Calorimetric and Computational Studies of Chlorocarbon Adsorption in Zeolites

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Abstract: Monte Carlo simulations on the adsorption of the two model chlorocarbons, chloroform and trichloroethylene, in three faujasite type zeolites, NaX, NaY, and siliceous faujasite (Si/Al = 1.2, 3.0, and ∞, respectively), are compared with the results of calorimetric measurements on the same systems. At low sorbate loadings, the heats of adsorption increase with increasing polarity of the zeolite host (siliceous faujasite < NaY < NaX), underlining the importance of the dipolar nature of the sorbates. For all six systems, quantitative agreement is found between the calculated and observed heats as a function of sorbate loading. Decomposition of the calculated heats into the short-range and long-range contributions shows that sorbate−sorbate interactions are important in all three hosts and lead to an increase in the adsorption heat with coverage in NaY and siliceous faujasite. The SIII′ cations play a specific role in the case of zeolite NaX, where a cancellation between the short-range and electrostatic interactions leads to a heat of adsorption that is invariant with coverage.

Introduction

Environmental issues relating to ozone-depleting chlorofluorocarbons (CFCs)[1] and to the removal of chlorinated solvent residues from contaminated groundwater and soils[2] are driving the development of new separation and catalytic conversion processes for halocarbons. Zeolites have recently been recognized as interesting alternatives to other separation media such as activated carbons.[3,4] As a consequence, a need is emerging for developing a better understanding of halocarbon adsorption in zeolites at a molecular level. Unlike zeolite/hydrocarbon systems, there is a dearth of definitive experimental information relating to halocarbon behavior in zeolites. For example, in previous structural studies by X-ray powder diffraction,[5] both the accuracy and the completeness of the sorption site geometries were partially limited by the difficulty of dealing with highly disordered adsorption sites. Similarly, only preliminary attempts have been made to model the properties of halocarbons/zeolites systems,[6] although a detailed X-ray and molecular dynamics study has shed considerable light on the behavior of 1,4-dibromobutane in NaY.[5c] The chemisorption of halocarbons in zeolites has recently been investigated by FTIR spectroscopy, including a new method for characterizing the zeolite basicity from chloroform adsorption[7] and a study of chloroethylene in Cr−Y zeolite.[8] In the present work, we use the combination of thermodynamic measurements and Monte Carlo simulations that utilize a newly developed force field[9] to treat some model systems, chloroform and trichloroethylene in siliceous faujasite, NaY, and NaX. Faujasite-type zeolites are acknowledged to exhibit powerful catalytic properties and high performance in separation processes. Our aim is to identify the driving forces of the halocarbon adsorption under equilibrium conditions by probing the influence of parameters such as the Si/Al ratio, the cation content, and the sorbate loading. The results yield new insight into the energetics and structures of zeolite/halocarbon systems and their impact on the potential applications of nanoporous materials for separation purposes.

There are three central elements to the interaction between chlorocarbons and zeolites: (i) strong van der Waals-type attractions between the polarizable chlorine atoms and oxygens of the host framework, (ii) electrostatic interactions between the chlorines and the nonframework cations, and (iii) hydrogen bonding between hydrogens and framework oxygens in the case

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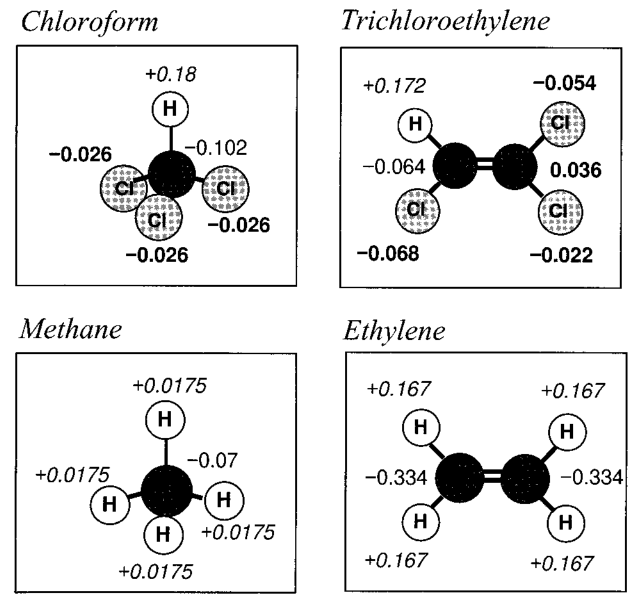

