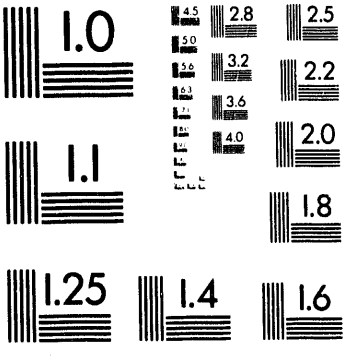
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Title: COMPUTER SIMULATIONS OF BENZENE IN FAUJASITE-TYPE ZEOLITES

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Submitted to: International Zeolite Association

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Computer simulations of benzene in faujasite-type zeolites

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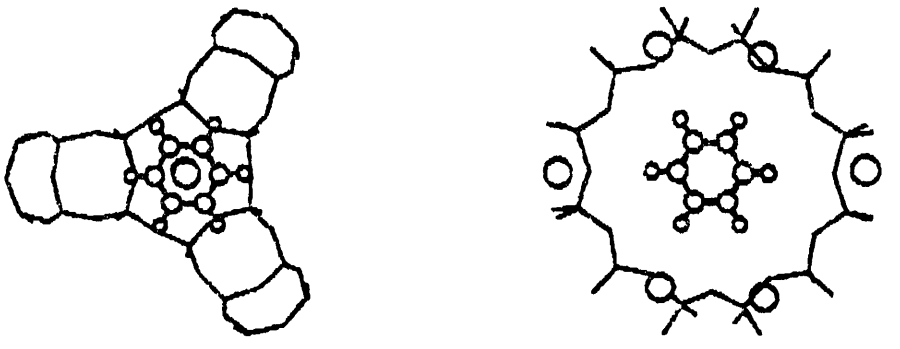
1. INTRODUCTION

The synthetic faujasite analogues, zeolites X and Y, are used extensively as catalysts in a variety of reactions and separation processes. For example, rare-earth and high-silica faujasites are excellent fluid cracking catalysts with good selectivity and high conversion rates, and the acidic nature of highly siliceous faujasites is also exploited in hydrocracking. [1] The properties of adsorbed hydrocarbons are central to the catalytic processes that take place within the cavities of zeolites and other shape-selective, microporous catalysts. Selectivity, for example, may be strongly influenced by the diffusivities of reactant and product molecules. [2] Neutron diffraction studies [3] have revealed two adsorption sites for benzene in Na-Y at low temperatures. The dominant site which is thought to be occupied exclusively at low coverages (~1 molecule per supercage), lies in the supercage, facially coordinated to the SII cation (Figure 1(a)), and the second, which appears at higher concentrations is centered in the 12-ring window (Figure 1(b)); these findings are consistent with infra-red studies. [4] The precise nature of the cation-benzene ring interaction is unclear, although quadrupolar terms are believed to be important. In relation to possible covalent interactions, quasi-elastic neutron scattering [5] has detected a weak perturbation of the benzene ring frequency, but an investigation using FYNES [6] showed no measurable change in the p^* energy levels.



(a) (b)

Figure 1 - The experimentally determined binding sites for benzene in Na-Y

The heat of adsorption of benzene in Na-X and Na-Y, which has been examined by several workers, [7] is known to increase as the Si/Al ratio decreases presumably reflecting the dominant cation sorbate interactions. Benzene mobility has been probed by a variety of

techniques, though the disparity between the results obtained from different methods is rather large. For example, the measured diffusion coefficients for benzene in Na-Y at 298K range from $1\times10^{-11}m^2s^{-1}$, from NMR studies, [8] to $3\times10^{-13}m^2s^{-1}$, from adsorption uptake studies. [9] A molecular dynamics simulation of benzene in Na-Y [10] gave a very high value for the diffusion coefficient ($4\times10^{-9}m^2s^{-1}$ at 326K), but a recent study on siliceous faujasite showed rather good agreement with experimental results obtained by ^{2}H NMR. [11]

Computer modelling of sorbates within zeolite cavities has been very successful in cases where sorbates are inert gases or simple hydrocarbons, or where the zeolite hosts are siliceous, [12] but there has been very little work on systems involving unsaturated hydrocarbons and cation-containing zeolites. In this paper we describe the results of computer simulation on a model zeolite-sorbate system of this type, benzene in Na-Y. It has been shown previously [13-15] that the concentration of sodium ions in the SII and SIII sites of ion-exchanged zeolite-X/Y samples has a profound effect on the behaviour of adsorbed benzene. In order to obtain a more detailed understanding of the influence of exchangeable cation on sorbate structure and dynamics, and to examine the quality of simulations in a system that is quite complex to model, we have used energy minimisation and Monte-Carlo methods to probe the location and energetics of benzene in sodium zeolite-X and -Y. Predicted values for the sorbate location, heats of sorption are compared to the corresponding experimental data. The sensitivity of the computational results to the forcefield and its parameterisation is explored.

