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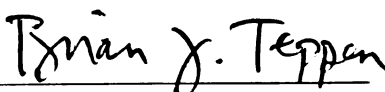
MOLECULAR SIMULATION OF COMPETITION BETWEEN WATER AND
TRICHLOROETHENE FOR ADSORPTION TO MINERAL SURFACES

presented by

Chunhui Li

has been accepted towards fulfillment
of the requirements for

M.S. degree in Crop and Soil Sciences


Major professor

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**MOLECULAR SIMULATION OF COMPETITION BETWEEN WATER AND
TRICHLOROETHENE FOR ADSORPTION TO MINERAL SURFACES**

By

Chunhui Li

AN ABSTRACT OF A THESIS

Submitted to

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2001

Professor Brian J. Teppen

ABSTRACT

MOLECULAR SIMULATION OF COMPETITION BETWEEN WATER AND TRICHLOROETHENE FOR ADSORPTION TO MINERAL SURFACES

By

Chunhui Li

Trichloroethene (TCE) is a chlorinated solvent that is a major environmental contaminant of soils and groundwater, and its interactions with minerals play a key role in the fate and transport of TCE. This molecular simulation study is complementary to experimental work on TCE sorption to hydrated zeolites. This research is the first to perform grand canonical Monte Carlo simulations of competitive TCE and water adsorption by zeolites. Potential energy parameters for the system were improved, and the resulting force field reproduces the properties of TCE, water, and aluminosilicates. For more complex systems, the force field predictions matched experimental data for water sorption by zeolite Y and for TCE sorption to hydrated zeolite Y. The structural and energetic features of adsorbates were examined in detail. Water and TCE domains remain quite separate in the zeolite, with very little mixing of the two species even when clusters of each are present in the same pore. Water-TCE competition was examined in zeolites that were empty or pre-equilibrated with either water or TCE. Two commercial force fields were also tested but our own modeling results were in far better agreement with the overall experimental data and especially the water sorption data.

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INTRODUCTION

Trichloroethene (C_2HCl_3 , TCE), a chlorinated solvent, was widely used for metal degreasing, for organic extractions, and as a chemical intermediate due to its effectiveness, noncorrosivity, and nonflammability. Figure 1.1 shows how the United States production of TCE changed over time (Doherty 2000). It has been produced since the early 1920s. By the 1960s, people began to notice its role in contaminating drinking water wells, as exemplified by the popularized case (Harr 1996) in Woburn, Massachusetts. After the 1970s, TCE production began to decrease due to several regulations and economic factors, but then during the late 1980s, TCE production increased again because it is a suggested replacement for other solvents, which were banned in 1990 amendments.

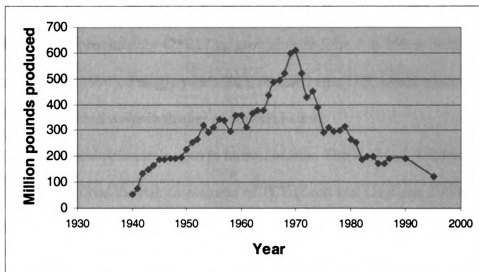


Figure 1.1. United States production of trichloroethene (TCE). (Doherty 2000)

TCE has commonly been found beneath landfills and industrial parks, and it is unfortunately difficult to degrade and persistent in subsurface environments. TCE is identified in at least 852 of the 1416 sites proposed for inclusion on the U.S. E.P.A. National Priorities list (Doherty 2000). TCE can enter surface waters via direct discharges or by seepage and can enter groundwater through leaching from disposal operations. The water solubility of TCE is ~ 1385 mg/L (Sabatini and Knox 1992). The density of TCE is 1.46 g/cm^3 . So it is moderately soluble in water and can leach from soils into groundwater, while it is also dense and can sink through groundwater as a dense non-aqueous phase liquid (NDAPL). The upper limit for TCE in drinking water is 0.005 mg/L, (Code of Federal Regulations 1993) which is just 0.00036% of its water solubility. In 1994 alone, 42 million pounds of TCE were released into the U.S. environment, as reported to the U.S. E.P.A. toxic release inventory (Doherty 2000). Suppose all of this TCE entered the groundwater at the legal upper limit of 0.005 mg/L. Since there are approximately 42×10^{17} kg groundwater from 0 to 250 m depth on earth, (Sigg and Stumm 1994), a single year's TCE release in the U.S. would place about 0.9% of the world's ground water in danger of contamination.

TCE is a probable carcinogen to human health. The National Academy of Sciences has described the risk assessment of TCE (Scott and Coglianò 2000). The hazard identification, dose response, and exposure have been addressed. TCE has been shown to cause liver and kidney cancer in experimental animals (Wartenberg, Reyner et al. 2000). Kidney cancer, liver cancer, non-hodgkin's lymphoma, cervical cancer, hodgkin's disease and multiple myeloma have been found to have an excess cancer

incidence among people with the most rigorous occupational exposure (Wartenberg, Reyner et al. 2000). Although these effects may be caused by several solvents together, TCE is likely one of these active agents.

The transport and fate of TCE are largely controlled by the interaction with minerals and organic constituents of soil and sediments. Even though sorption of organic contaminants to surface soils is dominated by a partitioning into the organic fraction of the soil, (Chiou, Peters et al. 1979; Green and Karickhoff 1990) the sorption of TCE by minerals also important to TCE fate and transport in soil, since the TCE can be sorbed by subsurface minerals and can leach to the groundwater from surface soil. Many aquifer materials contain only traces of organic matter and sorption to mineral phases must be invoked in order to explain observed transport results (Curtiss, Roberts et al. 1986; Stauffer, MacIntyre et al. 1989; Jackson, Lesage et al. 1992; Sabatini and Knox 1992). Sorption of TCE on fractions of whole soils has been studied experimentally (Pignatello 1990). Sorption correlated with organic carbon (OC) content, but an important contribution of the mineral fraction was also shown, since some fractions contributed more to sorption than they should have based on OC content. The literature is quite diverse on this point, with from 10 to 10^4 mg/kg TCE sorbs to low-organic-matter minerals (Stauffer and MacIntyre 1986; Estes, Shah et al. 1988; Stauffer, MacIntyre et al. 1989; Farrell and Reinhard 1994; Farrell and Reinhard 1994; Xing and Pignatello 1996; Werth and Reinhard 1997; Li and Werth 2001; Pires, Carvalho et al. 2001). Adsorption onto porous silicated minerals is often found to be high. For example, at 100% relative humidity, the montmorillonite Swy-1 sorbed 1300 mg/kg TCE while a silica gel sorbed up to 2000 mg/kg (Farrell and Reinhard 1994). Micropores, defined by IUPAC as pores

smaller than 20 Å in diameter, may be responsible for adsorption isotherm nonlinearity and slow desorption phenomena.

Zeolites are 3-dimension porous aluminosilicates that form naturally in volcanic deposits and are also widely synthesized. Approximately 121 different microporous structures have structure codes in the International Zeolite Commission (IZC) (Wagner and Davis 2000). Zeolites are composed of SiO_4 and AlO_4 tetrahedra, which are connected by corner-sharing oxygen atoms. The arrangement of these tetrahedra results in a variety of structures containing cavities and channels. Their unique structures provide many functions in industry, where zeolites are mainly used as adsorbents, catalysts, molecular sieves, and ion-exchangers in detergents.

TCE adsorption in three faujasite type zeolites, NaY, NaX, and siliceous faujasite FAU, has been studied by calorimetric experiments, inelastic neutron scattering and NIR-FT Raman spectroscopy (Mellot, Cheetham et al. 1998; Davidson, Mellot et al. 2000). These zeolites all have the same basic structure but differ in their charges, with cation-exchange capacities (CEC) of 418, 654, and 0 cmol/kg zeolite respectively. The calorimetric study (Mellot, Cheetham et al. 1998) showed that adsorption heat increases with increasing polarity of the zeolite host. At room temperature and in the zero loading limit, the adsorption heat of TCE is about 45, 55, 80 kJ/mol for dry and degassed siliceous Y, NaY, NaX zeolite, respectively. Up to 30-40 molecules per unit cell, the adsorption heat for these three types of zeolites increased to 55, 72, and 95 kJ/mol, respectively, in which indicates that favorable sorbate-sorbate interactions stabilize the system. The spectra (Davidson, Mellot et al. 2000) showed that in siliceous FAU, TCE interacts with zeolite by hydrogen bonds between hydrogen atoms in the sorbate and

oxygen atoms in the framework, and by van der Waals interactions between chlorine atoms in sorbate and oxygen atoms in framework. In dry zeolites NaX and NaY, there are also electrostatic interactions between chlorine atoms in the sorbate and sodium cations in the zeolite pores. The adsorbate-adsorbate interaction and the dipolar nature of the adsorbate are important to the adsorption. The sorbate/zeolite interactions are related to the basicity of the zeolite. Pires et al. (Pires, Carvalho et al. 2001) also measured TCE adsorption onto dried and degassed zeolites and pillared clays. For zeolite Y, about 0.44 g TCE/g zeolite were adsorbed to either the Na- or H-exchanged mineral.

The studies summarized above dealt with evacuated zeolites and provide useful background data, but the addition of water to the system is necessary to give environmental relevance to these model minerals. The thermodynamic properties of TCE adsorption by zeolite NaX in the presence of water have been studied by high-pressure liquid chromatography methods (Farrell, Hauck et al. 1999). Zeolite NaX is completely hydrophilic because of its high charge density, and the TCE adsorption enthalpy is about 20.3 ± 12.1 kJ/mol. Endothermic heats of adsorption are known to occur for solutes that are less strongly adsorbed than the accompanying solvent. Thus TCE adsorption on the zeolite is endothermic because it requires the displacement of water from hydrophilic pores. The competitive sorption mechanisms of TCE and tetrachloroethene (PCE) by hydrated zeolites have also been studied (Li and Werth 2001). Sorption of TCE from 30 mg/L solution onto four zeolites ranged from 1 to 100 mg/g, with lower sorption to the higher-charged zeolites. Competition between TCE (less favored) and PCE (more favored) adsorption by zeolites increases with increasing hydrophobicity and decreasing micropore width. The contribution to the adsorption potential is mainly from van der

Waals forces and electrostatic interactions. The authors reasoned that since PCE is more polarizable than TCE, PCE has a higher sorption potential and can displace TCE in strongly hydrophobic micropores. Since PCE is also slightly larger than TCE, PCE can displace TCE in moderately hydrophobic micropores with decreasing pore size. For the unsubstituted, siliceous zeolite silicalite, 200 mg TCE/g zeolite was sorbed rapidly from aqueous solution (Alvarez-Cohen, McCarty et al. 1993).

