Entropy driven separations in nanoporous materials
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CHAPTER 8

Exploiting Large-Pore Metal-Organic Frameworks for Separations using Entropic Molecular Mechanisms*

8.1 Introduction

Nanoporous materials such as zeolites [1, 2], metal-organic frameworks (MOFs) [3–7], and zeolitic imidazolate frameworks (ZIFs) [8] offer great potential as energy-efficient alternatives to conventional separation processes like distillation, absorption, and extraction. Besides being industrially relevant, they are scientifically very interesting to gain understanding of the fundamentals of the separation mechanisms governing adsorbed molecules in confinement. Separation in nanoporous materials relies on adsorption [9] and diffusion [10], and can be achieved by size/shape exclusion (steric separation), by differences in the adsorbate-adsorbent interactions and by adsorbate packing (thermodynamic equilibrium effect) and by differences in the diffusion rate of adsorbates within the adsorbent channels.

Zeolites and aluminosilicates are produced commercially and have relatively high thermal and chemical stabilities. These materials are based on TO$_4$ tetrahedra (where T is an aluminum or silicon atom), which results in 3-dimensional networks when all four corners of the tetrahedral are shared. The tetrahedra are primary building blocks, which form secondary building blocks (e.g. 4-rings, 6-rings, double 6-rings, etc.). These secondary units join together to form the about 225 different zeolite topologies we know today. In Figure 8.1 two well-known zeolites are shown: faujasite (FAU) and Mobile Five (MFI). For FAU we can see the 6-6, 6-2, 6, 4-2, 1-4-1, and 4 secondary building blocks forming a supercage. The nomenclature can be found in the zeolite atlas, but for example 6-6 stands

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Figure 8.1: Two well-known zeolites: (a) Faujasite (FAU), and (b) Mobile Five (MFI). The Faujasite family of zeolites is composed of sodalite cages linked through double 6-rings into an hexagonal layer. Color code: aluminum (green), silicon (yellow), extra-framework cation site I, I’, II and II’ (red), site III (blue, pink, yellow). MFI is a 3-dimensional network consisting of linear channels (‘L’), zig-zag channels (‘Z’) and intersections (‘I’). The unit cell has dimensions of $20.022 \times 19.899 \times 13.383$ Å; per unit cell there are 4 intersections, 2 zig-zag channels, and 2 linear channels. The channels are shown as an adsorption surface (inside as ‘gold’, outside view as ‘blue’), with hexane molecules adsorbed in the linear and zig-zig channel.

for a double 6-ring of T-atoms. FAU-type zeolites are widely used in separation processes and catalysis. There are many forms of the FAU topology, e.g. Ba-X, Na-X, Na-Y, siliceous Na-Y, and SAPO-37, which differ in their chemical composition. The FAU-type pore structure consists of sodalite cages arranged in 1.2 nm wide supercages accessible through 0.72 nm windows. MFI is a typical example of a three-dimensional channel structure with intersections at the crossing of the channels, and has been the focus of the pioneering computational zeolite work, starting with the works of June et al. [11, 12] and Snurr et al. [13]. The channels of MFI are wide enough to adsorb e.g. C6, C7, and C8 isomers, including benzene and xylenes.

In aluminosilicates, the ratio between aluminum and silicon determines the charge of the framework. This charge is compensated by the presence of extra-framework cations like Na+, Li+, K+, Ba2+ and Ca2+ which are distributed among different sites in order to maximize their interactions with the framework oxygens and minimize the cation-cation repulsion. Zeolites have relatively high framework densities, low surface areas, and low pore volumes, and in general show high selectivities because strong confinement allows for higher discrimination between adsorbing species.
MOFs are novel materials that, relative to zeolites, have moderate stability, high void volumes, and well-defined tailorable cavities of uniform size. These materials consist of building blocks that self-assemble into crystalline materials that, after evacuation, can find applications in adsorption, separations, air purification, gas storage, chemical sensing, and catalysis [14–17]. MOFs possess almost unlimited structural variety because of the many combinations of building blocks that can be imagined [18–20]. The clear advantage of MOFs is their very high pore volumes and surface areas. For development of next-generation porous materials it is highly desired to combine the high selectivity of zeolites with the large pore capacities of MOFs. Another scientifically extremely appealing property of MOFs is design. Düren et al. developed ‘in silico MOF design’, i.e. using information obtained from computer simulation these authors proposed a new, not yet synthesized, MOF with enhanced methane storage capabilities [21]. Sarkisov and Kim reviewed how the information obtained from computational characterization can be used in screening protocols to identify the most promising materials for a specific application before any costly and time consuming experimental effort is committed [22].

There is a conceptual difference between adsorption of small versus larger molecules. In contrast to larger molecules, small gas molecules such as CO₂, O₂, N₂, CH₄, etc. have little or no shape/size differences relative to the framework. They behave more like a fluid inside large pores of nanoporous materials [23]. The possible separation mechanisms are therefore limited to either small pore systems, or for larger pores limited to reduced separation selectivities. It is inherently hard for these systems to combine high selectivity with high pore volumes, because only the surface-adsorbed molecules “feel” the framework (while the remainder of the molecules interact mainly with other molecules). Selectivity therefore originates from the low loading regime where a few molecules interact with strongly selective sites, but selectivity is lost at higher loadings. This is unfortunate, because many industrial processes operate at saturation conditions (e.g. liquid-phase separations).

Separation mechanisms that are effective at saturation conditions have (in general) to be entropic in nature (saturation corresponds to the high-pressure part of adsorption isotherms). For molecules that have a bulky size and shape (relative to the framework) it is possible to exploit entropy effects to induce a difference in saturation loading. Molecules that fall into this class are for example alkanes (chain-like) and aromatics (flat in shape). For example, xylene isomers have the same mass and similar boiling points, and are also close in shape. The similarity of these properties is why they are so difficult to separate via traditional methods. Xylene isomers have a bulkiness of the shape and size of MOF cavities. If one specific isomer can stack or pack two molecules per channel-length, but the other isomers only one, then a significant difference in saturation loading leads to a very efficient separation. In this case, high selectivity can be combined with high pore volumes. Here, we will focus on systems of this type and on the methodologies to achieve this. Our focus lies heavily on computational work because in simulations all molecular level information is readily available and a wide range of
thermodynamic conditions can be examined.

8.2 Nanoporous materials for separations

Surface area, pore volume, and porosity have become the main characterization properties for bench-marking porous materials [24]. Geometric surface areas can be calculated using a simple Monte Carlo integration technique in which a nitrogen probe molecule is rolled along the surface [21, 25]. The obtained values usually compare well to BET surface areas once the appropriate consistency criteria are met [26]. For sorption applications, these molecular surface areas are physically more meaningful than e.g. Connolly surface areas [27]. The crystal volume per mass is a property directly computable from the crystallographic data of a nanoporous material, but it is the accessible volume (the volume accessible to the adsorbates per volume or mass of framework) that is the appropriate adsorption metric. The porosity can be computed using a methodology proposed by Talu and Myers [28], where the volume is probed with a non-adsorbing helium atom. An alternative is to use the \( r \to 0 \) limit of the pore size distribution function to determine the void fraction [24]. Once the helium void fraction and the crystal volume per mass are known, then the accessible pore volume or pore capacity can be calculated (by multiplying the two). The pore capacity is the volume accessible to adsorbates per framework mass and it takes the framework density and porosity into account. Relevant accessible pore volumes should not include volumes that are not accessible (from the main channel).