2. COMPUTATIONAL DETAILS

Energy minimisation calculations were performed using the Biosym's Solids_Docking tool , and the Discover program. [16] The calculations were carried out using a single unit cell of faujasite [17] with an additional 10Å shell of structure surrounding it to give some degree of periodicity, and a single benzene molecule per unit cell. Two forcefields were used for the calcul. The standard Biosym cvff forcefield was our starting point. The parameters are given in Table 1. In addition, we also used a forcefield of cff91 form as developed by Hill and co-workers [18] by fitting to *ab initio* potential energy hypersurfaces for silicate cluster models. The charges on the framework calculated from this method are quite typical of those reported based on quantum chemical calculations on discrete clusters. [19] Short-range interactions were represented by Lennard-Jones [9-6] potentials, and electrostatic interactions were calculated using a simple coulombic summation with a short-range cut-off. No special effort was made to fit the interaction parameters between the sorbate and the zeolite to experimental data. This point will be addressed later in the paper. The potential parameters used are summarised in Table 1.

The methodology employed in the Solids_Docking tool consists of the following steps :
(i) high temperature dynamics are initially performed on the sorbate to produce a database of sorbate conformations,
(ii) a series of random insertions of benzene into the zeolite model are made and their energies determined. Configurations with a favourable energy are accepted and a database of zeolite-sorbate configurations is created,
(iii) For each configuration in the database, the position of the sorbate is energy minimised with respect to the zeolite while the host atoms are held rigid.

Table 1 : A summary of the potential parameters used to represent the host-guest interactions

	cff91 forcefield			cvff forcefield		
	Charges	Non-bonding parameters		Charges	Non-bonding parameters	
		r^*_i (Å)	ε_i (kcal mol^{-1})		A_i (kcalmol^{-1}Å^{12})	B_i (kcalmol^{-1}Å^6)
Si	0.524	0.0001	0.0000	1.4	1.72×10^6	0.000
O	-0.262	3.4506	0.1622	-0.7	1.81×10^5	821.3
H	-0.153	2.9950	0.0200	-0.153	7.11×10^3	32.9
C	0.153	4.0100	0.0640	0.153	1.98×10^6	1126.0
Na	0.8	3.1440	0.5000	0.8	1.4×10^3	300.0

where :

$$E_{ij} = \epsilon_{ij}\left(2\left(\frac{r^*_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{r^*_{ij}}{r_{ij}}\right)^6\right)$$

$$r^*_{ij} = \left(\frac{1}{2}\left(r_i^{*6} + r_j^{*6}\right)\right)^{\frac{1}{6}}$$

$$\epsilon_{ij} = 2\frac{\sqrt{\epsilon_i \epsilon_j}\, r_i^{*3} r_j^{*3}}{r_i^{*6}+r_j^{*6}}$$

$$E_{ij} = A_{ij}/r^{12} - B_{ij}/r^6$$

$$A_{ij} = (A_i A_j)^{1/2}$$

$$B_{ij} = (B_i B_j)^{1/2}$$

The rationale for this procedure is to alleviate to some extent the problem of local minima in the configurational space search. Hopefully one of the minimised configurations will be the global minimum of the potential energy surface.

Six models for faujasite were used, each for a distinct Si/Al ratio :-

a) a purely siliceous model.

b) a Na-Y model (Si/Al=2.0) in which we fill all the SI' and SII sites in the structure with cations.

c) a Na-X model (Si/Al=1.4) in which in additional to occupying the cations sites as in the Na-Y model, we also occupy one sixth of the SIIIi sites.

d) a Na-X model (Si/Al=1.0) in which one third of the SIIIi sites are filled.

e) a Na-X model (Si/Al=1.4) in which one sixth of the SIII sites are filled.

f) a Na-X model (Si/Al=1.0) in which one third of the SIII sites are filled.