The study of water adsorption by zeolites showed that the adsorption of water by zeolites with similar structures largely depends on the chemical compositions of the framework, in which the Si/Al ratio plays an important role. The study of water adsorption by the zeolite mordenite showed that when the Si/Al ratio is less than 20, the volumes of adsorbed water and hydrocarbons were comparable, and when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is greater than 40, there is almost no water adsorbed. By contrast, hydrocarbon adsorption does not depend on the ratio between 40 and 90 (Chen 1976). Comparing with mordenite, the adsorption of water by dealuminated faujasite typically shows an inverse relationship with the Si /Al ratio (Li, Annen et al. 1991). The study of water adsorption isotherms on zeolite 4A, Y, ZSM-20 (Na and H form) at 298K and $P/P_0 = 0.8$ showed the adsorption amount is 0.25, 0.25, 0.28 g/g zeolite respectively (Pires and De Carvalho 1997). Water adsorption by zeolites 4A, 5A, B, X, Y, erionite, offretite, mordenite (Landolt 1971) has been studied at 298 K, and the adsorption amount of water by these zeolites is 0.25, 0.25, 0.20, 0.32, 0.28, 0.11, 0.16, 0.13 g/g zeolite respectively at $P/P_0 = 0.5$.

Computer simulation as a powerful research tool has been developed rapidly in recent decades with the proliferation of computer resources. Simulation saves time and

money compared with wet-lab experiments, especially when the experiment is difficult to perform. Simulations provide insight from the molecular level to macro-scale system properties. Nowadays more and more computational software is available to the researcher, so that both empirical and quantum *ab initio* simulations have become routine in many labs. The *ab initio* calculation, which only uses some basic physical constants, can provide electronic information about the system. The capacity and speed of computers limit electronic methods to smaller systems compared with empirical simulations. The advantages of the empirical molecular simulation are the speed to study large systems of many thousand atoms and consideration of solvent effects. Electronic information is not computed in empirical simulations, so bond information or other electron transfers may not be modeled. Still, empirical modeling can be a useful method to study mineral systems in general, including adsorption isotherms in particular. This is because many adsorption interactions are dominated by electrostatics and van der Waals forces that do not involve electron transfer. In addition to computing the adsorbate loading as a function of chemical potential, one can observe precisely which sites on the adsorbent are loaded first and the computation yields adsorption energy as a function of loading. A limitation on empirical modeling is the lack of effective potential energy parameters, especially when there are not many experimental data available, or when the system is too large to do first principles calculations, from which we can derive the potential functions and parameters for empirical modeling.

Monte Carlo simulation, one of the empirical molecular simulation techniques, has been successfully conducted on the sorption of zeolites for different species, such as alkanes, chlorocarbons, aromatic organic compounds, water and inorganic gases (Smit

and Siepmann 1994; Smit and Siepmann 1994; Smit 1995; Smit and Maesen 1995; Douguet, Pellenq et al. 1996; Bremard, Buntinx et al. 1997; Channon, Catlow et al. 1998; Klemm, Wang et al. 1998; Nascimento 1999; Shen, Jale et al. 1999). This technique has also been used to study the structures and properties of clay systems. TCE sorption by layer clay was found (Teppen, Yu et al. 1998) to occur by three distinct mechanisms: The most stable mode of sorption was by full molecular contact, coplanar with the clay surface. This kind of interaction is suppressed by increasing water loads. A second, more reversible interaction involves adsorption through single-atom contact between one chlorine atom and the mineral. In a third mechanism, TCE never contacts the clay directly but sorbs onto the external air/water interface. For TCE desorption (Teppen, Arands et al. 1998; Teppen, Yu et al. 1998) from kaolinite, TCE desorption kinetics are much faster from the hydroxylated aluminol surface than from the siloxane surface. Simulations of TCE adsorption by the dry zeolites NaX, NaY, and siliceous faujasite have been studied (Mellot, Cheetham et al. 1998). The calculated isosteric adsorption heats are in good agreement with the calorimetric experimental data. The adsorption heat was decomposed into short range and electrostatic component. For siliceous Y at “zero” loading the short range interactions accounts for 90% of the total adsorption energy. With the increase of TCE loading, the electrostatic component remains same at 4.2 kJ/mol. All the increase in adsorption heat is from dispersion component. For NaY at zero loading, the electrostatic contribution accounts for 14.2 kJ/mol, which give the higher affinity of TCE for charged zeolite compared with siliceous zeolite. For NaX at zero loading, the electrostatic contribution consists of 41.3 kJ/mol, which is 50% of the total adsorption energy. At fixed loading, TCE heats of adsorption increase in the

sequence of host basicity and cation content for these dry zeolites. The pair distribution functions also showed the central elements to the interaction between TCE and zeolites: 1) Cl atoms and O atoms van der Waals interactions, 2) Cl atoms and Na cation electrostatic interactions, and 3) H atoms and O atoms hydrogen bonding. The simulation of water adsorption isotherm by siliceous and aluminum containing Heulandite-type zeolites showed that the cation displacement is important to the polar molecule adsorption by zeolite (Channon, Catlow et al. 1998). The sorbed water formed water clusters by hydrogen bonding. At 300K for siliceous zeolite, there are 1.8 water molecules per simulation box at 2 atm. For aluminum containing zeolite, there are about 70 water molecules per simulation box at 0.5 atm, which is a loading rate of 0.072 g water/g zeolite. Molecular simulations of adsorption to zeolites were recently reviewed (Fuchs and Cheetham 2001). To date, Monte Carlo simulations have been mostly used for single component adsorption systems. There have been a few computational studies of binary competition for adsorption sites in zeolites, mostly focused on organic-organic competition. For water –organic competition, which is critical to understanding organic sorption in soils, we know of no previous studies. Even though simulation of binary mixture adsorption can be more complicated and time-consuming than the single component adsorption, it can give us more information on the adsorption processes, as they would be expected to occur *in situ* in a hydrated environment.

There are three reasons to study the system of TCE, H₂O competitive adsorption by zeolite in this work: First, people have proposed to use zeolites as TCE adsorbent because of their special physical and chemical properties (Alvarez-Cohen, McCarty et al. 1993; Weber, Bertrand et al. 1996). Their functions are similar to activated carbon for

sequestration and conversion of TCE. There is a need to understand TCE adsorption by zeolites at the molecular level. Meanwhile, the functional groups are the same as those of clay minerals. The understanding of adsorption mechanism by zeolite may provide insight into the mechanisms of TCE adsorption by the clay minerals, which play an important role in the transportation and fate of pollutants in the soil and ground water.

Second, technically, simulations of zeolites are somewhat easier than simulations of clay minerals. Zeolites have fixed cavity diameters, but for clays with the layer structure, the distance between layers changes with the water content. Zeolites can have a wider range of charge than the clay minerals, but pore-size distributions of zeolite are much less dependent on charge. Considering these factors, simulation of adsorption by zeolites is easier to control due to fewer variables.

Third, good force field parameters can be transferred to other mineral systems. This work will validate and improve the force field parameters of the zeolite and the organic solvent, which will increase the parameter database of the mineral systems and help in the study of more complex systems.

The objective of this work is to use grand canonical ensemble Monte Carlo (GCMC) simulations to study the competitive adsorption of TCE and water by zeolite. This goal can be separated into two subgoals:

The first goal is to use all available experimental and quantum mechanical data to produce a new and improved set of potential energy parameters for molecular mechanics simulations of TCE and H₂O adsorption by zeolite.

The second goal is to use simulations to determine the adsorption mechanisms and to study this adsorption at the molecular level. This mechanistic information will be

used to help interpret the macroscopic adsorption data for the competition between water and TCE at mineral surfaces.

Images in this thesis are presented in color.

METHODS

1. Force Field Methods

Force field methods are empirical computational methods, which use a set of mathematical functions and parameters to analytically describe the potential energy surface of a system as a function of the atomic coordinates. Force field simulations can handle large systems, such as condensed matter, macromolecules, inorganic crystals and organic interphases, because they bypass solving the electronic Schrödinger equation. In other words, empirical methods do not calculate the electronic energy for a given nuclear configuration. The basis of force field methods is that molecules tend to be composed of units that are structurally similar in different molecules, a small set of molecules are used to parameterize the force field, then these force field parameters are transferred to study other systems. The force field energy is decomposed into several parts:

$$E_{\text{FF}} = E(\text{bond stretch}) + E(\text{angle bend}) + E(\text{torsion}) + E(\text{inversion}) + E(\text{Cross term}) + E(\text{van der Waals}) + E(\text{electrostatic})$$

The first five terms on the right of above equation are the bond terms. The last two terms are the non-bonded terms. Some parts, especially the cross terms, are commonly ignored. Given this energy, the relative energy of a system can be calculated and the optimized geometry can be found by minimizing this energy. Since each atom has a unique atom type in the force field, the energy contribution of the individual atoms or classes of atoms can be analyzed.

Many kinds of force fields have been developed (Weiner, Kollman et al. 1986; Jorgensen and Tirado-Rives 1988; Allinger, Yuh et al. 1989; Halgren 1996; Halgren

1996; Halgren 1996; Halgren 1996; Halgren and Nachbar 1996; Sun 1998; Sun 1998; Sun, Ren et al. 1998; Newsam, Sun et al. 1999). Different force fields use different functions and parameters and are suitable for studying different systems. In general, force fields can be classified into three categories: 1. Broadly applicable force fields, which cover a broad range of the periodic table by using simple rules to create energy parameters. This type of force field can often predict molecular structure reasonably well, but the prediction of the other molecular properties is often limited. 2. Classical force fields: This type of force field generally has relatively simple functional forms and focuses on the application of certain areas, mainly biochemistry. 3. Second-generation force fields: This type of force fields can achieve higher accuracy in predicting various molecular properties; meanwhile they can still cover a broad range of the periodic table. In this research work, we will mainly talk about two commercial force fields, COMPASS and PCFF, which are both second-generation force fields. PCFF (Sun, Mumby et al. 1994) stands for Polymer Consistent Force Field and is an *ab initio* force field. Most parameters are derived from *ab initio* data using a least-squares fitting technique. The non-bond parameters were derived by fitting to molecular crystal data based on energy minimization calculations. COMPASS (Sun 1998) stands for Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies and was developed on the basis of PCFF. The valence parameters for molecular classes in the PCFF were transferred to the COMPASS. The nonbond parameters were reparameterized. COMPASS was also expanded to include the most common organic and polymer materials and inorganic materials.

