We used molecular simulations to test the adsorption selectivity for enantiomers in the chiral zeolites SOF, STW, and ITQ-37. This work is the first simulation study which demonstrates the chirality of SOF, STW, and ITQ-37. We obtain information at the molecular level that explains the nature of the chiral selectivity. We selected CHBrClF and 4-ethyl-4-methyloctane as the probe molecules for the study. We calculated pure component and racemic mixture adsorption isotherms, Henry coefficients, adsorption enthalpies, and radial distribution functions. While STW is enantioselective for the probe molecules studied, ITQ-37 is likely to be enantioselective for other chiral molecules, and SOF is not a candidate for chiral separation. Appropriate pore geometry, resulting in differences in the adsorption behavior between the two isomers, is required for observing chiral selectivity. We provide insight that could be used for the synthesis and characterization of new chiral structures aimed to separate specific isomers. Using the methodology described here, it could be possible to easily determine if a new zeolite structure would show adsorption selectivity for a given chiral molecule.

Introduction

The separation of a racemic mixture is of crucial importance for the pharmaceutical and agrochemical industries. For example, one of the isomers of a chiral molecule may have a therapeutic effect and the other one may have toxicological impact. During the past few years a wide variety of methods have been developed to achieve chiral separation, such as crystallization, asymmetric catalysis, or liquid chromatography.

Chiral porous materials usually have potential to selectively adsorb chiral molecules or to serve as a chiral reaction environment. The number of chiral porous materials showing enantioselectivity is relatively limited, although there has been a great advance in the synthesis of new chiral materials during the last years. Chirality has been induced in silicas and sol–gel materials. New materials have been synthesized using chiral templates, such as polymerized organogels by the use of chiral organic gelators. Chirality can also be induced in crystals with large surface area, such as zeotypes, zeolites, aluminophosphates, and metal–organic frameworks (MOFs). Frequently, the product obtained after the synthesis of these materials is an intergrowth of different polymorphs. Therefore, new approaches have been developed to create homochiral porous structures.

Zeolites are preferred to other porous materials in catalysis and separation applications due to their relatively low cost, permanent porosity, and high thermal and chemical stability. Zeolites can be modified to act as asymmetric catalysts. The most common methods to induce a chiral reaction environment in the zeolite are: (1) adsorption of chiral molecules in an achiral zeolite (chiral inductor method); (2) covalent bonding of chiral molecules to the achiral zeolite structure (chiral auxiliary method); and (3) a combination of the chiral inductor and the chiral auxiliary methods. The confined space and the nonframework cations present in the zeolite are believed to be responsible for the chiral induction. It has also been demonstrated that zeolite defects in the form of silanol groups can improve enantioselectivity in chirally modified zeolites. Chiral catalysis is also possible in mesoporous materials such as MCM-41 and SBA-15.

Only a few as-synthesized zeolite-like materials were identified as chiral, namely, BEA, CZP, GOO, OSO, and BSV. Recently, 20 other well-known zeolites have been identified as chiral, due to the fact that they have chiral asymmetric unit cells. Computational methods have been developed to help in the design of new chiral materials. The main conclusion of these computational studies is that in order to obtain an energetically stable chiral zeolite, some of the T atoms of the structure should be different from silicon and substituted by another type of atoms such as B, Be, Zn, Ge, or S. Following this approach, three new chiral germanosilicate materials were synthesized recently: SOF, STW, and ITQ-37. These zeolites crystallize in a chiral space group, so they have a gyroidal structure. It has been reported that SOF and STW are not stable in their pure silica form, so the inclusion of Ge in these frameworks is vital for their stability. SOF consists of straight, elliptical channels, which are crossed by zigzag channels. The twist of the zigzag channels defines the handedness of the structure (see Figure 1a). STW is formed by rectangular cages connected by two narrow and two wide windows. The cages have three different orientations, and the chirality is determined by the relative orientation of the cages and the windows between cages (see Figure 1b). ITQ-37 is a low density zeolite with extra large 30-ring windows. It consists
of two different types of cavities, each of them connected to other three cavities to form a complex, gyroidal channel system (see Figure 1c). One major advantage of these materials with respect to other chiral zeolites is that they are homochiral after synthesis without further modifications. This means that single crystals of each of these zeolites exhibit only one hand, and therefore they have an intrinsic chiral structure. After synthesis we would obtain a racemic mixture of these crystals. Experimental studies have been performed to favor one crystal polymorph in intergrown chiral zeolites. Recently, a simple abrasive grinding method has been successfully used to obtain single chiral crystals from an initially racemic mixture of conglomerate crystals. Similar procedures may be used to obtain only one type of zeolite crystal instead of a racemic mixture. To the best of our knowledge, experimental adsorption isotherms of chiral molecules in any of these three chiral zeolites have not been reported yet, and it is not clear if they show adsorption enantioselectivity for typical chiral guest molecules. It has been demonstrated experimentally that other chiral zeolites may provide enantioselectivity large enough to achieve chiral separation, such as GOO and BEA.

