Adsorption 11: 379–382, 2005

Adsorption of Various Hydrocarbons in Siliceous Zeolites: A Molecular Simulation Study

PIERRE PASCUAL
Laboratoire de Chimie Physique, UMR 8000 CNRS-Université Paris-Sud, Orsay, France

HÉLÈNE KIRSCH
Laboratoire de Matiriaux Minéraux, Mulhouse, France

ANNE BOUTIN
Laboratoire de Chimie Physique, UMR 8000 CNRS-Université Paris-Sud, Orsay, France

JEAN-LOUIS PAILLAUD AND MICHEL SOULARD
Laboratoire de Matiriaux Minéraux, Mulhouse, France

BERNARD TAVITIAN
Institut Français du Pétrole, Rueil-Malmaison, France

DELPHINE FAYE
Centre National d'Etudes Spatiales, Toulouse, France

ALAIN H. FUCHS*
Laboratoire de Chimie Physique, UMR 8000 CNRS-Université Paris-Sud, Orsay, France
fuchs@lcp.u-psud.fr

Abstract. The adsorption of linear, branched and cyclic alkanes in several siliceous zeolites is reinvestigated using a recently developed forcefield based on the anisotropic united atom (AUA) potential scheme with no further readjustment. The simulation model is shown to be reasonably well transferable from on guest-host system to another, enabling thus to predict adsorption equilibria in systems for which experimental data are scarce.

Keywords: adsorption, zeolites, molecular simulation, hydrocarbons

1. Introduction

The use of recently developed techniques allows the simulation of systems that a few years ago were considered impossible to study via computer experiments. Systems of relevance to applications such as normal and branched alkanes, benzene, alkyl benzene isomers and halocarbon molecules in aluminosilicate hosts are now being studied by molecular simulation (see the reviews of Fuchs and Cheetham, 2001; Smit and Krishna, 2003).

Among other interesting issues, molecular simulations have tried to reproduce the "kinks" observed in the adsorption isotherms of various guest-host systems at

---

*To whom correspondence should be addressed.

low temperature, instead of the usual smooth Langmuir (or "type I") isotherm. An inflection in the isotherm was predicted by Smit and coworkers (Smit and Maesen, 1995; Vlugt et al., 1999) in the case of n-hexane and n-heptane in silicalite, while for shorter and longer alkanes the usual type I isotherm was computed. This was attributed to a so-called "commensurate freezing" effect (Smit and Maesen, 1995; Vlugt et al., 1999). On the other hand, Van Well et al., (1998) have obtained a step in the computed isotherm of n-pentane in zeolite ferrerite in disagreement with the type I isotherms observed experimentally. These authors have tested another set of potential parameters proposed earlier by June et al. (1992). The simulation showed no kink anymore, but the loadings were greatly overestimated.

All the above-mentioned computer experiments rely on a very simple United Atom (UA) description of the guest hydrocarbon molecules together with the rigid framework hypothesis. Most of them also describe the guest-host interaction through a Lennard-Jones repulsion-dispersion term that acts between each oxygen atom of the framework and each UA of the host molecules (the so-called Kiselev approximation). Giving the difficulties in reproducing the observed kinks in the isotherms, whenever they exist, the validity of these simple forcefields is thus questionable. Whether or not some, or all of the above-mentioned hypothesis should be abandoned, at the expense of more accurate models (and often much more expensive calculations) is still an open question.