During Grand Canonical Monte Carlo simulation of adsorption (GCMC), we only consider nonbonded interactions, which include the Lennard-Jones 6-9 function for the van der Waals interaction and the Coulombic function for the electrostatic interaction.

$$E = E_{\text{elec}} + E_{\text{vdw}}$$

$$E_{\text{elec}} = q_i * q_j / (\epsilon * R_{ij})$$

Where q_i and q_j are the partial charges for atom i and j , R_{ij} is the distance between atoms i and j , and ϵ is the dielectric constant which here is 1.0 since we are working at the molecular scale.

$$E_{\text{vdw}} = D_0 (2(R_0/R)^9 - 3(R_0/R)^6)$$

Where D_0 is the well depth in kcal/mol, and R_0 is the equilibrium distance in angstroms. Tables 2.1 and 2.2 show the force field parameters of the zeolite-water-TCE system for both the COMPASS and PCFF force fields. (MSI 1999)

Force field type	Atoms in model	Partial Charge	VDW	
			R ₀ (kcal/mol)	D ₀ (Å)
Si4z	Si in zeolite	0.89	4.29	0.105
O2z	O between two Si	-0.4450	3.3	0.08
Al4z	Al in zeolite	0.7343	4.4	0.2
O2z	O between Al and Si	-0.4578	3.3	0.08
O3z	O between H,Al,Si	-0.3348	3.3	0.08
H1o	hydrogen	0.0839	1.087	0.008
H1o	H in H ₂ O	0.42	1.087	0.008
O2*	O in H ₂ O	-0.84	3.695	0.21
C3=	C in TCE	0.204	3.92	0.08
C3=	C in TCE	-0.0248	3.92	0.08
Cl1	Cl in TCE	-0.102	3.823	0.286
H1	H in TCE	0.1268	2.878	0.023

Table 2.1. Part of force field parameters from COMPASS for our adsorption simulation.
(MSI 1999)

Force field type	Atoms in model	Partial Charge	VDW	
			R ₀ (kcal/mol)	D ₀ (Å)
sz	Si in zeolite	0.5236	0.001	0.00
oss	O between two Si	-0.2618	3.4506	0.1622
az	Al in zeolite	0.5366	0.0001	0.00
oas	O between Al and Si	-0.2959	5.2591	0.0129
Hb	hydrogen	0.0839	1.2149	5.2302
Ob	O between H,Al,Si	-0.2515	5.2191	0.0135
Hw	H in H ₂ O	0.3991	1.098	0.013
O*	O in H ₂ O	-0.7982	3.608	0.274
C=	C in TCE	0.2040	3.9	0.064
Cl	Cl in TCE	-0.1020	3.92	0.2247
Hc	H in TCE	0.1268	2.995	0.020

Table 2.2. Part of force field parameters from PCFF for our adsorption simulation (MSI 1999)

2. MC:

The Monte Carlo technique as applied to molecular simulation was first introduced by Metropolis et al (Metropolis, Rosenbluth et al. 1953). It is a stochastic modeling method for obtaining optimized molecular structures and configurations based on the analysis of possible equilibrium configurations from a random sampling of the

potential energy surface. Monte Carlo methods can calculate the average property for any ensemble. In this work, we are using grand canonical ensemble Monte Carlo (GCMC) methods, in which the chemical potential, volume, and temperature are fixed and the numbers of molecules in the system are allowed to change during a simulation. GCMC is particularly useful for studying multilayer adsorption near a surface. For a GCMC simulation, there are two kinds of energy terms, Coulomb electrostatics interactions and van der Waals interactions.

In the GCMC adsorption system, there is a given crystal framework, which is the adsorbent, and one or more gas phases, which are adsorbates. Here we treat the adsorbate as an ideal gas whose chemical potential is determined only by the temperature and partial pressure. During the simulation, the chemical potential of the gas molecules and temperature are fixed while the number of molecules fluctuates. The volume of the adsorbent framework is also fixed and the framework and gas molecules are treated as rigid bodies.

At the beginning of a simulation, an initial configuration for the system is defined and the total potential energy is determined. There are four kinds of moves to generate the next configuration: Create, destroy, translate or rotate a gas molecule in the pores of the framework. The adsorbate model is randomly displaced to a new configuration in the adsorbent and a new energy is calculated. The new configuration, based on the energy change, is accepted or rejected by the Metropolis rules. If the energy of a new configuration is lower than the original, this configuration is accepted and the next displacement is continued. If the new configuration energy is greater than the original, the configuration is accepted or rejected depending on the comparison of a Boltzmann

distribution to a random number. If the value of Boltzmann distribution is less than the random number between 0 and 1, the configuration is accepted and used as the basis for a new displacement. Otherwise, the new configuration is rejected and the previous configuration is used for the next displacement. The chemical potential is translated into the partial pressure of each component until equilibrium is achieved. At this time, the temperature and chemical potential of the gas are equal to each other inside and outside of the framework.

The result of this simulation is a set of configurations that converge towards the specified chemical potential and temperature. A large number of configurations are generated after the equilibration period. The simulation takes several steps to equilibrate from its original random position. For accurate statistical results, the steps made prior to equilibration should be excluded in the analysis, and a large number of configurations should be generated after the equilibration period. These configurations can be sampled and saved as a trajectory. From a trajectory file, the adsorption energy, conformational structure, mass distribution, and loading amount can be analyzed as a function of adsorbate chemical potential, allowing construction of an isotherm along with the structural and energetic features underlying the isotherm.

3.MD:

MD is a deterministic molecular modeling tool that evaluates the forces on individual atoms using the same energy force field. Newton's differential equations of motion are used to compute new atomic positions after a short time interval (on the order of a femtosecond), then evaluation for a large number of time steps provides a time-dependent trajectory of all atomic motions.

4. Comparison of MC and MD:

The prime purpose of both Monte Carlo and molecular dynamics program is to compute equilibrium properties of classical many-body systems and MD simulations can also be used to follow nonequilibrium kinetics. Since all the atoms are labeled in the simulations, the exact atomistic behavior that causes the averaged data can be followed in order to determine the molecular mechanisms. Classical molecular dynamics and Monte Carlo simulations cannot provide any electron information, but instead need a set of empirical parameters to calculate the potential surface.

In MD simulations, all particle coordinates are updated simultaneously. In conventional MC simulations, only a few coordinates are changed in a trial move. As a consequence, collective molecular motions are not well represented by MC, and this may adversely affect the rate of equilibration. An advantage of MC is that, unlike MD, unphysical moves can be carried out. Moreover, in MC the system is not constrained to move on a hypersurface where some Hamiltonian is conserved. The time step in MD is limited by the need to conserve energy. Clearly, no such constraint applies to MC. The computation of time-average quantities distinguishes molecular dynamics from Monte Carlo simulation.

5. Model

In this research, we are going to study the zeolite HY80, which belong to the large class of faujasite-type zeolites. Figure 2.1 is one supercell zeolite (MSI 1999) with the composition of $\text{H}_5\text{Si}_{379}\text{Al}_5\text{O}_{768}$. Internal pores are mostly siloxane surfaces with elliptical

cross-section about 8 by 12 Å. Total surface area of the model is about 1240 m²/g. The accessible volume to a sphere with radius of 1.2 Å is about ~40% of total volume. Spheres with different radii give different estimates for accessible volume, and Table 2.3 gives the accessible volume and its percentage of total volume versus radius r of the probe molecule. The cell parameters for this supercell are: a = 50.06Å, b =25.03Å, c =25.03Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. Si atoms were substituted by Al atoms randomly by Loewenstein's rule, which asserts that no two aluminum atoms share a common oxygen atom. The model Si/Al ratio is 75.8, which is the closest approximation to the ratio 80 used in experiment while we can still keep the model size amenable to calculation. The substitution charges were balanced by exchangeable H⁺. The figure 2.1 is the zeolite viewing along the crystal direction (011) plane. The dominant pores are 12-member ring channels and 6-member ring cages.

Radius of probe sphere (Å)	Occupiable volume (Å ³ /unit cell)	Percent of total volume
1.0	13799	44
1.2	12541	40
1.4	11480	37

Table 2.3. The change of accessible volume and percent of total volume with the radius of probe sphere. The total volume is 31355 Å³/unit cell.

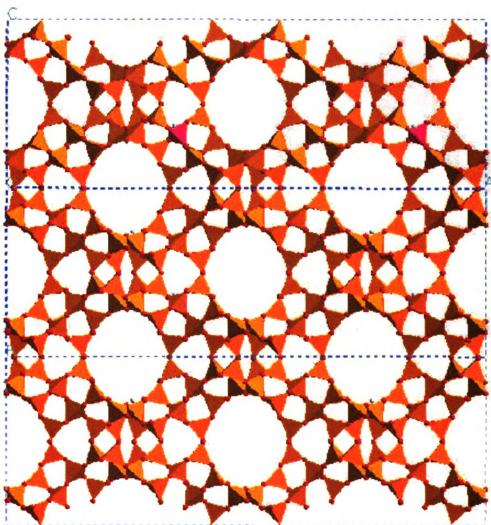


Figure 2.1. Zeolite viewed along (011) plane.

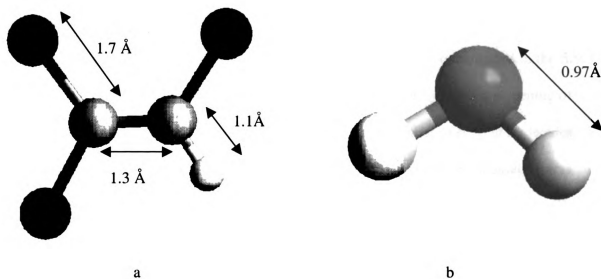


Figure 2.2. a. Single TCE molecule from MP2/6-311+G (2d, p) geometry optimization b. Single water molecule from energy minimization by COMPASS force field.