Computer simulations in chiral porous materials have studied different aspects of asymmetric catalysis and chiral selectivity. Due to the complexity of these systems, computer simulations on chiral adsorption selectivity are scarce. Molecular simulations in intrinsically homochiral zeolites are not available in the literature. Most simulations studies are centered around chirally modified zeolite Y and the different isomers of BEA. Avery et al. reviewed computer simulation studies on the structural aspects of enantioselective asymmetric catalysis, concluding that small energy differences along the reaction pathways to chiral products are decisive. Sivasubramanian et al. optimized the geometries of cation complexes in a chiral inductor and a chiral auxiliary modified zeolite Y using quantum chemistry calculations to explain the enantioselectivity of different chiral molecules and demonstrated the importance of the zeolite cations in asymmetric reactions. Willock et al. used hybrid Monte Carlo (MC) and Molecular Dynamics (MD) simulations to
explain the chiral modifier stability in protonated zeolite Y. Jirapongphan et al. 36 studied the interactions of chiral modifiers with chiral adsorbed molecules in zeolite Y by molecular simulations, relating the different binding motifs to the observed enantioselectivity. Bao et al. 37 obtained large separation factors for chiral hydrocarbons in the chiral MOF Cd-BINOL by MC simulations. In their study these authors also highlighted the importance of the different adsorption sites and their accessibility during chiral separations, concluding that the adsorbate–host interaction is the most important factor for enantioselectivity in this system. Van Erp et al. 38–40 used molecular simulations to show that adsorbed scalemic mixtures of chiral hydrocarbons induce an enantioselective environment in alumina-substituted zeolites. Clark et al. 41 studied the adsorption of chiral molecules in zeolite BEA and zeotype UCSB-7. They showed that there is a large enantioselectivity in the different channels of BEA due to small differences in adsorption energies and adsorption orientations of the different isomers.

In this work we explore the enantioselective capacity of the three newly synthesized chiral germanosilicates, SOF, STW, and ITQ-37, using molecular simulations. We will focus on the pore geometry of the zeolites and not on their chemical composition. We use bromochlorofluoromethane, CHBrClF, the simplest chiral organic molecule, as well as other halocarbons, and the hydrocarbon 4-ethyl-4-methyloctane as probes to test the adsorption selectivity of these materials. We explore the possibility of describing chiral selectivity in zeolites by molecular simulations, and its dependence on the characteristics of the adsorbed molecules and the pore geometry. We describe the reasons for the different behavior of chiral molecules in these zeolites, and the pore parameters that determine enantioselectivity in these chiral structures. We show that a chiral zeolite can show chiral selectivity depending on the nature of the adsorbed molecules. The remainder of this paper is organized as follows: in the next section we present the simulation force fields and methods. The following section contains the results and discussion, and we present our conclusions in the final section.