We reinvestigate here the adsorption of linear, branched and cyclic alkanes in several zeolites, using a recently developed forcefield based on the anisotropic united atom (AUA) potential scheme. As in the usual UA model, a CH_2 or CH_3 group is represented by a single center of force. In the AUA scheme, this center of force is no more located on the carbon atom but displaced towards the geometric center of the group by a small distance δ of the order of a few tenth of an Angström. Ungerer and coworkers (Ungerer et al., 2000) have proposed an AUA model that reproduces quite well the liquid-vapor phase equilibria of linear, branched and cyclic alkanes (Bourasseau et al., 2002a; Bourasseau et al., 2002b) as well as alkenes (Bourasseau et al., 2003). An extension of this forcefield for simulating adsorption in zeolites has been recently proposed (Pascual et al., 2003). Within the rigid framework and the Kiselev approximation, Lennard-Jones parameters for the framework oxygen atom of neutral silicalite were obtained by adjusting simulation results to experimental data in the case of n-butane. Once these two parameters (σ_O and ε_O) were fixed, all cross potential parameters for the individual UA groups were obtained using the Lorentz-Berthelot mixing rules. Adsorption quantities for linear and branched alkanes, have been very accurately reproduced (Savitz et al., 1998). This procedure allows extending the computation to any other system without further adjustment of the parameters, as long as the forcefield parameters for the bulk fluid are available. The simulation of alkenes as well as alkane-alkene mixtures adsorption in silicalite has provided a demonstration of this (Pascual et al., 2004). In this work, we are testing the possible transferability of this forcefield to several other guest-host systems.

2. Models and Methods

The adsorption of n-alkanes ($n = 1$–9) in zeolite TON, $n-$pentane in ferrierite (FER), 3-methylpentane in silicalite-1 (MFI), and cyclohexane in beta (BEA) have been computed using configurational bias Grand Canonical Monte Carlo simulations. The AUA parameters of the bulk fluid (Ungerer et al., 2000; Bourasseau et al., 2002a, 2002b, 2003) were used, together with the $\sigma_O = 3.00$ Å and $\varepsilon_O = 93.53$ K parameters derived from our earlier study (Pascual et al., 2003). We used the zeolite structures given in the Atlas of Zeolite. To relate the chemical potential to pressure, the ideal gas law was assumed. We have checked that this assumption is satisfactory below 1 MPa under the thermodynamic conditions used in this study, by separately simulating the gas phase properties.

Thermogravimetry under controlled vapour pressure (cold point method (Simonot-Grange, 1979)) was used to study the adsorption of cyclohexane in BEA and 3-methylpentane in silicalite-1. The equipment used is a modified TGA 92 from Setaram. Experimental adsorption isotherms at 295 K were drawn in graduated steps by increasing pressure in small successive increments, under pressure ranging from 10^{-2} to 10^4 mbar (1 Pa to 10^6 Pa). Zeolite samples were outgassed *in situ* under a vacuum of 1 Pa and a temperature of 823 K for 10 hours prior to the adsorption. Purely siliceous beta and silicalite-1 zeolites were provided by the Laboratoire de Matériaux Minéraux.

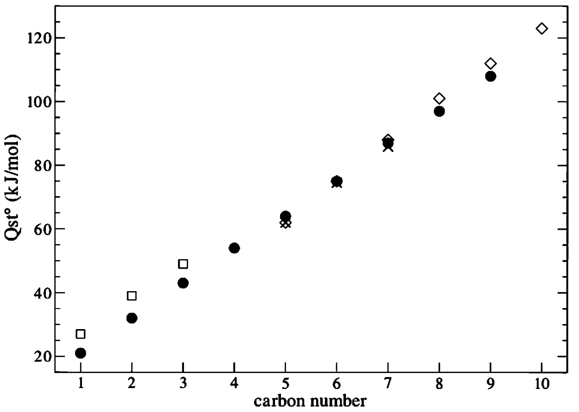

Figure 1. Isosteric heat of adsorption of linear alkanes in zeolite TON at 300 K. Simulation results from AUA model (filled circles) and UA model of ref. Maesen et al., 1999 (crosses) and experiments from ref. Savitz et al., 1998 (squares) and Denayer et al., 1998 (diamonds).

3. Results

As stated above, the framework oxygen Lennard-Jones parameters have been determined from a fit of the simulations to the experimental adsorption data of normal butane in silicalite-1 (MFI). It thus seems natural, as a first test of the transferability of the forcefield, to compute the adsorption properties of linear alkanes in some other zeolite framework. In Fig. 1, we report the isosteric heat of adsorption of several linear alkanes in TON. The agreement with experiments is quite good. The simulation results performed using the UA model (Maesen et al., 1999) also reproduce the increase of the isosteric heat with the chain length for linear alkanes. However simulations results slightly under predict the isosteric heats for shortest and longest studied alkanes.

