Molecular Modeling of Binary Liquid-Phase Adsorption of Aromatics in Silicalite

Shaji Chempath and Randall Q. Snurr
Dept. of Chemical Engineering and Center for Catalysis and Surface Science, Northwestern University, Evanston, IL 60208

John J. Low
UOP Research Center, Des Plaines, IL 60017

Adsorption in the zeolite silicalite from binary liquid mixtures of p-xylene, m-xylene, and toluene was investigated using grand canonical Monte Carlo (GCMC) simulations. The results obtained agree well with experimental excess adsorption isotherms from the literature. The agreement is very good when the zeolite is modeled using the PARA form of the silicalite structure, but the results obtained with the native ORTHO structure are in some cases even qualitatively wrong. This supports the previous suggestion that the structure of silicalite undergoes a transition from ORTHO to PARA upon adsorption of aromatic molecules. Molecular-level details of the energetics and siting within the zeolite provide insights into the macroscopic behavior. The simulated single-component and binary results were used to test ideal adsorbed solution theory for these systems. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 463–469, 2004

Keywords: GCMC, liquid phase adsorption, silicalite, xylene, toluene

Introduction

Grand canonical Monte Carlo (GCMC) simulations have been used successfully in recent years to study adsorption of gases in microporous materials such as zeolites (Fuchs and Cheetham, 2001). In theory, adsorption from a liquid phase can also be studied using the same simulation techniques. However, since the simulations must be done near full loading of the zeolite channels, more aggressive biasing techniques are required to ensure convergence in a reasonable time. From an experimental point of view also, adsorption from the liquid phase poses some problems. It is difficult to obtain the absolute amount of sorbate molecules adsorbed in a zeolite, and, usually, an excess isotherm is measured and reported instead. Because of these difficulties, almost all molecular simulations of adsorption in zeolites have been for gas-phase systems.

There are many industrial processes where multicomponent liquid mixtures need to be separated. Adsorption in a microporous solid can be an attractive alternative to distillation, especially when the relative volatility of the compounds in the mixture is close to one (Ruthven, 1984). An important example is the separation of *p*-xylene and *m*-xylene, where *p*-xylene is the desired compound because it is widely used in the production of polyesters. Usually, fractional crystallization or adsorption into a zeolite is used to separate *p*-xylene from its isomers or other alkyl benzenes. Adsorption based processes use techniques such as simulated moving bed (SMB), as in the Sorbex process (Broughton, 1984), which operates in the liquid phase. Recently, there has been interest in the use of MFI zeolite membranes for such separations (Min et al., 2003; Hedlund et al., 2002; Sakai et al., 2001; Xomeritakis et al., 2001; Gump et al., 2001). It should be noted that membrane based separations depend both on adsorption and diffusion characteristics of the compounds in the membrane. In this article we show that GCMC simulations can be used to estimate the adsorption from a liquid phase into a zeolitic phase. Comparisons are made to experimental data from the literature for binary aromatic mixtures in the zeolite silicalite. Information about the siting of molecules inside the zeolite channels for single component

---

Correspondence concerning this article should be addressed to R. Q. Snurr at snurr@northwestern.edu.

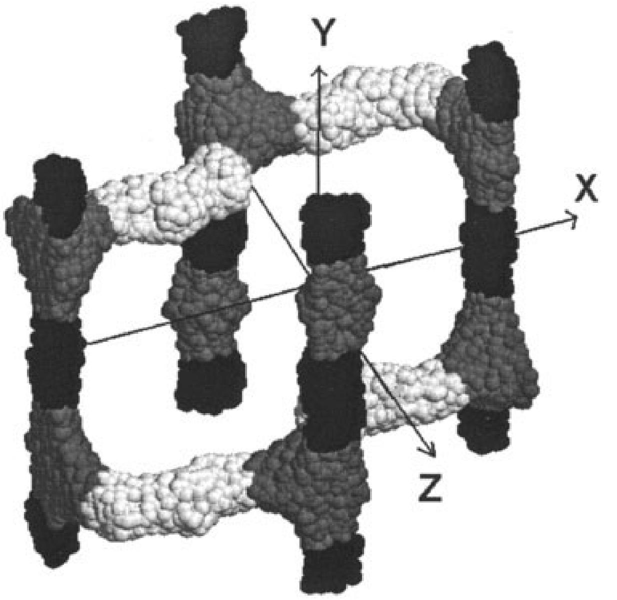

Figure 1. Channel structure and different sites in silicalite.

One unit cell is shown. The atoms of the zeolite are not shown for clarity. The spheres represent pore space available for adsorption. Black spheres represent the straight channel sections, light-gray spheres represent the zigzag channel sections, and the dark-gray spheres represent the intersections.

sorption and binary sorption also are given and used to shed light on the observed behavior.