In Figure 8.2 we plot surface areas and pore capacities as a function of the porosity for a wide range of MOFs, zeolites, COFs, and ZIFs. Note that the y-axes are in log-scale. The structures have been selected on the premise that
8.2 Nanoporous materials for separations

Figure 8.3: Two examples of MOFs: (a) An iron-based MOF with triangular 1D channels running in the z-direction. The linker molecule is 4,4-bis(1H-pyrazol-4-yl)biphenyl. The topology of the MOF is the same as Fe$_2$(BDP)$_3$ but has an additional phenyl-group in the linker. The channels are large enough to accommodate aromatics. (b) UiO-66 consisting of two types of cages in an alternating arrangement (left-view: small type cavities, right-view: large type cavities). We show a snapshot of 2,3-dimethylbutane at high loading at 433 K in $2 \times 2 \times 2$ unit cells. Each edge length of the unit cell is 20.7 Å.

their pores should be large enough to accommodate hexane molecules. In general, the pore capacities and surface areas of MOFs are an order of magnitude larger than for zeolites. MOFs therefore have the potential to revolutionize storage [29–31], CO$_2$ capture and adsorption [32–34], adsorption [35], separations [36], and catalysis [37–41], and to become just as widespread as zeolites.

Figure 8.3 shows two examples of MOFs: (i) an iron-based MOF with triangular channels and (ii) UiO-66 containing cavities accessible through windows. The iron-based MOF has iron-metal corners that are bridged by 4,4-bis(1H-pyrazol-4-yl)biphenyl linkers, creating a one-dimensional, triangular channel structure. The openness of the structure is striking. In contrast to zeolites, which are much denser, every MOF framework atom is in contact with the channel and the wall thickness is one atomic layer. The channels are large enough to accommodate aromatics without diffusion limitations. The UiO-66 pore system consists of two types of cages per unit cell that alternate: 4 octahedral cages of 1.1 nm in diameter and 8 smaller tetrahedral cages 0.8 nm in diameter [42]. About 50% of the structure is void. The UiO-66 structure is capable of efficiently separating hexane isomers [43].

What is also evident (beside noting the high pore volume) is that the structures are not as thermally stable as zeolites. MOFs consist of a coordinating metal atom (or cluster of atoms) with one or more ligands attached to it by so-called ‘coordination bonds’. These bonds (between 50 kJ/mol and 200 kJ/mol) are weaker than covalent bonds and its force is acting on a relevant distance of 1.5–2.5 Å. The strength of covalent bonds is about 200-800 kJ/mol and the force operates over shorter distances of the order of 1-2 Å [44]. In addition, and likely related to this, the structures are less water-stable than zeolites. The principles of designing...
water-stable MOFs are not yet well understood. Solvents, left over from synthesis, need to be removed, usually by heating and vacuum. But the temperatures that are attainable before thermal decomposition are not as high as for zeolites. And similar to zeolites, there are also issues of (partial) pore collapse and imperfections and stacking faults during crystal growth. However, the last years much progress has been made in the synthesis of (water-)stable MOFs [45].

There are several works that discuss guidelines and objective criteria for which the adsorptive delivery should be optimized [46, 47], taking the entire adsorption-desorption cycle into account (in a practical pressure range of 1-30 bar). A too strong affinity of adsorbates with the framework makes it very energetically costly to desorb, whereas a too low affinity leads to poor delivery. For example, for methane an optimal enthalpy value of around 20 kJ/mol has been found (at 254 K). Most small pore structures (like zeolites) have a significantly stronger interaction. MOFs seem to have an ideal adsorption behavior for many adsorbates, except perhaps for hydrogen adsorption (MOFs are still well below the DOE targets for hydrogen storage although progress is made [48]). For example, the record holder for methane-storage is a MOF [49]. However, because the building blocks of MOFs are expensive, it would be very costly to use MOFs for storage applications. For separation and catalysis applications the material can be immediately reused and the cost of the material itself is less of an issue (especially if the MOFs are very stable). The open structure of MOFs means that there are little or no diffusion limitations [50]. A wish list for a next-generation adsorbent would therefore be:

- sufficient thermal- and water-stability,
- high adsorption selectivity,
- large pore capacity,
- heats of adsorption that are not too low or too high,
- a diffusion selectivity that enhances the adsorption selectivity even further (or at least does not hamper the adsorption selectivity).

Operating at saturation conditions using large pore capacities is beneficial because then more fluid can be treated in a single adsorption-desorption cycle, thereby reducing the amount of cycles (and hence the costly desorption step). Especially for membrane applications, it is the product of both the diffusivity and adsorption selectivities that determines the efficiency. This creates an inherent difficulty, because usually (but fortunately not always) an increase in affinity decreases the diffusion rate.

8.3 Adsorption thermodynamics

The thermodynamics of physi-sorption of gases in porous solids is well developed (see refs. [51–53] and references therein). Excess adsorption is defined as “the difference between the number of moles of gas present in the system (sample cell
containing porous solid) and the number of moles that would be present if all the accessible volume in the system (both inside and outside the pores) were occupied by the adsorbate gas in its bulk state at the same temperature and pressure” [54]. Although experiments measure excess adsorption, it is much more convenient (and even necessary) to describe the theoretical framework in terms of absolute adsorption [54]. Simulations always compute absolute adsorption $n_a$, but (knowing the accessible pore volume $V_{\text{pore}}$ of the framework) $n_a$ can be converted to excess adsorption $n_{\text{exc}}$:

$$n_{\text{exc}} = n_a - \frac{pV_{\text{pore}}}{zRT} = n_a - \rho(p, T) V_{\text{pore}}$$  \hspace{1cm} (8.1)

$R = 8.31451 \text{ J/mol/K}$ is the gas constant, $z$ the compressibility in the bulk fluid phase, and $\rho$ is the density of the bulk fluid phase at temperature $T$ and pressure $p$.

The affinity of a molecule with the framework can be expressed as the binding energy, or more general, as the enthalpy of adsorption at infinite dilution $\Delta H$ [55]:

$$\Delta H = \Delta U - RT = \langle U_{hg} \rangle - \langle U_h \rangle - \langle U_g \rangle - RT$$  \hspace{1cm} (8.2)

where $\Delta U$ is the internal energy, and $\langle U_{hg} \rangle$, $\langle U_h \rangle$, and $\langle U_g \rangle$ are the average energy of the guest molecule inside the host-framework, the average energy of the host-framework, and the average energy of the guest-molecule, respectively. In simulations a common approximation is to assume the framework is rigid, and in this case the enthalpy of adsorption at infinite dilution can be understood to be the difference in internal energy of a single molecule outside and inside the confinement of the host framework. In the limit of zero temperature, the enthalpy of adsorption becomes the binding energy. Infinite dilution enthalpy of adsorption $\Delta H$ is related to the Henry’s coefficient $K_H$ as

$$\Delta H = -\frac{\partial \ln K_H}{\partial \beta}$$  \hspace{1cm} (8.3)

where $\beta = 1/(k_B T)$ is the inverse temperature, and $k_B$ the Boltzmann’s constant. The Henry’s coefficient is the slope of the isotherm at zero pressure/loading.

