

## Molecular Simulation Studies of Separation of Enantiomers in non-chiral zeolites

### 1.- Purpose of the visit

The purpose of my visit to the Katholieke Universiteit Leuven was to study the adsorption and separation properties of several enantiomers in zeolites containing different type of non-framework cations, using molecular simulations. The base of my work was to obtain the adsorption isotherms of both pure component and mixtures using Grand Canonical Monte Carlo simulations. To speed up the equilibration in my simulations I used the configurational-bias Monte Carlo technique in combination with two new movements developed by the host group. The good and accurate force fields that have been developed in my group for adsorption and diffusion of alkanes in zeolites with sodium and calcium as non-framework cations made of those cations a very good option for my study. As adsorbates I used (R, S) lactic acid enantiomers because they are computationally affordable, commercially interesting, and are known to diffuse easily through the MFI zeolite which make experimental verification possible. The host institution has a wide experience in experimental adsorption studies using zeolites which offers a unique possibility to test the theoretical findings directly in the laboratory. In a second step I plan to move to other chiral molecules such as terpenes and geraniols. As adsorbents I started with MFI and in a second stage I plan to study LTA4A (96 sodium cations) and LTA5A (32 calcium cations and 32 sodium cations).

The idea of this study stems from a previous collaboration between the two groups in which Tom Caremans, PhD student of the group in Leuven studied the enantioselective adsorption in achiral zeolites of 4-ethyl-4-methyloctane. In this project a fundamentally new mechanism was found to could ultimately lead to new pathways for enantioseparation. The principal novelty of this work was the discovery that enantioselective adsorption can occur in zeolites that are not chiral by themselves. For the adsorption of racemic mixtures the effect does not occur. However if one of the enantiomers (R or S) is in higher concentrations in the gas that adsorbs, this concentration can either increase further upon adsorption or decrease. These two types of enantioselectivity are called homoselective and heteroselective adsorption, respectively. The purpose of this new project is to continue whether this effect also exist for more commercially relevant molecules.

### 2.- Description of the work carried out during the visit

During my stay at the K.U. Leuven, at first I checked in the literature for previous models of lactic acid. As I could not find any, I tried to create a good definition of the enantiomers of lactic acid. I had to learn how to use some programs as "Materials Studio" or "Lammps" for this purpose. Then I had to adapt two new MC moves that have been developed by the host group to my own codes. Finally I applied this knowledge to study the chirality behaviour that MFI exhibits when silicon atoms are exchanged by aluminium.

As LAC is not in the gas phase at ambient conditions unlike the chiral alkanes studies previously, we used a pressure  $P=0.1$  kPa and  $T=300$  K. The average number of LAC molecules in the MFI zeolite is  $\pm 10$  molecules per unit cell which is much more than the saturation limit of 4 molecules per unit cell for the alkanes. In addition, we tried to simulate the conditions of an experimental study that examined the adsorption of LAC in MFI from an aqueous solution. For this case we simply fixed the total number of molecules (R+S-enantiomers) to the same 4 molecules per unit cell which was found to the average occupation in this experimental study.

At first we studied the adsorption on MFI zeolite of the two enantiomers (R, S) from lactic acid (LAC) separately. Then we combined these to enantiomers on different kinds of mixtures with different ratios of each component.

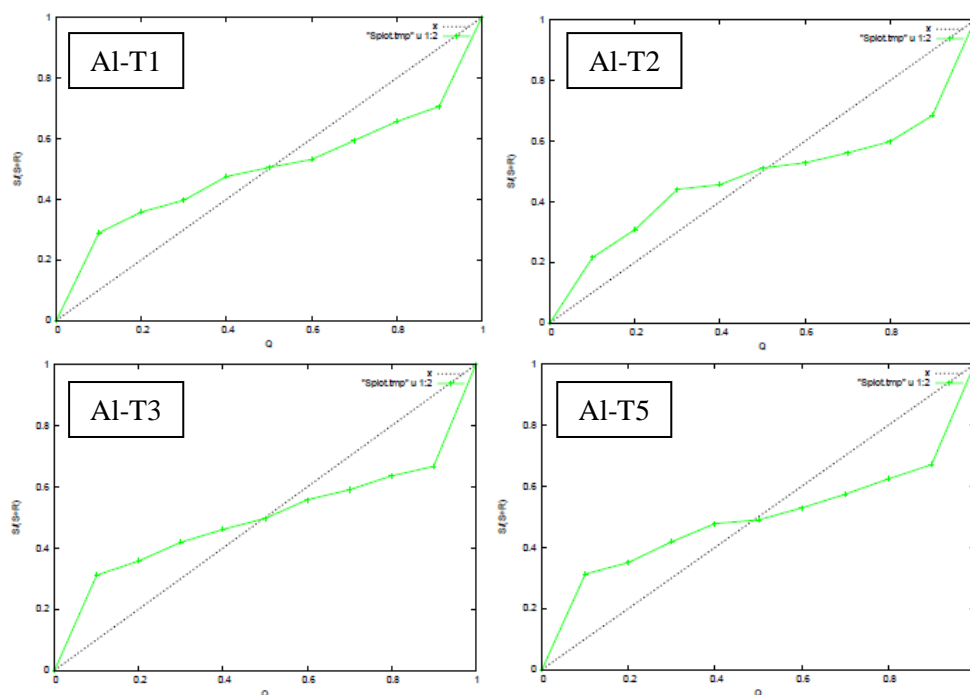
After that we analyzed the behaviour of the adsorbent, changing eight atoms of silicon from the structure by aluminium. To do that we had created 8 different frameworks by exchanging the aluminium atoms at different T-Site positions, this positions are T-Site 1, 2, 3, 4, 5, 6, 8 and 11. Positions 7, 9, 10 and 12 were not study, because they don't obey the Lowenstein's rule. To make zero the net charge of the framework after change the silicon by aluminium we added different type of cations. We first, tried with sodium cations, and secondly with calcium cations. Finally, we analyzed the enantioselectivity of all the frameworks and mixtures under study.