Figure 1. Estimated partial atomic charges for chloroform and trichloroethylene, compared with their hydrocarbon analogues, methane and ethylene (see text for details).

of hydrochlorocarbons. We have recently developed a new force field that embraces all of these features.[9] Parameters for the short-range host−guest interactions were obtained from values for Ar and hydrocarbons in various zeolites.[10,11] Regarding long-range interactions, framework partial charges were based upon previous computational[12] and high-resolution X-ray diffraction studies[13] and sorbate charges were derived from first principle calculations and scaled so as to reproduce the experimental dipole moments. Details of the force field have been published elsewhere,[9] but we wish to stress that no fitting to experimental data on halocarbons was used in the derivation of the parameters.

There are interesting contrasts between the behavior of hydrocarbons and chlorocarbons in zeolites, which can be identified as arising from two main sources. First, the molecular polarity is essentially inverted between the two types of systems (Figure 1), as a consequence of which there are striking differences in the disposition of halocarbon molecules within the zeolite cavities, especially in relation to their interactions with cations and the specific role of the hydrogen atom. Second, since the magnitude of van der Waals interactions is determined by the polarizability of the sorbate, it is expected to be considerably enhanced in the case of $CHCl_3$ when compared to the hydrocarbon analogue, CH_4. The ambient, zero-loading adsorption heats of CH_4 in NaY (15.2 kJ mol $^{-1}$)[14] and $CHCl_3$ in NaY (53 kJ mol $^{-1}$) are particularly illustrative of this point.

Computational Methods

Our Monte Carlo simulations used the Metropolis scheme in the canonical ensemble, at a constant volume V and temperature T. The three zeolite hosts were modeled as follows: (i) $Si_{192}O_{384}$ for the siliceous faujasite, (ii) $Na_{48}Al_{48}Si_{144}O_{384}$ for NaY, placing the Na cations in 16 sites SI and 32 sites SII, (iii) $Na_{88}Al_{88}Si_{104}O_{384}$ for NaX, placing Na cations in 32 sites SI′ and 32 sites SII and using our recent procedure for the placement of the 24 extra Na cations in sites SIII′.[15] We are aware that, by keeping the cation distribution fixed during the Monte Carlo runs, we are unable to allow for any cation movement that may happen upon adsorption. Future theoretical development should make this possible. In each system, the number of guest molecules, N, was varied from a single molecule per unit cell up to ∼30−40 molecules per unit cell, so as to reproduce the variation of loading in a fashion similar to the calorimetric measurements. All average energies were obtained over $(1-2) \times 10^6$ iterations, after an equilibration period of $(100-200) \times 10^3$ steps, with a short-range summation taken up to a cutoff radius of 12 Å and an Ewald summation regarding the electrostatic term. The software of the MSI Catalysis and Sorption Consortium was used for these simulations.[16]

Experimental Methods

The microcalorimeter for these measurements was the same Tian-Calvet instrument used in an earlier study of adsorbates on silicalite.[17] The sample and reference cells were Pyrex cubes, 2.5 cm on a side, which were surrounded by thermopiles on the bottom and four sides. Each sample (∼1 g) was pressed into wafers and placed into the sample cell. The corresponding dry weights of the samples, used in the calculations of loading, were determined from TGA measurements. The samples were then degassed by ramping the temperature of the sample cell from 20 to 110 °C, in a vacuum, over the course of 12 h, after which the temperature was further ramped to 350 °C over the next 12 h. Finally, the sample was held in a vacuum at 350 °C for an additional 12 h. After the sample was cooled to room temperature, adsorbates were dosed on to the samples by injection of vapor from a 50-cm^3 dosing loop on a six-way valve. As discussed elsewhere,[17] calibration of the instrument was accomplished by using the baseline shift measured when a current was passed through a Pt wire placed between the Pyrex sample cell and the thermopiles. The calibration was confirmed by using heats of adsorption of ethane in silicalite estimated from adsorption isotherms. The preparation of the siliceous faujasite sample has been described previously;[18] the Si:Al ratios of the NaY and NaX samples were 2.6 and 1.2, respectively.