Simulation Details

Details about the simulation parameters and models used can be found in the Supporting Information (Tables T1–T4). In this work, we will consider the pure silica version of the zeolites. This approximation is justified by the fact that the valences of Ge and Si are identical and their electronegativities are very similar. The spectroscopic electronegativities of Si and Ge are 11.33 and 11.80 eV, respectively. Therefore, we can safely assume that the partial charges of Si and Ge atoms in the zeolite are identical. In addition, the dispersive interaction of the T atoms in the zeolite is shielded by the oxygen atoms. As a result, the oxygen atoms of the zeolite are responsible of the most important contribution to the dispersive interaction between the zeolite and the adsorbed molecules, so that differences in the dispersive interaction of the T atoms can be neglected in a first approximation. Our SOF and STW force fields use this approximation, which is widely used for pure siliceous zeolites. For simplicity, we will name the molecules of 1-bromo-1-chloro-1-fluoroalkyl halide as C\textsubscript{n}BrClF, n being the number of carbon atoms in the molecule.

Results and Discussion

The pure component isotherms of the two CHBrClF isomers, as well as the isotherm of their racemic mixture in SOF, STW, and ITQ-37, were calculated as a function of the total fugacity at 298 K (see Figure 2). For SOF and ITQ-37 there are no large differences in adsorption between the two isomers, both for the pure components and in the racemic mixture. These differences are smaller than the error bars and are only appreciable near saturation. The differences in adsorption in SOF and ITQ-37 at saturation did not increase when the temperature was reduced, so we conclude that these structures do not provide enantioselectivity for the two isomers of CHBrClF. On the other hand, we found adsorption selectivity in STW for the racemic mixture. The R–CHBrClF isomer is preferentially adsorbed with an enantiomeric excess of 18%. We define the enantiomeric excess (ee) as
where $\theta_L$ and $\theta_R$ are the loadings of isomers L and R in the zeolite, respectively. The results provide evidence that the pore geometry of STW is an excellent environment for the adsorption separation of this molecule.

The separation of CHBrClF in STW takes place at high loadings, which suggests that the selectivity is caused by entropic effects. At low loadings the adsorption is equal, so that there is no selectivity in the Henry regime, and the pure component isomers of the two isomers are identical. We have computed the adsorption enthalpy at zero loading for the two isomers in STW at different temperatures (Figure 3). At temperatures below 150 K the R-isomer is preferentially adsorbed, while at temperatures above 150 K this is the L-isomer. This preference is reversed at the saturation loading at 298 K. This shows that the two isomers interact differently with the zeolite, in agreement with previous experimental and simulation studies. Dryzun et al. showed that the isomers of histidine have a different adsorption enthalpy in several chiral zeolites. Avery et al. showed that small differences in the conformation energy of different isomers in chirally active materials can lead to large effects in selectivity. In STW, the differences in the adsorption enthalpy at zero loading are not reflected in differences in the pure component adsorption isotherms, but the slightly different interaction with the zeolite can be a reason for the different adsorption in the mixture. We also computed the Henry coefficients and adsorption enthalpies at zero loading of CHBrClF in SOF, STW, and ITQ-37 at different temperatures (Supporting Information, Tables T5, T6, and T7 respectively). In SOF there is not a significant difference between the two isomers of CHBrClF, so we do not observe any selectivity. We find larger differences for ITQ-37 than for STW. We conclude that ITQ-37 does not show adsorption selectivity for CHBrClF because its pores are much larger than the pores of STW, so packing efficiency is less important for this structure.

