorption
H_{st} = isosteric heat of adsorption
I = ionization potential
k = Boltzmann constant
$k_{i,j}$ = binary interaction parameter
ℓ = bondlength
m = mass of an electron
M = number of simulation cycles
n = number of outer shell electrons
N = number of adsorbate molecules
$\mathbf{O}$ = orientation vector
p = probability
P = pressure of bulk gas
q = charge
Q = quadrupole moment
r = distance
R = gas constant
$\mathbf{R}$ = position vector
S = number of adsorbate sites
T = temperature
u = pair potential energy
U = potential energy
V = cavity volume
x = adsorbed phase mole fraction
y = gas phase mole fraction
Z = number of zeolite sites

Greek letters

α = polarizability, separation factor
β = adjustable parameter
δ = constant
ϵ = Lennard-Jones well depth
μ = chemical potential
σ = Lennard-Jones diameter
χ = diamagnetic susceptibility
Ω = unit axial vector

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