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EQUILIBRIUM AND STRUCTURAL PROPERTIES OF GAS MOLECULES ADSORBED IN ZEOLITE A

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Abstract—The equilibrium and structural properties of gas molecules confined within zeolite pore cavities were investigated via grand canonical ensemble Monte Carlo simulations. The Lennard-Jones 6-12 potential was chosen to be a representative model for the system of adsorbed argon gases inside 5A zeolites. The adsorption isotherm, the isosteric heat of adsorption, the energy distribution curve and the mass density profile were computed for the temperature of 203 K and 297 K over the bulk pressure range varying from 50 kPa to 400 kPa. The simulation results were compared with the experimental measurement, and, in the range of temperature and pressure considered here, the Monte Carlo data were shown to be in reasonable agreement with the available experimental values. It was observed that, at the higher surface coverage, adsorbate molecules formed the monolayer structure near the zeolite pore wall and promoted the second layer close to the cavity center under the influence of both argon-argon and argon-zeolite potential minima.

Key words: *GCEMC Simulation, Zeolite A, Adsorption Isotherm, Energy Distribution Curve, Mass Density Profile*

INTRODUCTION

Because of their unique structure with exceptional porosity and surface area, zeolite materials have played an important role in industrial applications such areas as purification, separation, catalysis and ion-exchange. In many cases the zeolite structure remains the fundamental factor responsible for these applications [Yang, 1987]. The pore size, shape and dimensionality of zeolites are dependent not only on the framework cavities but also on the type of cations contained in the non-framework structure. The replacement of neutralizing cations results in the different pore size and this process can take place readily by the ion-exchange method in an appropriate solution or molten salt. For instance, by exchanging the sodium cations in the A-type zeolite framework with the calcium cations, the effective aperture diameter is increased from about 4 Å (4A zeolite) to about 5 Å (5A zeolite) while the potassium cations reduce to about 3 Å (3A zeolite).

In order to facilitate the selection and optimization techniques required in the zeolite chemistry and engineering, it is desirable to investigate the related thermophysical properties at a molecular level. An alternative approach to this goal is the use of molecular-based computer simulations via Monte Carlo and molecular dynamics methods [Allen and Tildesley, 1987]. In principle, if one has an accurate knowledge of the zeolite structure and the interaction potentials among atoms or molecules, then it should be possible to obtain any macroscopic values from the microscopic information. These simulation studies have provided invaluable insight into both static and dynamic phenomena that are of direct importance on the catalytic activity and selectivity of zeolites. Current computational work in this area may be classified into two groups: those dealing with the idealized pore model as a reference system [Soto and Myers, 1981; Woods et al., 1988; MacElroy and Raghavan, 1990; Suh and Park, 1994] and those dealing with the more realistic model including complicated geometric factors [Yashonath et al., 1988; Woods and Rowlinson, 1989; Razmus and Hall, 1991; Cracknell and Gubbins, 1993]. A comprehensive review on this subject is recently written by Cheetham and Gale [1992] and also by Titiloye et al. [1992].

In the present work, we investigate the thermodynamic and energetic properties of argon gases trapped inside 5A zeolite cavities under equilibrium conditions with an external bulk phase. The microscopic behavior of adsorbate molecules in zeolite pore systems, particularly when the bulk fluid is gas or vapor, is very sensitive to the underlying molecular-scale event. In this case, as an intermediate between theory and experiment, reliable and unambiguous results will be necessary to eliminate any uncertainties involved in theoretical and experimental measurements. To this end, we performed here machine experiment (computer simulation) over various temperature and pressure conditions using the grand canonical ensemble Monte Carlo (GCEMC) method. Since the number of adsorbate molecules is allowed to fluctuate in the grand canonical ensemble, where the chemical potential, volume and temperature of the system are fixed, our GCEMC calculation is most appropriate for determining the adsorption characteristics in such model zeolite systems [Nicholson and Parsonage, 1982].