Silicalite is an all-silica zeolite with the MFI framework structure. The channel structure is shown in Figure 1. A set of straight channels run in the *y*-direction and zigzag channels run in the *x*-direction, as shown in the figure. We have divided the zeolite channels into three regions for analyzing adsorption of aromatic molecules: the intersections, straight channels, and zigzag channels. The exact definitions of these three sites are given below. Silicalite is known to exist in different crystal structures. The as-synthesized form of silicalite is called ORTHO silicalite. It was also found that silicalite may exist in another form referred to as PARA (van Koningsveld et al., 1989). PARA silicalite has the same connectivity and channel structure as ORTHO silicalite, but slight differences in pore size and shape lead to remarkable changes in adsorption characteristics of aromatic molecules. It is known that on adsorption of more than 4 molecules of *p*-xylene per unit cell silicalite changes from ORTHO to PARA (van Koningsveld et al., 1989; Fyfe et al., 1984). Single component adsorption of benzene and *p*-xylene in silicalite both in PARA and ORTHO form have been studied previously (Snurr et al., 1993b), and, based on several observations, it was argued that silicalite changes from ORTHO to PARA also upon adsorption of more than four molecules per unit cell of benzene. In this article we indirectly test if this also holds for other small aromatic molecules.

Mohanty et al. (2000) simulated adsorption of *p*-xylene and *m*-xylene isomers in silicalite and found that *p*-xylene is adsorbed preferentially in both forms of the zeolite. Their binary GCMC simulations were performed for equimolar mixtures of the gas phase. They observed that adsorption of *m*-xylene at high pressures is increased by the presence of *p*-xylene. Lachet et al. (1999) performed similar simulations of single and multicomponent mixtures of xylenes from the gas phase in zeolite Y.

Many authors have experimentally studied the adsorption of *p*-xylene in silicalite by techniques such as X-Ray diffraction, FT-Raman spectroscopy, and NMR (Fyfe et al., 1984; van Koningsveld et al., 1989; Mentzen and Vignemaeder, 1987; Ashtekar et al., 1998; Huang, 1996). Below the loading of four molecules per unit cell, it is found that *p*-xylene adsorbs at the intersections. At loading above four molecules per unit cell, *p*-xylene also adsorbs at the zigzag channels of the zeolite which is in its PARA form. The adsorption of *o*-xylene and *m*-xylene in silicalite was studied by powder X-ray diffraction (Nair and Tsapatsis, 2000). Based on the observations, it was suggested that framework flexibility is important in these systems and should be considered in atomistic simulations because adsorption causes considerable distortion of the channels.

Methodology

Thermodynamic equilibrium

Consider a closed system, as shown in Figure 2, where a binary liquid mixture is in equilibrium with a gas phase and an adsorbed zeolite phase. This system has two degrees of freedom. Fixing the temperature and one liquid phase mole fraction is enough to calculate all other intensive thermodynamic variables. This situation mimics the experimental conditions where the liquid mixture with zeolite crystals is kept in sealed tubes under temperature control. Note that the gas-phase pressure is not controlled, and it depends on the vapor pressures of the compounds in the liquid. Since the three phases are in equilibrium, the different compounds have the same chemical potentials in all three phases. At a given temperature and liquid composition, the partial pressures in the gas phase can be calculated using an equation of state (EOS). The Peng-Robinson equation was used in this work, and the calculations were done using the commercial software package HYSYS. A GCMC simulation can then be done to calculate the equilibrium between the gas phase and the zeolite phase. Gas-phase fugacities are used as input to the GCMC code (Gupta et al., 2003). For all systems studied here, the concentration of one compound in the liquid phase was varied (from 1% to 99%) and the number of molecules adsorbed in the zeolite at each composition was calculated using GCMC.

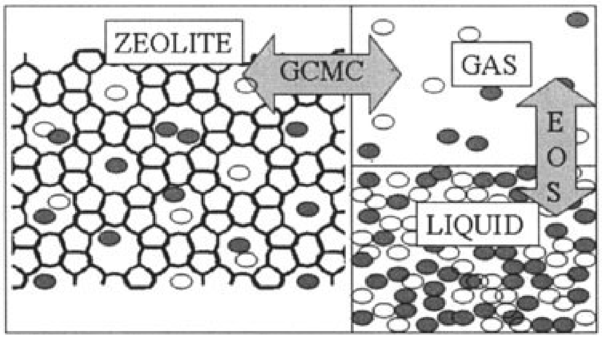

Figure 2. Binary-mixture three-phase equilibrium.

Equilibrium between liquid and gas can be calculated with an EOS model. GCMC simulations can calculate equilibrium between gas and zeolite.

GCMC simulations

GCMC simulations are done to generate configurations of a system for which μ, V, T are specified, where μ is the chemical potential, V is the simulation volume and T is the absolute temperature. GCMC usually consists of four types of moves: (1) insertion of a molecule at a randomly selected place in the system, (2) deletion of a randomly selected molecule from the system, (3) rigid body translation of a randomly selected molecule, and (4) rigid body rotation of a randomly selected molecule. Since the liquid-phase adsorption leads to high loading, more aggressive biasing techniques are required during the insertion attempts. Otherwise, very few insertions and deletions are successful and the simulations do not converge properly. Energy biasing and cavity biasing (Mezei, 1980) have been used previously (Snurr et al., 1993b) to study gas-phase adsorption of benzene and *p*-xylene in silicalite. We use the same techniques, also. However, the combined energy and cavity biasing is implemented in a more sophisticated fashion here, which we now describe.