Results and Discussion

In Figure 2a, the calorimetric heats of adsorption of chloroform at room temperature are compared with the values obtained with our Monte Carlo simulations in the three hosts, siliceous faujasite, NaY, and NaX. Our simulations capture our experimental findings remarkably well, as shown by the excellent agreement for all three host−guest systems. Two dominant features of chloroform adsorption are revealed: (i) an increase in adsorption energies over the whole loading range in the sequence siliceous faujasite < NaY < NaX (the slight decrease that is observed at low loadings in siliceous faujasite is probably due to a low concentration of silanol defects) and (ii) an increase in adsorption energies of more than 10 kJ mol $^{-1}$ upon loading in siliceous faujasite and NaY, in contrast to the chloroform/NaX system which shows a relatively flat profile.

To elaborate on these two important features of chloroform adsorption, the total host−guest interaction energies were decomposed into their short-range and long-range components (Figure 2b−d). Since the short-range interactions are very

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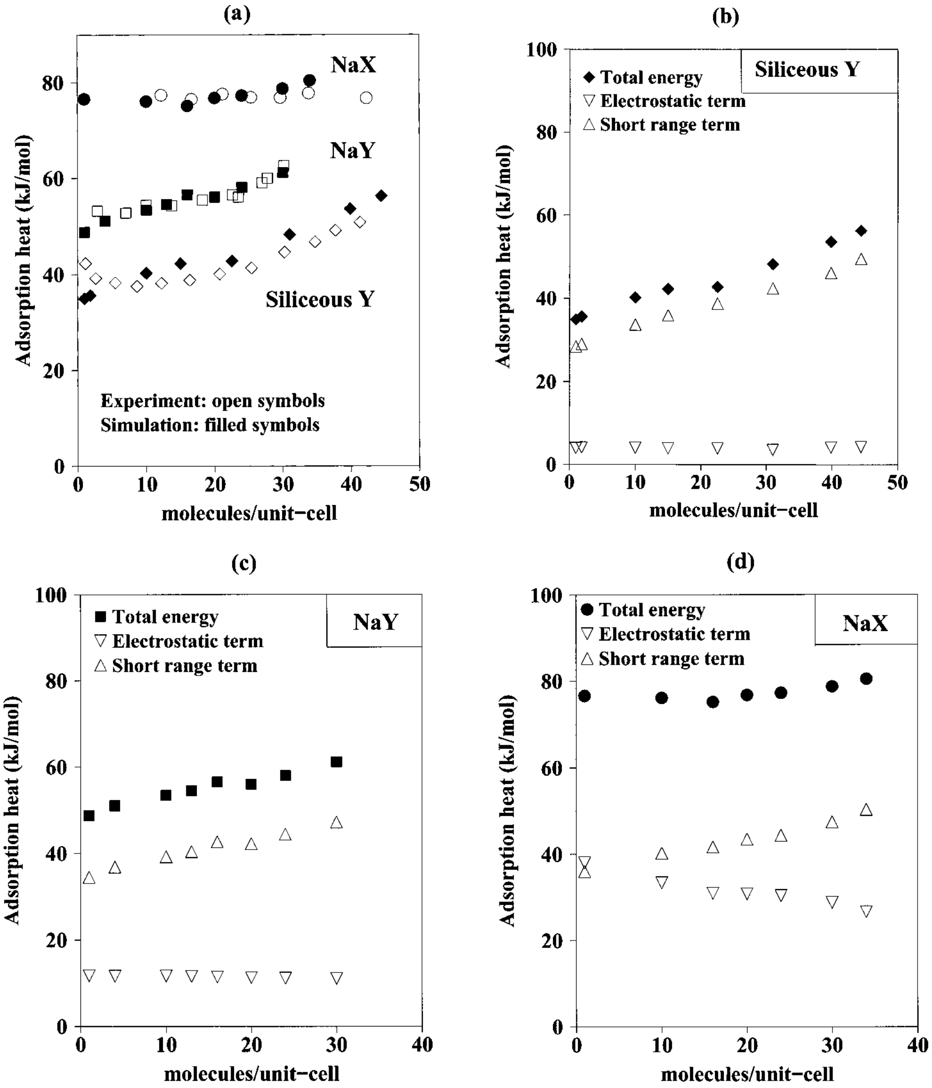

Figure 2. (a) Observed and calculated heats of adsorption of chloroform at room temperature in the three zeolite hosts, siliceous faujasite, NaY, and NaX (b, c, d) Calculated heats of adsorption for siliceous faujasite, NaY, and NaX decomposed into their short-range and long-range contributions.

