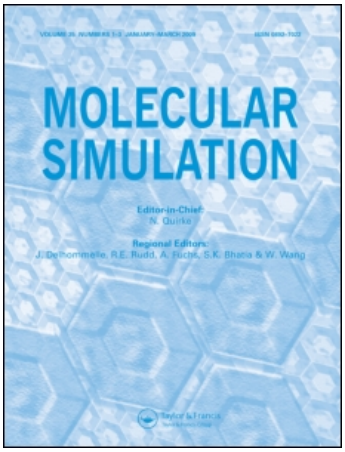

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular Simulation of Adsorption of Guest Molecules in Zeolitic Materials: A Comparative Study of Intermolecular Potentials

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To cite this Article Boutin, Anne , Buttefey, Séverine , Fuchs, Alain H. and Cheetham, Anthony K.(2001) 'Molecular Simulation of Adsorption of Guest Molecules in Zeolitic Materials: A Comparative Study of Intermolecular Potentials', Molecular Simulation, 27: 5, 371 — 385
To link to this Article: DOI: 10.1080/08927020108031359
URL: http://dx.doi.org/10.1080/08927020108031359

Molecular Simulation, Vol. 27, pp. 371–385
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MOLECULAR SIMULATION OF ADSORPTION OF GUEST MOLECULES IN ZEOLITIC MATERIALS: A COMPARATIVE STUDY OF INTERMOLECULAR POTENTIALS

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(Received May 2001; In final form July 2001)

Grand Canonical Monte Carlo simulation, together with an appropriate guest–host forcefield is shown to provide reasonably accurate predictions of adsorption properties of guest molecules in a variety of zeolitic materials. The use of a simple guest–host Kiselev-type potential permits the calculations to capture the essence of the behavior of simple guest–host systems such as rare gases or methane molecules in neutral $AlPO_4$-5. However, a full scale potential is needed in the more complex cases of large anisotropic molecules adsorbed in cationic zeolites (such as xylene isomers in faujasite). The guest–host potential model developed by Nicholson and coworkers is shown to allow an excellent transferability of the potential parameters from one guest/host system to another.

Keywords: Zeolites; Intermolecular potential; Transferability; Adsorption

INTRODUCTION

Zeolitic materials and related open-framework inorganic materials are gaining increasing importance in industrial applications. In two of the most widespread applications, i.e. molecular sieving and catalysis, a crucial role is played by adsorption and transport of the guest molecules. From a more academic point of view, the behavior of fluids in confined geometries has also attracted much

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interest in the past few years. While the macroscopic science of this field is well developed, there is a need for a more fundamental microscopic understanding of the phenomena, as well as means for predicting thermodynamics and transport properties in a variety of guest–host systems.

Molecular simulation, in conjunction with experiments, has played an important role in the past few years in developing our understanding of the relationship between microscopic and macroscopic properties of confined molecular fluids in zeolitic materials.

Two principal types of theoretical treatments of guest molecules in zeolite hosts can be found in the literature. On one hand, *ab initio* quantum chemistry techniques are used to address the problem of molecular chemisorption processes and reactions at Brønsted acid sites. On the other hand, classical Monte Carlo (MC)/Molecular Dynamics (MD) simulations are used to study adsorption and transport of molecules in zeolite pores.

The quantum chemistry approach is rather time consuming and, for this reason, calculations were often limited in the past to finite cluster models of zeolite. Modern *ab initio* MD codes can now be used to study larger systems, such as a methanol molecule interacting with the Brønsted site in a periodic model of chabazite [1,2].

The classical MC/MD approach has been widely used to study the behaviour of simple molecules (e.g. rare gases or simple hydrocarbon molecules) in silicious zeolites such as silicalite. A large number of different equilibrium configurations of the system can be generated through these techniques, enabling one to compute ensemble average quantities, that can be related to thermodynamics and transport properties of the guest molecules. This approach relies on semi-empirical intermolecular potentials, which constitutes a main drawback of the classical methods.

Bridging the gap between the quantum chemistry and the classical approaches is a major challenge in molecular simulation. Electronic density functional theory based MD codes are still far from being able to address long time diffusion and high loading adsorption processes. This is not only a problem of computing time. Basic problems remain open, such as the long range dispersion interaction between species which are still not properly handled in the theory. The development of mixed quantum/classical methods, once the embedding problems are solved, is expected to yield new powerful methods for zeolite catalysis studies.