For the purpose of energy biased insertions, the simulation volume is divided into a grid of small cubes of size 0.2 Å. Each cube is given a weight w proportional to $\exp(-\mathcal{V}/kT)$, where $\mathcal{V}$ is the energy of interaction between the zeolite and a probe particle placed at the center of the cube. For combined energy and cavity biasing, the simulation volume is also divided into larger cubes of size 1.0 Å. A list of all atoms in each large cube and another list of large cubes occupied by each atom are maintained. (This is similar to the cell index neighbor list method (Allen and Tildesley, 1987).) During an insertion attempt one of the small cubes is randomly picked according to its weight w, and the center of mass for the new molecule is placed in the small cube. The Eulerian angles for the molecule are chosen randomly and positions of all individual atoms of the new molecule are generated. With this new trial configuration, a check is made whether all atoms of the new molecule are inside cavities. An atom is said to be in a cavity if there are no other existing atoms in the large cube occupied by this atom. If all atoms are in cavities, then the molecule is said to be in a cavity. During each insertion move, N_c such trials are made and a running average of $N_{s,N}$, the number of molecules found to be in a cavity, is maintained. Note that $N_{s,N}$ is maintained for each value of N—the total number of molecules in the system. One of the configurations lying in a cavity is randomly picked, and the insertion is accepted or rejected with the Metropolis acceptance probability

$$P_{acc} = \min\left[1, \frac{N_{s,N}}{N_c W} \frac{fV}{(N+1)kT} \exp\left(-\frac{\mathcal{V}}{kT}\right)\right] \tag{1}$$

Here, f is the fugacity for the inserted species, V is the simulation volume, N is the number of molecules already in the system, k is Boltzmann's constant, T is the absolute temperature, and $\mathcal{V}$ is the energy of interaction between the inserted molecule and the rest of the system. The acceptance criteria for regular GCMC moves can be found in standard text books (Allen and Tildesley, 1987). We tested the new cavity biasing scheme by reproducing *p*-xylene adsorption isotherms from previous work (Snurr et al., 1993b).

Identity change moves were also used in binary GCMC simulations to obtain faster convergence (Cracknell et al., 1993). One of the two species in the binary simulation is picked randomly. One of the existing molecules of this species is then converted to the other species, keeping its center of mass and Eulerian angles the same. We have found that this move is essential for equilibrating multicomponent systems at full loading. These moves were accepted with acceptance ratio

$$P_{acc} = \min\left[1, \frac{f_2 N_1}{f_1 (N_2 + 1)} \exp\left(-\frac{\mathcal{V}_2 - \mathcal{V}_1}{kT}\right)\right] \tag{2}$$

Here, the subscripts 1 and 2 represent the initial and final species, respectively.

Forcefield

The forcefield used here has been used previously to study adsorption of aromatics in silicalite (Snurr et al., 1993a,b). All parameters were taken without modifications. The simulations done with these parameters reproduce the experimental values of isosteric heats of adsorption at low loading and Henry's constant reasonably well (Snurr et al., 1993a). The aromatic rings were modeled with carbon and hydrogen atoms with partial charges. The methyl groups were modeled as a united atom also with a partial charge. Atomic coordinates of the silicalite atoms are known from the X-ray work of Olson et al. (1981). The Lennard-Jones interaction of silicon atoms with the guest molecules was neglected in the force field, as is common. The zeolite framework was considered rigid and pretabulated potential maps were used for both Lennard-Jones and Coulombic interactions between all zeolite atoms and the adsorbed atoms with interpolation during simulation.

Definition of sites

The quantitative definition of the different sites in the channel structure of silicalite is done as follows. This method was initially used by June et al. (1991) to classify the sites of xenon adsorption in silicalite. A three-dimensional (3-D) grid is generated for the unit cell of silicalite, and the energy of interaction between a probe particle and the zeolite is calculated at each point in the grid. An approximate Lennard-Jones benzene sphere of σ equal to 5.27 Å and ϵ/k equal to 440 K was used as the probe particle in these calculations. After all points are tabulated, a steepest descent energy minimization is done starting from each of the grid points. All points which minimize to a particular minimum belong to a particular site. Based on this scheme, there were 12 minima in the unit cell of silicalite: 4 in the intersections, 4 in the straight channels, and 4 in the zigzag channels. Figure 1 shows the sites belonging to these minima. During GCMC studies, an adsorbed molecule is said to be in a particular site if its center of mass lies in the region covered by that site.