MODEL AND COMPUTATIONAL METHODS

Zeolites are a class of crystalline aluminosilicate materials, in which the open framework cavities are interconnected each other with the three-dimensional network of molecular dimensions. The

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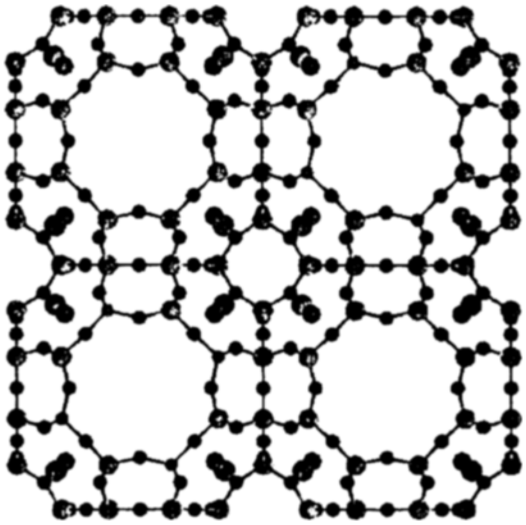

Fig. 1. The two-dimensional crystal structure for the 2×2×2 unit cell of 5A zeolites with the zeolite framework as ball-and-sticks and cations as spheres.

pore cavities consist of an extensive linkage of SiO_4 and AlO_4 groups joined together through the oxygen atoms and the resulting cage-like structure generates highly microporous media. The possible building units of zeolite cavities are the primary building units of SiO_4 and AlO_4 tetrahedra and the secondary building units of linked SiO_4 and AlO_4 rings. The neutralizing cations are located in the non-framework to offset the negative charge introduced by the (AlO_2) groups. For dehydrated 5A zeolites, the chemical composition can be represented by the formula, $Ca^{+2}_4Na^{+1}_4[(AlO_2)_{12}(SiO_2)_{12}]$, where the square bracket contains the framework atoms and the remaining eight cations reside in specific sites near the center of six-membered oxygen rings.

The two-dimensional diagram of dehydrated 5A zeolites is presented in Fig. 1 with the silicon/aluminium/oxygen framework as ball-and-sticks and cations as spheres in the 2×2×2 unit cell. The atomic coordinates for the crystal structure were taken from the refined atomic positions by the X-ray crystallographic analysis [Szostak, 1992]. As shown in this figure, the framework pore structure is a simple cubic arrangement and each cavity is interconnected to their six adjacent cavities. The larger pore cavity forms the nearly spherical structure with the diameter of ca. 11.4 Å. The lattice constant is ca. 12.3 Å and the window between the cavities is an eight-membered oxygen ring with a free diameter of ca. 4.3 Å. For computational simplicity, we model the rigid zeolite system, in which the positions of both the framework atoms and the cation atoms are fixed. In this model the zeolite structure does not alter with the loading of adsorbate molecules during the sorption simulations.

We consider here the system of argon gases to be adsorbate molecules and 5A zeolites as sorbents. The interaction energies are atomistically calculated using the simple potential function of a pairwise Lennard-Jones 6-12 model. The atomic potential parameters for pure elements are the same as described elsewhere [Razmus and Hall, 1991; Titiloye et al., 1992]. For the argon-zeolite interaction potentials, the mixing parameters for length and energy terms in the Lennard-Jones mixture model are determined by means of the conventional combining rules, known as the Lorentz and the Bertholet rule [Lee, 1988]. The possible induced effects due to the electric fields are ignored in modelling the argon-zeolite potentials since the polarizability of argon is known to be sufficiently small. In fact the long-ranged charge distributions in many silicalite materials are largely delocalized [Cheetham and Gale, 1992; Ramdas, 1989]. Consequently, the electrostatic interactions can be neglected for the small and nonpolar molecules confined within zeolites. It should be pointed out, however, that such an assumption used in our case of argon may not be valid for larger and more polarizable molecules in zeolites, for example, xenon [June et al., 1990] and hydrocarbon molecules [Catlow et al., 1991].

