Polychlorinated Aromatics Adsorption in EMT-Type Zeolite: A Combined Experimental-Simulation Approach


J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.8b02115 • Publication Date (Web): 25 May 2018

Downloaded from http://pubs.acs.org on May 25, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.
Polychlorinated Aromatics Adsorption in EMT-type Zeolite: a Combined Experimental-Simulation Approach

Joharimanitra Randrianandraina¹,²,a, Irena Deroche¹,²*, Laetitia Bullot¹, Régis Stephan¹,², Marie-Christine Hanf¹,², Gérald Chaplais¹,², T. Jean Daou¹,², Angélique Simon-Masseron¹,², Joël Patarin¹,², Philippe Sonnet¹,²

¹ Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France
² Université de Strasbourg, France

* to whom correspondence should be addressed: irena.deroche@uha.fr

ᵃ Present adress : Université de Bourgogne Franche Comté, France
ABSTRACT

Combination of molecular simulation tools with the gravimetric experiments have been employed in order to explore at the microscopic scale the adsorption of dichlorinated aromatics in EMT-type zeolite. A suited combination of classical and quantum simulation tools provided a clear overall picture of the adsorption process, from both local and global points of view, well matching with the gravimetric measurement data. The adsorbate preferential locations, adsorbate / zeolite interaction nature and geometry, as well as the adsorption energy were extracted from Density Functional Theory calculations. Furthermore, on the basis of classical force fields, the Gibbs ensemble Monte Carlo simulations made possible to predict room temperature dichlorobenzenes adsorption isotherms in EMT-type zeolite in both, purely siliceous and aluminosilicate forms. Finally, we accomplished a detailed analysis of the microscopic mechanism of the adsorption process, with a special highlight to understanding of the interaction geometry of the molecule with the sodium cation, according to its crystallographic site. Thus, we could depict that adsorbates under study preferentially adsorb within the smaller cage, called hypocage. Then, the larger cages, designed as hypercages, start filling only once all hypocages are at least partially occupied.
INTRODUCTION

Polychlorinated aromatics (PClAs) (such as polychlorinated benzenes, phenols or biphenyls) are highly toxic water and atmospheric contaminants\(^1\), essentially originating from the waste incineration with as principal contributors the medical, hazardous and municipal waste\(^2\). The ambient presence of PClAs also arises from their long term extended industrial processing in a large number of manufacturing sectors such as medical and agricultural chemicals or paints\(^2, 3\). This class of compounds has been shown harmful towards environment (in particular seawater and aquatic organism)\(^1\) and human health, due to its ability to easily achieve systemic circulation, and further internal organs, including brain\(^4\). Moreover, those species gather physico-chemical properties such as semi-volatility, high thermal stability and important liposolubility rendering them undegradable and bioaccumulative\(^5\). Finally, the PClAs’ high thermal stability also induces their incomplete combustion, at standard combustion temperatures, producing even more hazardous species such as polychlorodibenzo-dioxins (PCDDs)\(^2\).

Faced with an evidence of such important toxicity of PClAs, the US Environmental Protection Agency decided to rank those compounds among the priority pollutants\(^2, 6\). Consequently, there is an urgent need to define an efficient and environment friendly PClAs removal strategy.

A recovery of PClAs through a selective adsorption technology based on porous materials seems to constitute an attractive solution\(^7\). In particular, zeolites appear as ideal candidates for such application\(^8\), through their particularly adapted structural (well controlled pore size distribution, excellent thermal, chemical and mechanical stability) and textural (large surface area and high microporous volume) properties\(^9\), combined with environmental safety. Besides, through varying their chemical composition, from a purely siliceous to an aluminosilicate one with charge compensating cations, one can achieve a fine tuning of the zeolite / adsorbate
interactions. Finally, zeolites were found 8-12 times more efficient compared to activated carbons in retention of various chlorinated organic compounds.

Although an important research effort has been devoted during last decades to the adsorption of halogenated hydrocarbons by diverse porous adsorbents, the PClAs were scarcely addressed. Besides, the PClAs adsorption properties in various microporous materials such as Metal-Organic Frameworks (MOFs), zeolites, activated carbons or carbon nanotubes have been predominantly explored in the liquid phase. The evaluation of the gas or vapor phase PClAs adsorption performances, more appropriate when forecasting an air clean-up strategy, remains uncommon. Concerning porous carbons, Li et al. applied the thermo-gravimetric analysis to investigate the gas phase chlorobenzene adsorption in activated carbons while Bell et al. determined the influence of surface functional groups on adsorption properties of several PClAs within the microporous carbons. Concentrating on zeolite adsorbents, Hernandez et al. used the inverse gas chromatography technique in order to describe the adsorption of chlorobenzene in dealuminated clinoptilolite. Further, applying the pulse chromatography technique, Canet et al. examined the adsorption of volatile organic compounds including chlorobenzene in faujasites, by revealing that the zeolite chemical composition can influence the adsorption isotherms, especially in the Henry domain. Finally, some of us recently described the adsorption of dichlorobenzene in the *BEA and/or FAU-type zeolites, respectively from the experimental and simulation point of view.

The present study aims to elucidate the adsorption properties of ortho- and meta- dichlorinated benzenes (called o-DCIB and m-DCIB, respectively) within EMC-2 zeolite (EMT-type structure), joining a kinetic and gravimetric experiment to ab-initio and force-field based molecular simulations. In particular, we intend to bring a microscopic insight into the adsorption
phenomena, with two special highlights: (1) the role of the extra framework charge compensating Na+ cations and (2) the specificity of the EMT topology contrasted to the much more frequently addressed FAU one. For that purpose a suited combination of Gibbs Ensemble Monte Carlo and DFT simulations has been applied. Whereas other electronic structure methods, such as coupled-cluster theory\textsuperscript{32}, are known to give more accurate results compared to DFT ones, they are usually limited to the study of relatively small systems. Thus, DFT approach presents an excellent compromise between accuracy, size of system and computational cost\textsuperscript{33}. Especially, the dispersion corrected version, commonly designed as DFT-D\textsuperscript{34} is well suited for the study of adsorption in nanoporous materials\textsuperscript{35}.

