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Mechanism of adsorption of *p*-cresol uremic toxin into faujasite zeolites in presence of water and sodium cations – A Monte Carlo study

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ABSTRACT

Atomistic Monte Carlo simulations on the adsorption of *p*-cresol and water in faujasite zeolites have been performed. Two types of zeolites were used, namely a hypothetical, pure silica faujasite and the NaY one. The comparison of the results obtained for both zeolites on the adsorption of *p*-cresol shows that the molecules are mainly adsorbed at the supercage and few of them are located at the cage windows. The presence of the sodium cations in the framework of NaY does not modify substantially the qualitative observations made for pure-silica faujasite. By contrast, the presence of the cations modifies notably the shape of the adsorption isotherm of water (either in presence or absence of *p*-cresol molecules in the zeolite pores) which can be correlated with the energetics of interaction between the species in the system.

1. Introduction

Zeolites are microporous crystalline materials with pores having the diameter of the order of few angstroms (3–12 Å) [1]. The porous nature of the material is used in several industrial applications ranging from catalysis, ionic exchange, phase separation and so on [2–4]. Recently, the shape selectivity property of zeolites is inherited in the dialysis procedure for the removal of uremic toxins [5,6]. The main necessity for the zeolitic usage in dialysis procedure is due to the inefficient removal of protein-bound uremic toxins in conventional dialysis method. Recent studies show that the conventional hemodialysis method using polymer membranes are good at removing only small toxins that are present in blood as free, solute species (e.g. urea, creatinine). On the other hand, a very small [7] amount of protein-bound uremic toxins is eliminated. The presence of such toxins at high concentration can cause many biological, biochemical and physiological disturbances in patients with uremia [8,9]. One such prototype of protein-bound toxin is paracresol (hereafter termed *p*-cresol) which causes intoxication in patients when concentration of the molecule increases in the serum [9–12]. An alternative to the use of polymeric membranes with mitigated efficiency is the design of selective adsorbant such as zeolite, a route that we are investigating for several years.

This work is devoted to the adsorption study of *p*-cresol and water in two different faujasite zeolites to gain detailed insights into the effect of cationic presence within the framework. The need to gather information at the molecular scale on the zeolites–sorbates pair interplay has promoted the usage of molecular simulations. So far, many atomistic simulations devoted to the studies on the adsorption in faujasite zeolites have been reported. Wender et al. [13] has extensively studied the adsorption of several linear alkanes starting from ethane to decane in faujasite zeolites at various temperatures. The results obtained from these Monte Carlo simulations are reportedly in good agreement with the experimental results. Bates et al. [14,15] simulated, using Monte Carlo with configurational-biased technique, the adsorption of the alkane series from butane to decane to predict the conformation and heat of adsorption of the adsorbates in various all-silica zeolites (MFI, FAU, MOR, RHO, LTA, FER). The authors tried to correlate the shape and energies of the adsorbates with the pore diameter of the zeolites. It was found that there is good driving force for adsorption when the pore size is greater than 4 Å, and the adsorption energy increases with increase in alkane chain length. The investigation of adsorption energy as a function of pore diameter led to the conclusion that the sorbate molecules are much more localized at smaller pore channels rather than being uniformly distributed throughout the structure. Adsorption and diffusion simulation studies of benzene

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in various zeolites were investigated using molecular dynamics by Rungsirisakun et al. [16].

Beauvais et al. [17] studies on the distribution of cations in faujasite gives an idea of the effect of water adsorption on cation distribution. On dehydrated faujasite, it mainly depends on the Si/Al ratio. By contrast, in hydrated faujasite, the cations are redistributed upon adsorption quantity above 150 molecules. Interestingly, the configuration observed at low loading is recovered when there is huge adsorption of water molecules. Zeng et al. [18] work on benzene adsorption in all-silica Y type and NaY type zeolite shows that the latter one adsorbs significantly more benzene than the former type because of the presence of cations in the framework. The work by Lachet et al. [19] on the adsorption of *p*-xylene, *m*-xylene and their mixtures in the NaY zeolite suggested that *m*-xylene has stronger binding capacity when compared to its isomeric *p*-xylene. Even in the mixture adsorption, irrespective of the concentration of the isomers in the mixtures, NaY zeolite exclusively prefers *m*-xylene for adsorption. The influence of Si/Al ratio on the adsorption of hydrocarbons has been studied by Daems et al. [20] who found a selective adsorption of aromatics on Y type when compared to X type zeolites.

The present work is devoted to the Monte Carlo simulation study of the adsorption of *p*-cresol and water in pure silica and NaY faujasite zeolites. To our knowledge, no work has been reported on the adsorption of uremic toxins in faujasite zeolites by means of molecular simulations. The main objective of the work is to understand the effect of cation upon adsorption process. The paper is presented as follows. Initially, we present the methodology we used in our simulations which includes the molecular models for the adsorbates and zeolites. Subsequently, we discuss the adsorption of *p*-cresol in faujasite zeolites and cationic influence. Finally, we study the coadsorption of water in faujasite zeolites and propose a mechanism for the coadsorption process.