The GCEMC simulations adopted in this work are based on the asymmetric sampling algorithm proposed by Adams [1975]. The main loop consists of two independent steps. In the first step, a particle is randomly moved within a given maximum displacement. The move is either accepted or rejected subject to the total potential energy change. This procedure is exactly the same as the traditional Monte Carlo method in the canonical ensemble [Nicholson and Parsonage, 1982; Allen and Tildesley, 1987]. The second step generates new trial configurations by attempting an addition or removal of a randomly chosen particle. The success of either an addition or removal is controlled both by the potential energy change and by the chemical potential parameter. This compound event is repeated as many times as is desired and the equilibrium properties are evaluated at each step. A more detailed GCEMC algorithm is described in our previous studies for the hard-sphere [MacElroy and Suh, 1986, 1987; Suh and Park, 1994] and Lennard-Jones systems [MacElroy and Suh, 1989; Suh et al., 1991] confined within various porous media.

The initialization procedure was first to construct the computer-generated zeolite structure, and then proceeded directly to the sorption simulations in the accessible pore volume. In order to minimize the system size effects the nearest image convention using periodic boundary conditions was applied in the fundamental cubic box consisting of the 2×2×2 unit cell (384 oxygens, 96 silicons, 96 aluminiums and 64 cations). A spherical cut-off distance was taken as half the simulation box length, i.e., 12.3 Å. During the initial stages of sorption simulations the configurations generated were not representative of the equilibrium ensembles and were discarded from the averaging process. In all cases reported here configurations were equilibrated for 1×10^5 steps before accumulating data and the ensemble averages were obtained during the final 2 million simulation steps.

RESULTS AND DISCUSSION

The GCEMC simulations were performed at the temperatures of 203 K and 297 K over the bulk pressure ranges varying from 50 kPa to 400 kPa. In Fig. 2 the adsorption isotherm at a given temperature, constructed from the ensemble averages of the number of adsorbed molecules per unit cell, is presented as a function of bulk pressure. The value of bulk pressure in the gas phase is calculated from the corresponding chemical potential with the assumption that the ideal gas law applied. Also shown in this figure as solid curves are the experimental data for the adsorption isotherm measured by Miller et al. [1987]. These experimental data were represented in terms of the modified Langmuir equation with correlation parameters available in their work. The GCEMC simulation results are shown to be in good agreement with those of the experimental isotherm. This indicates that the atomic-type potentials based on a Lennard-Jones model is, at least

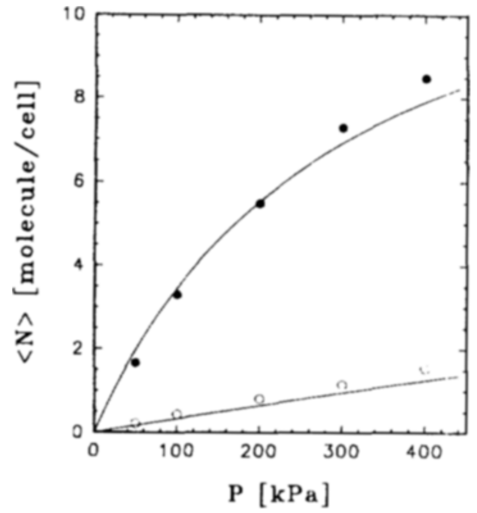

Fig. 2. Adsorption isotherms as a function of bulk pressure.
● GCEMC results for T=203 K; ○ GCEMC results for T=297 K; — experimental data [Miller et al., 1987].