To study the influence of molecular packing in the separation of CHBrClF isomers in STW, we calculated the radial distribution functions (RDF) of the molecules adsorbed at 298 K and a total fugacity of 100 kPa. At these conditions there is a clear separation in the equimolar mixture. The R-isomer preferentially adsorbed (see Figure 2). A given type of molecule packs more efficiently than others when more molecules of the first type can fit in the same volume inside the porous material. The RDF is related to the average distance between molecules of the same type. One molecule will pack more efficiently than another if the peaks of the RDF of the former molecule are higher and at lower distances than in the RDF of the latter. The C–C RDFs of the pure component and racemic mixture of CHBrClF isomers are shown in Figure 4. The Br–Br, Cl–Cl, F–F, and H–H RDFs can be found in the Supporting Information (Figures S2–S5). A mixture of different molecules of handedness provides the most efficient packing. On the other hand, the packing of the R-isomer is much more efficient when adsorbed as pure isomer than in the mixture, while there is only a small improvement in the packing efficiency for the L-isomer in the mixture compared to the pure isomer. As a consequence, the loss of packing efficiency of the R-isomer in the presence of L-isomer molecules causes a small excess of R molecules in the adsorbed phase of the racemic mixture. The RDFs also show that, when the packing efficiency is optimal, the distance between Cl atoms of different molecules is maximal (Supporting Information, Figure S3). This suggests that the adsorption separation at saturation conditions is due to steric effects.

To understand the adsorption mechanisms of CHBrClF isomers in STW, in Figure 5 we show snapshots obtained during the MC simulations at saturation conditions of the pure isomers L and R. Every cage of STW can contain up to two CHBrClF molecules. The large windows connecting the cages of STW are marked with dashed lines. The molecules are adsorbed close to both types of windows of STW. Molecules adsorbed close to the large windows have one of its atoms in the middle of the window, while the rest of the molecule is at the cage. In most cases, the atom at the large window is Cl in the case of the L-isomer and Br for the R-isomer. Molecules can also be adsorbed with one of its atoms at the middle of a small window, although the orientation of molecules at the small window does not follow a clear trend. Nevertheless, this configuration is not favored due to the reduced size of the small window. The main difference in the adsorption behavior between isomers takes place at the center of the large window. This is in agreement with previous experimental and simulation studies. Dryzun et al. showed that the isomers of histidine have a different adsorption enthalpy in several chiral zeolites. Avery et al. showed that small differences in the conformation energy of different isomers in chirally active materials can lead to large effects in selectivity. In STW, the differences in the adsorption enthalpy at zero loading are not reflected in differences in the pure component adsorption isotherms, but the slightly different interaction with the zeolite can be a reason for the different adsorption in the mixture. We also computed the Henry coefficients and adsorption enthalpies at zero loading of CHBrClF in SOF, STW, and ITQ-37 at different temperatures (Supporting Information, Tables T5, T6, and T7 respectively). In SOF there is not a significant difference between the two isomers of CHBrClF, so we do not observe any selectivity. We find larger differences for ITQ-37 than for STW. We conclude that ITQ-37 does not show adsorption selectivity for CHBrClF because its pores are much larger than the pores of STW, so packing efficiency is less important for this structure.

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The large windows parallel to the page are marked with a dashed line. The different atoms of the molecule are also colored: Br = gray; Cl = yellow; F = green; H = white. The large windows perpendicular to the page are marked with a dashed line. The large windows parallel to the page are marked with a dashed line.

with experimental results in chirally modified zeolites, which demonstrates that a tight fitting between the reactant and the chiral inductor is needed to achieve enantioselectivity. In the case of CHBrClF, Br and Cl atoms have the larger van der Waals radius, so these atoms interact more tightly with the zeolite and therefore play the most active role in the zeolite–molecule interactions.