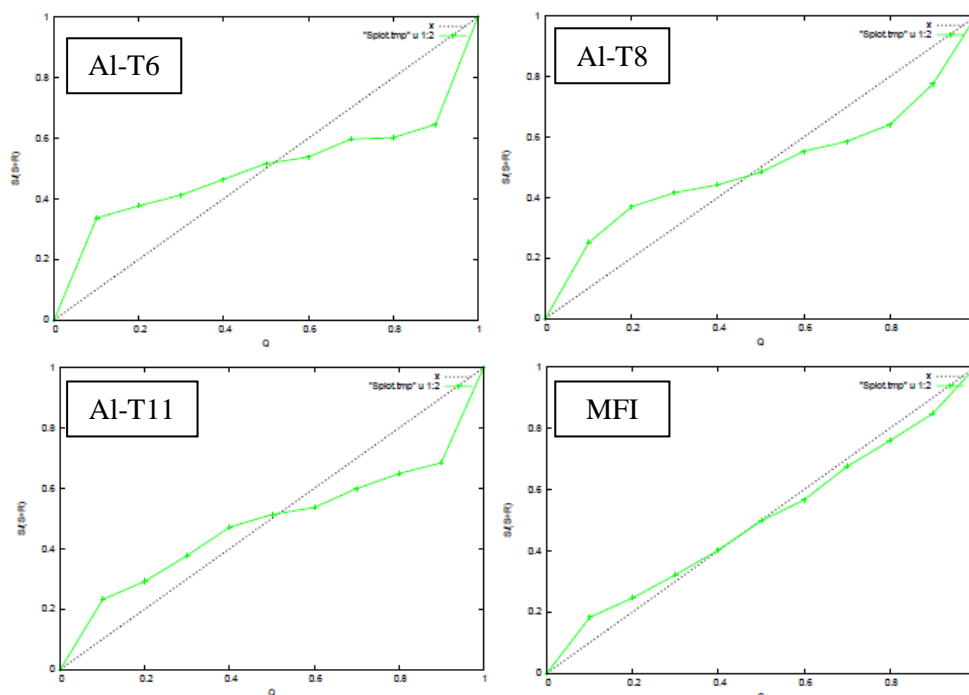
### 3.- Description of the main results obtained

To get a good statistic is necessary to run very long simulations for these systems and further analysis to make definite conclusions.

With the results from the outputs of the simulations, we use a program developed by the Dr. Titus van Erp, to determine the kind of adsorption of the molecules at the structure (homoselective or heteroselective). In all cases the adsorption of both enantiomers from lactic acid at MFI zeolite presents a hard heteroselectivity adsorption. Below we show some preliminary results obtained for the structures containing sodium cations. The simulations with calcium cations are still running.

The results are very different from the previously studied alkanes. In that case  $\text{Ca}^{2+}$  mostly showed homoselective and  $\text{Na}^{+}$  heteroselective adsorption. For LAC all systems seem to give heteroselective adsorption. Also, all Si-MFI seems to give some effect, contrary to previous study, although the presence of cations enhances the effect considerably. The explanation for this is that LAC is polar and is not only sitting in the intersections like 4-ethyl-4-methyloctane.





The results based on LAC seem to give a completely different picture than the previously studied 4-ethyl-4-methyloctane. The heteroselective effect seems rather strong. Still, we did not find a similar strict ordering between cations and adsorbate molecules as was found for the chiral alkane study. The polarity of the adsorbate and their extended mobility make the system much more complex. Also, we should realize that it might take a rather long time before the MC simulations find a new type of ordering. Previous results were based on much longer initialization runs before statistics was gathered. We should, therefore, realize that results can also change qualitatively wherever simulations are run much longer.

#### 4.- Future collaboration with host institution

After my grant at the K.U. Leuven I plan to keep active collaboration with this group. We will continue with the current project, which is far from been over. We are also thinking of extending our collaboration in new projects. Particularly we are pondering about the possibilities to do similar studies with other chiral molecules such as terpenes and geraniols which might be relevant in scientific research by their applications. Also we want to study the behavior of these molecules on other structures as MEL, MOR, LTA4A or LTA5A.

#### 5.- Projected publications/articles resulting or to result from your grant

We are still waiting for some simulations results. Therefore, a first step is to extend the present simulation to much longer simulation times. In a second step, we should try to understand why LAC behaves so differently than 4-ethyl-4-methyloctane. If we achieve this, this would certainly an important step forward that might lead to new applications. In our opinion such a result would certainly deserve to be published in a high-quality journal of broad interest.

The first manuscript resulting from this collaboration will be submitted for publication within the next months. In our opinion such a result would certainly deserve to be published in a high-quality journal of broad interest.