6. Research work method

In this research work, the two commercial force fields COMPASS and PCFF were first tested for TCE and water adsorption isotherm by zeolite HY80. Tables 2.1 and 2.2 contain the relevant force field parameters for COMPASS and PCFF respectively. Based on the analysis of these force field functions and parameters, and also based on the results of the first few simulations, we refined the parameters for the whole system and then created a new force field. Using this force field, the adsorption isotherms of TCE and water by zeolite were also studied.

The first step of this work is to refine the charges for chlorine atoms in the TCE using *ab initio* calculations including the solvent effect. The chlorine atoms in the TCE are highly polarizable, as are the oxygen atoms inside the zeolite framework. We expected that their interactions are important to the adsorption isotherm, especially when

we include solvent effects in each simulation. The effect of a solvent may be divided into two major parts: 1) Specific solvation or short-range effects, concentrated in the first solvation sphere, and 2) Macroscopic or long-range effects, involving screening of charges (solvent polarization), which requires a large number of solvent molecules. To consider the effect of solvent water in the simulation, the quantum calculation was performed under the condition that a polarized continuum of water was added. The polarizable continuum model (PCM) (Cossi, Barone et al. 1996) employs a van der Waals surface type cavity, a detailed description of the electrostatic potential, and parameterizes the cavity/dispersion contributions based on the surface area. Charges for TCE are from an MP2/6-311+G (2d, p) (Moller and Plesset 1934; Hehre, Radom et al. 1986) geometry optimization, which applies the perturbation theory to calculate the approximate electron correlation energy, followed by a ChelpG analysis, (Chirlian and Francl 1987; Breneman and Wiberg 1990; Francl, Carey et al. 1996) which finds partial atomic charges that correspond to the *ab initio* molecular electrostatic potential. The final charges for TCE are given in Table 2.4. Since in our force field, we did not separate the two chlorine atoms in the same side of carbon double bond, the partial charges for these two chlorine atoms were averaged to the same number. The charges we used (Table 2.4) were very close to those used in another successful study (Mellot, Cheetham et al. 1998) of TCE adsorption to dry zeolites. Notably, our charges on Cl atoms of TCE were somewhat more negative due to our inclusion of the polarizable continuum in the quantum calculations.

The second step is to refine the van der Waals parameters for TCE by molecular dynamics fitting. After fixing the TCE charges, the van der Waals potential were refined

by molecular dynamics simulation at room temperature. A liquid TCE box with 64 TCE molecules was built. According to the following approximate thermodynamic calculation, the liquid TCE potential energy of one unit cell should be about -247 kJ/mol.

$$E = U = PE + KE$$

$$H = U + PV$$

$$\Delta H_{\text{vap}} = \Delta H_{\text{gas}} - \Delta H_{\text{liq}}$$

$$\begin{aligned} \Delta H_{\text{vap}} &= (U + PV)_{\text{gas}} - (U + PV)_{\text{liq}} \\ &= (PE + KE + PV)_{\text{gas}} - (PE + KE + PV)_{\text{liq}} \end{aligned}$$

Assume that $KE_{\text{liq}} = KE_{\text{gas}}$ at the same temperature

$$PV_{\text{liq}} = 0, PV_{\text{gas}} = nRT$$

$$\text{Then } \Delta H_{\text{vap}} = -PE_{\text{liq}} + PE_{\text{gas}} + nRT$$

$$PE_{\text{liq}} = -\Delta H_{\text{vap}} + PE_{\text{gas}} + nRT$$

$$\text{At } 25^\circ\text{C } \Delta H_{\text{vap}} = 34.54 \text{ KJ/mol (Lide 1995)}$$

$$PE_{\text{liq}} = -34.54/4.18 + 8.312 \cdot 298/4.18 \cdot 1000 + PE_{\text{gas}} \text{ (kcal/mol TCE)}$$

$$PE_{\text{gas}} = 3.81 \text{ kcal/mol TCE}$$

$$PE_{\text{liq}} = -3.86 \text{ kcal/mol TCE}$$

$$PE_{\text{liq}} / \text{unit cell} = 64 \cdot (-3.86) = -247.04 \text{ kcal/mol}$$

The equilibrated TCE liquid box containing 64 unique TCE molecules is shown in Figure 2.3. Using molecular dynamic simulation on this TCE liquid box, the van der Waals potential parameters for TCE were refined by trial and error each time until the final density of the TCE box was 1.466 g/cm^3 , which is in agreement with the experimental data of 1.46 g/cm^3 at 293 K. The final potential energy is -249.97

kcal/mol, which is also in good agreement with the results of the above calculation, - 247.04 kcal/mol. The mathematical functions and parameters of bond-terms of TCE for molecular dynamic simulation are shown on Table 2.4, which are all from the PCFF force field. The charges for TCE are from the above *ab initio* calculation. Our van der Waals terms for chlorine atoms are quite similar to the parameters in PCFF, which means the solvent effect does not change the van der Waals terms for chlorine atoms too much.

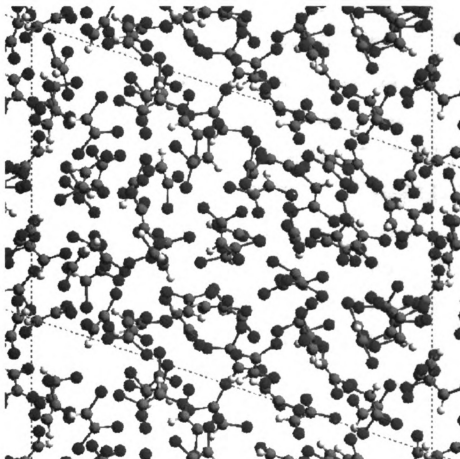


Figure 2.3. Equilibrated liquid TCE box with 64 TCE molecules per unit cell after 100ps of NPT molecular dynamics.

Bond stretch			K_b (kcal/molÅ ²)	R_0 (Å)	d	
C=2	C=1	Quartic	1090.5	1.4	-1.8	
H1	C=2	Quartic	731.5	1.1	-1.9	
Cl1	C=1	harmonic	557.0	1.7		
Cl2	C=2	harmonic	557.0	1.7		
Angle bend			K_0 (kcal/molÅ ²)		θ_0 (°)	d
H1	C=2	C=1	Theta quar	70.6	124.9	-0.50
H1	C=2	Cl2	Theta harma	75.0	120.0	
Cl2	C=2	C=1	Theta harma	72.4	120.0	
Cl1	C=1	Cl1	Theta harma	120.0	120.0	
Cl1	C=1	C=2	Theta harma	72.4	120.0	
Torsions				Barrier (kcal/mol)		Period
H1	C=2	C=1	Cl1	Dihedral	8.2	2.0
Cl2	C=2	C=1	Cl1	Dihedral	8.2	2.0
Inversions				K_0 (kcal/mol)		
C=1	Cl1	C=2	Cl1	Wilson avg	16.0	
C=2	Cl2	C=1	H1	Wilson avg	15.0	

Table 2.4. Atom types and force field functions and parameters of TCE from PCFF force field. C=1 and C=2 stands for the carbon atoms, Cl1 and Cl2 stands for the chlorine atoms, and H1 stands for hydrogen atoms.

The partial charges for the zeolite atoms are from previous work by Teppen et al. (Teppen, Rasmussen et al. 1997). The charges were derived from the CHELPG method using MP2-optimized geometries of several small aluminosilicate molecules. The partial charges for silicon and oxygen of zeolite in PCFF and COMPASS are from Hartree-Fock calculations, (Hill and Sauer 1994; Hill and Sauer 1995) which do not include electron correlation effects. The charges in PCFF are also rather artificial because only half of the *ab initio* calculation charges were used in the force field. This 0.5 factor was given (Hill and Sauer 1994; Hill and Sauer 1995) because organic force fields generally use low charges and the authors believed that better structure prediction could be achieved by also decreasing the zeolite charges.

After refining these parameters, our field force was used to simulate the adsorption isotherms. The sorption module in the Cerius² software from MSI was used for all the sorption simulations. Ewald summation methods were used for calculating non-bond interaction at 0.025 kcal /mol accuracy (Karasawa and Goddard 1989). Periodic boundary conditions were used to remove the surface effects, resulting in simulation of adsorption by an infinitely large zeolite crystal.

Force field type	Atoms in model	Partial Charge	VDW	
			R ₀	D ₀
sz	Si in zeolite	1.4	3.8	0.05
oss	O between two Si	-0.7	3.85	0.26
az	Al in zeolite	1.2	3.9	0.06
oas	O between Al, Si	-0.9	3.8	0.26
H+	hydrogen cation	1.0	ignore	ignore
hw	H in H ₂ O	0.41	1.145	0.015
O*	O in H ₂ O	-0.82	3.7	0.26
C=1	C in TCE	0.0367	3.9	0.064
C=2	C in TCE	-0.0441	3.9	0.064
Cl1	Cl in TCE	-0.0374	3.92	0.236
Cl2	Cl in TCE	-0.0966	3.92	0.236
H1	H in TCE	0.1788	2.995	0.02

Table 2.4. Atom type and force field parameters used in our simulation.

RESULTS AND DISCUSSION

Experimental description:

These are unpublished data from Dr. James Farrell's group at the University of Arizona and their methods generally follow their previous studies of TCE sorption and desorption (Farrell and Reinhard 1994; Farrell and Reinhard 1994; Farrell, Grassian et al. 1999; Farrell, Hauck et al. 1999). The experimental results will be very briefly presented here and then discussed in more detail along with the simulation results.

a. Farrell's group measured the water adsorption isotherm by zeolite both by continuous gas chromatography (GC) and gravimetric methods at 278, 283, 293, and 320 K.