The next system of interest is *n*-alkanes in ferrierite. This system is particularly interesting since it provides a very demanding test case for the simulation models because the adsorbate molecules fit tightly in the zeolite pore. We report, in Fig. 2, the computed adsorption isotherm of *n*-pentane in ferrierite at 298 K and compare it to available experiments and also to simulations that we have performed, at this temperature, using van Well et al.'s model (Van Well et al., 1998). This provides a clear confirmation of the ability of the AUA model used here to reproduce the type-I isotherm obtained experimentally. An analysis of the molecular conformations shows that *n*-pentane molecules occupying the so-called 10-ring channels are in their all-*trans* conformation. Adsorption in the 8-ring cages is accompanied by a *trans-gauche* conformation transition (or strictly speaking an *anti-gauche* transition). More details on the adsorption mechanisms of linear alkanes in ferrierite can be found elsewhere (Pascual and Boutin, 2004).

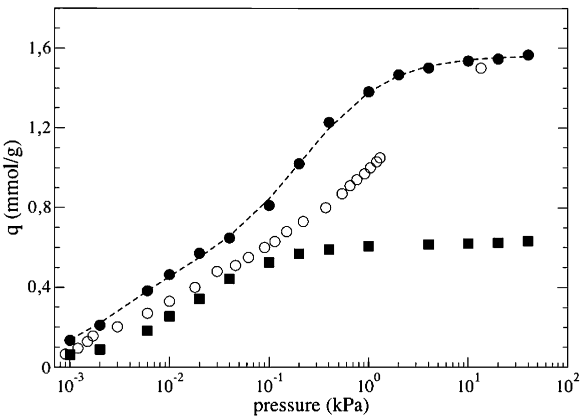

Figure 2. Adsorption isotherms of *n*-pentane in ferrierite at 298 K. AUA simulation (filled circles) fitted by a Dual Site Langmuir model (dashed line), van Well et al. simulations (Van Well et al. 1998) and experiments (Eder and Lercher, 1997) (open circles).

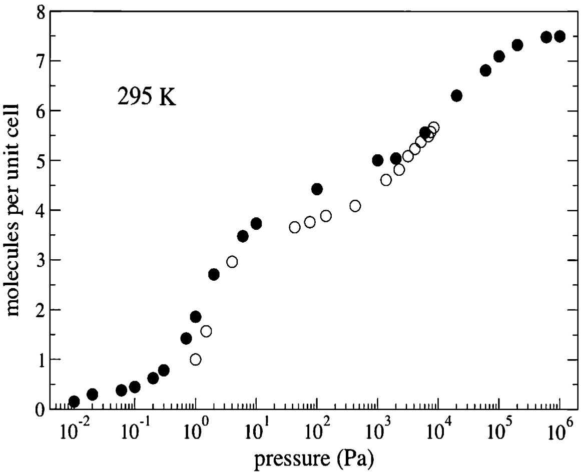

Figure 3. Adsorption isotherms of 3-methyl-pentane in silicalite-1 at 295 K. Experiments (open circles) and simulation (filled circles).

We now turn to a system in which the host framework is silicalite-1 and the guest molecule is 3-methyl-pentane. As can be seen in Fig. 3, the agreement between simulation and experiments is quite good. The sub-step in an experimental alkane-siliceous zeolite isotherm, whenever it exists, is satisfactorily reproduced.

Finally, a first investigation of the adsorption properties of cyclohexane in zeolite BEA is shown in Fig. 4.