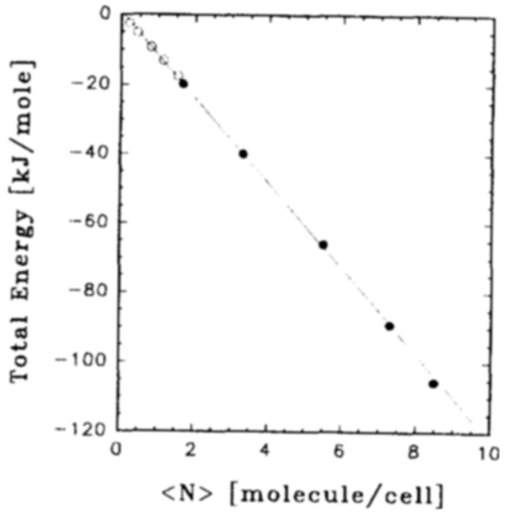

Fig. 3. Total potential energies as a function of the amount adsorbed in the unit cell.
● GCEMC results for T=203 K; ○ GCEMC results for T=297 K; — the least-square curve fitting.

qualitatively, of reasonably accuracy to predict such equilibrium and thermodynamic properties for the ranges of temperature and pressure considered here.

At the limit of very low surface coverage, known as the Henry's law regime, the adsorbate-adsorbent energies dominate the adsorbate-adsorbate energies. The initial increase in the adsorption isotherm results primarily from the attractive interactions due to the argon-zeolite potentials. For higher bulk pressure or larger surface coverage, the cavity-filling effects are significantly increased due to the increasing importance of the repulsive interactions among adsorbate molecules. The attractive energies may enhance the degree of equilibrium adsorption whereas the repulsive energies reduce the adsorption process. Under these conditions the larger deviation from Henry's law at higher pressure regions will be caused by the thermal energy balance between the argon-argon and the argon-zeolite interactions. It can be expected, if this were our case, that the repulsive influence among adsorbate molecules will be gradually exerted than might be inferred from the simple Lennard-Jones interactions. This explains in part why the less predictive results were obtained with increasing bulk pressures.

The experimental value for the isosteric heat of adsorption was measured to be 14.02 kJ/mol for the system of argon in 5A zeolites [Miller et al., 1987].This agrees well with our GCEMC simulation results of 13.84 kJ/mol, which was determined from the slope of the total potential energy versus the amount adsorbed in the unit cell (Fig. 3). The good agreement between simulation and experiment again confirms the quality and accuracy of our GCEMC calculation. As can be seen in this figure, the isosteric heat of adsorption for lower loading is nearly independent of the coverage, suggesting that the gas adsorption simulated in the range of lower pressure regions occurs on the sterically homogeneous surface.

A similar physical interpretation of this observation follows from thermodynamic arguments to those widely used in the theories of adsorption isotherms including the adsorption models of Langmuir, Freundlich and BET [Yang, 1987]. However, in these theoretical equations, the structural effects are oversimplified with assumptions that the adsorption sites are identical and that the pre-existing adsorption sites are static and do not change with loading. One may argue that the Langmuir equation of adsorption would be appropriate to predict the equilibrium properties of small and nonpolar molecules in zeolites. Even though such a simple model may provide an initial groundwork as a first approximation, this is not the case for the higher loading systems.

This last point is clearly illustrated in Fig. 4, where the contour maps of mass density profiles are plotted in the xy-plane passing through the unit cell. Figs. 4a and 4b, respectively, correspond to the temperatures of 203 K and 297 K both at the same bulk pressure of 400 kPa. For the larger cavity-filling in Fig. 4a, where some eight admolecules are occupied per unit cell, the actual pore configurations are shown to be the monolayer structure close to the zeolite wall with the promotion of the second layer formation near the cavity center. The similar structural effects were also observed for other temperature and pressure conditions. As a consequence of the three-dimensional symmetry in the unit cell of 5A zeolites, there are the eight equivalent sites near cations located in the framework cavities. In the simulation studies for xenon in the NaA alpha cage [van Tassel et al., 1991, 1992, 1993], it was found that closely spaced adsorption sites caused xenon to avoid each other and hence the sites were not entropically independent. In this sense more specified configurations would be required to develop the predictive adsorption theory for higher adsorbate loadings, and, ultimately, to understand the temperature, pressure and framework dependence of adsorption sites in zeolites.