From a practical point of view, the EMC-2 zeolite has been selected for this study since gathering interesting structural, textural and chemical properties for PClAs adsorption. First, the EMT topology presents a three-dimensional structure and a large porosity, supposed to permit a fast mass transfer inside and outside the crystalline structure\textsuperscript{36}. Further, the presence of charge compensating cations within its porosity arises an electric field\textsuperscript{37}, enhancing the affinity for the PClAs. Finally, the EMT zeolite topology possesses attractive textural parameters, such as high specific surface area, microporous volume (respectively of \( \sim 800 \text{ m}^2 \text{ g}^{-1} \) and \( 0.33 \text{ cm}^3 \text{ g}^{-1} \)) and high pore opening (12-MR \( \sim 0.73 \text{ nm} \))\textsuperscript{38}.

**MATERIALS AND METHODS**

**EXPERIMENTAL SECTION: GRAVIMETRIC MEASUREMENT**

The \( o \)-DCIB and \( m \)-DCIB adsorption kinetics were evaluated using the SETSYS Vapor Sorption (Setaram) applying dynamic conditions setup. After an activation of the EMC-2 zeolite, (heating at the temperature of 473 K during 4 h), the \( o \)-DCIB and \( m \)-DCIB adsorption kinetics
were measured at 298 K, applying the relative pressure of $p/p^* = 0.5$ (with $p$ corresponding to the vapor pressure and $p^*$ the saturation vapor pressure at a given temperature). The experimental setup consisted of a carrier gas ($N_2$) and auxiliary gas ($N_2 + DClB$) whose pressures were adjusted to 1.0 bar at the inlet of the oven. At the outlet the gas flow rate was measured controlling the DClB relative pressure value set as $p/p^* = 0.5$. The stabilized value of the gas flow rate was 70 mL.min$^{-1}$. The EMC-2 sample mass variation induced by the adsorption phenomenon was recorder throughout the zeolite was brought into contact with the DClB. This way, allowed obtaining the kinetic adsorption curve.

**COMPUTATIONAL METHODOLOGY**

**MICROSCOPIC MODEL FOR THE EMT-TYPE ZEOLITE**

The EMC-2 zeolite has a hexagonal unit cell with following lattice parameters: $a = b = 17.215$ Å, $c = 28.082$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. In order to bring to light the role of the charge compensating Na$^+$ cations in the DClBs adsorption phenomenon, the zeolite has been considered in, purely siliceous (hypothetical one) and aluminosilicate chemical compositions. For the purely siliceous EMT-type zeolite only Si and O atoms are placed on the respective crystallographic positions. For the dehydrated aluminosilicate EMC-2 zeolite, the unit cell chemical formula was $Na_{20}Si_{76}Al_{20}O_{192}$, reproducing the experimental EMC-2 framework Si/Al molar ratio of 3.8. The distribution of Al atoms strictly respects the Löwenstein’s Al–O–Al avoidance rule$^{39}$ and the Na$^+$ compensating cations were distributed in agreement with the model experimentally determined by Lievens et al.$^{40}$ According to this model, the distribution along the crystallographic sites is defined as follows: 1 cation in site Ia (situated inside the hexagonal prism), 9 cations located within the sodalite cages (4 in the I’a and 5 in the I’b site). Finally, 10 cations are within the
supercages whence 6 in the site IIa (within the hypercage) and 4 in site IIb (inside the hypocage). Note that for steric reasons, only cations in sites II are accessible to adsorbate molecules. For the Monte Carlo simulation part, the zeolite system is assumed to be semi-ionic with atoms carrying the following partial charges (in electron units): Si (+2.4), Al (+1.4), O (−1.2) and Na (+1)\(^1\).

**MICROSCOPIC MODEL FOR THE DICHLOROBENZENES**

DFT optimized molecular models of the investigated DCIB molecules obtained by Rai *et al.* were applied\(^2\). For the purpose of subsequent Gibbs ensemble Monte Carlo (GEMC) simulation the adsorbate molecules were described *via* the explicit hydrogen model, each atom constituting a single, partial charge bearing, interaction site. Both the aromatic cycle and attached exocyclic atoms were considered as rigid entities, consequently no intramolecular interactions were taken into account. The partial charges distribution along atoms forming DCIB molecules is presented in Table S1.

**INTERACTION POTENTIAL**

The intermolecular sorbate/sorbate and sorbate/zeolite interactions were modeled using a sum of repulsion-dispersion and electrostatic potential expressed via the Lennard-Jones and the Coulombic terms, respectively, according to the Equation 1:

\[
U_{ij}^{\text{Inter}} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \quad \text{(Equation 1)}
\]
where $q_i$ and $q_j$ are the atoms partial charges, $r_{ij}$ corresponds to the distance separating two atoms and $\varepsilon_{ij}$ and $\sigma_{ij}$ are the Lennar-Jones interatomic potential parameters. The parameters for adsorbates corresponding to those terms have been taken from the Transferable Potential for the Phase Equilibrium (TraPPE)\textsuperscript{42} force field, initially fitted to reproduce the liquid/vapor coexistence curves. Additionally, the parameters for zeolite were extracted from the Clay force field\textsuperscript{41}. The full set of all applied parameters is reported in Table S1. The Lennard-Jones cross-terms were calculated through the Lorentz-Berthelot combination rule.