similar in magnitude in all three hosts, the higher affinity of chloroform for the more polar zeolites clearly stems from the stronger electrostatic interactions occurring in these cation-containing systems; at zero loading, the electrostatic interactions consist of 47% of the total adsorption heat in NaX, 24% in NaY, and 11% in siliceous faujasite. This establishes the role of the chloroform dipole moment (1.06 D) in the adsorption process in terms of its interaction with the electric field generated by the structure. In NaY, our calculations show clear evidence for the three interactions mentioned above: (i) short-range $Cl\cdots O_{zeolite}$ interactions (ii) electrostatic $Cl\cdots Na(SII)$ interactions, and (iii) $H\cdots O_{zeolite}$ hydrogen bonding. This system has been described in detail previously.[9] In the case of NaX, our results point to the possibility that the Na cations in site SIII′ are involved in additional interactions with the sorbate, in comparison with NaY. With the aim of unambiguously elucidating the role of SIII′ sodiums in the adsorption process, the location of chloroform was investigated by docking and energy minimization calculations (at zero K) in the NaX structure. We show a typical binding site geometry in Figure 3, where new features in comparison with siliceous faujasite and NaY are clearly visible. The attraction of the chlorine atoms toward the Na cations in sites SIII′ controls the orientation of the molecule in the 12-ring window, leaving Cl atoms at a distance of 3.2 Å from these cations. This position still allows chloroform to accommodate $Cl\cdots O_{zeolite}$ van der Waals interactions and $C-H\cdots O_{zeolite}$ hydrogen bonding in a fashion similar

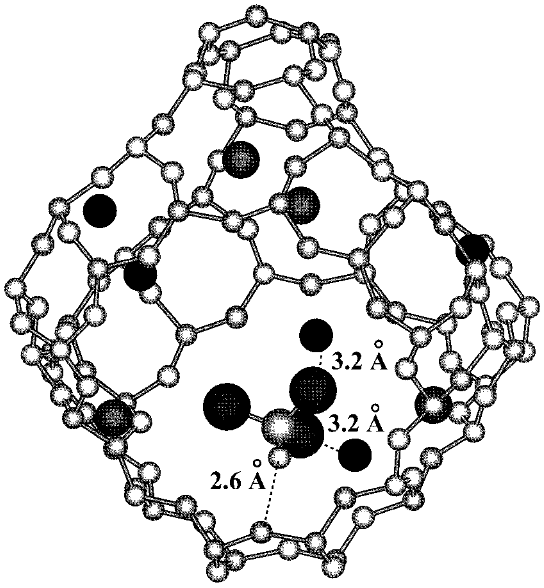

Figure 3. Binding site geometry for chloroform in zeolite NaX, estimated from Monte Carlo docking calculations (zero K).

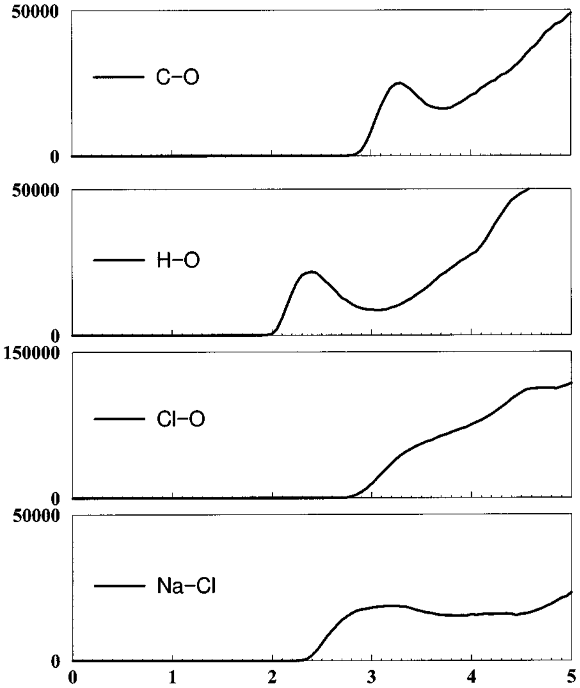

Figure 4. Partial radial distribution functions for chloroform in zeolite NaX, taken from the room-temperature Monte Carlo simulations at low loading (1 molecule per unit cell). Distinct features in the C−O and H−O figures arise from hydrogen bonding.

to that in siliceous faujasite and NaY. The coexistence of these three interactions, even at room temperature, is nicely illustrated by a series of partial radial distribution functions taken from our Monte Carlo simulation at zero loading (Figure 4).