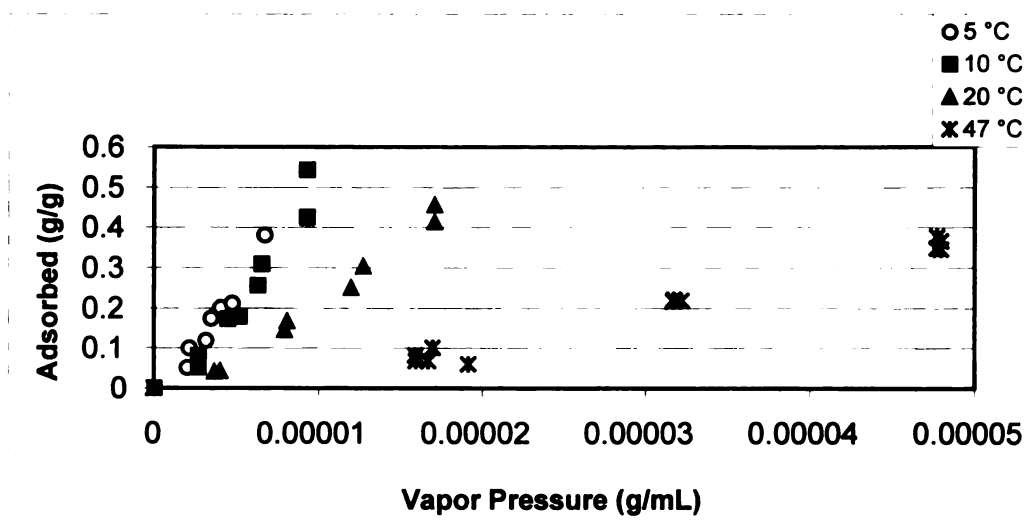


Figure 3.1. Experiment data for pure water adsorption by zeoliteHY80 at different temperatures. (James Farrell, unpublished)

b. Farrell's group measured desorption isotherms for TCE interacting with hydrated zeolites by two methods. In the first, oven-dried zeolite was allowed to equilibrate simultaneously with both water and TCE, each at saturation vapor pressures. The

relative humidity was then maintained at 100% in the GC gas stream, while the TCE content of the gas stream was gradually lowered. The quantities of sorbed TCE in equilibrium with various partial pressures of TCE gas and 100% relative humidity are shown in the “oven-dried” series of Fig 3.2. Adsorption and capillary condensation of water and TCE on the outside of the particles is a problem for experiment. There is an inflection point (i.e. change in sign of the second derivative) at about 20% of P_{sat} (loading = 0.45 g/g) in the experimental data, Figure 3.2. This inflection point is where capillarity condensation begins. Most likely the capillary condensation that begins at this point is on dry spots on the zeolite surface.

c. The second type of measurement of TCE-water competition by Farrell’s group was gathered by pre-equilibrating the zeolite with a stream of 100% relative humidity and no TCE over night. Then, desorption isotherms in the presence of 100% humidity and various TCE contents were gathered as above, and the results are plotted as the “pre-equilibrated with water” series in Fig 3.2. On this graph, no inflection point appear until about 90% of P_{sat} , indicating approximately 0.38 g/g TCE sorption within the zeolite. Thus, pre-equilibrating the mineral with water seems to reduce TCE sorption by about 10 to 20%, although TCE sorption remains quite substantial.

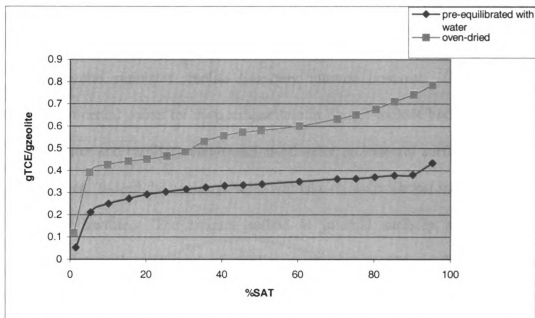


Figure 3.2. Experimental data for water and TCE adsorption by zeolite HY80 at 308K

Simulation results and discussion

1. At 308K, our simulation results for pure water adsorption by the model for zeolite HY80 is 0.27 g/g zeolite at 100% humidity. The pore space in the HY80 is enough to hold about 0.33 g/g zeolite water according to the free volume calculation. Since the sphere with 1.2 Å radius was used to measure the pore space in zeolite and the water molecule is larger than this sphere, this 0.33 g/g amount should be an upper limit amount for water. Our results are in good agreement with measured experimental data for water adsorption, 0.28 g/g zeolite Y (Landolt 1971) or 0.25 g/g zeolite Y (Pires and De Carvalho 1997) at 298K. Comparing with Farrell's experimental water adsorption by zeolite HY80 at different temperatures (discussed above), our results are also in the right range of the data between 293K and 320K.

Experimentally, water adsorption to a zeolite powder is somewhat difficult to compare with simulation results, because the real powder has external surfaces while the simulated zeolite has only internal porosity. Thus, the highest experimental points for each temperature in Fig.3.1 include both internal sorption of water and capillary condensation of water on external surfaces of the zeolite powder. Indeed the zeolite powder will take up water almost indefinitely, beyond 1 g/g zeolite. The amount sorbed to internal surfaces alone is therefore experimentally uncertain. Farrell's group tried to address this uncertainty by measuring water sorption at 303 K to two different zeolite columns (data not shown) in a stream of 100% relative humidity. The two duplicated columns show the same water uptake until 0.38 g/g, which may be regarded as an upper limit on water sorption to zeolite internal surfaces. Beyond that point (i.e. after longer equilibration) water condensation depends on the packing density of the columns and the two uptake profiles diverge. In Figure 3.1, the water sorption data at 278 and 283K clearly show inflection points at 0.2 to 0.25 g/g zeolite that may indicate the extent of internal pore filling of zeolite HY80 by water and would agree with both our simulations and other experimental data (Landolt 1971; Pires and De Carvalho 1997).

Figure 3.4 shows a) zeolite before adsorption b) the snapshot of the final configuration (as representative of the equilibrium state), and c) mass cloud of sorbate in zeolite. These figures show that water occupied all the 12-member rings channels and 6-member ring channels. It is apparent that water occupies nearly all of the available porosity.

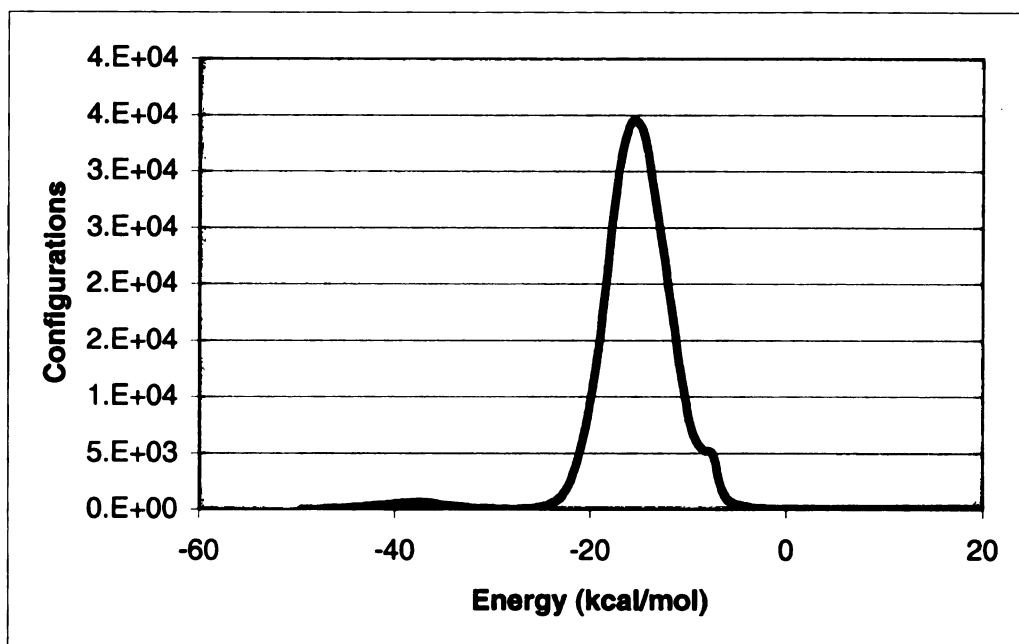


Figure 3.3. Energy distribution for pure water adsorbed by zeoliteHY80.

Figure 3.3 shows that there are two peaks for the energy distribution for pure water adsorbed by zeolite HY80. The energy for the high peak is about -15 kcal/mol, for the small peak is about -38 kcal/mol. The former represents the bulk of the pore water in the zeolite, while the latter represents the few water molecules that are directly coordinated to exchangeable cations.

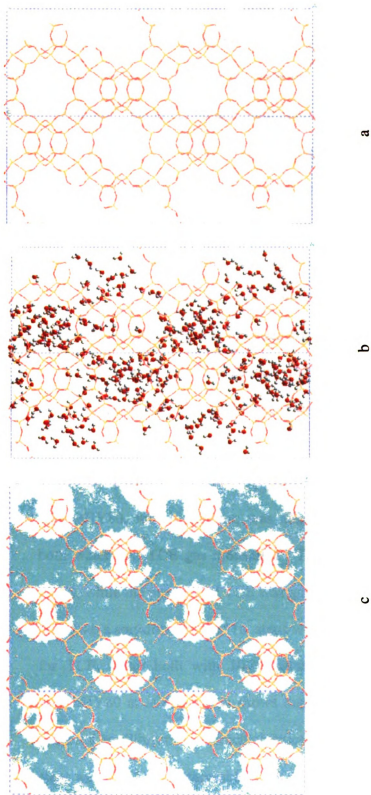


Figure 3.4. a. Zeolite before adsorption. b. The snapshot for the pure water adsorption by zeolite at 308K. c. The mass cloud of sorbate for the water adsorption by zeolite at 308K.

The COMPASS and PCFF force fields have also been tested for water adsorption. Even though there are no TCE competing with water in these simulations, there are only 0.00076 g/g zeolite and 0.0035 g/g zeolite water sorbed by the zeolite for the two force fields, respectively. These results are consistent with previous results (Channon, Catlow et al. 1998) using the PCFF force field, in which little or no water sorbed to siliceous pores in a Heulandite zeolite. For each one unit cell, there is no more than one water sorbed by the zeolite. This means that the zeolite in these two force fields is much more hydrophobic than the zeolite as modeled by our force field. Both PCFF and COMPASS use lower charges than our force field. Since electrostatic interaction in this system accounts for the large part of the whole interaction, these lower charges apparently result in the greater hydrophobicity of the zeolite. In this respect, our force field agrees much better with the experimental data and is superior to either of the commercially available force fields.