**DFT SIMULATION PARAMETERS**

The starting configurations for the geometry optimizations on the DFT level have been obtained by the classical (force field based) Canonical Monte Carlo simulation based approach, implemented in the Sorption Module of the Accelrys Materials Studio package\textsuperscript{43}. An equilibration period (consisting of $1.0 \times 10^7$ Monte Carlo steps), was followed by a production period which allowed us to select the lowest energy configurations for every investigated system ($o$- and $m$-DClB adsorbed respectively in the purely siliceous and the aluminosilicate EMC-2 zeolite). The subsequent optimizations have been achieved using the periodic density functional theory calculations, performed on the solids in both the absence and the presence of $o$- or $m$-DClBs. The aim of this approach was to determine the preferential location of the adsorbate molecule, the major interactions with the framework atoms and the confined molecule / atom geometries. The full geometry optimizations (simultaneous relaxation of both atomic positions and unit cell volumes) of these structures were achieved using the PBE GGA functional\textsuperscript{44} with D2 dispersion correction\textsuperscript{45} and pseudopotentials described by the projector-augmented wave method (PAW)\textsuperscript{46} as implemented in the Vienna Ab-initio Simulation Package\textsuperscript{47}. The periodic
conditions were applied without any symmetry constraint, i.e. the geometry optimizations were carried out in P1 symmetry. The plane wave cutoff was set to 400 eV. The total number of atoms was 288 and 308 for the purely siliceous and aluminosilicate EMT-type zeolite, respectively. Due to the large cells size, only the \( \Gamma \) point (center of the reciprocal space cell) was used to sample the Brillouin zone for each system. The convergence criterion based on the residual forces calculation, exerted on atoms calculated through the Feynman method, was set up to 0.01 eV/Å. The charge difference isosurfaces are visualized using the visual molecular dynamics software developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign\textsuperscript{48,49}.

In order to set a reference state of the adsorbate molecules, both the \( o\)- and \( m\)-DCIB geometries have also been separately optimized, in a box with the dimensions of a unit cell of the EMT zeolite structure.

**GIBBS ENSEMBLE MONTE CARLO SIMULATION DETAILS**

The \( o\)- and \( m\)-DCIB absolute adsorption isotherms were simulated at 298 K in the purely siliceous (EMT-SiO\(_2\)) and aluminosilicate (Na-EMT) zeolites, applying the Configurational-bias Monte Carlo (CBMC) simulation method using the isobaric–isothermal version of the Gibbs ensemble\textsuperscript{50}, implemented within the code Towhee\textsuperscript{51}. The osmotic version of the Gibbs ensemble was employed, where only the adsorbate molecules can be transferred between explicit adsorbate reservoir and zeolite. Such simulation procedure closely imitates the experimental set up and moreover, does not need any chemical potential calculation. For all simulations, our system contained a total of 500 adsorbate molecules, distributed among gas phase reservoir and
adsorbed phase in the zeolite porosity. Through our GEMC simulation procedure, we evaluated the average number of adsorbed molecules in equilibrium with the explicit bulk phase reservoir at given pressure and temperature. In order to achieve a higher efficiency of the MC scheme, we have applied the configurational-biaised algorithm. Thus, when inserting molecules in an energetically favorable phase space, we reach a better acceptance probability. The simulation box consisted of 4 unit cells, namely unit cell replicated in x and y space directions. The framework atoms (Si, Al and O) were maintained fixed during the simulation, whereas all Na\(^+\) compensating cations were allowed to relax during the MC run. The periodic conditions were applied in all space directions. A typical Monte Carlo run consisted of 1.0x10\(^7\) steps for the equilibration phase and the same number of steps for the production phase. Each step corresponded to a single MC move, including a center of mass translation, molecule rotation, volume exchange (this move was applied exclusively between the reservoir phase and the ideal gas bath, not to the zeolite framework), particle transfer move between the explicitly simulated reservoir and the zeolite containing box. Finally, the Ewald summation method was applied in order to calculate the electrostatic part of the interaction energy and the short-range interactions were truncated at a cut-off distance of 14.0 Å.

RESULTS AND DISCUSSION

DFT RESULTS

INFLUENCE OF ADSORPTION PHENOMENON ON ADSORBATE AND ADSORBENT GEOMETRIES AT LOW COVERAGE
First, based on the DFT-D2 level geometry optimization, we could observe the influence of the adsorption phenomenon on the geometry of both the adsorbate molecule and the EMT topology zeolite framework. For that purpose, we compared the basic geometry parameters (such as bond lengths and bond angles) of the DCIB species respectively in gas phase and adsorbed within the zeolite, as well as the empty microporous framework with the adsorbate molecule containing one. Thus, we have evidenced a very limited influence of the adsorption on the molecules geometry: bond lengths and bond angles variations are inferior to 1% and 0.4%, respectively.