For the time being, the classical, semi-empirical, approach is the only feasible way of addressing thermodynamic and transport phenomena in complex guest/host systems in which no chemical reactivity takes place. Recently developed techniques allow the simulation of systems that a few years ago were

considered impossible to study via computer simulation. Systems of relevance to commercial applications, such as normal and branched alkanes [3], benzene [4], alkyl benzene isomers [5] and halocarbon molecules [6] in aluminosilicate hosts are now being studied by molecular simulation. The MC algorithms used to obtain reliable thermodynamic data (adsorption isotherms and heats) as well as the newly developed semi-empirical forcefields which allow a better transferability of the parameters from one guest/host system to another have been reviewed recently [7].

In this paper, we address the specific question of reliability and transferability of the forcefield. Most authors agree on the fact that there is no single optimum force field for predicting adsorption properties. Some of them believe in an "engineering" approach in which the simplest (and cheapest) potential function should be used, and the potential parameters be readjusted whenever a quantitative prediction is needed. Others try to develop new strategies to derive semi-empirical potentials on a firmer basis. The performance of these two approaches is compared here, for several guest/host systems: argon and methane/$AlPO_4$-5, xylene isomers/faujasite. It is shown that simple, Kiselev type, force fields can do a good job for the so-called "simple" systems (small guest molecules in a neutral framework). Full scale potentials are needed, however, to model complex systems. These latter forcefields allow a better transferability of the parameters from one system to another, and still make use of a limited number of adjustable parameters.

COMPUTATIONAL METHODOLOGIES

Monte Carlo (MC) Simulations

MC simulations are particularly convenient for computing equilibrium thermodynamic quantities such as the average number of adsorbed molecules $\langle N \rangle$, the isosteric heat of adsorption, q_{st}, and the Henry's constants K. In addition, MC simulations provide detailed structural informations, in particular the location and distribution of adsorbed molecules in the pores.

Adsorption quantities have been computed in the Grand Canonical (GC) statistical ensemble in which the chemical potential (μ), volume (V) and temperature (T) are fixed [8]. These thermodynamic conditions are close to the experimental conditions where one wants to obtain information on the average number of particles in the porous material as a function of the external conditions. At equilibrium, the chemical potentials of the fluid bulk phase and the adsorbed phase are equal. The pressure in the reservoir fluid can be calculated from an

equation of state, and it is thus directly related to the chemical potential in the adsorbed phase. The ensemble average number of molecules in the zeolite, $\langle N \rangle$, is computed directly from the simulation. By performing simulations at various chemical potentials, at a given temperature, one obtains the adsorption isotherm. Experimental adsorption isotherms yields the *excess* number of molecules adsorbed in the porous medium which is not, in principle directly comparable to $\langle N \rangle$. Since zeolite pores are small, the correction is negligible under normal conditions.

A full development of the statistical mechanics of the μVT ensemble, the description of the corresponding Monte Carlo algorithms, and the bias MC moves that have been suggested in order to increase the acceptance probability of the insertion/deletion step for anisotropic molecules such as xylene isomers, have been given in several publications e.g. [8–10] and will not be repeated here.

Potential Energy Models

The potential energy model is an important input to a molecular simulation. Although the guest–host interaction is the most significant part of the total potential energy, some attention should be paid to the accuracy of the guest–guest interaction as we will see in the discussion section.

The zeolite is usually modeled as a rigid crystal. Following Kiselev [11], most authors have used a rather simplified guest–host potential function U_{GH}. In this model, a Lennard–Jones repulsion–dispersion term acts between the atoms of the guest adsorbate (G) and the oxygen atoms (O) and M^+ cations of the host material (H). In the case where the adsorbate molecules are multipolar, an electrostatic term is added, which acts between all atoms of the zeolite (Oxygen, tetrahedrally coordinated (T) atoms and M^+ cations) and of the adsorbate:

$$U_{GH}^{Kiselev} = \sum_{G,H \in O,M^+} 4\varepsilon^{GH} \left\{ \left(\frac{\sigma^{GH}}{r_{GH}} \right)^{12} - \left(\frac{\sigma^{GH}}{r_{GH}} \right)^{6} \right\} + \sum_{G,H \in T,O,M^+} \frac{q^G q^H}{r_{GH}} \qquad (1)$$

where r_{GH} is the distance between the guest G and the host H atoms, and q^G and q^H are the partial charges borne by the guest and host atoms, respectively. Some authors have used formal charges for the framework atoms, but usually partial charges are assigned using some quantum chemistry calculation. In most studies, the other part of the potential function, i.e. the host–host interaction, takes the form of an effective two-body potential derived from bulk simulations. In both the guest–host and guest–guest potentials, the well-known Lorenz–Berthelot combining rules are used to handle cross interactions.