Excess adsorption

In general it is experimentally difficult to obtain the absolute number of molecules adsorbed in a microporous phase from a liquid phase. Usually, an excess adsorption is measured. Definitions of different excess quantities can be found in textbooks on adsorption (Rouquerol et al., 1999). In order to measure excess, the concentrations in the liquid phase are measured

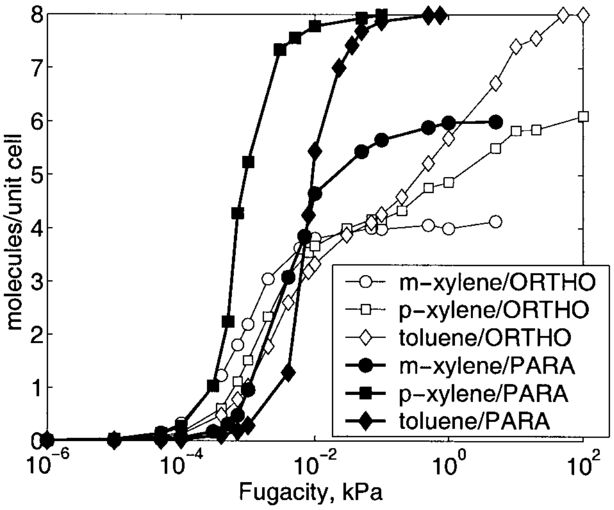

Figure 3. Single component isotherms at 300 K.

before and after the adsorption. "Reduced surface excess" (Rouquerol et al., 1999) of species 1 is defined as

$$e_1 = \frac{N_t}{m}(x_{0,1} - x_{f,1}) \tag{3}$$

where N_t is the total number of moles in the liquid initially, m is the mass of sorbent, $x_{0,1}$ is the mole fraction of species 1 in the solution initially, and $x_{f,1}$ is the mole fraction after adsorption. It can be shown that this is equivalent to

$$e_1 = \frac{N_z}{m}(x_{z,1} - x_{f,1}) \tag{4}$$

where N_z is total number of moles (species 1 and 2) adsorbed in the zeolite, and $x_{z,1}$ is the mole fraction in the adsorbed phase. Equation 4 is used for calculating excess from simulation of binary sorption.

IAS calculations

Ideal adsorbed solution (IAS) theory was developed by Myers and Prausnitz (1965). Given only the single component isotherms, IAS aims to predict multicomponent sorption. Details can be found in the original reference (Myers and Prausnitz, 1965). The assumption involved is that the adsorbed phase activity coefficients are equal to one. We generated single-component adsorption isotherms of xylenes and toluene in both forms of silicalite. The integrals required for estimating the surface pressure were evaluated by applying Simpson's rule. Predictions for binary sorption were then made using IAS. The comparisons between IAS predictions and the values obtained by doing full multicomponent simulations are given in the results section.

Results

Single component adsorption

Simulations were done for adsorption of single components in silicalite at 300 K. *p*-xylene, *m*-xylene, and toluene were simulated in both forms of silicalite, and the isotherms are shown in Figure 3. The averages of the potential energies for molecules adsorbed at the intersections and zigzag channels are given in Table 1. These averages are obtained by calculating the energy of each individual molecule in a site with the rest of the system. Such a calculation leads to double counting of sorbate-sorbate interactions. To obtain the total energy of the system, the values in each column of Table 1 should be multiplied by the respective number of molecules in that site, and then the sorbate-zeolite energy and half of the sorbate-sorbate energy should be added together. The zeolite-sorbate interactions do not vary significantly with amount adsorbed. However, the sorbate-sorbate interactions given depend on the amount of sorbate molecules present. The table corresponds to values obtained at saturation of the zeolite pores with adsorbed molecules. The position of the center of mass determines whether a molecule lies in an intersection or zigzag channel. Very few of these aromatic molecules adsorb in the straight channel segments at these conditions.

In ORTHO silicalite, *m*-xylene adsorbs only at the intersections, and the isotherm plateaus at four molecules per unit cell. Molecules orient themselves such that the methyl groups point into zigzag or straight channels. In PARA form, the saturation loading is six molecules per unit cell. In this case the zigzag sections are found to be energetically very favorable. The zeolite-sorbate interaction energy at the intersections is −56.2 kJ/mol as opposed to −70.4 kJ/mol in the zigzag channel. Even though there is a huge difference in energy, the molecules fill both zigzag channels and intersections equally because there is more freedom at the intersections, whereas the molecules adsorbed in the zigzag sections are tightly confined. Adsorption in the intersections is, thus, entropically favored. At saturation, the intersections contain 3.6 molecules per unit cell, and the zigzag channels contain 2.4 molecules per unit cell.

p-Xylene can adsorb up to 8 molecules in ORTHO silicalite, but only at very high fugacities. Energy in the zigzag section is −53.8 kJ/mol and at the intersection is −64.4 kJ/mol. At low loading, the adsorption is thus in the intersections only. At high loadings, the high energy zigzag channel sites also get occupied. In PARA silicalite the zigzag sections are filled first and then the intersections, as shown in Figure 4. The energies in the intersections and zigzag channels are −60.1 and −71.9 kJ/mol, respectively. *p*-xylene molecules at the intersection orient themselves such that the methyl groups point to the straight channel sections, in agreement with experimental observations in the literature (van Koningsveld et al., 1989; Mentzen and

Table 1. Energies of Molecules Adsorbed in Intersection(I) and Zigzag(Z) Channels for Single-Component Adsorption at Saturation Loadings, at 300 K*

System	V_I^{SZ} kJ/mol	V_Z^{SZ} kJ/mol	V_I^{SS} kJ/mol	V_Z^{SS} kJ/mol
m-xylene/ORTHO	−66.6	—	−3.7	—
p-xylene/ORTHO	−64.4	−53.8	−8.0	−12.7
toluene/ORTHO	−63.5	−51.2	−12.7	−12.3
m-xylene/PARA	−56.2	−70.4	−10.1	−13.3
p-xylene/PARA	−60.1	−71.9	−16.6	−16.2
toluene/PARA	−52.1	−62.6	−14.1	−13.6

*The superscripts *SZ* and *SS* represent sorbate-zeolite interaction and sorbate-sorbate interaction, respectively.