The adsorption phenomenon also induces quite a limited distortion of the zeolite framework, which can be evidenced by contrasting the unit cell parameters of empty and DCIB molecules containing zeolite, reported in Table S2. We can observe a slight unit cell contraction consecutive to the adsorption of both DCIB molecules (cell volume decrease of ~2% for the purely siliceous material and of ~0.5% for the aluminosilicate one) (Table S2). Such an observation agrees well with our previous study of adsorption of o-DCIB and m-DCIB in FAU-type zeolite\textsuperscript{31}, as well as with theoretical and experimental outcomes brought out for zero coverage caffeine adsorption within the UiO-66(Zr)-type MOFs\textsuperscript{53}, or for low loading of i-butane in ZSM-5 zeolite\textsuperscript{54}. Moreover, upon adsorption in the aluminosilicate EMC-2 zeolite we have looked into the adsorption induced by the redistribution of the compensating cations. Cations interacting with o- or m-DCIB were found to be shifted from their initial crystallographic site. Comparing the distance separating the cations from the center of the 6-MRs before and after adsorption we obtained differences comprised between 0.1 Å and 0.3 Å (further detailed) demonstrating partial detrapping of Na\textsuperscript{+} cations under influence of the interaction with DCIB molecules. Moreover, for the nearest cations interacting with the o-DCIB molecules, both localized in the SIIb crystallographic position, the shortest Na\textsuperscript{+} - O(z) distances pass from 2.25 Å
to 2.32 Å, and from 2.21 Å to 2.25 Å. The cations are displaced in such a way to simultaneously coordinate the oxygen atoms from the zeolite 6-membered ring (6-MR) and the most negatively charged atoms of the DCIB adsorbate, i.e. the aromatic carbon atoms opposite to chlorine atoms, as it will be detailed in the next section.

LOCATION OF ADSORBATE MOLECULES WITHIN THE ZEOLITE FRAMEWORK AND ADSORPTION GEOMETRY: QUALITATIVE AND QUANTITATIVE INTERACTION DESCRIPTION

Further, DFT level geometry optimizations starting from the Monte Carlo simulation revealed most stable configurations and enabled us to find the zero coverage preferential adsorption site of the adsorbate molecules as well as a qualitative and quantitative description of the interactions taking place between the DCIB molecules and zeolite surface. Based on such DFT level optimized structures, it appears that in the purely siliceous EMT-type zeolite both DCIB molecules adsorb preferentially within the hypocages, as illustrated in Figure 1 (a) and (c), respectively. In o-DCIB adsorption, the molecule located above the junction between a 6-MR and adjacent 4-MR, adopts a strictly parallel geometry to the 6-MR (the angle formed by the planes respectively of o-DCIB and 6-MR is 4°), with shortest distances of 2.6 Å measured between hydrogen atoms opposite to chlorine atoms and zeolite oxygen atoms (located on the 4-MR neighboring the 6-MR one). Then, the Cl atoms lie close to two 4-MR (adjacent the 6-MR), each one separated from three nearest-neighbors oxygen atoms by a distance of about 3.5 Å. In m-DCIB adsorption, the molecule lies inside the hypocage close to the 12-MR. Analogously to the o-DCIB, the shortest distances of 2.6 Å are measured between m-DCIB hydrogen atoms (neighboring chlorine atoms) and oxygen atoms located in the 12-MR. Moreover, the m-DCIB
molecule is orientated in order to enable both chlorine atoms to anchor through interaction with oxygen atoms belonging simultaneously to the hypocage defining 12-MR and to two adjacent 4-MR, with characteristic distances $d(Oz - Cl_{m-DCIB}) = \sim 3.5 \text{ Å}$, identical to the $o$-DCIB case. Furthermore, in our recent study of the DCIB adsorbates within FAU-type zeolite, similar shortest distances were observed between oxygen atoms and DCIB hydrogen atoms (2.6 Å)$^{31}$. Such distances suggest interactions of hydrogen-type bond. Alike interactions have been previously shown in benzene and phenol adsorption in MFI topology zeolites$^{55,56}$.

The DCIB adsorbates preferential locations and interaction geometries in the aluminosilicate EMC-2 zeolite significantly alter from its zeosil (pure siliceous) counterpart. According to the DFT optimized geometry depicted in Figure 1b, one can notice that, although the $o$-DCIB molecule is still located preferentially in the hypocage, but the plane of the molecule is not parallel to the 6-MR anymore, forming an approximate angle of 48°. The geometry adopted by the $o$-DCIB molecule makes possible a simultaneous interaction with both hypocage contained Na$^+$ cations, located in (opposite) crystallographic sites IIb. Identical shortest distances between Na$^+$ cations and DCIB adsorbates are observed for the chlorine atoms $d(Na^+ - Cl_{DCIB}) = 2.8 \text{ Å}$ and for the carbon atoms opposite to the chlorines $d(Na^+ - C_{DCIB}) = 2.8 \text{ Å}$.

(a)  
(b)
**Fig. 1.** Structures with DFT optimized geometries of o-DClB adsorbed within the purely siliceous (a) and aluminosilicate (b) EMT-type zeolite (Si:Al = 3.8) and m-DClB adsorbed within the purely siliceous (c) and aluminosilicate (d) EMT-type zeolite (Si:Al = 3.8). Red, yellow, pink, purple, green, grey and white colors correspond to O, Si, Al, Na, Cl, C and H atoms, respectively. Only the hypocage containing the adsorbate molecule is shown for sake of clarity.

Furthermore, in aluminosilicate EMT-type zeolite, the shortest distance separating the DCIB hydrogen atoms opposite to the chlorine atoms from the nearest oxygen atoms is reduced (comparing to the purely siliceous composition) from 2.6 Å to ~2.4 Å suggesting a strengthening of the hydrogen bond in the aluminosilicate form compared to the purely siliceous one. This distance becomes even shorter when compared to o-DClB adsorbed within the NaX zeolite (2.6 Å)\(^{31}\).