2. The experiment (b) by Farrell's group (described above) was also simulated.

ZeoliteHY80, initially vacant, was allowed to equilibrate simultaneously with both water and TCE gas molecules. The relative humidity was maintained at 100%, while the pressure of TCE was gradually lowered. For each TCE chemical potential, a sorption run of 2×10^7 steps was completed. Figure 3.5 is the trajectory for TCE, water both with 100% saturation pressure adsorbed by oven-dried zeoliteHY80 at 308K, which shows that after about 1×10^7 steps, the adsorption achieved equilibrium. For each chemical potential, the data from 1×10^7 to 2×10^7 steps were used as the ensemble for statistical mechanical analysis.

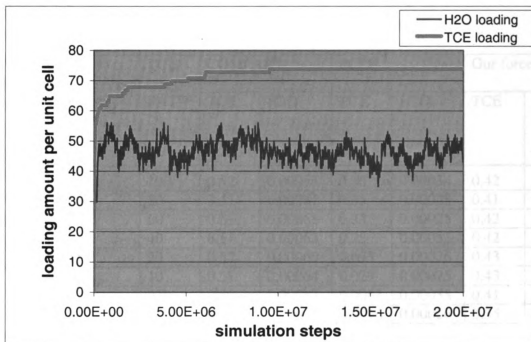


Figure 3.5. Trajectory for TCE and water adsorption simultaneously by zeolite at 308K.

TCE pressure (kPa)	TCE SAT%	COMPASS		PCFF		Our force field	
		TCE	H2O	TCE	H2O	TCE	H2O
15.75	100	0.52	0.00056	0.36	0.00034	0.42	0.036
12.60	80	0.51	0.00061	0.35	0.00028	0.41	0.039
9.45	60	0.51	0.00068	0.33	0.00025	0.42	0.036
6.30	40	0.51	0.00063	0.28	0.00031	0.42	0.033
3.15	20	0.52	0.00060	0.095	0.00026	0.43	0.033
1.58	10	0.51	0.00064	0.029	0.00025	0.43	0.035
0.32	2.0	0.50	0.00063	0.0063	0.00038	0.41	0.033
0.032	0.2	0.085	0.00070	0.0016	0.00026	0.35	0.053

Table 3.1. Different force fields for adsorptions of TCE and water by zeolite at 308K.

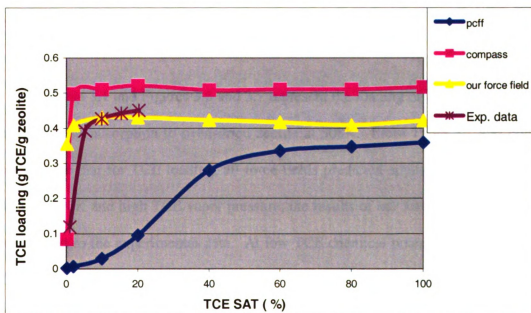


Figure 3.6. Comparison of experimental results with molecular simulations for TCE adsorption by zeolite at 308K with the competition of water at 100% relative humidity.

In each case, the zeolite pores were initially empty.

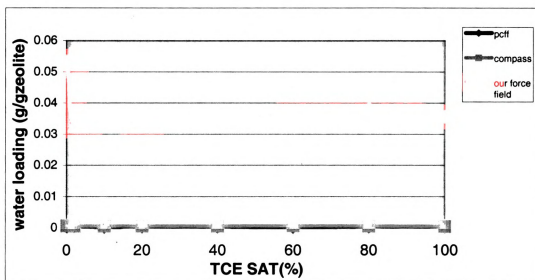


Figure 3.7. Comparison of experimental results with molecular simulations for H₂O adsorption by zeolite at 308K with the competition of TCE at 100% saturation. In each case, the zeolite pores were initially empty.

Table 3.1 and Figures 3.6 and 3.7 represent the loading of TCE and water through simultaneous adsorption to oven-dried zeolite at 308K. From Table 3.1 and Figure 3.6, we can see that for TCE loading, all force fields predicted approximately the amount of TCE at 308K and high TCE vapor pressure; the results of our force field, 0.42 g/g zeolite are closest to the experimental data. At low TCE chemical potential, our force field and COMPASS somewhat overpredicted the amount of TCE sorption, while the PCFF force field strongly underpredicted sorption below about 50% of the TCE saturation vapor pressure. At high TCE pressures, the experimental data are again difficult to interpret because of condensation on external surfaces as discussed above, but 0.45 g TCE/g zeolite is the experimental estimate based on the inflection point in Farrell's data (Figure

3.2). Furthermore, this value agrees well with the measurements of another group (Pires, Carvalho et al. 2001) who found 0.44 g TCE/g zeolite adsorbed to either H-exchanged or Na-exchanged zeolite Y.

The pore-space in the zeolite is enough to hold about 0.48 gTCE/g zeolite, which is the upper limit of the adsorption amount since the pore space was measured using a 1.2Å sphere. Since TCE is much larger, the volume accessible to TCE is much smaller. Comparing these three force fields, both COMPASS and PCFF under-predicted the amount of water adsorption by zeolite, which also happened in pure water adsorption by zeolite as described above. Even with our force field, competition from TCE suppressed water sorption by 80 to 90%. Notice that the partial charges on atoms of the zeolite lattice have much less impact on the amount of TCE sorbed than on the amount of water sorbed. This is to be expected since the partial charges on TCE itself are small. This may be the reason that PCFF and COMPASS are widely used even though the previous section shows they poorly predict water sorption to the zeolite. While there are no reported measurements of water sorption in the presence of TCE, our prediction of 3 to 4% by weight is plausible given that the pores are filled and that the TCE sorption agrees with experimental data.

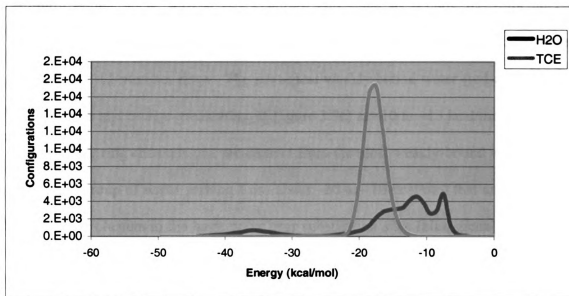


Figure 3.8. Energy distribution for TCE and water during simulation of TCE and water competitive adsorption by zeolite at 308K.

Figure 3.8 shows the simulated TCE and water energy distributions in zeolite HY80. The small peak between -30 and -40 kcal/mol corresponds to the nonbonded energy for water molecules adsorbed directly to the H^+ cations in the zeolite. Figure 3.8 shows that 12-member ring channels with diameter about $10\text{-}11\text{\AA}$ can hold both TCE and water, while the 6-member ring channels with diameter about $5\text{-}6\text{\AA}$ can only adsorb water molecules. This remained the same in the whole framework. Water molecules were occasionally sorbed in all the 12-member ring channels, but were far more common as small cluster in those 12-member ring channels that contained Al-substitution sites and H^+ cations.

The energy distribution in Figure 3.8 can be subdivided to show the locations of sites of a specific energy (Figures 3.9 and 3.10). As indicated above, the most strongly bound water molecules are coordinated directly to H^+ cations (Figure 3.10 a). The least

strongly bound water sorb at 6-9 kcal/mol and seem to occupy the 6-member ring channels (green areas in Figure 3.10c). Less frequently, this loosely bound water is found in the 12-member rings. The next-most weakly bound water (red-orange areas of Figure 3.10c and orange-green areas of Figure 3.9c) at -10 to -13 kcal/mol sorbs in a set of 6-member ring channels that are distinct from the most weakly-bound water then there is a broad group of water sorbing from about -20 to -10 kcal/mol that are mostly found in the water clusters in the large pores near substitution sites (blue-green areas of Figure 3.9c). These water molecules seem to be found in the second and third coordination spheres around the H^+ cations.

TCE molecules sorb at a single broad energy from -13 to -22 kcal/mol (Figure 3.8), centered at about -18 kcal/mol. This value agrees very well with experimental calorimetric measurements (Mellot, Cheetham et al. 1998) of 17.2 kcal/mol for the heat of TCE sorption to dry zeolite NaY. Comparison of all TCE (red areas of Figure 3.9b) versus the more weakly-bound TCE (blue areas of Figure 3.9c) show little trend other than TCE molecules near water cluster having somewhat lower energies, TCE seems to adopt a rather smooth distribution of energies regardless of their location in the large pores of the zeolite.

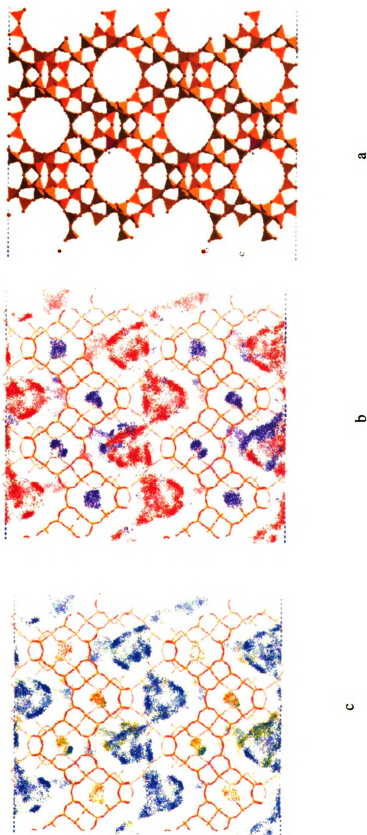


Figure 3.9. a. Zeolite before adsorption. b. Mass cloud for sorbate after adsorption. Red stands for TCE and purple stands for water. c. Mass cloud for energy after adsorption. Blue stands for energy about -18 kcal/mol and yellow stands for about -10 kcal/mol.