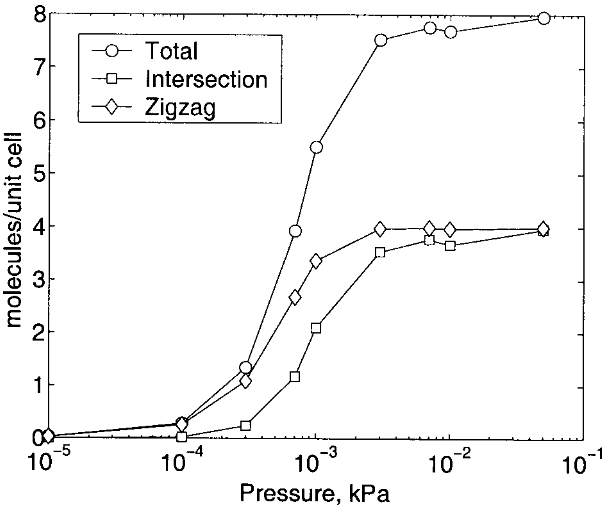

Figure 4. Distribution of *p*-xylene among different adsorption sites in PARA silicalite at 300 K.

Vignemaeder, 1987). Molecules in the zigzag sections orient so that the methyl groups point toward the intersections.

Toluene adsorbs up to 8 molecules in both forms of silicalite. In ORTHO silicalite, the intersections are preferred with a zeolite-sorbate energy of −63.5 kJ/mol, as opposed to −51.2 kJ/mol in zigzag sites. In PARA it is reversed. The zigzag sections are preferred with −62.6 kJ/mol, as opposed to −52.1 kJ/mol at the intersections. Toluene also orients itself so that a molecule at the intersection points the methyl group into a straight channel, and a molecule in the zigzag section points the methyl group to an intersection.

Binary mixture adsorption

The absolute number of molecules adsorbed from a liquid mixture at 300 K was calculated with GCMC for *p*-xylene/*m*-xylene, *p*-xylene/toluene, and *m*-xylene/toluene mixtures in PARA and ORTHO silicalite. Excess adsorption was then calculated with Eq. 4. The experimental values reported here are taken from the literature (Lee and Chiang, 1989). From the experimental values, the order of preference of adsorption is *p*-xylene > toluene > *m*-xylene.

The excess adsorption of *p*-xylene from *m*-xylene/*p*-xylene solution is shown in Figure 5. The values from simulations in PARA silicalite agree well with experiment. The simulations in ORTHO silicalite give qualitatively wrong results and even predict a negative excess adsorption of *p*-xylene at high liquid phase mole fractions of *p*-xylene in contradiction to what is observed experimentally. The results obtained for *m*-xylene/toluene and *p*-xylene/toluene are shown in Figures 6 and 7. In both cases the values from simulations in PARA silicalite agree well with experiment. Simulations of *m*-xylene/toluene in ORTHO silicalite show a maximum excess that is considerably lower than in experiment, and simulation of *p*-xylene/toluene in ORTHO silicalite shows even the wrong selectivity, suggesting that toluene is preferred whereas experiments and simulations in PARA show that *p*-xylene is preferred. In all cases, the zeolite-sorbate energy of interaction for each species in the binary GCMC simulations was found to be very close to the values (within ±1 kJ/mol) for their single component cases.

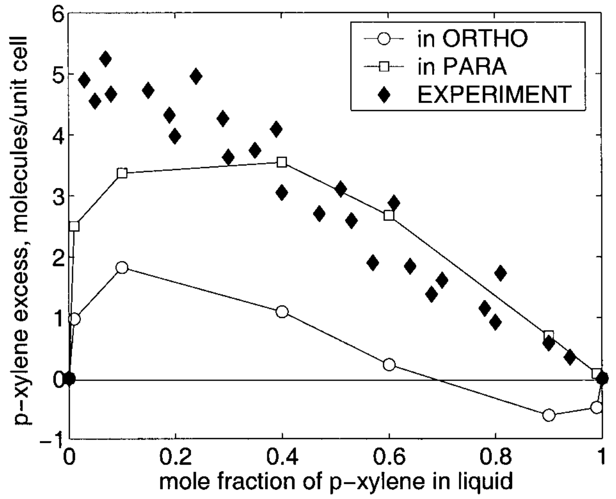

Figure 5. Reduced excess adsorption of *p*-xylene for *m*-xylene/*p*-xylene mixtures at 300 K.

GCMC results in both ORTHO and PARA silicalite are compared with experimental results from the literature (Lee and Chiang, 1989).