Pellenq and Nicholson have developed a full scale guest–host semi-empirical potential (hereafter called the PN potential) with the aim of obtaining a more accurate and transferable potential model [12–20]

$$U_{GH}^{PN} = U_{el} + U_{pol}^{PN} + U_{disp}^{PN} + U_{rep}^{PN} \tag{2}$$

in which the first term is the electrostatic interaction calculated in the same way as in the Kiselev potential. Induced interactions, due to the partial charges of the framework species are calculated using the first term of the multipole expansion

$$U_{pol}^{PN} = -\frac{1}{2}\sum_{i\in G}\alpha_i E_{T,O,M^+}^2 \tag{3}$$

where α_i, is the dipole polarizability of atom i of a guest molecule and E is the electrostatic field at the position occupied by atom i due to the partial charges carried by all the host species. The back-polarization and higher order terms are neglected.

The dispersion interaction includes the r^{-6}, r^{-8} and r^{-10} terms, as well as the three-body dispersion Axilrod–Teller term:

$$U_{disp}^{PN} = \left[\sum_{G,H\in T,O,M^+} -\frac{C_6^{GH}}{r_{GH}^6} - \frac{C_8^{GH}}{r_{GH}^8} - \frac{C_{10}^{GH}}{r_{GH}^{10}}\right] + U_{3\,body} \tag{4}$$

where the three-body interaction involving triplets of species i, j and k can be expressed in terms of geometrical factors W^{ijk} and electronic functions Z^{ijk} in the following general form:

$$U^{ijk}(l_1, l_2, l_3) = \sum_{l_1}\sum_{l_2}\sum_{l_3} Z^{ijk}(l_1, l_2, l_3) W^{ijk}(l_1, l_2, l_3) \tag{5}$$

The dispersion coefficients in Eq. (4) are estimated from a knowledge of the dipole polarizabilities and the partial charges of all interacting species. The calculation of the three-body dispersion term requires the same set of parameters as the two-body terms. All atoms of the framework are considered here, not only the oxygen atoms as in the Kiselev potential.

Finally, the repulsion interaction is represented with an exponential Born–Mayer term:

$$U_{rep}^{PN} = \sum_{G,H\in T,O,M^+} A^{GH}\exp(-b^{GH} r_{GH}) \tag{6}$$

In this latter case, Böhm–Ahlrichs combining rules are used to handle cross interactions:

$$A^{ij} = (A^{ii}A^{jj})^{1/2}, \quad b^{ij} = \frac{2b^{ii}b^{jj}}{b^{ii} + b^{jj}} \tag{7}$$

Usually, the repulsive interaction between the adsorbate and the T atoms can be neglected since the guest molecules are only sensitive to the repulsion from the oxygen atom and the extra-framework cations (when they are present).

Although the PN potential is more sophisticated and rather more time consuming to use in simulations than the Kiselev potential, it should be stressed here that no extra adjustable parameters are introduced in the full scale PN potential. Since the dispersion coefficients C_{6-10}^{GH} are calculated from a knowledge of dipole polarizabilities and the effective number of electrons of the interacting species, the only adjustable parameters are the A's and b's of the repulsion energy.