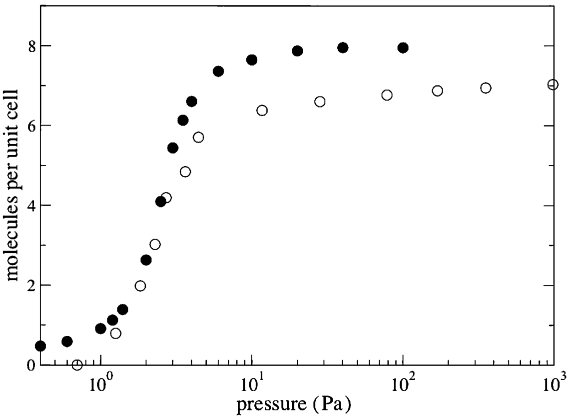

Figure 4. Adsorption isotherms of cyclohexane in zeolite BEA at 298 K. Experiments (open circles) and simulation (filled circles).

The agreement between simulations and experiments in the intermediate pressure regime is good. The inflexion point of the adsorption isotherm is particularly well predicted. At very low loading however the simulation over predicts the adsorbed quantities. The discrepancy is even more significant at full loading. There is a one molecule per unit cell difference between the computed and the experimental data. This discrepancy is not well understood for the time being. Both theoretical (the cyclohexane forcefield) and experimental problems (pore blocking) could be invoked, and there is a need for further studies in order to clear up this point.

4. Conclusion

This work provides some evidence that a carefully designed effective forcefield is able to capture the essential features of hydrocarbons adsorption in siliceous zeolites, even though the model used is based on rather crude assumptions such as rigid framework, united atom description of the host molecules and the Kiselev approximation for the guest-host interaction. Work is in progress to investigate the transferability of this model to cationic zeolites.

References

Bourasseau, E., P. Ungerer, A. Boutin, and A.H. Fuchs, *Mol. Simulation*, **28**, 317 (2002a).

Bourasseau, E., P. Ungerer, and A. Boutin, *J. Phys. Chem.*, **106**, 5483 (2002b).

Bourasseau, E., M. Haboudou, A. Boutin, A.H. Fuchs, and P. Ungerer, *J. Chem. Phys.*, **118**, 3020 (2003).

Denayer, J.F.M., G.V. Baron, J.A. Martens, and P.A. Jacobs, *J. Phys. Chem.*, **102**, 3077 (1998).

Eder, F. and J.A. Lercher, *J. Phys. Chem. B*, **101**, 1273 (1997).

Fuchs, A.H. and A.K. Cheetham, *J. Phys. Chem. B*, **105**, 7375 (2001).

June, R.L., A.T. Bell, and D.N. Theodorou, *J. Phys. Chem.*, **96**, 1051 (1992).

Maesen, T.L.M., M. Schenk, T.J.H. Vlugt, J.P. de Jonge, and B. Smit, *J. Catal.*, **188**, 403 (1999).

Pascual, P., P. Ungerer, B. Tavitian, P. Pernot, and A. Boutin, *Phys. Chem. Chem. Phys.*, **3684**, 3684 (2003).

Pascual, P., P. Ungerer, B. Tavitian, and A. Boutin, *J. Phys. Chem. B*, **108**, 393 (2004).

Pascual, P. and A. Boutin, *Phys. Chem. Chem. Phys.* **6**, 2015 (2004).

Savitz, S., F. Siperstein, R.J. Gorte, and A.L. Myers, *J. Phys. Chem. B*, **102**, 6865 (1998).

Simonot-Grange, M.-H., *Clays and Clay Minerals*, **6**, 423 (1979).

Smit, B. and T.L.M. Maesen, *Nature*, **373**, 42 (1995).

Smit, B. and R. Krishna, *Chem. Eng. Sci.*, **58**, 557 (2003).

Ungerer, P., C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau, and A.H. Fuchs, *J. Chem. Phys.*, **112**, 5499 (2000).

Van Well, W.J.M., X. Cottin, J.W. de Haan, B. Smit, G. Nivarthy, J.A. Lercher, J.H.C. van Hoof, and R.A. van Santen, *J. Phys. Chem. B*, **102**, 3952 (1998).

Vlugt, T.J.H., R. Krishna, and B. Smit, *J. Phys. Chem. B*, **103**, 1102 (1999).