For the siliceous model, we took the structure from the recent diffraction study of Hriljac and co-workers, [20] whereas for the cationated models we used the structure and nomenclature of Hseu. [21] In each case, the most favourable binding sites and binding energies for benzene were determined and compared to experimental data,where available.

the simulation only contains one benzene per unit cell, the lack of location of the SIII site is not surprisingly. Indeed, if the minimisation is started with a benzene in the experimentally determined 12-ring, it moved around the wall of the supercage to an adjacent 6-ring site. However, if we block all adjacent SII sites with benzene and repeat the minimisation, we find that the 12-ring position is now stable (figure 4). Both forcefields predict a binding energy at the SII site which is well within the range measured experimentally. The benzene-cation distance is found to be ~2.50Å for the cvff forcefield, and ~2.77Å for the cff91 forcefield. The conformation of the benzene with respect to the 6-ring is also incorrect as we predict that the hydrogens point towards the silicons rather than the oxygens. This suggests that the dominant interaction is a steric one rather than an electrostatic one.

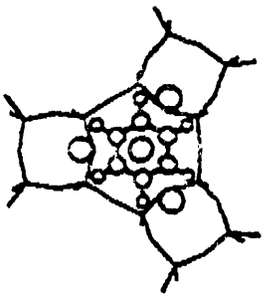
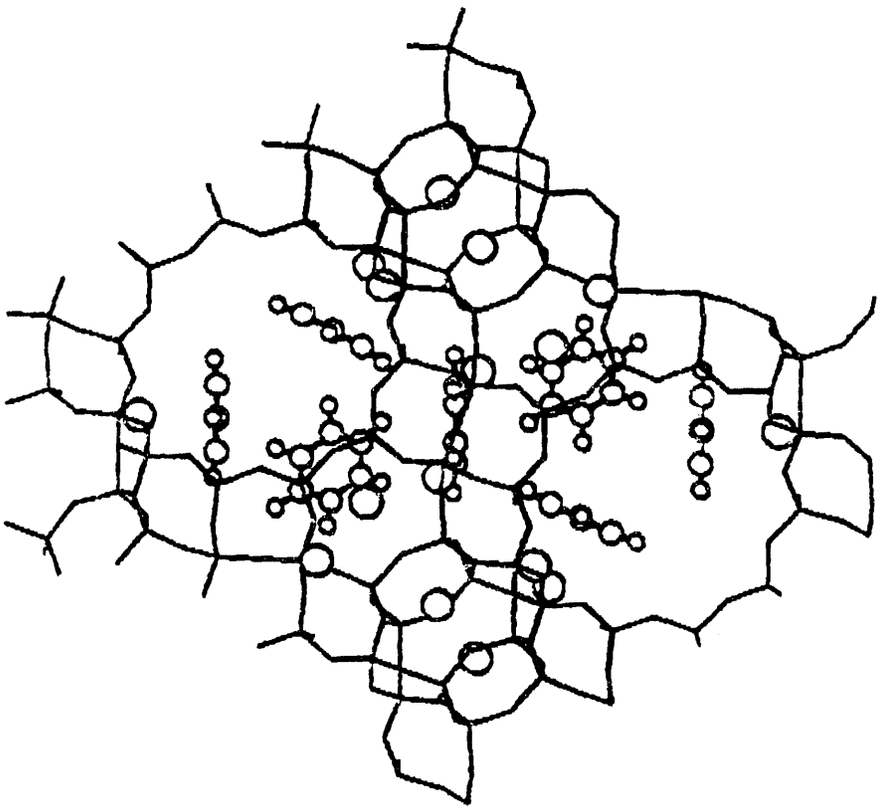


Figure 3 - Predicted benzene binding site in Na-Y

Figure 4 - Predicted 12-ring binding site for benzene in Na-Y at high loading



3. RESULTS AND DISCUSSION

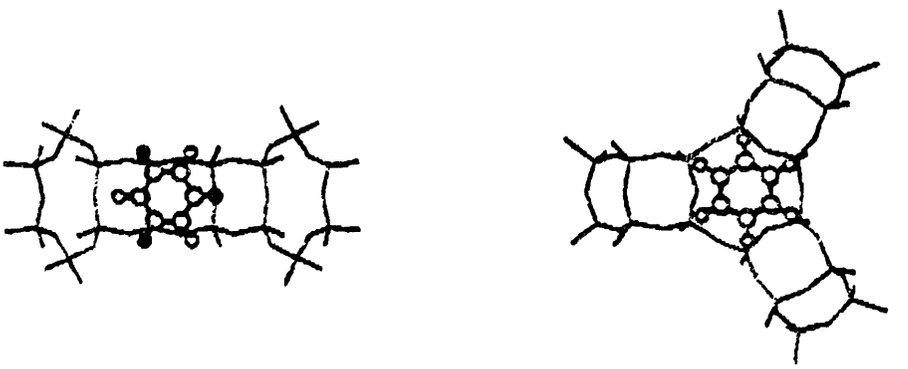
The sorption energies for the six-ring binding site in each of the zeolite models with the two forcefields are summarised in Table 2.