A siting analysis of binary mixture adsorption was done to see how molecules of a particular species are distributed among sites. For the cases of *m*-xylene/*p*-xylene/PARA and toluene/*p*-xylene/PARA, molecules were distributed equally between the intersection and zigzag sites. In the case of *m*-xylene/toluene/PARA, *m*-xylene preferred the intersections and toluene preferred the zigzag channels. Single component simulations in ORTHO silicalite for *m*-xylene had shown that *m*-xylene adsorbs only at the intersections. In the case of *m*-xylene/*p*-xylene mixtures in ORTHO, a *m*-xylene loading of up to 1.5 molecules/unit cell was found in the zigzag channels. This suggests that in ORTHO silicalite the adsorption of *p*-xylene in the intersections favors the adsorption of *m*-xylene in the zigzag channels. This observation also emphasizes the fact

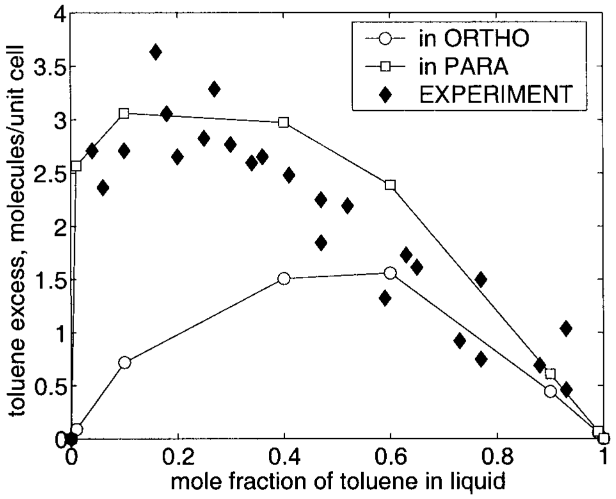

Figure 6. Reduced excess adsorption of toluene for *m*-xylene/toluene mixtures at 300 K.

GCMC results in both ORTHO and PARA silicalite are compared with experimental results from the literature (Lee and Chiang, 1989).

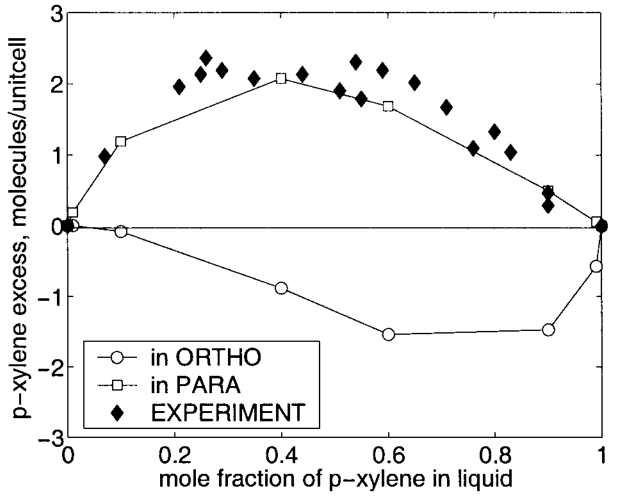

Figure 7. Reduced excess adsorption of *p*-xylene for *p*-xylene/toluene mixtures at 300 K.

GCMC results in both ORTHO and PARA silicalite are compared with experimental results from the literature (Lee and Chiang, 1989).

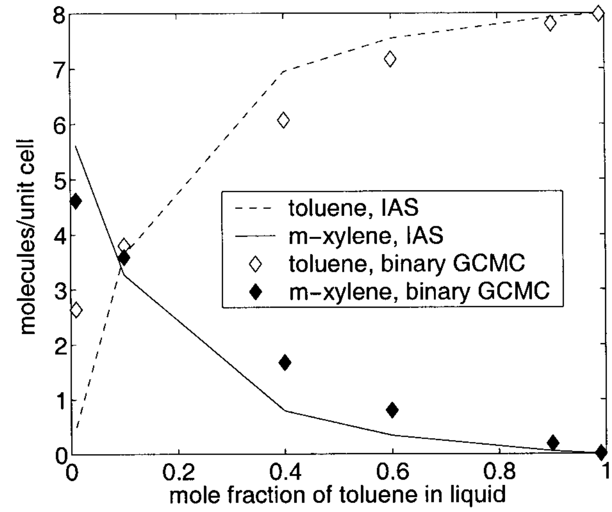

Figure 9. Adsorption isotherms from IAS vs binary GCMC for *m*-xylene/toluene mixtures in PARA silicalite at 300 K.

that sorbate-sorbate interactions are very strong in the systems studied here. This effect has been observed previously by other authors (Mohanty et al., 2000), where more *m*-xylene was absorbed in the mixture simulations than in the single-component simulations.

One of the reasons for agreement between the simulated isotherms in PARA and the experimental values is the fact that PARA allows easy adsorption in the zigzag channels, whereas ORTHO allows only *p*-xylene and toluene to adsorb inside zigzag channels at very high fugacities. Crystallographic studies (van Koningsveld et al., 1989) have previously shown a transition from ORTHO to PARA upon adsorption of more than four *p*-xylene molecules per unit cell. The studies here suggest that a transition also occurs for other aromatics from ORTHO to some other structure which allows adsorption in the zigzag channels. This new structure may be close to the structure of PARA. From our simulations (which are done at high loading), there is no way of concluding whether this change in structure with adsorption is continuous or sudden.