In terms of the variation of adsorption heat with sorbate coverage, all three systems (Figure 2b−d) show an identical increase in the short-range contributions with increasing coverage that arises from the changes in the chloroform distribution as a function of loading. At the zero-loading limit, chloroform is typically adsorbed in the region of the 12-ring window where it can benefit from the different interactions described previously. As the loading increases, an additional contribution to the total energy arises from intermolecular attractions between chloroform molecules detected by frequent Cl···Cl van der Waals contacts throughout the Monte Carlo simulations, although the local framework environment of each chloroform molecule is largely maintained. This aggregation effect is of a purely dispersive nature, arising because of the high atomic polarizability of the chlorine atoms, and leads to an inhomogeneous and disordered distribution of the sorbate molecules over the micropores.

On account of the above findings, the case of NaX is particularly striking since the flat profile for the total adsorption heats obtained in this case (Figure 2d) suggested, in the first instance, the possibility of a different adsorption process. However, the Monte Carlo simulations indicate that aggregation takes place in exactly the same way in all three hosts, as shown by the similar slope of the short-range term as a function of coverage in the three systems. Unexpectedly, however, and in contrast to the siliceous faujasite and NaY systems, this increase is canceled out in NaX by a decrease in the electrostatic interactions over the whole range of loading. We believe that this diminution in the electrostatic term reflects the limited availability of the favorable sorbate locations of the type shown in Figure 3; as the loading increases, the sorbate molecules are forced to occupy less favorable sites with respect to the SIII′ cations, thus leading to a cooperative decrease in the electrostatic interactions. By contrast, the flat profile of the electrostatic term in both siliceous faujasite and NaY reflects a potential surface that is reasonably uniform with respect to the electric field.

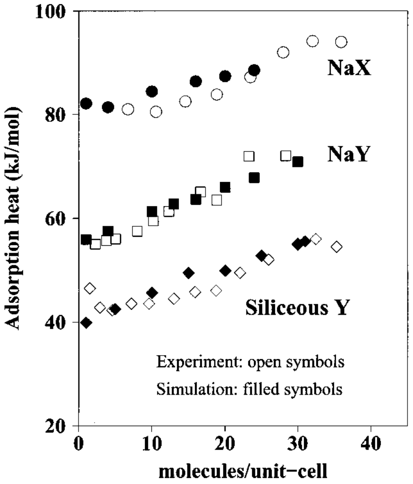

Figure 5. Observed and calculated heats of adsorption of trichloroethylene at room temperature in the three zeolite hosts, siliceous faujasite, NaY, and NaX.

The flat heat profile observed for NaX could be interpreted (incorrectly) in terms of Langmuir's theory as adsorption of molecules on a set of equivalent and independent sites without interactions between bound molecules. However, the frequently observed constancy of the heat of adsorption in zeolites[19] is actually due to internal compensation of the competing effects of surface nonuniformity and attractive gas−gas interactions. Although the cancellation of errors inherent in the Langmuir model is well-known,[20] Figure 2d is the first interpretation of this phenomenon with a detailed molecular model.

In order for our model to be of general utility for chlorocarbons in zeolites, it is important that it should be transferrable to other zeolite hosts and to other sorbate molecules. The data on trichloroethylene in our three faujasite hosts, presented in Figure 5, demonstrate clearly that it is indeed quantitatively transferrable to the case of unsaturated chlorocarbons. The only changes from the chloroform calculations are those pertaining to the partial charges of the sorbate itself (see Figure 1). The three driving forces identified with chloroform adsorption are also dominant in the case of trichloroethylene. Details will be published elsewhere.[21] In future publications, we shall show that our model is also applicable to other hosts such as ZSM-5.

In conclusion, our results show that a simple, well-parametrized model, comprising Lennard-Jones and Coulombic terms, affords a quantitative description of zeolite/chlorocarbon systems over a range of host composition, sorbate type, and sorbate loading. Furthermore, the simulations provide an important bridge between the structural and thermodynamic features of systems that are virtually impenetrable by conventional diffraction methods. The challenge now is to harness the power of this approach in the design, at a fundamental molecular level, of zeolite-based separation processes for halocarbon molecules.

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