The \(m\)-DClB (Figure 1d) in the aluminosilicate EMT-type zeolite also locates within the hypocage, as well coordinated to both present extra-framework cations in SIIb crystallographic sites. Analogously to the \(o\)-isomer, the Na\(^+\) cations coordinate both the chlorine atoms of the \(m\)-DClB molecule and the C atoms opposite to the Cl, with identical distances of 2.8 Å. Likewise
for o-isomer, we observed the shortest distance between H atoms of m-DCIB adsorbate and nearest oxygen decreases from 2.6 Å in the zeosil framework to 2.4 Å in the aluminosilicate framework. Moreover, in order to assess the interaction strength between the EMC-2 zeolite and both DCIBs isomers, we calculated the adsorption energies from the DFT level geometry optimized structures, according to the Equation 2:

\[
E_{\text{ads}} = E_{(\text{EMT + adsorbate})} - [E_{(\text{EMT})} + E_{(\text{adsorbate})}] \quad \text{(Equation 2)}
\]

where \(E_{(\text{EMT + adsorbate})}\) is the energy of the adsorbate molecule containing EMT-type zeolite, and \(E_{(\text{EMT})}\) and \(E_{(\text{adsorbate})}\) are the energies of the empty EMT-type zeolite and the isolated adsorbate molecule, respectively. The adsorption energies for both isomers adsorbed within purely siliceous and aluminosilicate EMT-type zeolite are displayed in Table S3. Similar values of adsorption energies can be observed for both adsorbate molecules within the purely siliceous zeolite whereas they are more or less doubled in the aluminosilicate form.
**Fig. 2.** Graphical representations of isosurfaces of charge differences induced by the adsorption phenomenon of \( o\)-DCIB adsorbed within the purely siliceous EMT-type zeolite at isosurface values of 0.004 e/Å\(^3\) (a) and 0.002 e/Å\(^3\) (b) and \( m\)-DCIB adsorbed within the purely siliceous EMT-type zeolite at isosurface values of 0.004 e/Å\(^3\) (c) and 0.002 e/Å\(^3\) (d). Red, yellow, green, olive and white colors correspond to O, Si, Cl, C and H atoms, respectively. Black and white isosurfaces correspond to electronic density decrease and increase, respectively.

Doubling adsorption energy when passing from the purely siliceous to the aluminosilicate zeolite composition could result from establishing additional electrostatic interactions between \( Na^+ \) cations and adsorbate molecules, interacting either via chlorine atoms or via aromatic carbon atoms opposite to the chlorine atoms. Further, roughly doubling of adsorption energy for various chlorinated hydrocarbons adsorption when passing from a purely siliceous to the aluminosilicate form of zeolite, has been already reported in the literature from both experimental and simulation points of view\(^{19,31}\). These DFT level calculated adsorption energy values are consistent with our previous results and other available data from literature.

Moreover, the DFT calculations enabled us to further analyze qualitatively the interactions between the adsorbate molecules and the adsorbent surface. We display the isosurfaces of charge difference between isolated species (adsorbate molecules in gas phase and empty zeolite in vacuum, both without further relaxation) and adsorbed phase (DCIB molecules adsorbed within the zeolites), which allows depicting the local charge reorganization induced by the adsorption phenomenon\(^{57}\). Figures 2 and 3 present the charge difference isosurfaces respectively for \( o\)- and \( m\)-DCIB isomers adsorbed within the purely siliceous EMT-type zeolite (Figure 2) and its aluminosilicate form (Figure 3). In order to evidence both the substantial and the fine charge perturbations for each system, we used two isosurface values; namely 0.004 and 0.002 e/Å\(^3\) for
purely siliceous EMT-type zeolite and 0.02 and 0.009 e/Å³ for the aluminosilicate form. One can notice in Figures 2a and 2c that the guest / zeolite interaction induced charge increase in the vicinity of the chlorine atoms in the direction of the closest oxygen atoms. In parallel is evidenced a charge decrease adjacent to the hydrogen atoms opposite to chlorine atoms and a simultaneous charge increase nearby the closest oxygen atoms, both along the axis H_{DCIB} - O_{zeolite}. The last observation evidences a hydrogen bond establishment, while the former ones attests an electrostatic interaction between chlorine atoms and oxygens. In Figures 2b and 2d, one can observe that at lower isosurface values (0.002 e/Å³), in addition to still more pronounced charge differences on the molecules, the oxygen atoms are subject to local charge redistributions: a general charge increase is observed in oxygen atoms in the neighborhood of the molecular hydrogen atoms whereas a charge decrease besides oxygen atoms situated close to DCIB chlorine atoms. Then, according to Figures 3a and 3c, we can point out that in the aluminosilicate EMT-type zeolite, a redistribution of the charge is observable even at higher isosurface values (0.02 e/Å³). Similarly to the purely siliceous framework, the initial intramolecular charge redistribution is evidenced essentially along the adsorbate molecule (Figures 3a and 3c). The representation of the higher charge difference isosurface for the o-DCIB molecule adsorbed in aluminosilicate EMT-type zeolite (Figure 3a) brings to light substantial charge increases (1) nearby chlorine atom in the direction of the Na⁺ cation and (2) close to the DCIB carbon atoms opposite to chlorine atoms, pointing also towards the Na⁺ cation. Thus, in both cases, those perturbations result in an electrostatic interaction between the Na⁺ cations and the above described charge gained species. In parallel, a charge loss is evidenced on hydrogen atoms situated closest to the oxygen atoms, along the H – O_{zeolite} axis, consistent with the
formation of a hydrogen bond. Quite a similar situation is observed for the \textit{m}-DCIB isomer adsorbed within the aluminosilicate EMT structure.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Graphical representations of isosurfaces of charge differences induced by the adsorption phenomenon of \textit{o}-DCIB adsorbed within the aluminosilicate EMT-type zeolite (Si:Al = 3.8) at isosurface values of 0.02 e/Å³ (a) and 0.009 e/Å³ (b) and \textit{m}-DCIB adsorbed within the aluminosilicate EMT-type zeolite (Si:Al = 3.8) at isosurface values of 0.02 e/Å³ (c) and 0.009 e/Å³ (d). Red, yellow, pink, purple, green, olive and white colors correspond to O, Si, Al, Na, Cl, C and H atoms, respectively. Black and white isosurfaces correspond to electronic density decrease and increase, respectively.}
\end{figure}