The PN potential function has been successfully used in a variety of systems: rare gases and small molecules in silicalite [12–16], faujasite [21] and $AlPO_4$-5 [22,23], and benzene and xylene molecules in faujasites [5,10,21]. In the

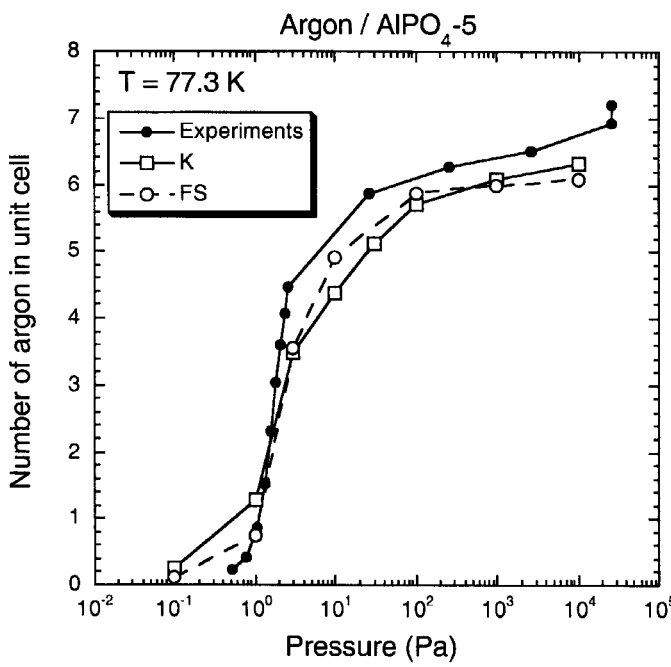

FIGURE 1 Adsorption isotherms of argon in $AlPO_4$-5.

TABLE I Parameters sets of the guest–guest and guest–host potentials used in this work (**existence of a step in the computed isotherm)

Set	*Guest–guest*		*Guest–host*	
1	Ar–Ar	LJ 12–6 [3] ε/k_B = (120.0 K, σ = 3.405 Å	Ar–O	LJ 12–6 from [24] ε/k_B = (86.893 K, σ = 3.4375 Å
2 [22,23]			Ar–O	LJ 12–6 [26] ε/k_B = (124.0 K, σ = 3.03 Å
3 [22,23]			Ar–O	Full scale
			Ar–Al	
			Ar–P	
4 [24]**	CH_4–CH_4	LJ 12–6 [24] ε/k_B = (148.0 K, σ = 3.73 Å	CH_4–O [24]	LJ 12–6 [24] ε/k_B = (96.5 K, σ = 3.6 Å
5			CH_4–O	LJ 12–6 [22,23] ε/k_B = (100.0 K, σ = 3.233 Å
6 [22,23]		LJ 12–6 [36] ε/k_B = (148.2 K, σ = 3.817 Å	CH_4–O	LJ 12–6 [22,23] ε/k_B = (100.0 K, σ = 3.233 Å
7**			CH_4–O	LJ 12–6 [24] ε/k_B = 96.5 K, σ = 3.6 Å
8**			CH_4–O	Full scale [22,23]
			CH_4–Al	
			CH_4–P	
9**		LJ 20–6 [37] ε/k_B = (148.0 K, σ = 3.73 Å	CH_4–O	LJ 12–6 [24] ε/k_B = 96.5 K, σ = 3.6 Å
10 [22,23]**			CH_4–O	Full scale [22,23]
			CH_4–Al	
			CH_4–P	

following section, we revisit some of the key results obtained by using different types of potential models. We then discuss the usefulness of either using the simple effective model or the full scale model. We also suggest some further developments in the methods used for modeling adsorption of complex mixtures (such as water+hydrocarbons) in cationic zeolites, which constitutes a major challenge for the future.

RESULTS

Adsorption of Argon in $AlPO_4$-5

The aluminophosphate $AlPO_4$-5 is a microporous crystal with a neutral framework. It consists of alternate tetrahedral aluminium and phosphorus atoms bridged by oxygen atoms. The crystalline lattice is hexagonal space group *P6cc* for ordered Al and P, and was taken from X-ray scattering and neutron powder diffraction studies. The full model has been described in earlier publications [22,23]. The micropores are not interconnected and form unidimensional channels of ~7.3 Å diameter parallel to the crystallographic *c* direction (AFI structural network). The rather simple $AlPO_4$-5 inner surface consists of a regular hexagonal array of oxygen atoms.

The computed adsorption isotherms of argon in $AlPO_4$-5 are shown in Fig. 1, where they are compared to experiments. The first set of data (*K* for Kiselev-like potential) was obtained using oxygen–argon (O–Ar) Lennard–Jones parameters (see Table I, parameters set 1) obtained from a combination of Smit *et al.*'s oxygen–alkane potential [24,25] and argon–argon potential parameters [26] using Lorentz–Berthelot combination rules. A rather good agreement is obtained between simulation and experiments. Very similar results were obtained previously [22,23] using slightly different O–Ar potential parameters (Table I, set 2). The computed isotherm obtained through the use of the Full-Scale (FS) potential (Table I, parameters set 3) is also shown in Fig. 1. It also agrees quite well with experiments.