2. Simulation details

2.1. Structures and force fields

Zeolites are microporous crystalline materials. The framework consists of tetrahedral silicon atoms bridged together by oxygen atoms. The faujasite porous network is made up of cuboctahedral sodalite cages having a diameter of 6.5 Å which are linked together in tetrahedral manner by six oxygen atoms forming cavities called supercages. These supercages have a diameter of 12.5 Å which are interconnected by the same tetrahedral manner by 12–membered ring windows of diameter 7.5 Å. A single unit cell of faujasite consists of 192 SiO_2 units having eight supercages and eight sodalite cages belonging to Fd3m space group with a lattice parameter of 25.03 Å. The presence of aluminum atoms in the framework imparts charge defects which are compensated by non-framework cations (Na^+). The Si/Al ratio varies from one faujasite to another. In the case of pure silica faujasite, there was no presence of charge defects in the framework and hence the faujasite is free from compensating cations. When the Si/Al ratio is greater than 1.5, the zeolite is termed as Y zeolite. The location of the sodium cations in the faujasite deserves discussion. From literature, it was found that the sodium cations can be placed at four different sites namely I, I′, II and III (see Fig. 1) [21,22]. In our simulations the Si/Al ratio was set to be 3 by having the full occupancy for I and II sites.

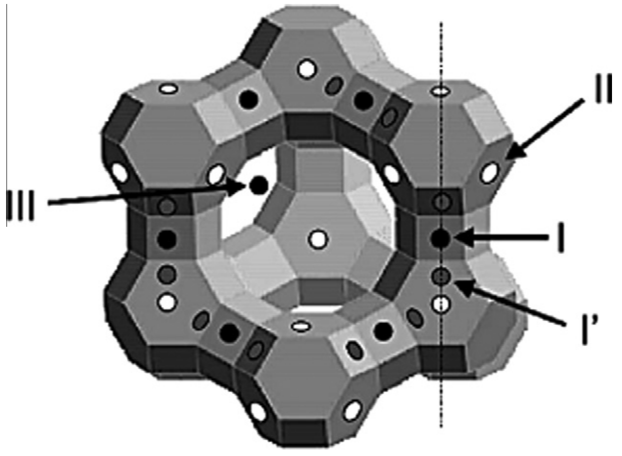

Fig. 1. Schematic representation of faujasite zeolite and location of extra framework cations.

All the Monte Carlo simulations were carried out using the simulation package “Towhee version 6.2” [23]. The Amber force field [24] for the adsorbate molecules (*p*-cresol and water) and the Clay-FF [25] one for the faujasite zeolites were used in the simulations. The framework zeolite atoms are fixed at their crystallographic positions. The TIP3P model is embedded in Amber force field for the parameterization of water molecules. Thus, water molecules were kept rigid in the simulations. Intramolecular energies arising from bonds, angles and torsions were accounted for in the case of *p*-cresol molecules. The computation of these energy terms is compulsory when using configurational-biased techniques.

All the atoms in the system bear a point charge which is used to calculate the electrostatic energy. The charges for *p*-cresol are obtained using density-functional methods [26,27] by fitting the electrostatic potential created by the electron density. The PBE functional [28] were used with the 6–311 G(d,p) basis set [29]. The Gaussian03 program package was used to calculate charges on *p*-cresol [30]. Charges for water are from TIP3P model, and charges for the pure silica faujasite are +2.4|e| for silicon and −1.2|e| for oxygen atoms. For NaY faujasite the charges for silicon is +1.40|e|, oxygen is −0.82|e| and sodium is +1.0|e|, respectively. Table 1 gathers the charges used in the simulations. The zeolite and the sorbates do interact through a pairwise additive potential. The 12–6 Lennard-Jones and Coulomb potentials are used to model these non-bonding intermolecular interactions. The whole Coulomb energy of the system that originates from sorbate–sorbate and sorbate–zeolite interactions is calculated using the Ewald summation method that separates the long-range term, evaluated in the reciprocal space, from the short one, evaluated in the real space. The bonded energy terms in the *p*-cresol molecule are modelled with the simple harmonic motion of the bond stretching and bond bending terms, and truncated Fourier series are used to account for the torsional energy.

Table 1
Atomic charges used in the simulations to calculate the electrostatic interaction energy.

Molecules	Atom type	Charges in unit of electrons
Pure silica faujasite	Silicon	2.4
	Oxygen	−1.2
NaY faujaite	Silicon & aluminum	1.40
	Oxygen	−0.82
	Sodium	1.0
P-cresol	Ring carbon	−0.25
	Methyl carbon	−0.30
	Carbon holding methyl group	0.20
	Carbon holding hydroxyl group	0.35
	Ring hydrogen	0.20
	Methyl hydrogen	0.10
Water	Hydrogen	0.40
	Oxygen	−0.80