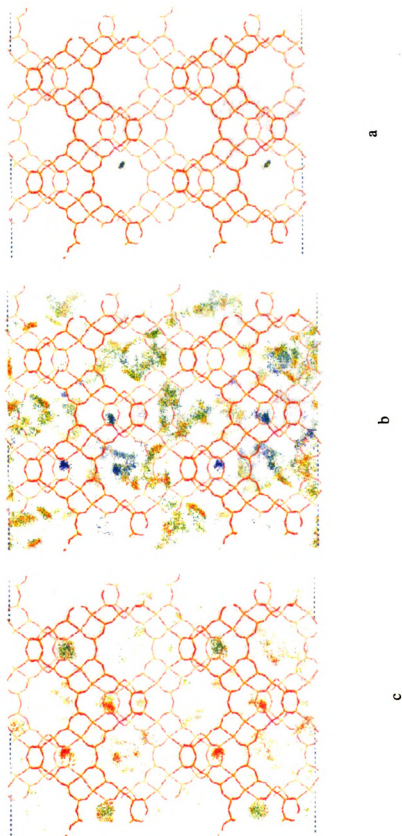


Figure 3.10. Mass cloud of energy for TCE and water adsorption by oven-dried zeolite. a. From -40 to -25 kcal/mol. b. From -20 to -12 kcal/mol. c. From -12 to 0 kcal/mol.

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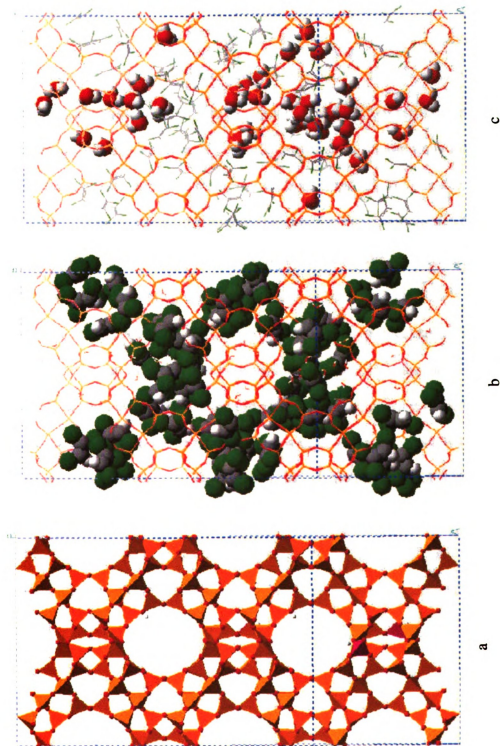


Figure 3.11. a. Zeolite before adsorption b. TCE locations inside zeolite after TCE and water coadsorption. c. water locations inside zeolite after TCE and water coadsorption



Note from Figure 3.9 b that there is little mixing of TCE and water in the zeolite structure, despite their simultaneous coadsorption. This is consistent with hypotheses (Corley, Hong et al. 1996; Farrell, Hauck et al. 1999) of capillary-phase separation as a factor controlling sorption of dissimilar solvents in microporous media. Figure 3.11 is another representation of the localized separation of TCE and water in this zeolite. Figure 3.12 is the radial distribution function for chlorine atom in TCE and oxygen atom in zeolite. The closest distance from chlorine atoms to oxygen atoms is about 3.0 angstrom, which is in agreement with the sum of the van der Waals radii of chlorine and oxygen. The positions of the hydrogen cations in the zeolite have a considerable influence on the TCE and water adsorption. Figure 3.13 is the radial distribution function for H^+ in zeolite and oxygen atom in water. The first maximum for the distance between them is about 1.6 to 1.8 angstrom, which agrees with the van der Waals radii of hydrogen and oxygen. The oxygen in water can form a hydrogen bond with H^+ in zeolite, then other water molecules can interact with these water molecules via more hydrogen bonds and may form water clusters. Comparing with Figure 3.11, we can see that chlorine atoms do not interact with H^+ closely because water is preferentially adsorbed near the cation.

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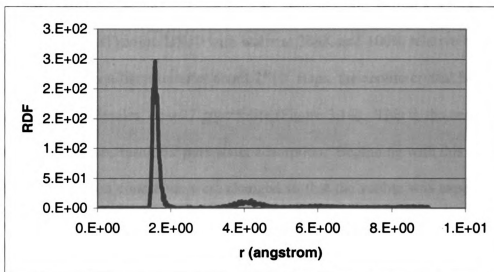


Figure 3.12. Radial distribution function for hydrogen cation in zeolite and oxygen atom in water.

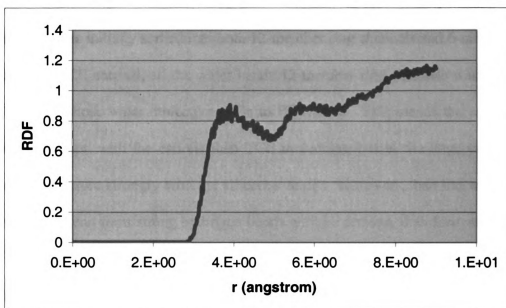


Figure 3.13. Radial distribution function for chlorine atoms in TCE and oxygen atoms in the zeolite.

3. In order to simulate experimental system c of Farrell's group, we pre-equilibrated the model zeolite HY80 with water at 308K and 100% relative humidity for 4×10^7 steps. After equilibration after about 2×10^7 steps, the zeolite crystal had adsorbed about 370 water molecules, or 0.27 g/g zeolite (Figure 3.14). This is the same endpoint reached in our previous result for pure water adsorption. Beginning with this equilibrated system, the simulation conditions were changed so that the zeolite was exposed to both TCE and water at 308K and their respective saturation pressures. From 2×10^7 steps to 1×10^8 steps, water was slowly displaced by TCE (Figure 3.14). From 1×10^8 steps to 2.5×10^8 steps, the displacement was faster, and after 2.5×10^8 steps the equilibrium was achieved again. The final equilibrium adsorption amount for water is 0.038 g/g zeolite, and for TCE is 0.44 g/g zeolite. Figure 3.15 compares the pure zeolite before adsorption, a snapshot at 4×10^7 steps when the zeolite is full of water, and a snapshot at 3×10^8 steps, when water has mostly been replaced by TCE. Comparing these three pictures, we can see that water was initially sorbed into both 12-member ring channels and 6-member ring channels. As TCE entered, all the water inside 12-member ring channels was displaced by TCE except those water molecules close to H^+ cations. This means the water has a stronger interaction with the cations than TCE molecules, but in the large cavities the TCE interacted more strongly with the siliceous zeolite framework than did water. The water molecules can form strong hydrogen bonds with H^+ cations, then form small water clusters, which are shown on Figure 3.15. The water inside 6-member ring channels cannot be replaced by TCE because it is difficult for TCE with its larger size to enter into these channels.

The final result for this simulation, with 0.44 g TCE/g zeolite and 0.04 g H₂O/g zeolite adsorbed, agrees very closely with the equilibrium achieved when TCE and water competed for the empty zeolite as reported in section 2 above. Thus, preequilibration of the mineral with water had no effect on the simulation equilibrium that was eventually attained. This is in contrast to the experimental result (Figure 3.2) in which preequilibration with water reduced TCE sorption as compared with TCE-water competition for sites in the degassed zeolite. The experimental system is hysteretic but the simulated system does not seem to be. Possible reasons for the deviation of the simulation results from experimental data might include a) In the experimental system, preadsorption of water may have blocked external sites at pore entrances and thus inhibited the uptake of TCE by the zeolite. No such kinetic artifacts exist in the simulation system. b) The force field methodology that we have created may still over-predict TCE-zeolite binding and under-predict water-zeolite binding, despite the fact that TCE and water sorption agreed quite well with experimental data in sections 1 and 2 above. c) The simulation was at 100% TCE vapor pressure, while the experiment ended at 95% of saturation. At that point the experimental adsorption was 0.44 gTCE/g zeolite, which would agree perfectly with the simulation result, but the experimental value probably included some sorption to zeolite external surfaces or water films.

Investigations to further test the force field simulations of the system should include GCEMC modeling of the entire TCE adsorption isotherm for comparison with Figure 3.2. A potential difficulty is that simulation at lower TCE pressures may take even greater computational effort before equilibrium is reached (see Figure 3.14).

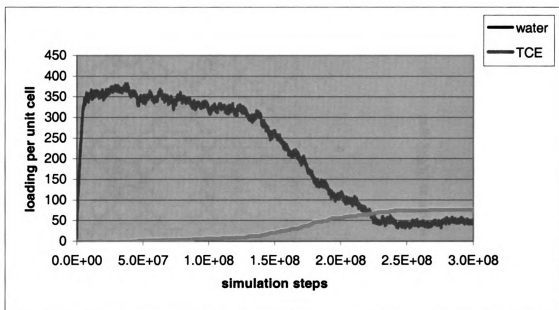


Figure 3.14. Trajectory for water and TCE adsorption by zeolite pre-equilibrated with 100% humidity water at 308K.

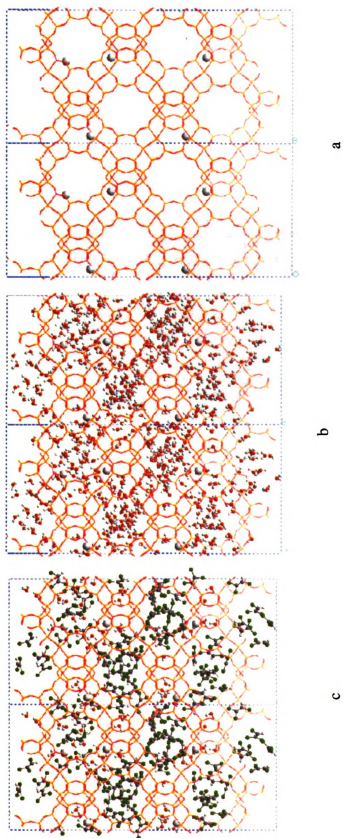


Figure 3.15. a. Zeolite before adsorption. b. Zeolite after equilibration with water at 308K and 100% humidity. c. Zeolite after TCE and water coadsorption onto system b.

4. TCE and water competition for a zeolite that was pre-equilibrated with TCE.

In order to investigate another approach to equilibrium, we also modeled pre-equilibration of the zeolite with TCE alone, followed by competition between TCE and water.

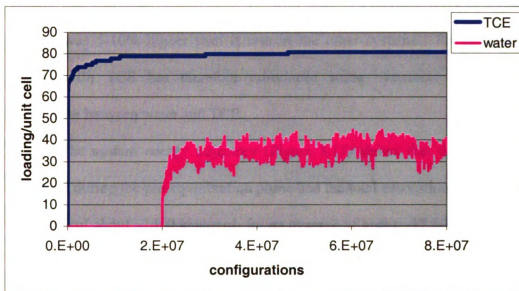


Figure 3.16. Trajectory for competitive TCE and water adsorption by zeolite after pre-equilibration with TCE alone.