The Helmholtz free energy $\Delta A$ of adsorption can be computed using Widom test-particle insertion. At infinite dilution the Gibbs free energy is related to the Helmholtz free energy by

$$\Delta G = \Delta A - RT$$  \hspace{1cm} (8.4)

The entropy difference of a molecule outside and inside the framework is given as

$$\Delta S = \frac{\Delta U - \Delta A}{T} = \frac{\Delta H - \Delta G}{T}$$  \hspace{1cm} (8.5)

The Gibbs free energy of adsorption consists of a change in enthalpy $\Delta H$ and a (temperature) change in entropy $T\Delta S$

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (8.6)

So, when a molecule adsorbs it transitions from the free fluid phase to an adsorbed phase with two common contributions.
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Figure 8.4: Thermodynamic adsorption properties of (a) hexane (nC6) and (b) 2,2-dimethylbutane (22DMB) as a function of channel size. The zeolites are in order of smallest to largest: MTW, VET, SPE, BEA, SSZ-31, MOR, CON, OFF, GME, AFI, CFI, MAZ, ADR, DON, AET, MEI, LTL, and FAU. Lines are guides to the eye. Data taken from Ref. [56].

1. it (usually) gains favorable energy (ΔH is negative) because of attractive interactions with the framework, and

2. the molecule has an increased confinement compared to the gas phase, thereby loosing entropy (ΔS is negative, −TΔS is positive, leading to increased and less favorable ΔG).

Adsorption will occur only when ΔG is negative and this is possible only if ΔH < TΔS. The process is (usually) exothermic (ΔH < 0). Figure 8.4 plots ΔG, ΔH, and −TΔS as a function of pore size at 533 K. The data is taken from Schenk et al. [56]. For hexane, the adsorption strength ΔG is stronger in the tighter MTW channels, even though the hexane molecule is more confined, as this is offset by a larger enthalpy-gain with the structure. For hexane the ΔG nicely correlates with the channel diameter, but for 2,2-dimethylbutane there is an optimal channel width somewhere in between FAU and MTW (i.e. AFI with pore size of 7.3 Å) [56, 57]. In general, the interplay of enthalpy and entropy is difficult to predict.

As another example, we show in Table 8.1 the values of ΔH, ΔG and −TΔS for hexane isomers in UiO-66. At low loading, the hexane isomers prefer the small-type cages in UiO-66 and at high loading also occupy the large-type cages. The branched hexane isomers are preferred in these small cages over the mono-branched and linear hexane. At 300 K, the 2,3-dimethylbutane is preferred, while at higher temperatures 2,2-dimethylbutane is preferred. This is exclusively due to entropy. In structures like UiO-66 the molecules are well separated in small cavities and inter-molecular interactions for hexane isomers are low. In general, because there are two types of cavities in UiO-66, molecules of a certain type can preferentially adsorb in one of the two types of cage (or transition between them) depending on temperature and loading [58]. Entropy differences between components in a
mixture can be substantial, even at low loading, and mixture simulations can be driven by rotational entropy [43, 59].

At the start of an adsorption process, \( \Delta H < T \Delta S \) and \( \Delta G < 0 \), and the process transfers molecules in the direction of lower free energy (which results in adsorption). As the adsorption process continues the \( \Delta H \) and \( T \Delta S \) terms change until \( \Delta H = T \Delta S \) and \( \Delta G = 0 \), and equilibrium is achieved. At finite loading, the enthalpy of adsorption \( \Delta H \) can be computed in the grand-canonical ensemble \( \mu VT \) (fixed chemical potential \( \mu \), fixed volume \( V \) and fixed temperature \( T \)) from a fluctuation formula [60, 61]:

\[
\Delta H = \frac{\langle U \times N \rangle_\mu - \langle U \rangle_\mu \langle N \rangle_\mu}{\langle N^2 \rangle_\mu - \langle N \rangle^2_\mu} - \langle U_g \rangle - RT \quad (8.7)
\]

The chemical potential in the adsorbed \( \mu_a \) and gas phase \( \mu_g \) are defined as

\[
\mu_a = \left( \frac{\partial G_a}{\partial n_a} \right)_{T,p} \quad (8.8)
\]

\[
\mu_g = \left( \frac{\partial G_g}{\partial n_g} \right)_{T,p} \quad (8.9)
\]

When equilibrium is reached, the chemical potential of the adsorbed phase becomes equal to the gas phase chemical potential

\[
\Delta G = (\mu_a - \mu_g) \ dn_a = 0 \rightarrow \mu_a = \mu_g \quad (8.10)
\]

### Table 8.1: Thermodynamic adsorption properties of hexane isomers at infinite dilution in UiO-66 at 300, 400 and 500 K. The structure of UiO-66 is shown in Figure 8.3.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>adsorbate</th>
<th>( \Delta G ) [kJ/mol]</th>
<th>( \Delta H ) [kJ/mol]</th>
<th>(-T \Delta S) [kJ/mol]</th>
<th>( \Delta S ) [J/mol]</th>
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</thead>
<tbody>
<tr>
<td>300</td>
<td>22DMB</td>
<td>-50.6</td>
<td>-71.9</td>
<td>21.3</td>
<td>-70.8</td>
</tr>
<tr>
<td>300</td>
<td>23DMB</td>
<td>-55.7</td>
<td>-77.5</td>
<td>21.8</td>
<td>-72.8</td>
</tr>
<tr>
<td>300</td>
<td>2MP</td>
<td>-44.8</td>
<td>-70.4</td>
<td>25.6</td>
<td>-85.3</td>
</tr>
<tr>
<td>300</td>
<td>3MP</td>
<td>-48.8</td>
<td>-72.8</td>
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<td>-80.2</td>
</tr>
<tr>
<td>300</td>
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<td>26.8</td>
<td>-89.2</td>
</tr>
<tr>
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<td>-56.0</td>
<td>-71.5</td>
<td>15.5</td>
<td>-38.9</td>
</tr>
<tr>
<td>400</td>
<td>23DMB</td>
<td>-46.1</td>
<td>-77.3</td>
<td>31.2</td>
<td>-78.0</td>
</tr>
<tr>
<td>400</td>
<td>2MP</td>
<td>-35.3</td>
<td>-69.1</td>
<td>33.7</td>
<td>-84.3</td>
</tr>
<tr>
<td>400</td>
<td>3MP</td>
<td>-42.3</td>
<td>-71.8</td>
<td>29.4</td>
<td>-73.6</td>
</tr>
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<td>400</td>
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<td>-62.8</td>
<td>39.8</td>
<td>-99.4</td>
</tr>
<tr>
<td>500</td>
<td>22DMB</td>
<td>-51.3</td>
<td>-71.3</td>
<td>20.0</td>
<td>-40.0</td>
</tr>
<tr>
<td>500</td>
<td>23DMB</td>
<td>-39.8</td>
<td>-77.0</td>
<td>37.2</td>
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<tr>
<td>500</td>
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<td>39.7</td>
<td>-79.4</td>
</tr>
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<td>-70.0</td>
</tr>
<tr>
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<td>nC6</td>
<td>-15.3</td>
<td>-61.4</td>
<td>46.0</td>
<td>-92.0</td>
</tr>
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</table>
Adsorption is usually described through isotherms, i.e. the amount of adsorbate on the adsorbent at constant temperature as a function of pressure or fugacity. A common, generic isotherm-model is the $n$-site Langmuir-Freundlich (LF) model (also known as ‘Sips’ model):

$$q(x) = \sum_{i} q_{i,\text{sat}} \frac{b_{i}x^{\nu_{i}}}{1 + b_{i}x^{\nu_{i}}}$$