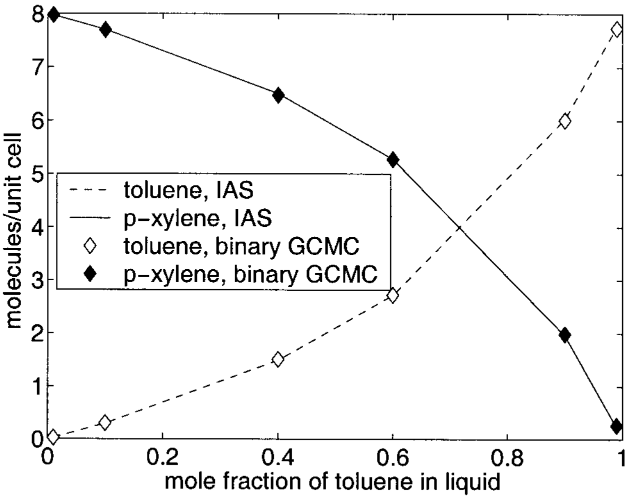

Figure 8. Adsorption isotherms from IAS vs binary GCMC for *p*-xylene/toluene mixtures in PARA silicalite at 300 K.

The agreement between simulation and experiments also depends on how good the forcefield parameters are. The forcefield parameters used here yield good agreement with experimental data for single component adsorption (Snurr et al., 1993a,b) and our results show also very good agreement for the mixtures. This provides additional support for the suggestion (Siperstein and Myers, 2001) that if GCMC parameters work well for single component systems, they should also yield useful prediction for mixtures. This has been shown here to be true also for liquid-phase adsorption.

Comparison of IAS and binary-GCMC simulations

Application of IAS is expected to give good results when the total adsorption area is the same (in other words, when the saturation loading is the same) for both compounds and the molecules adsorbed at the sites do not interact strongly with each other. Figure 8 shows that isotherms predicted by IAS agree very closely with isotherms generated by binary GCMC for the case of *p*-xylene and toluene in PARA silicalite. Note that, at the simulation temperature (300 K), the binary liquid mixtures give rise to partial pressures of about 1.0 to 4.0 kPa. Figure 3 shows that, at this pressure, the single component isotherms of *p*-xylene and toluene saturate at 8 molecules/unit cell. *m*-Xylene has a different saturation loading (6 molecules per unit cell in PARA), so we do not expect the IAS predictions for *m*-xylene/toluene or *m*-xylene/*p*-xylene to agree as well with binary GCMC results. The comparison of isotherms predicted from IAS and binary GCMC for *m*-xylene/*p*-xylene mixtures in PARA silicalite is shown in Figure 9. The IAS prediction is still quite good, but not in quantitative agreement, as in Figure 8. IAS predictions for *m*-xylene/toluene mixtures show agreement with GCMC similar to that in Figure 9 (not shown).

Conclusions

We have shown that GCMC simulations with energy biasing, cavity biasing, and identity change moves can be used to estimate multicomponent sorption from a liquid phase into microporous materials. The experimental and simulated values of excess adsorption isotherms in silicalite agree well for binary mixtures of *m*-xylene, *p*-xylene, and toluene. The agreement is good only when the PARA form of the silicalite is used in the simulations. Since this agreement is good for all three mixtures studied, we can argue that, after adsorption of aromatics from a liquid phase, the silicalite changes structure from the ORTHO to another form close to the structure of PARA silicalite. The main difference between the ORTHO and PARA structures is the availability of more space for adsorption in the zigzag channels of PARA. Predictions from IAS theory are found to give reasonable estimates of binary adsorption for these liquid-phase systems.

Acknowledgment

Please note for GCMC moves with combined energy and cavity biasing, the weight w_i for small cube i is defined as $V/V_{\text{cube}} \exp(-\mathcal{V}_i/kT)/\sum_j \exp(-\mathcal{V}_j/kT)$.

This work has been supported by the National Science Foundation CAREER program.

Literature Cited

Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids,* Oxford University Press, Oxford (1987).

Ashtekar, S., J. J. Hastings, and L. F. Gladden, "FT-Raman Studies of Single-Component and Binary Adsorption in Silicalite-1," *J. Chem. Soc., Faraday Trans.,* **94,** 1157 (1998).

Broughton, D. B., "Production-Scale Adsorptive Separations of Liquid-Mixtures by Simulated Moving-Bed Technology," *Sep. Sci. Technol.,* **19,** 723 (1984).

Cracknell, R. F., D. Nicholson, and N. Quirke, "Grand-Canonical Monte-Carlo Study of Lennard-Jones Mixtures in Slit Shaped Pores," *Mol. Phys.,* **80** (1993).

Fuchs, A. H., and A. K. Cheetham, "Adsorption of Guest Molecules in Zeolitic Materials: Computational Aspects," *J. Phys. Chem. B,* **105,** 7375 (2001).

Fyfe, C. A., G. J. Kennedy, C. T. Deschutter, and G. T. Kokotailo, "Sorbate-Induced Structural-Changes in ZSM-5 (Silicalite)," *J. Chem. Soc.-Chem. Commun.,* **8,** 541 (1984).