In Fig. 5 the normalized energy distribution curves are presented in order to illustrate the manner in which the energy distributions change with respect to temperature and pressure conditions. Compared with the resulting distributions for 400 kPa (Fig. 5b), the larger statistical errors exhibited in those for 50 kPa (Fig. 5a) are related directly to the larger thermal motion of admolecules at the lower surface coverage. The distribution energies are shown to be the two-peaked curves in shape. Those distribution curves correspond to the energetically distinct regions in the zeolite cavities. The energy peak around −18 kJ arise from

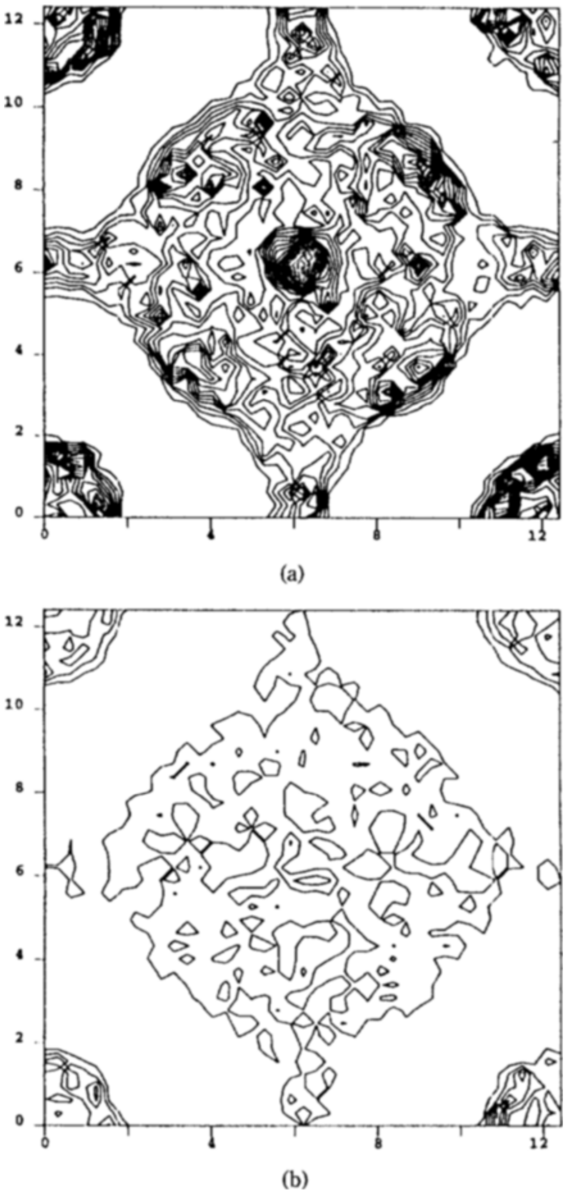

Fig. 4. Contour maps of mass density profiles at P=400 kPa for (a) T=203 K and (b) T=297 K.