(8.11)

where $x$ can be pressure or fugacity, $n$ is the number of types of sites, and $q_{i,\text{sat}}$ (the saturation loading for site $i$), $b_{i}$ and $\nu_{i}$ are fitting constants. The constant $\nu$ is often interpreted as the heterogeneity factor [62]. Values of unity indicate a material with homogeneous binding sites and Eq. 8.11 reduces to the $n$-site Langmuir model.

Our knowledge on the peculiarities of isotherm behavior has grown tremendously the last two decades. Hexane and heptane in MFI show inflections in the isotherms due to ‘commensurate freezing’ [63]. The length of these molecules is commensurate with the length of the zig-zag channels. In Figures 8.5(a) and 8.5(b) we show the density of hexane atoms in the MFI structure. The pictures can be considered an average over millions of snapshots. Hexane fits very snugly, and packs nicely in the zig-zag channels without sticking out into the intersections. Only the hexane molecules that are in the linear channels can stick out into the intersection.

By fitting the isotherms to a model and by examining simulation snapshots of the system a lot of information can be obtained [24]. Branched alkanes in MFI can be described by the dual-site Langmuir model [64], which signals the absence of significant inter-molecular interactions. In Figure 8.5(c) we show the adsorption isotherms of linear alkanes [65] and their dual-site LF fits (Table 8.2). The model describes the isotherms well. Linear alkanes smaller than hexane have a lot of rotational freedom (i.e. several molecules can fit at the channels and intersections) and there is much heterogeneity. For small molecules the intersections are comparatively unfavorable owing to a high potential energy and low entropy [66]. Adsorption in the straight or zig-zag channels have very similar potential energies, but the zig-zag channel is slightly more favored due to its higher entropy [66, 67]. Hexane is the most commensurate with the zig-zag channel and is the onset of the behavior for longer alkanes, all of which have large inflections. They are no longer ‘hidden’ inside the zig-zag channels, and after 4 molecules per unit cell have to interact with each other. The magnitude of the inflection increases for lower temperatures (which signals an energetic origin).

In hindsight, almost all isotherms in nanoporous materials have inflections. The underlying cause of inflections is an energetic and entropic difference between sites in the structure. If the sites differ greatly in the energetics, then first the lowest energy site is filled up before the next site is (example: branched alkanes in MFI), and this second filling requires significantly more pressure. For smaller energy differences, the adsorption occurs concurrently, but is mostly in favor of the lowest energy site. The magnitude of an inflection is so strongly related and so sensitive to
Figure 8.5: Commensurate freezing of hexane and heptane in MFI: (a) front-view of the density of hexane atoms in MFI, (b) top-view of the density of hexane atoms in MFI, (c) single component isotherms of linear alkanes in MFI at 303 K. The solid lines are dual Langmuir-Freundlich fits through the isotherm data. For hexane, a dashed line shows the fit of a single Langmuir-Freundlich fit (there is a small difference at 7.5 molecules per unit cell). The simulation were run long enough to make sure the error bar was smaller than the symbol size [65].

Table 8.2: Dual-site Langmuir-Freundlich parameters for pure component linear alkanes at 303 K in MFI.

<table>
<thead>
<tr>
<th></th>
<th>site A</th>
<th>site B</th>
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<tbody>
<tr>
<td></td>
<td>$q_{i,A,sat}$ [molec. uc$^{-1}$]</td>
<td>$q_{i,B,sat}$ [molec. uc$^{-1}$]</td>
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<tr>
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<td>nC5</td>
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</tr>
<tr>
<td>nC9</td>
<td>4.00</td>
<td></td>
</tr>
</tbody>
</table>

8.4 Enthalpic separation mechanisms

Most studies aim to improve the separation (and storage) efficiency of materials focusing on tuning the enthalpy of adsorption, because it is much harder to elucidate the entropy contribution as a function of topology. The entropy effects can (in
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The larger polarizability and quadrupole moment of CO\textsubscript{2} over N\textsubscript{2}, H\textsubscript{2}, CO and CH\textsubscript{4}, allows for its separation by selective binding of CO\textsubscript{2} with either the unsaturated metal atoms (M) of Cu-BTC\cite{69, 70}, Cu-TDPAT\cite{71}, M-MOF-74\cite{72–77}, the extra-framework cations of NaX zeolite \cite{78} and rho-ZMOF\cite{79} (a charge framework) or with the functional groups (-NH\textsubscript{2}, -OH, CH\textsubscript{3}, Cl, F, Br, CN) in the MOFs linkers \cite{80–82}. D’Alessandro et al. and Zhang and co-workers have given excellent reviews on CO\textsubscript{2} capture and separations \cite{83, 84}. Differences in the quadrupole moments of N\textsubscript{2} and O\textsubscript{2} favor N\textsubscript{2} adsorption in both LTA-4A and LTA-5A \cite{85} and also in C\textsubscript{6}(BTC)\textsubscript{2}, Fe(DOBDC)\cite{86} and Cu-BTC\cite{87}. Differences in their magnetic susceptibilities are believed to be responsible for the higher affinity of O\textsubscript{2} over N\textsubscript{2} in MOF-177\cite{88}. Hydrogen bonds are responsible for the selective adsorption of CHCl\textsubscript{3}, MeOH and H\textsubscript{2}O in Zn\textsubscript{2}(bptc), but not hexane or pentane \cite{89}. More effective van der Waals interaction between C\textsubscript{2}H\textsubscript{2} in M(HCO)\textsubscript{2} (M=Mg,Mn) could be responsible for the separation of C\textsubscript{2}H\textsubscript{2} from CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}, O\textsubscript{2} and H\textsubscript{2} \cite{90}. \(\pi\)-Interactions between the metals and the double bonds of alkenes are responsible for the separation of alkane/alkenes mixtures. Wang et al. \cite{69} showed separation of ethylene over ethane in Cu-BTC, which is a consequence of the interactions between the \(\pi\)-electrons in ethylene double bond and the positive charge of the Cu(II) sites in the framework. Yoon et al. \cite{91} and Lamia et al. \cite{92} showed separation of propylene over propane in Cu-BTC and Hartmann et al. \cite{93} showed separation of isobutene and isobutane in Cu-BTC.