Gump, C., V. Tuan, R. Noble, and J. L. Falconer, "Aromatic Permeation through Crystalline Molecular Sieve Membranes," *Ind. Eng. Chem. Res.,* **40,** 565 (2001).

Gupta, A., S. Chempath, M. J. Sanborn, L. A. Clark, and R. Q. Snurr, "Object-Oriented Programming Paradigms for Molecular Modeling," *Mol. Simul,* **29,** 29 (2003).

Hedlund, J., J. Sterte, M. Anthonis, A. J. Bons, B. Carstensen, N. Corcoran, D. Cox, H. Deckman, W. de Gijnst, P. P. de Moor, F. Lai, J. McHenry, W. Mortier, and J. Reinoso, "High-flux MFI membranes," *Microporous Mesoporous Mat.,* **52,** 179 (2002).

Huang, Y., "An FT-Raman Study of Sorbate-Induced Structural Changes in Zeolite ZSM-5," *J. Am. Chem. Soc.,* **118,** 7233 (1996).

June, R. L., A. T. Bell, and D. N. Theodorou, "Transition-State studies of xenon and SF_6 diffusion in silicalite," *J. Phys. Chem.,* **95,** 8865 (1991).

Lachet, V., A. Boutin, B. Tavitian, and A. H. Fuchs, "Molecular Simulation of *p*-xylene and *m*-xylene Adsorption in Y Zeolites. Single Components and Binary Mixtures Study," *Langmuir,* **15,** 8678 (1999).

Lee, M. L., and A. S. T. Chiang, "Adsorption of Binary Aromatic Solutions on Silicalite," *J. Chi. Inst. Chem. Eng.,* **20,** 113 (1989).

Mentzen, B. F., and F. Vignemaeder, "Characterization and Localization of the para-xylene Molecule in a Pentasil Type Zeolite—the Complexes Formed by 2 Boralites with *p*-xylene," *Mater. Res. Bull.,* **22,** 309 (1987).

Mezei, M., "A Cavity-Biased (t,v,μ) Monte-Carlo Method for the Computer-Simulation of Fluids," *Mol. Phys.,* **40,** 901 (1980).

Min, J. S., Y. Kiyozumi, and N. Itoh, "A Sealant-Free Preparation Technique for High-Temperature Use of a Composite Zeolite Membrane," *Ind. Eng. Chem. Res.,* **42,** 80 (2003).

Mohanty, S., H. T. Davis, and A. V. McCormick, "Shape Selective Adsorption in Atomistic Nanopores—a Study of xylene Isomers in Silicalite," *Chem. Eng. Sci.,* **55,** 2779 (2000).

Myers, A. L., and J. M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.,* **11,** 121 (1965).

Nair, S., and M. Tsapatsis, "The Location of *o*- and *m*-xylene in Silicalite by Powder x-ray Diffraction," *J. Phys. Chem. B,* **104,** 8982 (2000).

Olson, D. H., G. T. Kokotailo, S. L. Lawton, and W. M. Meier, "Crystal-Structure and Structure-Related Properties of ZSM-5," *J. Phys. Chem.,* **85,** 2238 (1981).

Rouquerol, F., J. Rouquerol, and K. Sing, *Adsorption by Powders and Porous Solids,* Chapter 5, Academic Press, London, pp. 142–148 (1999).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes,* Wiley-Interscience, New York (1984).

Sakai, H., T. Tomita, and T. Takahashi, "*p*-xylene Separation with MFI-Type Zeolite Membrane," *Sep. Purif. Technol.,* **25,** 297 (2001).

Siperstein, F. R., and A. L. Myers, "Mixed-Gas Adsorption," *AIChE J.,* **47,** 1141 (2001).

Snurr, R. Q., A. T. Bell, and D. N. Theodorou, "Molecular Simulation of Low Occupancy Adsorption of Aromatics in Silicalite," *Proc. from Ninth Int. Zeolite Conf., Montreal 1992,* Volume II, R. von Ballmoos, J. B. Higgins, and M. M. Treacy, eds., Butterworth-Heinemann, Stoneham, MA (1993a).

Snurr, R. Q., A. T. Bell, and D. N. Theodorou, "Prediction of Adsorption of Aromatic Hydrocarbons in Silicalite from Grand Canonical Monte Carlo Simulations with Biased Insertions," *J. Phys. Chem.,* **97,** 13742 (1993b).

van Koningsveld, H., F. Tuinstra, H. van Bekkum, and J. C. Jansen, "The Location of para-xylene in a Single-Crystal of Zeolite H-ZSM-5 with a New, Sorbate-Induced, Orthorhombic Framework Symmetry," *Acta Crystallogr. Sect. B-Struct. Commun.,* **45,** 423 (1989).

Xomeritakis, G., Z. P. Lai, and M. Tsapatsis, "Separation of Xylene Isomer Vapors with Oriented MFI Membranes made by Seeded Growth," *Ind. Eng. Chem. Res.,* **40,** 544 (2001).

Manuscript received May 22, 2003, and final revision received Sept. 2, 2003.