Figure 3c representing the higher charge difference isosurface (0.02 e/Å³) indicates exclusively intramolecular charge perturbations, consisting mainly of charge increase in the vicinity of a chlorine atom and the opposite carbon atom, both charge increases being oriented towards the adjacent Na⁺ cations, located in the hypocages (crystallographic sites IIb). Finally, at
the lower charge difference isosurface value for both DCIB isomers (0.009 e/Å³) (Figures 3b and 4d) there is major intramolecular charge redistribution at the DCIB molecules level, whereas the charge of the oxygen atoms remain quite unperturbed, excepted a limited charge gain for the oxygen atoms forming hydrogen bond. In conclusion, the major interactions revealed between investigated DCIB isomers and aluminosilicate EMT-type zeolite are (1) hydrogen bonds and (2) electrostatic interactions between Na⁺/chlorine atoms and/or Na⁺/aromatic carbon atoms opposite to chlorine ones.

**GRAVIMETRIC EXPERIMENT AND GEMC RESULTS**

**SIMULATED AND EXPERIMENTAL ADSORPTION ISOTHERMS**

Figures 4a and 4b present the absolute adsorption isotherms of both DCIB isomers in the purely siliceous and aluminosilicate EMT-type zeolite respectively, obtained by the Gibbs ensemble Monte Carlo simulation at 298K. As it is usually observed in rigid microporous adsorbents, such as zeolites, all the isotherms are of type I with a well defined plateau (Figure 4a). The saturation adsorbed amounts are of 12.8 (o-/Na-EMT-), 13.0 (m-/Na-EMT), 14.0 (o-/EMT-SiO₂) and 14.3 (m-/EMT-SiO₂) molecules per unit cell for o- and m-DCIB respectively in aluminosilicate and purely siliceous EMT-type zeolite.
Fig. 4. Absolute adsorption isotherms simulated at 298K of o-DCIB (circles) and m-DCIB (triangles) respectively in purely siliceous (empty symbols) and aluminosilicate (full symbols) EMT-type zeolite (Si:Al = 3.8). The numbers of adsorbed molecules per unit cell are presented as function of absolute pressure in linear scale (a) and as function of relative pressure (p/p₀) in the semi-log scale (b). Experimental kinetic adsorption isotherms of o-DCIB (black) and m-DCIB (red) in aluminosilicate EMT-type zeolite (c), presented as the number of adsorbed molecules per unit cell as function of time of contact between the zeolite sample and the adsorbate vapor at relative pressure of p/p₀ = 0.5.

The experimentally measured kinetic adsorption isotherms of both DCIB isomers are reported in Figure 4c, obtained for the partial vapor pressure of p/p₀ = 0.5. At such a relative pressure, the available porosity of an exclusively microporous sample is totally filled. Consequently, the total saturation adsorbed amount determined from the simulated isotherm plateau values can be directly contrasted with the experimentally achieved adsorbed amounts. A slightly higher adsorbed amount has been measured for the m-DCIB isomer (15.3 molecules / unit cell), in comparison with the o-DCIB that experimentally achieved a saturation amount of 12 molecules / unit cell. Thus, an excellent agreement of experimental and simulated adsorbed amounts at saturation is observed for o-DCIB molecule adsorption, whereas the simulation slightly underestimates experimental adsorbed amount for the m-DCIB. Nevertheless, the same tendency is brought out by both simulation and experiment: m-DCIB total adsorption capacity in EMT-
type zeolite is higher compared to the o-isomer. Moreover, Figure 4b shows the adsorption isotherms plotted in semi-log scale, that evidence a major difference in the zeolite porosity filling relative pressure between the aluminosilicate and siliceous composition of EMT-type zeolite. The aluminosilicate zeolite starts to adsorb at \( p/p^o = 10^{-5} \) whereas this phenomenon occurs for a value which is more or less two orders higher (\( p/p^o = 10^{-3} \)) for the purely siliceous EMT-type zeolite. Interestingly, these porosity filling relative pressures can be compared with those previously obtained for o- and m-DCIB molecules in purely siliceous and aluminosilicate FAU-type zeolite\(^{31}\). We can thus observe that for both DCIB isomers whereas the aluminosilicate zeolite (NaX) starts filling at lower pressures compared to the aluminosilicate EMC-2 zeolite (\( p/p^o = 10^{-6} \)), the purely siliceous FAU-type zeolite porosity fills at slightly higher relative pressures. The lower Si/Al molar ratio and consequently the higher Na\(^+\) cation concentration within the NaX zeolite (Si/Al = 1.1) compared to the aluminosilicate EMC-2 zeolite one (Si/Al = 3.8) may explain the lower filling relative pressures in the case of aluminosilicate zeolites. Additionally, although EMT and FAU topologies have similar structural and textural properties, the hypocages contained within EMT framework have smaller diameter compared to FAU supercages. The lower relative pressure of porosity filling could originate in this subtle difference between these structures. Further, we can observe that neither the porosity filling pressure nor the saturation adsorbed amount are significantly influenced by the relative positions of the chlorine substituent, since the simulated adsorption capacities for o- and m-DCIB isomers are relatively similar. Whilst we have shown above that the chemical composition of the adsorbent plays a key role in the porosity filling pressure, it does not seem to influence in a major fashion the adsorption capacities, since the difference in adsorbed quantities for both isomers; respectively in siliceous and aluminosilicate zeolites is quite low. A slightly higher
saturation adsorbed amount in purely siliceous FAU-type zeolite in comparison with its aluminosilicate analogue has been previously reported in the literature for the p-cresol adsorption by Narasimhan\textsuperscript{58} as well as by our anterior work\textsuperscript{31}. The steric hindrance exerted by the charge compensating cations present in the porosity might explain this adsorption capacity difference.