MOFs differ from zeolites in that they can possess unsaturated (also called ‘open’) metal-sites. These sites can be very strong and selective, and have opened up a promising future for MOFs as catalysts. Zeolites on the other hand, can possess strong electric field gradients when cations are incorporated. Zeolites that are used in industry usually contain cations, \textit{e.g.} Na-X, Ba-X, Na-Y, and LTA-4A (sodium ions) and LTA-5A (sodium and calcium ions). Introducing cations in MOFs can lead to increased affinity for certain adsorbates. For example, several studies used lithium-doping as a method to increase the affinity of hydrogen with the MOF \cite{94–96}, to provide the desired binding enthalpies in the range of 20-30 kJ/mol for hydrogen. Mulfort and Hupp \cite{95} reasoned that framework reduction might increase affinity by: (a) increasing the polarizability of organic struts, thereby strengthening adsorbate/ framework van der Waals interactions,
8.5 Entropic separation mechanisms

8.5.1 Entropy

In a mixture, one component can drive another out at high pressures. Differences in adsorption loading of a mixture can be caused by energetic difference in the affinity of the components and by entropic effects. There are several tests to get to the root-cause of the expulsion effect:

- Examine the heat of adsorption and compare to the average energy (as a function of loading).

Each point of the isotherm is equilibrium and hence \( \Delta H = T \Delta S \). At infinite dilution, the enthalpy is directly related to the difference in internal energy (see Eq. 8.2). So when one plots \( \Delta H \) as a function of loading (at constant temperature) any sudden changes signals a sudden change in entropy. And when compared to \( \langle U_{hg} \rangle - \langle U_h \rangle - \langle U_g \rangle - RT \) the effect of enthalpy can be examined. By comparing the difference in behavior one can elucidate whether the effect is enthalpic or entropic. For example, in Figure 8.6a we plot the enthalpy of adsorption as a function of loading for hexane and 2,3-dimethylbutane in MFI. For hexane, energetics and entropy goes hand-in-hand: the hexane molecules at loadings higher than 4 molecules per unit cell have significant favorable inter-molecular interactions which confines the molecules more and more. The dibranched molecule adsorbs in the intersec-

\[ \Delta H = T \Delta S \]

\[ \langle U_{hg} \rangle - \langle U_h \rangle - \langle U_g \rangle - RT \]

\[ \text{Figure 8.6: Elucidating enthalpy vs. entropy: (a) Enthalpy of adsorption and average energy in MFI at 433 K for hexane and 2,3-dimethylbutane, (b) Average energies (total, adsorbate-host, and adsorbate-adsorbate energy [intra-molecular energy not shown]).} \]

(b) introducing charge-compensating cations capable of binding gas molecules via charge/ quadrupole or more specific interactions, and (c) coulombically displacing interwoven frameworks, thereby enhancing accessible surface area.
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Figure 8.7: Elucidating enthalpy vs. entropy: component loading of an equimolar C2,C4,C6-mixture in TON-type zeolite at (an approximately) fixed total loading of 0.9 mol kg\(^{-1}\) (dashed line) as a function of temperature.

Molecules may be separated by selective adsorption on the basis of differences of MFI first (see Figure 8.1b for the structure of MFI), and as soon as these are filled (4 molecules per unit cell), the dibranched molecules are pushed into the linear and zig-zag channels, thereby creating an additional adsorption lattice that was not energetically favorable before. Doubling of the amount of available sites causes a sudden jump in the entropy. The creation takes a large additional driving force (as the channel sites are energetically unfavorable for the branched isomers) leading to large inflections in the isotherms. We will discuss this further in the section ‘configurational entropy’. Note the large scatter in $\Delta H$ at high loading. The fluctuation method relies on the efficiency of insertion and deletions of the particle during the simulation, and therefore generally fails close to saturation loadings.

- Change the interaction model of the atoms to a hard-sphere model [97]. If the attractive part of the Lennard-Jones potential is removed from the framework-adsorbate and adsorbate-adsorbate interactions and the repulsion term is extremely strong then the atoms are treated as impenetrable spheres that cannot overlap in space. Such a ‘hard sphere’ model has no energy scale and the only driving force is entropy. If in a mixture, one of the components is driven out at high pressures, then this must be because of entropy.

- Investigate the effect as a function of temperature. The lower the temperature, the more energetics dominates. Vice versa, entropy becomes increasingly important at high temperatures. In Figure 8.7 we show the component loading in a C2,C4,C6 equimolar mixture in TON-type zeolite at constant total loading. As can be observed, with an increase in temperature and hence $T\Delta S$, the smallest component will win (this will be further discussed in ‘size entropy’ and ‘length entropy’).
in their molecular shape [98]. Krishna et al. reviewed entropy effects affecting the adsorption of mixtures of alkanes [99] and packing effects in microporous materials [100]. Smit and Maesen reviewed adsorption and shape selectivity in zeolites [101, 102].

For alkanes three entropy effects were discovered: (i) size entropy [103], (ii) length entropy [103], and (iii) configurational entropy [64, 97, 104]. The prominent geometric property that characterizes linear alkanes is the chain-length. Branched alkanes, compared to its linear isomer, exhibit a decreased length but also an increased width. Recently two new entropic effects were found for adsorption of a mixture of aromatics. The typical characteristic of aromatics is their relatively small ‘height’ compared to their width and length (i.e. the aromatic ring is flat). We will first discuss the closely related ‘size entropy’ and ‘length entropy’ effects. Next, we will discuss ‘configurational entropy’, and afterwards we will discuss two more recently discovered entropic mechanisms: ‘commensurate stacking’ and ‘face-to-face stacking’ (i.e. ‘pringling’).

### 8.5.2 Size entropy

Size entropy favors smaller molecules over larger molecules [103, 105]. At low loadings, the larger molecules adsorb the strongest (highest adsorption strength and Henry coefficients) but at high loadings, because the smaller molecules can fill the vacant sites more easily, their saturation loading is usually significantly higher than for longer molecules, in terms of molecules per unit cell (uc). The entropy gain is so strong that replacing one C6 by two C2 is favorable, even though the number of carbon atoms becomes less (so it is misleading to think of entropy in terms of e.g. the total amount of carbon atoms). The higher saturation capacity of the smaller molecules increases the entropy of the system (and reduces the Gibbs free energy) favoring the adsorption of smaller molecules over larger molecules at saturation conditions. This has been observed for alkane mixtures that differ in chain-length (and hence in molecular volume) in MFI at saturation conditions [106–108]. In all cases, the more bulky component adsorbs the strongest at low loading but is eventually overtaken by the smallest one.