For the pre-equilibration phase, 2×10^7 GCEMC steps were run at 308K with a TCE pressure of 15.75 kPa, or 100% of its saturation vapor pressure. The TCE loading of the zeolite during this phase of the simulation was 0.45 g TCE/g zeolite, which is just 2 to 7% higher than the TCE loadings we observed previously in competition with water. After this pre-equilibration, the GCEMC simulation conditions were changed to a competition between water and TCE, both at 100% of their saturation vapor pressures.

The simulation was run for a further $6 \cdot 10^7$ steps (for a total simulation of $8 \cdot 10^7$) and the overall trajectory is depicted in Figure 3.16. After the competition between TCE and water had resolved to equilibrium, the zeolite contained 0.029 g H₂O/g zeolite and 0.46 g TCE/g zeolite. The water adsorption for this system was thus about 20% less than that for the other systems, where TCE and water competed for either an empty zeolite or a zeolite that had been pre-equilibrated with water. Conversely, TCE sorption for this system was 5-10% higher than it was in the other systems. Pre-equilibration of the zeolite with TCE has therefore introduced some hysteresis into the competitive interaction between water and TCE.

The system energy trajectory (Figure 3.17) shows that the 79 TCE molecules adsorbed during the pre-equilibration phase had the total adsorption energy (for the whole unit cell) of about -1400 kcal/mol, for an average of about -17.5 kcal/mol TCE. Figure 3.18 shows that this average energy was very smoothly distributed over a continuum of sites, indication that there were no especially strong interactions between TCE and the H⁺ cations in the zeolite. This is plausible since the partial charges on TCE atoms are so low. (Table 2.4)

The radial distribution function for this interaction between Cl atoms of TCE and H⁺ cations in the zeolite is given in Figure 3.19.

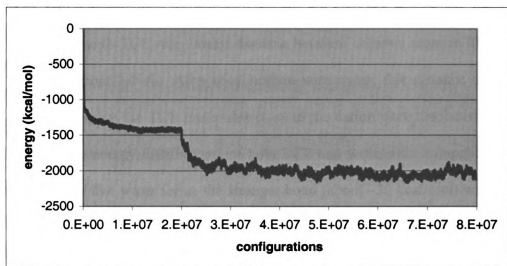


Figure 3.17. Energy change for the adsorption of TCE and water by zeolite that was pre-equilibrated with TCE.

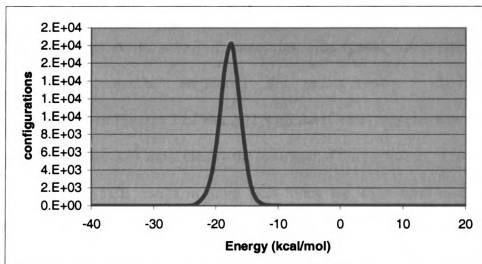


Figure 3.18. Energy distribution for pure TCE adsorbed by zeolite HY80 in the absence of competition from water.

The radial distribution function in Figure 3.19 shows that when there is no water competing with TCE, the closest distance between chlorine atom in TCE and hydrogen cation is about 2.0 Å. After equilibration with water, this distance changed to 4.0 Å. This means that the TCE molecules close to the cation were displaced by water (Figure 3.20). The energy distributions of both TCE and water after competition (Figure 3.21) again show that water forms the stronger bond (about -35 kcal/mol) with the cation than the TCE interaction with the cation. But unlike the results discussed in section 3, since TCE molecules enter into the zeolite first, these molecules tend to occupy all the sites near the cations. Even though water can replace the TCE close to cations, the larger water clusters are not able to form, so there is somewhat less water adsorption and slightly more TCE adsorption than the situation in which water entered the zeolite lattice first. Water cannot displace the TCE inside 12-member ring channels at locations far from hydrogen cations. Water molecules also enter into the 6-member ring channels, which are not available to TCE molecules. The spatial distribution of water and TCE after their competitive sorption to this zeolite system is shown in Figure 3.22. Comparison of Figures 3.22 and 3.21 with the results from previous simulations (Figure 3.8 and Figure 3.9) show clearly the locations of the hysteresis. Pre-equilibration of the zeolite with TCE results in more TCE filling the large pores near H^+ cation sites at energies near -20 kcal/mol. Once water is introduced, some of these TCE molecules prevent the expansion of water clusters (at water sorption energies of -10 to -20 kcal/mol) that were able to form in the absence of pre-equilibration with TCE.

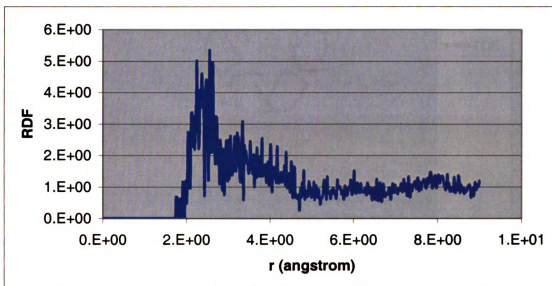


Figure 3.19. Radial distribution function for the hydrogen cation in zeolite and chlorine atoms in TCE in the absence of competition by water.

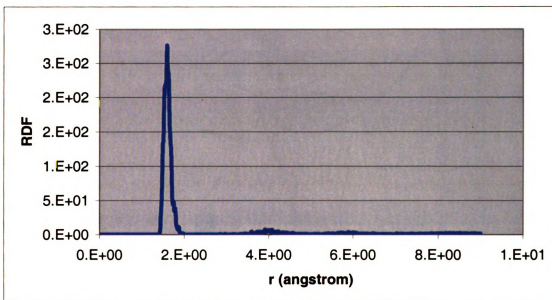


Figure 3.20. Radial distribution function for the hydrogen cation in zeolite and oxygen atoms in water after the entire simulation summarized in Figure 3.16.

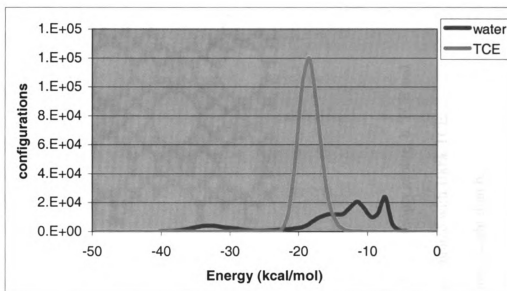


Figure 3.21. Energy distribution for TCE and water adsorbed by zeolite HY80 pre-equilibrated with 100% TCE.

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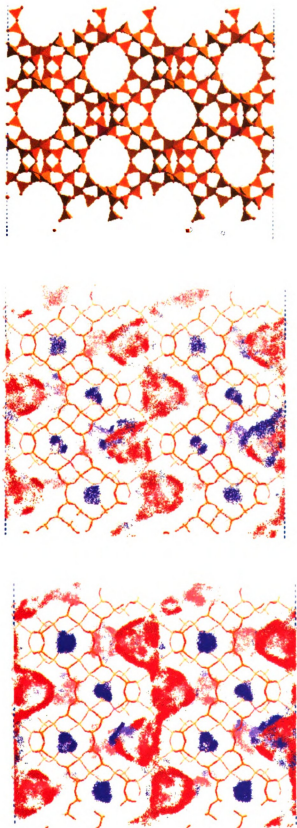


Figure 3.22. The mass cloud of sorbate for TCE and water adsorption to zeolite HY80. a. Empty zeolite. b. TCE and water simultaneously sorbed by zeolite. c. TCE and water sorbed by zeolite pre-equilibrated with 100% TCE. Since the simulation steps for c is 1×10^8 and b is 2×10^7 , the sorbate color in c is more bright than b.

CONCLUSIONS

This study demonstrates the feasibility and utility of grand canonical Monte Carlo simulations of binary TCE and water adsorption by zeolite. Potential energy parameters for the system were improved using both quantum mechanical results and empirical adjustment for internal self-consistency. The resulting force field is able to reproduce the densities and heats of vaporization for bulk TCE and bulk water phases, as well as the structures of numerous aluminosilicates. When applied to more complex systems, the force field predictions matched experimental data for water sorption by zeolite Y and for TCE sorption to hydrated zeolite Y. These data indicate that the zeolite HY with Si/Al ratio 80 is moderately hydrophilic in that the zeolite adsorbs 0.27 g H₂O/g zeolites from the vapor phase. When TCE and water are simultaneously adsorbed into the zeolite HY80, the TCE outcompetes water and occupies most 12-member channels. Many water molecules are relegated to the 6-member channels, which TCE cannot enter due to its larger molecular size. Some water molecules are adsorbed strongly near the H⁺ cations in the zeolite, and other waters interact with them to form small water clusters in the 12-member channels. Water and TCE domains remain quite separate in the zeolite, with very little mixing of the two species even when clusters of each are present in the same pore.

The same equilibrium is reached in the molecular simulations whether TCE and water compete for an empty zeolite or for a zeolite that has been pre-equilibrated with pure water. Pre-equilibration of the zeolite with pure TCE results in a slightly different final equilibrium in which somewhat more TCE and somewhat less water is sorbed.

These simulation findings are somewhat in contrast to the experimental results, in which pre-adsorption of water reduces TCE adsorption by about 10%. The experimental data are somewhat difficult to compare with the simulations owing to capillary condensation on external surfaces in the experimental system, while the simulated zeolite has no external surfaces.

Two commercial force fields (PCFF and COMPASS) were tested and compared with our force field. All force fields predicted the amount of TCE adsorption by the zeolite in approximate agreement with experiment at high TCE pressures, but PCFF predicted sorption that was much too low at low TCE pressures. The zeolite as modeled by COMPASS and PCFF is too hydrophobic overall because their predictions of water sorption are much smaller than the experimental data. Our simulation results are in far better agreement with the overall experimental data and especially for the water sorption data.

Suggested projects for further validation and improvement of our force field include simulations of zeolites with other exchangeable cations that might be allowed to be mobile within the zeolite pores, and simulations of broader parts of the isotherm in the case of TCE-water competition for zeolites that have been pre-equilibration with water. The latter might be expected to be the most relevant GCEMC molecular modeling systems for studying TCE sorption to zeolites and other minerals in the environment. In this respect, simulation and experimental studies of sorption to minerals at high water activity and low TCE activity should be pursued.

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