Adsorption of Methane in $AlPO_4$-5

This system displays an interesting kink (or "step") in the experimental adsorption isotherm [27] at low temperatures, instead of the usual smooth Langmuir (or "type I") isotherm. This step is akin to a phase transition of the confined methane fluid and has first been reproduced by Boutin *et al.* [22,23] through GCMC simulations, using a PN-type potential function. In the first

instance, it was thought that a full-scale potential form was presumably needed in order to reproduce such subtle effects as a kink in the isotherm. This was based on the fact that these authors could not find the step using a Kiselev-like potential (with the parameters set 6 given in Table I).

Later, Maris *et al.* [24] found that this step could be reproduced by using a simple Kiselev-like potential. This has been checked here by performing GCMC simulations, using exactly the same potential parameters (Table I, set 4). As shown in Fig. 2, the step is indeed obtained in such conditions. The hysteresis observed in Ref. [24] is presumably due to the poor convergence of the simulations in the transition region. A long enough simulation ($\geq 10^8$ steps) leads to the single adsorption–desorption branch shown in Fig. 2.

It is worth mentioning that Maris *et al.* [24] claimed that the step could actually be obtained by using the Kiselev-type potential parameters used in Refs [22,23]. We have fully revisited this point here and we are unable to reproduce their results. We find that the use of the parameters set 6 (Table I) does not lead to a step in the computed isotherm. Different grid spacings in the guest–host potential have been tested and no significant change was found in the resulting form of the isotherms. The same was true when using a combination of Maris *et al.* and our parameters (set 5, Table I). We thus conclude that, within the Kiselev scheme, slight changes in the methane–oxygen parameters (5% change or less), can transform the type I into a stepped isotherm displaying the known phase transition. Adsorption isotherms obtained using different parameter sets are shown in Fig. 3.

In Fig. 4 is shown the evolution of the pressure at which the step is found in the isotherm, versus temperature. The data obtained with the use of the parameters set 10 in a full-scale potential agree extremely well with experiments. This is not the case with the Kiselev-type potential (parameters set 4) although the slope of the transition pressure is well reproduced.

One important point raised by these studies is the sensitivity of the adsorption data to very small changes in the guest–host steric potential parameters (or to the details of the zeolite structure). This will be a somewhat general conclusion of this survey. Such sensitivities have also been observed in other systems such as pentane/ferrierite [28] and *p*-xylene/silicalite [29], and could partly be attributed to the rigid framework assumption made in the simulations.

Adsorption of Xylene Isomers in Faujasite

Lachet *et al.* [5,10,30,31] have studied in some details, the adsorption of *p*-xylene and *m*-xylene in several X and Y faujasite zeolites. They were able to reproduce fairly well, the equilibrium adsorption properties using a guest–host potential

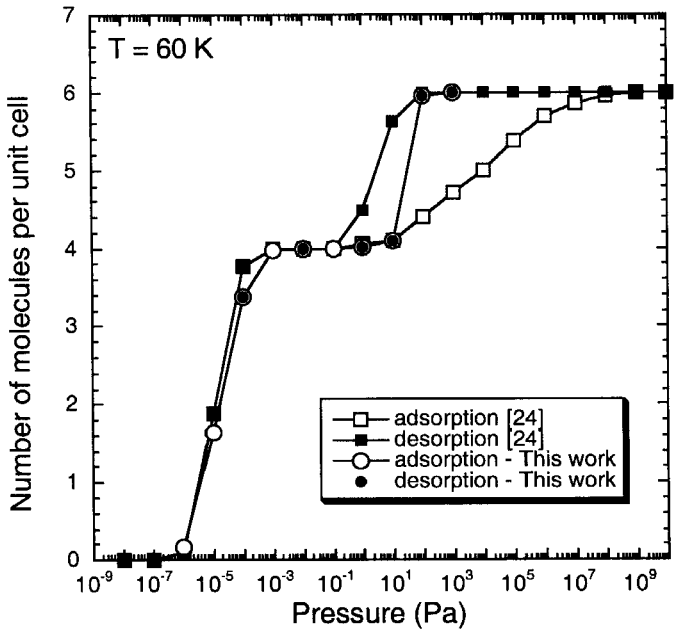

FIGURE 2 Calculated adsorption and desorption isotherms of methane in $AlPO_4$-5 at 60 K.