<table>
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<tbody>
<tr>
<td>23DMB</td>
<td>116.35</td>
<td>86.81</td>
<td>6.71</td>
<td>6.21</td>
<td>4.04</td>
</tr>
<tr>
<td>22DMB</td>
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<td>7.11</td>
<td>5.71</td>
<td>5.44</td>
</tr>
<tr>
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<td>86.10</td>
<td>7.83</td>
<td>6.00</td>
<td>3.43</td>
</tr>
<tr>
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<td>85.4</td>
<td>8.24</td>
<td>5.87</td>
<td>3.98</td>
</tr>
<tr>
<td>nC6</td>
<td>116.28</td>
<td>85.26</td>
<td>9.85</td>
<td>4.42</td>
<td>3.64</td>
</tr>
</tbody>
</table>

Table 8.3: Molecular properties of hexane isomers: surface area (vdW), volume (vdW), and shadow lengths [109], calculated using Materials Studio [110] by projecting the molecular surface on three mutually perpendicular planes. The molecules are first rotated to align the principal moments of inertia with the X, Y and Z axes.
In Figure 8.8 we show this behavior for an equimolar C2/C4/C6 mixture of linear alkanes in TON-type zeolite. The TON-type zeolite is a one-dimensional channel zeolite consisting of apertures of 8-rings of about 5.7 Å in diameter. At low loadings, C6 has the strongest affinity (heat of adsorption at infinite dilution and 300 K are C2=-50 kJ/mol, C4=-77 kJ/mol, C6=-100 kJ/mol) and highest Henry coefficient because it has more carbon atoms. However, as the fugacity increases, C6 molecules are replaced by C4 molecules and afterwards by C2 molecules. This is because at saturation conditions the dimensions of TON channels restrict the adsorption of C6 to two molecules per unit cell, of C4 to five molecules per unit cell and of C2 to ten molecules per unit cell (as shown in Figure 8.8b) which increases the overall entropy of the system. The size entropy effect counters the energetic effect of the larger number of carbon-atoms which favors the adsorption of the larger molecule and the adsorption of C6 in TON is eventually overtaken at higher fugacities by the smallest component C2.

In Figure 8.7 the loading of C2, C4 and C6 at a total mixture loading of 1.5 molecules per unit cell as a function of temperature is presented. We can see that at low temperatures TON is C6 selective, but with increasing temperature the system becomes more C2 selective. This means that C2 is entropically favored over C4 and C6 and (C4 over C6). If the temperature increases, the entropic effects become dominant over the enthalpic effects.

The size entropy separation mechanism requires a difference in the molecular volume of the components. For example, when we examine the same equimolar C2/C4/C6 mixture of linear alkanes in FAU-type zeolite (which has a large, roughly spherical cavity) we observe the same behavior: the smallest C2 molecule wins at high pressures. It does not depend on the topology of the framework but on the differences in saturation loading. In Table 8.3 we list geometric properties of hexane isomers; and in Figure 8.9 we show the pure component adsorption of hexane isomers in FAU-type zeolite. As can be seen, because the hexane isomers have similar molecular surface areas and volumes (with the exception of
8.5 Entropic separation mechanisms

2,2-dimethylbutane), size entropy is of no use here. For this, we need to turn to ‘length entropy’ which makes use of differences in the length-direction of the isomers (‘L’ in Table 8.3).

### 8.5.3 Length entropy

Although ‘size entropy’ is not able to separate a mixture of hexane isomers in a large pore structure like e.g. FAU (hexane isomers have more or less the same volume, see Table 8.3), it is possible to modify the effective size of a molecule. For example, by lining up the hexane isomers in one-dimensional channels, the dominant effective size that comes into play is its length (Table 8.3 shows that length $L_x$ of the hexane isomers are significantly different). The length entropy concept is schematically depicted in Figure 8.10. Basically, in one-dimensional channels size is best described in terms of length. Length entropy has been highlighted by Talbot [103] and the term is derived from the decreasing linear dimension of the

![Figure 8.9: Single components isotherms of C6 isomers at 300 K in FAU.](image)

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>$L$ [Å]</th>
<th>$L$ [Å]</th>
<th>$L$ [Å]</th>
<th>infinite dilution properties in kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 Pa</td>
<td>$10^3$ Pa</td>
<td>$10^5$ Pa</td>
<td>$\Delta G_0$</td>
</tr>
<tr>
<td>23DMB</td>
<td>6.54</td>
<td>5.35</td>
<td>4.67</td>
<td>-33.8</td>
</tr>
<tr>
<td>22DMB</td>
<td>6.63</td>
<td>6.33</td>
<td>6.29</td>
<td>-31.0</td>
</tr>
<tr>
<td>3MP</td>
<td>7.59</td>
<td>6.32</td>
<td>4.74</td>
<td>-30.9</td>
</tr>
<tr>
<td>2MP</td>
<td>8.12</td>
<td>7.39</td>
<td>6.33</td>
<td>-30.5</td>
</tr>
<tr>
<td>nC6</td>
<td>9.28</td>
<td>8.62</td>
<td>6.85</td>
<td>-28.9</td>
</tr>
</tbody>
</table>

**Table 8.4:** Molecular properties of hexane isomers in AFI at 300 K: molecular projected lengths along the channel axis at different fugacities, enthalpy of adsorption at infinite dilution. The lengths are the end-to-end distance taken along the channel-axis with 3.76 Å added for vdW radius of CH₃.
Figure 8.10: Length entropy of C6 isomers in one-dimensional channels. The projected lengths size are $nC6 > 2MP > 3MP > 22DMB > 23DMB$. In a mixture it is entropically more favorable to adsorb more molecules with a smaller effective size. In one-dimensional channels (when all the isomers are able to fit in), the isomer with the smallest effective length will be preferentially adsorbed at saturation conditions. Note that 3MP has two configurations that are very close in energy (less than 1 kJ/mol difference in the gas phase in favor of the isomer in brackets), but that the more compact isomer is favored in adsorption due to more favorable vdW interactions.

We use AFI as an example of a length-entropy system. Following Schenk et al. [57], we first measure the effective length of hexane isomers. The results are provided in Table 8.4 and at infinite dilution these lengths agree very well with the molecular shadow length given in Table 8.3. These differences in channel-occupation translate immediately to different saturation loadings, with the most compact molecule having the highest saturation loading. The pure component isotherms of hexane isomers in AFI are shown in Figure 8.11. If a structure has channels large enough to accommodate di-branched isomers while still inducing a parallel adsorption arrangement of the adsorbates, then the sorption hierarchy of that structure will be di-branched $>$ mono-branched $>$ linear. This is simply because the linear isomers will occupy the largest segment of the channel, as compared to the other isomers, while the di-branched isomers (the most compact ones) can arrange a larger number of molecules in the same given channel segment [99, 112, 113].

Note that the concept of length entropy is limited to small pores and that the effective length depends on pressure. By compressing the molecules more and more, for example in AFI at $10^8$ Pa (see Table 8.4), the adsorbates reoriented and also can change their internal configuration [57]. If the isotherms in Figure 8.11 would be extended to higher pressure, then e.g. 3-methylpentane would win over 22DMB. Jiang and Sandler studied the length and configurational effects in carbon nanotubes as a function of channel size [114]. In the smallest channel, only the linear alkane can adsorb, excluding all branched molecules. In slightly larger channels the adsorption order was neoC5 $>$ iC5 $>$ nC5 due to length entropy. But for even larger channels the order is $nC5 \geq iC5 > neoC5$.

