Entropy driven separations in nanoporous materials
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Citation for published version (APA):
Torres Knoop, A. (2016). Entropy driven separations in nanoporous materials
6.1 Introduction

Nanoporous materials such as zeolites, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs) offer considerable potential as energy-efficient alternatives to conventional separation processes like distillation, absorption, and extraction. Separation in nanoporous materials relies on adsorption and/or diffusion properties and can be achieved by size/shape exclusion (steric separation), by differences in the adsorbate-adsorbent interactions and/or adsorbate packing interactions (thermodynamic equilibrium effect) or by differences in the diffusion rate of the adsorbates within the adsorbent channels.

At low loadings (i.e. the Henry regime) adsorbate-adsorbate interactions are of little importance. The selectivity is mainly driven by enthalpic effects, and is in favor of the molecule that has the strongest interaction with the framework. This is the principle behind most separations of mixtures of light gaseous compounds, where a common feature is that saturation conditions are often not reached. For example, the selective adsorption of CO$_2$ from mixtures containing N$_2$, H$_2$, CO, and CH$_4$ by selective binding of CO$_2$ with either the metal atoms (M) of CuBTC [1], Cu-TDPAT [2], M-MOF-74 [3], or the extra-framework cations

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of NaX zeolite [4] and the selective adsorption of N₂ from O₂ based on the larger quadrupole moment of N₂ in both LTA-4A and LTA-5A [5].

However, many industrially used setups operate close to saturation conditions, e.g. liquid-phase adsorption. At these conditions, adsorption is dominated by entropic effects and therefore highly influenced by adsorbate-adsorbate interactions and packing efficiency. Up to date several entropy effects have been discovered and exploited for mixture separations: (1) size-entropy, (2) configurational-entropy, (3) commensurate stacking, and (4) length-entropy [6]. “Size entropy” effects arise from the fact that smaller molecules can fit easier in the “gaps” between adsorption sites, leading to higher saturation capacities with decreasing molecules size. An example is the separation of alkanes in MFI [7]. “Configurational-entropy” effects favor molecules with better packing within the pores structure. The length and topology of one of the mixture components is comparable with the channels leading to “commensurate freezing” [8]. This is the case in the separation of linear from branched alkanes in silicalite-1, where the linear n-hexane (nC₆) is favor over the di-branched isomers 2,2-dimethylbutane (22DMB) and 2,3-dimethylbutane (23DMB) [9, 10]. “Commensurate-stacking” occurs when the packing arrangement of one of the components is commensurate with the channel size, which allows this component to stack like books on a bookshelf. This is observed in the adsorption of o-xylene in MIL-47 and p-xylene in MAF-X8 [11]. “Length-entropy” effects favor molecules with the shortest length (footprint) in one-dimensional channels, since they can be pack more efficiently within the channels. A good example is the separation of hexane isomers in AFI channels, where selectivity relies on the smaller footprints of the branched isomers 22DMB and 23DMB [12–15]. In this article, we describe a new entropy-based separation mechanism in one-dimensional channels at saturation capacity. In this mechanism, the selectivity relies on a loading driven reorientation of one of the mixture components into a “pile” configuration where all the molecules are in a “face-to-face” orientation. We demonstrate this effect in two systems: (i) o-xylene and benzene in AFI and MAZ zeolite channels (which can be efficiently separated from m-, p-xylene and ethylbenzene), (ii) and 1,3,5-trichlorobenzene in a triangular MOF (which can be efficiently separated from 1,2,4-/1,2,3-trichlorobenzene).

6.2 Methodology

The force fields and methodology used in this chapter are the same as the ones used in chapter 5.

6.3 Results and discussion

AFI zeolite possesses one-dimensional channels with corrugated pore topology; the channel diameter at the narrow constrictions is 7.3 Å and at the protracted segments is 8.4 Å. MAZ zeolite is slightly smaller than AFI; the channel diameter at the narrow and protracted segments are 6.7 Å and 7.4 Å, respectively. Figure
Figure 6.1: Snapshots of benzene, o-, p- and m-xylene and ethylbenzene in AFI (left) and MAZ (right) channels at saturation conditions. Benzene and o-xylene are able to change their orientation from parallel to perpendicular (relative to the channel axis). At high loadings this leads to a “face-to-face arrangement that reduces their “footprint” compared to p-, and m-xylene and ethylbenzene.

6.1 shows snapshots of benzene, o-, p-, m-xylene and ethylbenzene at saturation loading. The height and width of o-xylene and benzene are both smaller than 8.4 Å and 7.4 Å, allowing a perpendicular alignment (with respect to the channel axis) within the protracted channel segments in both AFI and MAZ. For m-, p-xylene and ethylbenzene, either the height or width is too large to allow vertical alignment; consequently their orientations within the channels are aligned obliquely.

Because of the perpendicular alignment, o-xylene and benzene reduce their effective footprint and achieve much higher saturation capacities as shown in Figure 6.2a where Configurational-Bias Continuous Fractional Component Monte Carlo (CB/CFCMC) simulations [16] of pure component isotherms for hydrocarbons in AFI at 433 K are presented. The simulations are in very good qualitative agreement with the experimental data (at 303 K) of Chiang et al. [17] and provide the means to understand why. For MAZ zeolite, the simulation results show the same difference in saturation capacity between adsorbates that can change their orientation compared to those that cannot (Figure 6.2b). In MAZ however, a difference between benzene and o-xylene shows up that is not present in AFI. This is because MAZ is slightly smaller than AFI and although o-xylene is able to align perpendic-
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Figure 6.2: Single component isotherms in (a) AFI and (b) MAZ zeolite at 433 K. At saturation conditions, benzene and o-xylene can reach higher loadings because of molecular reorientation. This can be exploited as a separation mechanism in liquid conditions. The smaller channel of MAZ compared to AFI allows for a better reorientation of benzene.

ular, the tighter confinement does not allow for a complete “face-to-face” stacking at this range of pressures. This suggests that a 1D channel slightly smaller than that observed in MAZ would be perfect to separate benzene from other aromatics. Benzene is the main precursor for ethylbenzene, cumene and cyclohexane, used for the production of styrene/polystyrene, resins and Nylon.