We have analyzed the influence of pore size distribution in the host framework on enantioselectivity for the CHBrClF molecule. We have generated modified SOF, STW, and ITQ-37 structures by stretching and shrinking the distances between framework atoms in steps of 10% and calculated their pore size distributions (Supporting Information, Figure S6). We have computed the racemic mixture isotherms of CHBrClF in these modified SOF, STW, and ITQ-37 structures (Supporting Information, Figure S8). CHBrClF is not adsorbed in SOF shrunk by more than 10%, and STW by more than 20%, due to the reduced pore size of the host frameworks. For SOF we only obtain a low enantiomeric excess of 4% when the atomic distances are increased 10%. For STW, we find adsorption separation in all the structures tested, although for the stretched structure adsorption only occurs at very large fugacities. The stretched structure of STW provides a larger enantiomeric excess than the original and shrunk structures. Finally, the ITQ-37 structure provides a large enantiomeric excess of 40% only when its size is reduced 30% (Supporting Information, Figure S8). According to our results, a tight fitting of the molecules adsorbed is a necessary condition to achieve separation in one porous material. The material has to contain pores with a diameter of the same order as the van der Waals diameter of the larger branches of the chiral molecule. The van der Waals diameters of the Cl and Br atoms in our CHBrClF model are 6.94 and 7.3 Å, respectively. The investigated structures which provide enantioselectivity have pores with mean diameters between 6.3 and 8.7 Å. Furthermore, structures which provide large enantioselectivity have two different types of pores, both with a diameter similar to the diameter of the larger atoms in the molecule. The difference in diameter of these two types of pores is on the order of 0.2–0.4 Å, which is in the range of the difference between the van der Waals diameters of the Br and Cl atoms. It is noteworthy that, when the difference in the Henry coefficients and adsorption enthalpies at zero loading of the two isomers in one zeolite type is larger (see Tables S6, S7, and S8), the enantioselective excess obtained in its stretched or shrunk versions is also larger. These pore characteristics are necessary to provide enantioselectivity for the CHBrClF molecule, but they are not sufficient. MFI has two pores with diameters 8.1 and 8.4 Å (Supporting Information, Figure S7) and therefore satisfy the previous conditions for enantioselectivity. Nonetheless, this zeolite is not enantioselective for CHBrClF. We believe that, apart from having a tight fitting between the host and the guest molecule, to obtain enantioselectivity the chiral molecule needs to encounter a chiral environment. The conclusion is that only the zeolites that are chiral can show enantioselectivity provided that the former conditions are met.

To check the adsorption selectivity of large chiral molecules in SOF, STW, and ITQ-37, we computed pure component and 50/50 mixture isotherms of 4-ethyl-4-methyloctane in these structures at 200 and 298 K. 4-Ethyl-4-methyloctane is not adsorbed in SOF. This is due to the small pore diameter and low pore volume of SOF. The pore volumes of SOF, STW, and ITQ-37 calculated by MC simulations are 0.145, 0.204, and 0.719 cm³/g, respectively. The pore volume of SOF is 12% smaller than that for MFI (0.164 cm³/g), another zeolite with a similar channel system, where 4-ethyl-4-methyloctane molecules can be adsorbed using the same simulation techniques. Although the straight channels of SOF are formed by large 12-rings, the channel sections and the windows between straight and zigzag channels are elliptical, which may hinder the adsorption of large branched molecules.

The racemic mixture isotherms of 4-ethyl-4-methyloctane in STW at 200 K and ITQ-37 at 298 K are shown in Figure 6. We obtain large error bars for the adsorption of 4-ethyl-4-methyloctane. The acceptance probability for insertion moves, although significant, was low. STW shows a small adsorption selectivity for 4-ethyl-4-methyloctane, which is only evident at low temperatures. At 200 K, the adsorption isotherm yields an enantiomeric excess of 20%. In the case of ITQ-37, we do not find any evidence of differences in adsorption.

In Figure 7 we show a snapshot of a racemic mixture of 4-ethyl-4-methyloctane adsorbed at 200 K and at saturation conditions in STW. The C₅H₁₂ branches of the molecules are preferentially pointing in the direction of the small windows. The C₅H₁₂ branch of the L-isomer crosses one of the large windows, entering the neighboring box, while the tip of the C₅H₁₂ branch stays close to the center of the other large window of the same box. In the case of the R-isomer, the chiral center is much closer to one of the large windows, and the C₅H₁₂ branch of the molecule enters nearly completely into the neighboring box. The tip of the C₅H₁₂ branch of the R-isomer stays close to the center of the other large window of the same box. Therefore, the L-isomer can adsorb in STW occupying less space than the R-isomer, so it is the component preferentially adsorbed at high loadings.