** ADSORBATE MOLECULES LOCATION AND ARRANGEMENT **

Figure 5 presents typical arrangements adopted by both investigated DCIB isomers within the EMC-2 zeolite porosity respectively at low and saturation coverage, extracted from the snapshots obtained during the Monte Carlo simulation runs. At low loading (2 molecules / unit cell), DCIB molecules locate preferentially within hypocages, as can be observed from Figure 5a and 5c. For the \textit{o}-DCIB, the depicted preferential location is a hypocage. The snapshot represented in Figure 5a is a typical low coverage location of \textit{o}-DCIB. Molecule is in the center of the hypocage allowing a simultaneous interaction with both Na\textsuperscript{+} cations in site IIa, i.e. on the one hand through the Cl atom (typical distance of 2.8 Å) and on the other hand through the aromatic C atoms opposite to chlorine atoms (typical distance of 2.9 Å). Then, for the \textit{m}-DCIB adsorbate at low loading, one molecule is situated inside the hypocage, whereas the other one is in the 12-MR window separating hypo- and hypercages (Figure 5c), both molecules interacting with a Na\textsuperscript{+} cation initially located in site IIa, with similar typical distances as in for the \textit{o}-DCIB. As it can be observed from Figures 5b and 5d at high loading (12 molecules / unit cell) similar configurations are adopted by both DCIB isomers within the zeolite porosity: four molecules are located in the hypercage; whereas two more molecules occupy the 12-MR window separating hypo- and hypercage (stick rendering on the Figures). Three of the DCIB cycles are mostly parallels to each other whereas the fourth one is rather perpendicular to the three others with the closest distance.
separating two DCIB molecules of ~3.4 Å. Identical DCIB molecules packing have already been pointed out for the FAU-type zeolite\textsuperscript{31}.

![Typical arrangements of o-DCIB (a, b) and m-DCIB (c, d) molecules within aluminosilicate EMT-type zeolite (Si:Al = 3.8) zeolite respectively at low (a and c) and high (b and d) coverage. Red, yellow, pink, purple, green, grey and white colors correspond to O, Si, Al, Na, Cl, C and H atoms, respectively.](image)

**Fig. 5.** Typical arrangements of o-DCIB (a, b) and m-DCIB (c, d) molecules within aluminosilicate EMT-type zeolite (Si:Al = 3.8) zeolite respectively at low (a and c) and high (b and d) coverage. Red, yellow, pink, purple, green, grey and white colors correspond to O, Si, Al, Na, Cl, C and H atoms, respectively.

### INFLUENCE OF THE CHARGE COMPENSATING CATION

#### CRISTALLOGRAPHIC SITE

Additionally, through plotting the radial distribution function (RDF), related to the probability of the presence of an atom situated at a particular distance from another atom, we investigated possible correlations between the cationic crystallographic site and the cation / molecule interactions. Only sodium cations accessible to adsorbate molecules, located within both hypocages (sites SIIb) and hypercages (SIIa) have been considered, since cations within sodalite
cages (SIa’ and SIb’) are inaccessible to almost all adsorbates. For the o-DClB adsorption, Figures 6a and 6b report RDFs for interaction between the hypercage located Na\(^+\) cations (SIIa) and (1) chlorine o-DClB atoms (6a) and (2) aromatic carbon atoms opposite to chlorine atoms (6b), respectively. Figures 6c and 6d report alike interactions for hypocage located Na\(^+\) cations. The evolution of the RDFs with the increasing loading indicates that at very low coverage the o-DClB molecules locate exclusively within hypocages, predominantly interacting with the Na\(^+\) cations in the SIIb crystallographic site, through a Cl atom of the o-DClB. The interaction between Na\(^+\) cations in SIIb site and aromatic carbon atoms opposite to Cl atoms is shown to be considerably less frequent (7d). When the coverage increases, the o-DClB start to locate within hypercages (Figure 6a), thereby interacting with the Na\(^+\) cations in crystallographic site SIIa. The Na\(^+\) within the hypercages also predominantly coordinate the Cl atoms of o-DClB molecules compared to aromatic carbon atoms, however the frequency of both interactions increase with coverage (Figures 6a and 6b). The quasi exclusive interaction of Na\(^+\) cations in particular for a cation located in site SII (which is coordinated to oxygen atoms of 6-MR) with Cl atoms of o-DClB adsorbate has already been evidenced in the NaX zeolite\(^{31}\).
Fig. 6. Radial distribution functions for interactions $\text{Na}^+_{\text{SIIa}}$ - Cl$_{\text{o-DCIB}}$ (a), $\text{Na}^+_{\text{SIIa}}$ - C$_{\text{o-DCIB}}$ (b) $\text{Na}^+_{\text{SIIb}}$ - Cl$_{\text{o-DCIB}}$ (c) $\text{Na}^+_{\text{SIIb}}$ - C$_{\text{o-DCIB}}$ (d) respectively for loadings of 1 (black); 3 (blue); 6 (cyan); 12 (pink); 24 (red); 46 (green) molecules per simulation box composed of 4 EMT unit cells (simulation box: EMT unit cell doubled in x and y direction).

