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Adsorption Kinetics of Mixtures of n-Hexane and 2-Methylpentane on Silicalite by Nonequilibrium Molecular Dynamics.

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1. Introduction

In the context of the separation processes of mixtures the use of nanoporous systems has been revealed as a good complement to classical distillation procedure when the molecules have very similar boiling points as it is the case for many isomers. This has been done successfully for instance with xylene isomers. In gasoline, branched alkanes have higher octane numbers compared to normal ones and they are for this reason more desirable. The aim of this work is to describe, at a molecular level, the mechanism implied in the kinetics of adsorption of mixtures of two valuable compounds, n-hexane (HEX) and 2-methylpentane (2MP), on an infinite membrane of silicalite.

2. Model and simulation details

Transient nonequilibrium molecular dynamics (NEMD) simulation was used here to mimic gravimetric uptake experiments [1] of equimolar mixtures of hexane on silicalite.

The initial system consisted of an infinite membrane of silicalite with an external surface perpendicular to the straight channel (*y* direction) in contact with a gas of HEX and 2MP mixture. With time, by integrating the equation of motion, the adsorbate entered the pore until equilibium is reached. The thickness of the zeolite was three unit cells in the *y* direction (about 60 Å), two and three unit cells in *x* and *z* directions, respectively (about 40 Å). Three equimolar mixtures were studied containing 20, 40 and 80 molecules of n-hexane, we will refer to as first, second and third mixture in the text.

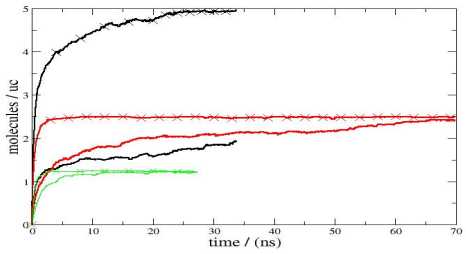

Fig 1. Uptake curves of the 3 mixtures. In green first case (20), in red second case (40), in black third case (80). The lines with X on them are the 2MP (lower curves) while the simple lines refer to HEX.

The silicalite and the alkanes were simulated using an all atom and an united atom model, respectively. Both the silicalite and the hexane were flexible and they interacted via Lennard-Jones potentials. Simulation details can be found elsewhere [1].

3. Results and discussion

Figure 1 show the comparison of the uptake of the three mixtures, due to computational limitations the third did not end but the trends are clear enough to be discussed. As expected from previous simulations on pure n-hexane and pure 2MP, the n-hexane was adsorbed faster than the 2MP, its self diffusion coefficient was 2 oders of magnitude higher. HEX had barely the same kinetics in the first and second mixtures but it was much lowered in the denser system. As the amount of 2MP increased its adsorption kinetics decreased, being 6 times slower from 20 to 40. Compared to the pure compound, the presence of HEX strongly reduced the diffusion of 2MP in the pore.

An analysis of the molecular position can give insight to explain these differences. HEX in the pores was located in the straight and zig-zag channels and in their intersections, while 2MP was only located in the intersections. 2MP is much more cumbersome than n-hexane. It has to cross a high-energy barrier to go from an intersection site to another one, which is not the case for HEX. In the first and second case the number of 2MP was not sufficient enough to occupy all the intersections, HEX molecules had then enough free intersections to diffuse nearly as if they were alone. This was not the case for 2MP. Here, as a prerequisite for a jump, it is required that the other intersection is free, that no HEX molecule is located in the channel and that its conformation is favorable. The probability to move is then highly dependent on the density of HEX.

At high loading, case 3, 2MP filled nearly all the intersections and both the kinetics of n-hexane and 2MP was reduced. However, the flexibility of HEX was large enough to overtake 2MP, the kinetics of HEX was then faster than 2MP.

3. Conclusion

Using NEMD, we have shown that two isomers with very different shapes (n-hexane and 2-methylpentane) exhibit a very different behaviour when they are adsorbed together on silicalite. The uptake curve for HEX is similar to the pure compounds except for high loading of 2MP. At the contrary the adsorption kinetics of 2MP decreases when the density of HEX increases. This difference is related to the diffusion “style” of the two molecules, 2MP diffuses in the pores by jumps while HEX exhibits a liquid-like diffusion.

Reference

[1] J.M Simon, A. Decrette, J.P. Bellat, J. M. Salazar, Mol. Sim. 30 (2004) 621.