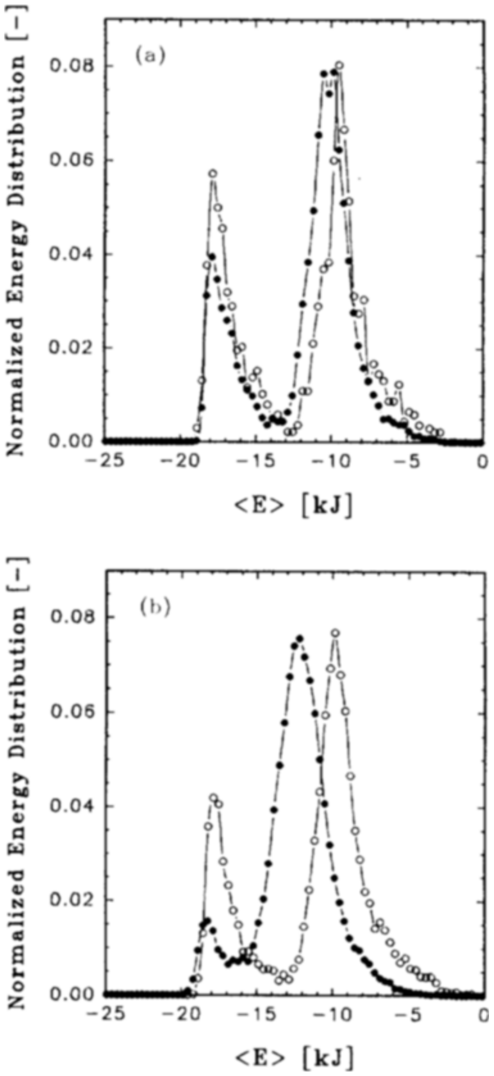

Fig. 5. Normalized energy distribution curves for (a) P=50 kPa and (b) P=400 kPa.

● GCEMC results for T=203 K; ○ GCEMC results for T=297 K.

argon trapped near the localized adsorption sites, whereas the peak in the higher energies around -10 kJ--12 kJ from those located in the less favored regions. These two main peaks are essentially associated with the different adsorption positions, and, obviously, the latter is more mobile because it is occupying the higher energy sites. This indicates that the interaction energy of adsorbed molecules is a strong function of the adsorption sites in the zeolite pore cavities.

A similar trend was observed in the more complex systems studied by Woods and Rowlinson [Woods and Rowlinson, 1989]. In their simulation work, they attempted to understand the structural behavior of xenon and methane adsorbed in the systems of zeolite X and also zeolite Y. The molecular structure of methane is approximately spherical in shape and the hard-sphere diameter of methane is roughly equal to that of xenon. The resulting density profiles for methane were qualitatively the same as those for xenon. At the low pressure region adsorbate molecules formed a predominantly monolayer structure in contact with the cavity wall. There was a second layer near the cavity center with increasing pressure and a distance between two layers was found to be approximately equal to the equilibrium molecular separation. The computational and experimental measurements of xenon [McCormick and Chmelka, 1991] and methane [Cohen de Lara et al., 1989] in the systems of zeolite A also found that adsorbed molecules were bound close to the cavity wall corresponding to the potential minima. Although the exact comparison with our GCEMC results is not expected, the structural and energetic effects explained in this work are in agreement with these observations.

CONCLUSION

In this paper, the system of argon gases adsorbed within 5A zeolite cavities was investigated by means of molecular-based computational approaches. The grand canonical ensemble Monte Carlo calculations, coupled with the Lennard-Jones 12-6 model as an input potential, have been performed to reproduce the equilibrium and structural properties such as the adsorption isotherm, the isosteric heat of adsorption, the energy distribution curve and the mass density profile. The Monte Carlo results were shown to be in reasonable agreement with the experimental data appeared in the literature. Our simulation results also provided the detailed information about the related structural and energetic properties at a molecular level. It was observed in the mass density profiles that, at the higher surface coverage, the pore structure formed the monolayer arrangement near the zeolite pore wall and the second layer was promoted close to the cavity center under the influence of both argon-argon and argon-zeolite potential minima. The resulting energy distribution was found to be the two-peaked curve in shape, which corresponds to the energetically distinct regions in the zeolite cavities. Although we have restricted our attention to the case of argon in 5A zeolites using the relatively simple model potentials, it would be of great interest to investigate other zeolite systems in order to verify a number of the conclusions obtained in this work, which may be difficult to probe by the experimental measurement. More precisely defined molecular interactions could be required to handle this application computationally. Confirmation of obtaining this possibility is currently under investigation and further simulation results will be reported in the near future.

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