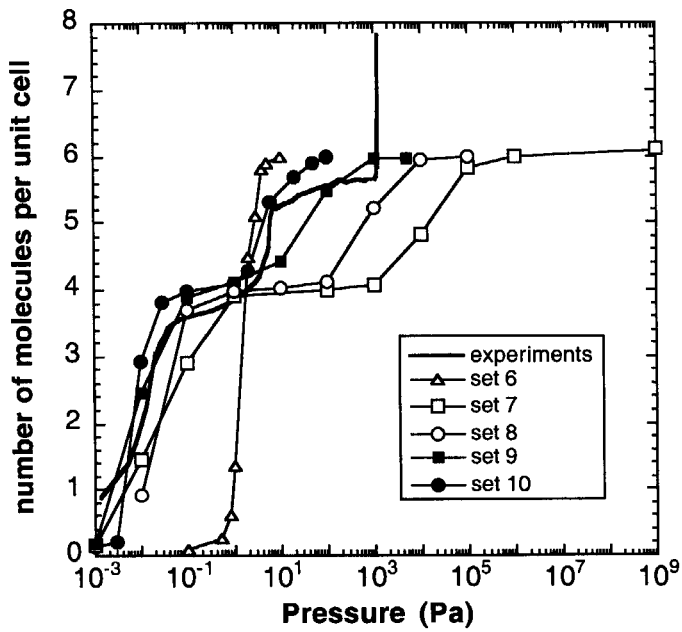

FIGURE 3 Adsorption isotherms of methane in $AlPO_4$-5 at 77.3 K calculated using different potential parameter sets compared to experiments.

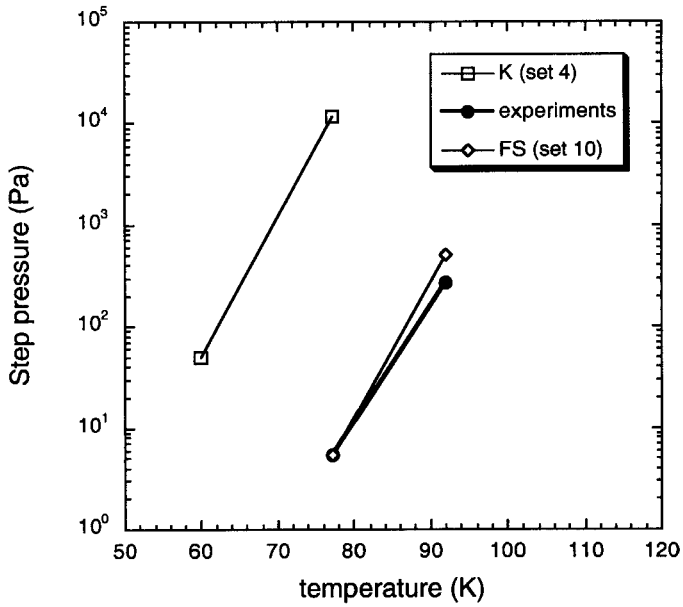

FIGURE 4 Evolution of the pressure at which the step is found in the isotherm versus temperature.

derived from the PN scheme (Fig. 5). The transferability of the potential function, from one system to another, has been tested here for these two isomers in NaY and KY faujasites. The potential parameters were fitted to the experimental data for the *m*-xylene/NaY system. As shown in Table II, the maximum loading in the isotherm is rather well reproduced in all three other systems, without readjusting the potential parameters. The same calculation has been performed with a Kiselev-type potential, which was obtained by fitting the Lennard–Jones oxygen–xylene atoms parameters in order to reproduce the experimental adsorption isotherm of *m*-xylene in NaY. As seen in Table II, attempts to transfer this latter potential function to the other xylene/faujasite systems without further readjustment clearly breaks down.