In Figure 6.3 we show the CB/CFCMC simulation isotherms (inset) and the simulated breakthroughs at 100 kPa for an equimolar mixture of o-xylene/p-xylene/m-xylene/ethylbenzene in AFI at 433 K. The CB/CFCMC mixture simulations for the 4-component mixture are in excellent agreement with the IAST calculations based on pure component isotherms fits (fit parameters are provided in the SI of ref. [18]). The isotherms clearly show AFI selectivity for o-xylene at saturation conditions. The sequence of breakthroughs show that the breakthrough of o-xylene occurs significantly later than that of ethylbenzene and p- and m-xylene. This ensures highly selective separation of o-xylene from the other components and demonstrates the possibility of separation of a 4-component o-xylene/m-xylene/p-xylene/ethylbenzene mixture on the basis of molecules reorientation provided pore saturation conditions are attained. Our results are in good agreement with Hu et al. [19, 20] transient breakthrough experiments.

The experimental results of Chiang et al. [17] already suggest that benzene and o-xylene arrange in a “face-to-face” configuration in AFI. By dividing the loading per channel by the channel-length it is clear that the footprint of the molecules is small, but the experimental data is insufficient to elucidate how and why. Chiang et al. purported that even at low loading benzene molecules would prefer to be orientated perpendicular in AFI. But this is not the case. It is not an energetic, but an entropic effect. We note that perpendicular alignments of aromatics has been observed before by Lucena et al. [21, 22] in AEL and AFI zeolite and by
6.3 Results and discussion

Figure 6.3: Breakthroughs simulation at 100 kPa and mixture isotherms (inset) for an equimolar mixture of o-xylene/p-xylene/m-xylene/ethylbenzene in AFI zeolite at 433 K. The breakthrough simulation methodology is the same as that used in chapter 5. The reorientation of o-xylene allows higher saturation capacity and drives the other mixture components out of AFI zeolite. This makes AFI an o-xylene selective structure. Diffusion considerations do not change this.

We found that the effect is not caused by the corrugation of the wall. Even without walls (in simulations we achieve this by omitting the framework and in-
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Figure 6.4: Distribution of the angle between the aromatic ring of o-xylene and the channel axis of AFI at 433 K for different loadings. As loading increases, molecules orient with the aromatic ring perpendicular to the channel axis (90°). The flat black line represents the distribution of an ideal gas.

Figure 6.5: Infinite dilution heat of adsorption of benzene, o-, m-, p-xylene and ethylbenzene in (a) AFI and (b) MAZ zeolites at different temperatures. For AFI zeolite, our results agree qualitatively with the experimental results of Chiang et al. [17]. In the Henry regime, benzene is the least strongly adsorbed species in both zeolites.

Instead restrict the molecules to a volume and shape corresponding to a channel) the effect can be observed. Also, the effect is largely independent of the molecular properties at the Henry regime. A weaker adsorbing molecule that is able to reorient wins at saturation from a stronger adsorbate that is unable to reorient. This is the case of benzene in AFI and MAZ zeolite. In both cases, benzene has a higher saturation capacity than p-xylene, m-xylene or ethylbenzene, but a lower heat of adsorption (Figure 6.5).
A class of molecules that have a reduced footprint by reorientation are aromatics, but the effect should be applicable to any adsorbate with one dimension significantly smaller than the other two. The effect is also not limited to the smallest molecules in a mixture. If the larger molecule is (when reoriented) close to the dimensions and shape of the channel and able to change its orientation, but the smallest is not, then the largest molecule will be both entropically and energetically favored at saturation conditions.

As an example on how to exploit the reorientation, we predicted the separa-
tion of 1,3,5-trichlorobenzene from its isomers based on the reorientation into a pile configuration of this isomer in a modified Fe$_2$(BDP)$_3$ metal organic framework. In the modify structure the BDP linkers (BDP=1,4-benzenedipyrazolate) were substituted by 4,4- bis(1H-pyrazol-4-yl) biphenyl linkers [24] to increase the channel size (Figure 6.6). Figure 6.7a shows that the small differences in the isomers shape are enough to only permit the 1,3,5-trichlorobenzene to reorient and reduce its footprint within the channels allowing this isomer to reach a higher saturation capacity (Figure S5). In Figure 6.7b the CB/CFCMC simulated mixture isotherms of an equimolar mixture of trichlorobenzene isomers are presented. The reorientation into a pile of 1,3,5-trichlorobenzene leads to a very efficient separation, especially under saturation conditions.

6.4 Conclusions

When in a mixture of components only one of them has the right size to rotate inside the channels, this mechanism can lead to important differences in saturation capacities. Therefore, highly selective separations can be achieved by proper choice of one-dimensional channel sizes at saturation conditions. Our CB/CFCMC and breakthrough simulations clearly underscore the potential of adopting separation strategies that relies on differences in molecular footprints, rather than adsorption strengths.

Acknowledgements

This material is supported by the NWO/CW through a VIDI grant (D. Dubbeldam) and by an ERC Starting Grant ERC-StG- 279520 Grant (S. Calero).
References