Table 2 - The variation in energy of the six-ring binding site as a function of Si/Al ratio

model	(a)	(b)	(c)	(d)	(e)	(f)
Si/Al	-	2.0	1.4	1.0	1.4	1.0
cff91 Energy ($kJmol^{-1}$)	9.1	61.0	80.1	80.6		
cvff Energy ($kJmol^{-1}$)	36.8	73.8			76.8	80.0

3.1 Siliceous Faujasite

In the case of the purely siliceous system containing no cations, we find that the potential energy surface is quite flat and a large number of sorption sites of similar geometry are found. Generally these are located over the four-rings in the wall of the supercage and in the region of the six-ring site (see figure 2), with the four-ring sites being of slightly lower energy. Although there has been no calorimetric measurements made on the system, extrapolations of the available thermochemical data on other faujasites of varying Si/Al ratio in the literature would suggest a value around 40-50 $kJmol^{-1}$. The cff91 predicted energy severely underestimates this value, whereas with the cvff forcefield, the sorption energy is much closer to the estimated value. A low temperature neutron diffraction study on this system failed to locate the sorbate at 4K, [20] corroborating the view that there are a large number of equally favourable sites of low symmetry contributing to the overall scattering from the sample.



(a) (b)

Figure 2 - Predicted benzene binding site in siliceous faujasite : (a) 4-ring site. (b) 6-ring site

3.2 Na-Y Faujasite

As has been previously mentioned, an experimental study on this system detects two cation binding sites. One located symmetrically above the SII cation position with the centroid of the benzene at a distance of ~2.70Å, and the other, that is only detected at high sorbate loading, in the 12-ring window. We only find the SII site in this work (figure 3), although since

3.3 Na-X Faujasites

Once the SIIIi cation sites are filled, we are entering a regime in which there is no structural data available on the location of benzene. Diffraction studies have shown that despite the possibilities of binding to an SIII cation in this system, once again the benzene in only located at the SII site as in Na-Y. From previous measurements in the heat of sorption with decreasingly Si/Al, we also know that the sorption heat increases as more cations are added to the system For the two models studied, we again find a large number of SII binding sites of similar energy to that in Na-Y. However,we also see a number of sites in which the benzene is partially coordinated to both an SII cation and an SIIIi cation (see figure 5 for a typical geometry); these are found to be slightly more favourable than the SII site. However, we note that the displacement from the symmetrical binding position is only slight and probably insufficient to be detected in the diffraction experiments. The binding energy for the model with the higher cation concentration is found to be slightly larger, which correlates with experiment (see table 2).

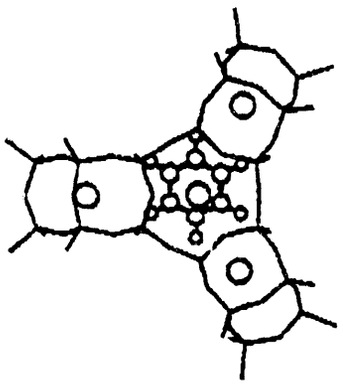


Figure 5 - Predicted binding site for benzene in Na-X

3.4 The Effect of the Forcefield

In general, both of the forcefields used here predict similar binding sites for each of the systems, however it can clearly be seen that the final energies predicted are very sensitive to both the form and parameterisation of the forcefield. Indeed the cff91 forcefield, which we considered to be in some ways more rigorous predicts less accurate results for energies. This is most marked in the case of the sorption energies for siliceous faujasite. Clearly further work needs to be performed to refine the forcefield especially in the area of zeolite-sorbate interactions, To this end, we are currently performing *ab initio* quantum mechanical calculations to probe the fine details of the cation-benzene interaction, and improve the predictions of sorption energies that can be made using this method.

ACKNOWLEDGEMENTS

NJH acknowledges the Science and Engineering Research Council (UK), Los Alamos National Laboratory, Biosym Technologies and the University of California for support. This work made use of MRL Central Facilities supported by the National Science Foundation under Award No. DMR-9123048.

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