TABLE II Maximum number of adsorbed molecules in the faujasite supercage

Zeolite	*NaY*		*KY*	
isomer	*m-xylene*	*p-xylene*	*m-xylene*	*p-xylene*
Experiments	3.62	3.34	2.95	3.10
Full scale	3.54	3.31	2.82	3.12
Kiselev-like	3.60	3.05	1.88	2.16

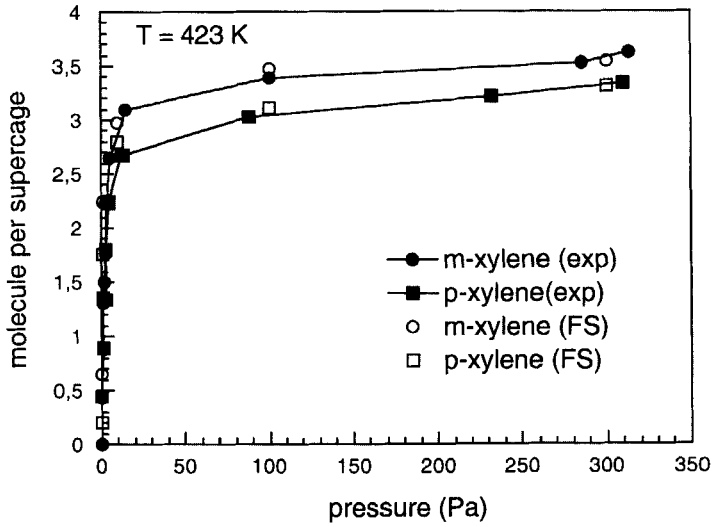

FIGURE 5 Adsorption isotherms of *meta* and *para*-xylene isomers in NaY faujasite.

CONCLUSIONS

Grand Canonical Monte Carlo simulation (using statistical biasing for studying large anisotropic molecules such as xylene isomers), together with an appropriate guest–host forcefield (the Kiselev potential in the simplest cases, a full scale potential in the more complex cases), may provide a reasonably accurate prediction of single component as well as binary mixture adsorption data [5,7].

However, in spite of their impressive results to date on a variety of systems, further progress is still needed in order to reach an acceptable accuracy in the simulations on certain types of systems. Guest–host systems in which the adsorbate molecules fit tightly in the zeolite pores provide extremely interesting and demanding test cases for the simulation models. The observed sensitivity to small changes in the Kiselev potential terms (or in the zeolite structure) is deemed to be largely unnatural and it illustrates the need to improve the potential models for these (and other) systems. Furthermore, it is in problems such as these that the inclusion of host structure flexibility is probably essential.

We suggest here some further developments in the method used for modeling adsorption of complex mixtures (such as water+hydrocarbons) in cationic zeolites. In these cases, the electrostatic and polarization terms will become dominant and we believe that computing higher order terms of the polarization energy in a self-consistent manner will become necessary. Along these lines, Smirnov [32] has suggested an interesting way of treating molecular partial

charges redistribution during adsorption of a highly polar molecule using the electron equalization method.

The guest–guest interaction potential is not the dominant term in the total Hamiltonian of the system, but at high loadings (where most of the interesting features are obtained), details of the intermolecular potential may become crucial. We suggest revisiting the intermolecular forcefields derived from bulk properties, in the manner described by Bayly *et al.* [33], Kranias *et al.* [34] and Delhommelle *et al.* [35]. The main point raised by these authors is that the use of partial charges located only at the atomic sites cannot lead to a good description of the electrostatic potential of the molecule. Using additional electrostatic centers of forces, calculating the partial charges by fitting the *ab initio* electrostatic potential, together with a stabilisation process in order to deal with ill-defined charges in the fitting procedure, leads to very accurate and transferable electrostatic potential terms. This strategy then leaves only two "effective" terms (the repulsive and dispersive ones) that contain adjustable parameters. It has been successful in obtaining transferable potential functions for bulk fluids simulations [35]. The same strategy should now be tested in the case of adsorption. Finally, in view of the unnatural sensitivity of adsorption data to small changes of the potential parameters, the methods used for computing framework partial charges should also be revisited, in order to test the accuracy of the electrostatic field created by the inorganic material at each point in the porous geometry.

Refinement of the simulation models along the lines described above are expected in the near future. They should lead to improved direct predictions of binary mixture adsorption (and presumably transport) properties, and may then help in the rational design of adsorbents.

Acknowledgements

This work was supported by the United States Department of Energy under grant no. DE-FG03-96ER14672, by the French Ministry of Education and the CNRS.

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