This observation was then explained by the quite constrained geometry of this crystallographic site favoring an “axial interaction” such as the one with Cl atoms. On the contrary, the site SIII’ in NaX (situated in the plane of a 12-MR thus constituting much more open site) gives rise to the interaction with carbon aromatic atoms. In EMT topology zeolite with a Si/Al molar ratio of 3.8, only cationic sites II are occupied. In our opinion, the predominant interaction in EMT-type zeolite is $\text{Na}^+$ - Cl (Figure 6c) accordingly to our explanation for NaX zeolite because of the geometry of the SIIb crystallographic site. The reason why one may observe a non-negligible RDF intensity for $\text{Na}^+_{\text{SIIb}}$ - C$_{\text{aromatic}}$ (Figure 6d) is that the SIIb sites located within the same hypocage are relatively close (separated by ~7 Å), enabling adsorbate molecule at low coverage to coordinate simultaneously both Na$^+$ cations, through interaction with Cl for one and with aromatic C for the other. However, this particular interaction geometry is possible only for molecule located in the hypocage, crystallographic sites SIIa located in the hypercage are separated by a longer distance (~9.1 Å), not enabling a o-DCIB molecule to interact simultaneous with 2 charge compensating cations. This hypothesis is confirmed by an extremely low RDF intensity for $\text{Na}^+_{\text{SIIa}}$ - C$_{\text{aromatic}}$ (Figure 6b). Thus, the observation we did previously for
cations in sites SII in NaX zeolite is similar to the one detailed here for site SIIa in EMC-2 zeolite: the o-DCIB molecules coordinate Na\(^+\) cations located in sites SII, preferentially via the Cl atom.

Analogous RDFs are represented for the m-DCIB adsorption in Figure 7. We can also observe in Figures 7a and 7b the RDFs reported for interactions between charge compensating Na\(^+\) cations in site SIIa and hypercage situated m-DCIB molecules coordinate respectively through Cl atom (7a) and opposite aromatic carbon atoms (7b). It is evidenced that even if at very low coverage there are m-DCIB molecules located in the hypercage and interacting with the SIIa crystallographic site located Na\(^+\) cation through the Cl atoms (7a), the frequency of this interaction is significantly lower (approximately a third) compared to the analogical one within the hypocage (Figure 7c). Then, as it was observed for the o-isomer, the interaction of molecule with the cation is preferentially realized through Cl atom as can be concluded by comparing Figures 7a to 7b for hypercage and 7c to 7d for hypocage.

![Radial distribution functions](image)

**Fig. 7.** Radial distribution functions for interactions Na\(^+\)\(_{\text{SIIa}}\) - Cl\(_{\text{m-DCIB}}\) (a), Na\(^+\)\(_{\text{SIIa}}\) - C\(_{\text{m-DCIB}}\) (b) Na\(^+\)\(_{\text{SIIb}}\) - Cl\(_{\text{m-DCIB}}\) (c) Na\(^+\)\(_{\text{SIIb}}\) - C\(_{\text{m-DCIB}}\) (d) respectively for loadings of 3 (blue); 6 (cyan); 24 (red);
46 (green) molecules per simulation box composed of 4 EMT unit cells (simulation box: EMT unit cell doubled in x and y direction).

CONCLUSION

The adsorption of DCiB molecules within purely siliceous and aluminosilicate EMT-type zeolite was investigated through combining gravimetric experiments, DFT as well as classical molecular simulation tools. A good agreement has been observed between the experimental and simulated adsorbed amount values. Further, on the basis of the DFT level optimized geometries, we could evidence the preferential adsorption sites of adsorbate molecules in both siliceous and aluminosilicate EMT-type zeolite structure, and also the associated adsorption geometries and energies. Then, we accessed a detailed description of the DCiB / EMT-typezeolite interaction. Thus, we showed that in the purely siliceous zeolite (hypothetical), the basic interaction is the hydrogen bond, between oxygen atoms of the zeolite framework and hydrogen atoms (opposite to the chlorine atoms) of the adsorbate molecule. For the aluminosilicate form, besides the hydrogen bond, extra interactions between Na\textsuperscript{+} cations and adsorbate molecules have been to take into account. Applying the Gibbs ensemble Monte Carlo simulation, in combination with suited interaction potentials, we could simulate the whole adsorption isotherms of the ortho- and meta- substituted dichlorobenzenes. A validation of those results through a successful comparison to experimental outcomes, enabled us subsequently to describe microscopic adsorption mechanisms at different coverages of both adsorbates within EMT-type zeolite. Further, we could extract, directly from the Monte Carlo simulation, the RDF related to the adsorbate molecules adsorption geometry within the zeolite. The interaction with Na\textsuperscript{+} cations with adsorbate molecules, via particularly the Cl atoms and the carbon aromatic atoms was observed. We concluded that the Na\textsuperscript{+} cations located in both SII crystallographic sites (site SIIa
in hypercage and site SIIb in hypocage) are predominantly coordinated to Cl atoms. Furthermore, we showed that a relative proximity of sites SIIb in hypocage make possible a simultaneous coordination of both Cl and aromatic carbon atoms.

This original work combining DFT and MC simulations provides new insights at the atomic scale of molecular adsorption in zeolites, complementary to experimental results and helpful to their analysis.

ASSOCIATED CONTENT

Supporting Information. Comparison between the DFT fully relaxed simulated cell parameters of the EMT-type zeolite (P1 symmetry) in the purely siliceous (EMT (SiO$_2$)) and aluminosilicate (Na-EMT) forms in the absence (empty) and in the presence of the o- and m-DClBs adsorbates.

AUTHOR INFORMATION

*E-mail: irena.deroche@uha.fr

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

The authors would like to acknowledge Habiba Nouali for her help with adsorption measurements. All the simulation work has been accomplished at the HPC Equipex Meso in Strasbourg; the authors would like to acknowledge the Mesocentre for the technical support.

REFERENCES


TOC Graphic
学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，
提供一站式文献检索和下载服务”的24小时在线不限IP的图书馆。
图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：
图书馆首页 文献云下载 图书馆入口 外文数据库大全 疑难文献辅助工具