Apart from size, the main difference between the CHBrClF and the 4-ethyl-4-methyloctane molecules is that the former...
contains pseudoatoms carrying a partial charge. We checked the influence of the charge in the separation efficiency of CHBrClF isomers in STW. For this purpose, we performed MC simulations in the canonical ensemble. We use as a starting configuration the final configuration of the grand-canonical MC simulation of CHBrClF in STW at 298 K and 100 kPa (5.75 molecules/uc of L-isomer, 6.25 molecules/uc of R-isomer). In these simulations, we scaled all the partial charges of the CHBrClF pseudoatoms by factors ranging from zero to 1.4. The molecule remained charge neutral in this process. The enantiomeric excess obtained as a function of the charge scaling factor is shown in Figure 8. The enantiomeric excess follows a nearly linear trend, with one sudden increase at a scaling factor of 0.6. When the partial charges are zero, we still obtain adsorption separation, although at a low enantiomeric excess of 1.2%. This confirms that the STW structure studied here is enantioselective for molecules that have a tight fitting in its pores and that the selectivity increases when the interaction of the isomers adsorbed is larger.

The adsorption isotherms of the racemic mixtures of C2BrClF and C3BrClF in STW and 298 K are shown in Figure 9. The adsorption isotherms of the racemic mixtures of CnBrClF molecules up to n = 6 in SOF, STW, and ITQ-37 at 298 K can be found in the Supporting Information (Figures S9–S12). We do not observe any adsorption selectivity for these molecules, while there is clear adsorption selectivity for the two different isomers of CHBrClF. We believe that one chiral molecule, apart from having a tight fitting with a chiral environment, needs to have certain asymmetry in order to present adsorption selectivity. The only difference between CHBrClF and C2BrClF is the...
substitution of the H of the first molecule by a CH$_3$ group. The sigma parameter for the H pseudoatom is 2.5 Å while the CH$_3$

Lennard-Jones size parameter is 3.76 Å. This last value is similar to the sigma parameters of Cl (3.47 Å) and Br (3.65 Å).

Therefore, in the C$_2$BrClF molecule there are three branches with a very similar van der Waals diameter, destroying the original asymmetry of the CHBrClF molecule.

Conclusions

Our calculations show that the STW structure is enantioselective for both CHBrClF and 4-ethyl-4-methyloctane isomers, while SOF and ITQ-37 are not. We obtain adsorption selectivity without making any distinction between the Ge and the Si atoms of the structure. Therefore, the adsorption selectivity is caused only by the pore geometry of the zeolite and not by the Ge substitution in the zeolite. Radial distribution functions show that the reason for the adsorption selectivity is the different packing efficiency of the different isomers when adsorbed as pure components or in the mixture. Furthermore, the different isomers adsorb differently at the points where the interaction with the zeolite is tighter. As a result, the separation factor is proportional to the point charges of the molecules, so that the electrostatic interaction of the molecule with the zeolite is stronger.

The SOF and ITQ-37 structures were scaled in size in order to obtain a tight fitting environment for the probe molecules. While ITQ-37 showed adsorption selectivity when it was shrunk by a factor of 30%, we did not observe selectivity in SOF for any of the scaled structures tested. There are two possible explanations for this difference: the zeolite has to contain adequate pore geometries to provide enantioselectivity, or the two isomers have to interact differently with the zeolite. This last point can be revealed by comparing the Henry coefficients and adsorption enthalpies at zero loading of the two isomers. Finally, we found that if the branches of the chiral molecule are made symmetrical in terms of interactions with the zeolite, the enantioselectivity disappears. Therefore, a chiral zeolite may show chiral selectivity depending on the nature of the molecules adsorbed.

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References and Notes