Length entropy occurs when there is a difference in the saturation loading arising from the difference in the effective length of the molecules in the structure. It relies on molecules being restricted to adsorb only in certain configuration, and therefore a one-dimensional channel confinement is a requirement. Some typical
8.5 Entropic separation mechanisms

Examples of one-dimensional nanoporous materials that can accommodate linear and branched alkanes are AFI, FER, MAZ, MOR, and LTL. Schenk et al. computed thermodynamic properties ($\Delta G$, $\Delta H$, and $\Delta S$) for (branched) alkanes in many one-dimensional channel systems and showed that length entropy drives the isomerization reaction toward the effective most compact isomer [56]. These entropy (stacking) effects only occur at high loadings, in which adsorbate-adsorbate interactions are important. These authors provided a thermodynamic explanation for the high branched-paraffin yield in n-C16 hydroconversion. Adsorption entropy not only affects the activity, but also the selectivity of many zeolite-catalyzed conversions. Shape selectivity states that molecules will not (trans-)form if they are too bulky to fit inside a channel of a zeolite. Inverse shape selectivity was proposed by Santilli et al. [115] to explain the high yield of dibranched alkanes in AFI-type of zeolites, and states that those molecules form that have an optimal fit within the channels. Schenk et al. demonstrated that the molecular basis of inverse shape selectivity is related to entropic effects inside the zeolite pores under conditions where the zeolites are (almost) fully saturated [57].

8.5.4 Configurational entropy

Knowledge on branched alkanes in silicalite was limited in the 90’s, although a few experimental studies were published [116–119]. The peculiar isotherms shapes of especially branched alkanes in MFI were highlighted by Vlugt et al. [104] using simulations. This is mainly because in the range of experimentally accessible pressures the longer dibranched alkanes do not exceed the 4 molecules per unit cells. The simulations could cover a range up to very high pressures and unearthed the generic shape of the isotherms. These authors provided a molecular mechanism (using snapshots): the dibranched molecules sit in the intersections of MFI, and
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Figure 8.12: Configurational entropy of hexane isomers in MFI at 300K: (a) pure component isotherms (b) components loadings in a 5-component equimolar mixture as a function of loading.

It requires significant additional pressure to push them into the zig-zag and linear channels. It was soon realized that this entropy effect could be exploited to separate linear from mono-branched alkanes in the C5-C7 carbon range [64], and more generally to separate linear, mono-branched and di-branched molecules [97]. In a mixture, the branched molecules are ‘squeezed out’ from the silicalite and replaced by linear alkanes. This ‘squeezing out’ effect was found to be entropic in nature; the linear alkanes have a higher packing efficiency. This configurational effects was later studied in more detail [112, 120–122] and also experimentally verified.

The MFI zeolite is a 3D channel system with two types of channels: (i) linear channels and (ii) zig-zag channels, and (iii) intersections (see Figure 8.1b). The zig-zag channel is slightly wider than the linear channel; the zeolite atlas list the maximum diameter of a sphere that can diffuse through the zig-zag channel as 4.70 Å, and the diameter of the linear channel as 4.46 Å, respectively [123]. The linear, mono-branched, and di-branched molecules have very different interactions with each of the three types of adsorption sites. The channels of MFI are 10-rings, but can expand somewhat upon adsorption allowing more bulky molecules like di-branched alkanes and even aromatics to adsorb. However, a linear alkane is at the channel-site energetically and entropically favored over a mono-branched molecules and even more strongly favored over a di-branched molecule. Vlugt et al. confirmed the entropic origin by performing simulations using a hard-sphere model [97]. Figure 8.6a shows that the replacement of branched molecules by linear molecules is mostly due to entropy, but also (albeit much less) due to the energetics.

In Figure 8.12 we show the pure-component and 5-component equimolar mixture isotherm for hexane isomers in MFI. The inflections at 4 molecules per unit cell in the pure component isotherms are related to the amount of intersections (4 per unit cell). Below the inflection the adsorption sites for branched molecules are only the intersections. It takes significant pressure to ‘push’ them into the
Figure 8.13: Relation between enthalpy, configurational entropy and size entropy: 13-component equimolar mixture of C5-C7 isomers at 433K in MFI. In the enthalpic regime the molecules do not strongly interact. In the configurational entropy regime the linear molecules start to replace the mono- and di-branched and the mono-branched start to replace the dibranched alkanes. Inevitably, size-entropy prevails at very high pressures.

Note that the cross-over points are hard to determine because from the figure it is not immediately clear which species replaces another one. However, the nC5 has an inflection which is clearly caused by configurational entropy, and the start of the influence of size entropy is around the point where nC7 goes down (as this can not be caused by configurational entropy which favors linear molecules over linear and zig-zag channels. In a mixture, competition between the isomers drives first the di-branched molecules out with respect to the linear and mono-branched molecules. The behavior of the mono-branched molecules is right in between the linear and di-branched.

Even a mixture of C5/C6/C7 that differs in chain-length will at medium to high pressures be ordered according to degree of branching [99]. In Figure 8.13 we show a 13-component equimolar mixture of C5-C7 isomers. The molecule now differ in degree of branching and size, leading to three regimes:

1. The enthalpic regime where molecules hardly interact and the hierarchy is determined by the affinity of the molecules with the framework,

2. The configurational entropy regime where linear molecules replaces mono- and di-branched alkanes, and mono-branched alkanes replace dibranched alkanes (the hierarchy is determined by the degrees of branching),

3. The size entropy regime where the molecules with the smallest size wins (the hierarchy is determined by the size of the molecules).

Note that the cross-over points are hard to determine because from the figure it is not immediately clear which species replaces another one. However, the nC5 has an inflection which is clearly caused by configurational entropy, and the start of the influence of size entropy is around the point where nC7 goes down (as this can not be caused by configurational entropy which favors linear molecules over
branched species; instead this is because C5 is smaller than C7). In the limit of high pressure, size entropy will dominate. Also note, that because of the interplay between the three different effects, the loading of a molecule in the mixture can go up, then down, and then up again.

Configurational entropy is observed in 3D structures of channels with intersections. Figure 8.6a shows that for dibranched alkanes the forced relocation from the intersection site to the channel site results in an unfavorable entropy change. The linear hexane molecule shows the opposite, and its relocation results in a favorable entropy contribution. However, configurational entropy is generic in the sense that any structures with multiple sites that strongly differ in energetics and local topology/structure (i.e. the volume accessible to the adsorbate) could potentially be exploited for separations.

8.5.5 Commensurate Stacking

Ortho-xylenes in MIL-47 have a very efficient stacking arrangement [124–126]. They form two layers of molecules that are sandwiched between two walls. The arrangement was later coined ‘commensurate stacking’ by Krishna and van Baten [127]. They also noted a similar ‘bookshelf’ structure is afforded by Co(BDP), and predicted that this MOF could therefore have the potential for separation of C8 hydrocarbon mixtures. The Co(BDP) channel dimension of about 10 Å is close to the length of para-xylene, but larger than the length of ortho- and meta-xylene. Para-xylene could therefore potentially stand ‘upright’, like a book in a bookshelf, adsorbed at the wall and its methyl groups favorably interacting with both the ‘floor’ and the ‘ceiling’.

Figure 8.14a shows the concept of stacking of ortho- and para-xylene in a manner commensurate with the framework. A structure with 8.5 Å channels is commensurate with ortho-xylene. That structure would be ortho-xylene selective because para-xylene cannot be stacked “upright”. It would have to align obliquely, thereby increasing its effective size and hence have a lower saturation loading. For para-selective structures, we thus need a channel dimension of about 10 Å. Then, para-xylene is able to make use of all available pore-volume with both methyl-groups strongly interacting with the framework.

Torres-Knoop et al. realized the potential for commensurate stacking but formulated stronger geometric requirements [128]. Firstly, if nothing is anchoring the molecules at the wall, then the obtained configurations will be too disordered and not exhibit the desired ‘array of upright molecules’. Therefore a periodic anchoring along the channel direction commensurate with the ‘width’ of the xylene would be required. This anchoring should be just enough to hold the molecules in place, but not so strong to impede diffusion. Secondly, a cuboid channel allows xylene to adsorb at opposite walls, but in this arrangement the ‘ceiling’ and ‘floor’ are blocked at that channel position (only the rotated orientation can fit, but this means disorder and a larger channel-length occupation of the xylene). Since the empty space between the molecules would be wasted (and leads to too much disorder) it would be better to have a rectangular channel with the adsorbates
8.5 Entropic separation mechanisms

Figure 8.14: Schematic of “commensurate stacking” of xylenes in rectangular channels: (a) the molecule has to be of the right size, (b) an ideal para-xylene structure would form a double layer where the adsorbate is commensurate with the framework in all directions. The yellow arrows denote the characteristic length of the molecules, which have to be commensurate with the channel dimensions.

forming layers. An idealized stacking for para-xylene would schematically look like Figure 8.14b. For molecules with different dimensions (meta-, ortho-xylene, benzene and ethylbenzene) four effects occur:

- ‘Wider’ molecules (e.g. ortho-, and meta-xylene) will be able to stack less molecules per channel length.
- ‘Longer’ molecules (e.g. ethylbenzene) have to align obliquely and therefore also stack less molecules per channel.
- ‘Shorter’ molecules (e.g. ortho-, and meta-xylene) will have a less optimal interactions with the pore structure.
- More bulky and non-flat molecules (e.g. ethylbenzene) are unable to form commensurate layers and will therefore have a lower saturation loading. That is, commensurate stacking also provides a mechanism to separate flat from not-flat molecules. MIL-47 is particularly effective at separating styrene from ethylbenzene [129].

8.5.6 Orientational entropy (“pringling”)

Aromatics have a particular shape; their height is much smaller than their respective length and width. Torres-Knoop et al. exploited the flatness by selecting channels of such size that one of the isomers is able to change its orientation perpendicular to the channel [130]. The other isomers remain mostly parallel to the channel and occupy more channel space per channel length. The selected component that is able to re-orient at high loading has a significantly higher saturation
capacity than its isomers. The packing of this component is very reminiscent of
the configuration of chips in the “pringles” snack.

The concept is explained in Figure 8.15. As long as one can avoid that molecules
can pack side-by-side in the channel (as would occur in rectangular channels)
the effective channel occupancy can be significantly reduced by reorienting the
adsorbate. To use pringling for separations, ideally only one of the isomers must
be able to reorient. Aromatics pack particular well, because there rigidity prevents
internal configuration changes (as happens with flexible alkanes in length entropy).
Ellipsoid or diamond-shaped channels could potentially be para-xylene selective.

8.5.7 Discussion entropic separation mechanisms

It is in principle always possible to separate molecules that differ in size using
“size entropy”. The principle does not dependent on the difference in adsorption
energetics, but on the crossover point where entropy wins. Since experimental
equipment and industrial setups are limited in pressure, the size entropy effect
might not always be usable in practice for molecules that differ too much in size (and hence the adsorption affinity which has to be overcome).

The other entropy effects can be applied to isomers, which have usually similar adsorption affinity with the framework, but also to mixtures that differ in molecular size. The ranges to which the size can vary depend on the particular system and on the affinity of the molecules with the framework. Commensurate stacking is the most sensitive entropic effect to the low loading part, since the saturation loadings of the isomers can be the same for some of the components. It is both an enthalpic and entropic mechanism.

In nanoporous materials, the entropy is related to the amount of molecules adsorbed. The larger the amount of molecules, the larger the entropy contribution. This means that, at high pressures, the adsorption selectivity will favour the mixture component with the highest saturation capacity. In this sense, all discussed entropy effects share one important feature: the effective smallest one wins at high pressure because it can obtain the highest saturation capacity. Therefore, all the above mentioned entropy effects are derived from size entropy. They differ on what size means and the details of how size reduction is achieved. In size entropy, the effective smallest literally refers to the smallest component in the mixture (lower number of atoms). For length entropy, the effective smallest is the mixture component which projected length (footprint) is the smallest. For orientational entropy, the effective smallest is the component that can reorient and upon reorientation has the smallest projected length. In commensurate stacking, the effective smallest is the component that inside the structure can be “packed” in the most compact way. In configurational entropy, the difference in saturation capacities arises from the difference in “accessibility” of the mixture components to the adsorption sites. The accessibility per site is determined by a “size entropy” effect per site. If the pressure is high enough, all entropy effects reduce to size entropy and the smallest molecules are preferentially adsorbed. In order to exploit entropy effects it is therefore important not only to known in which type of systems they occur, but also in which range of pressures/loadings.

8.6 Conclusions

This review highlights the potential of adopting separating strategies that rely on the differences in effective molecular size, rather than adsorption affinity. Size entropy is not readily extendable to large pore structures because the pressure needed to reach pore saturation can be high in e.g. MOFs. Pore saturation is needed for a smaller component to win entropically and overcome the enthalpic penalty due to a lower affinity with the framework. Length and configurational entropy are linked to small pore frameworks such as 8-, 10-, or 12-ring channel zeolites. Because the effect is due to confinement (by the framework) it is difficult to extend to more open pores. Commensurate stacking and the orientational entropy mechanism are also due to confinement, but by the framework and by other adsorbates. Hence, these mechanisms are able to operate at saturation conditions.
in systems with very open pores (large capacity) while still achieving high selectivities. All the mentioned entropy effects are derived from size entropy. In all off them, the effective smallest mixture component wins at saturation conditions. The difference between the effects is how this size reduction is achieved. Large pore volumes of MOFs for industrial separation applications are primarily suitable for separating large molecules.

Simulations Methodology

The adsorption computations of single and multi-components are usually performed in the grand-canonical ensemble [131, 132]. Reference [133] reviews state-of-art adsorption simulation methodologies. The presented adsorbent/adorbate systems can nowadays accurately be modeled in full atomistic detail using calibrated classical force fields. Common force field include TraPPE [134] and OPLS [135] for adsorbates like alkanes and xylenes, respectively; and TraPPE-Zeo [136] and DREIDING [137], UFF [138] for the modeling of zeolites and metal-organic frameworks, respectively. Using the dual-site Langmuir-Freundlich fits of the pure component isotherms, breakthrough calculations can be carried out by solving a set of partial differential equations for each of the species in the gas mixture [139]. The molar loadings of the species at any position along the packed bed and at any time are determined from Ideal Adsorbed Solution Theory calculations.

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References


Chapter 8. Exploiting Large-Pore Metal-Organic Frameworks for Separations using Entropic Molecular Mechanisms


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