A molecular dynamics study on light olefin diffusion in ZIF-8

Bernd Schmidt, Louis Vanduyfhuys, Veronique Van Speybroeck
[a] *Center for Molecular Modeling, Ghent University, Technologiepark 46, 9052 Zwijnaarde, Belgium*

In context of the current energy crisis, improving the efficiency of highly energy-consuming processes is more relevant than ever. One of the most energy-intensive chemical processes is the separation of alkanes and alkenes, which accounts for 0.3% of the world's energy consumption[1]. The most common way to separate alkanes and alkenes is via cryogenic distillation. However, a significant improvement in energy retention could be achieved by applying room temperature sieving of the molecules. For this purpose, membranes composed of nanoporous crystalline materials such as zeolitic imidazolate frameworks (ZIFs) are being investigated for their high selectivity in separation of ethane from ethene (C2) and propane from propene (C3) species at room temperature[2,3].

In this work, the impact of diffusion on the C2/C3 separation behavior in ZIF-8 is investigated by means of molecular simulations. To this end, molecular dynamics (MD) simulations are performed with flexible force fields derived using QuickFF[4,5] augmented with MM3 non-bonding contributions[6]. The diffusion process of C2/C3 species through ZIF-8 is modeled using umbrella sampling (US), an enhanced MD technique in which a series of bias potentials, harmonic in the collective variable (CV), are centered at subsequent positions along the diffusion path to restrict the guest molecule to a given interval of the CV. This results in an effective way to sample all relevant parts of phase space, construct the free energy profile (FEP) of diffusion using the Weighted Histogram Analysis Method[7], extract diffusion coefficients and investigate the diffusion mechanism.

The FEP can be deconvoluted into enthalpic and entropic contributions, as seen in figure 1. The enthalpic contribution can be further deconvoluted into covalent (host deformation due to gate opening, see further) and non-bonding (guest-host interaction) energies. As such, it is found that the transition state at CV = 0 Å corresponds with a maximum in enthalpy and entropy. Entropy is a difficult property to calculate but can be achieved through the FEP. Furthermore, by using a deprojection method on the 1D FEP as implemented in ThermoLIB[8], we could also construct the 2D FES in terms of the gate aperture and the original CV and quantify the gate opening magnitude as well as the required energy (see figure 1b). This advanced insight, both from the energy deconvolution into enthalpy and entropy and from the gate size can be used to find or engineer new host systems with high efficiency in C2/C3 species separation.

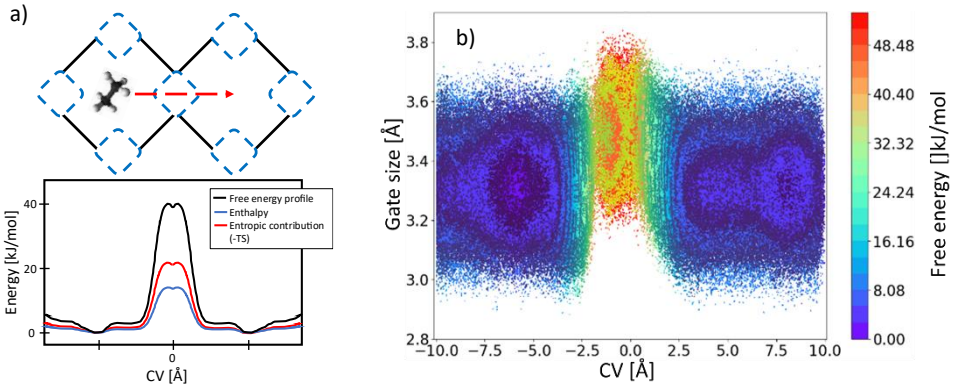

Figure 1: (a) Schematic view of an ethane molecule diffusing in a host molecule coupled with a schematic free energy profile and a sketch of the enthalpic and entropic contribution to the free energy profile. (b) 2D plot of the calculated gate sizes, colored in with the respective free energy of the system, against the CV, or position of the diffusing species in respect to the gate.

1. Stephenson, A. *et al. J. Mater. Chem. A* **7**, 25521–25525 (2019).
2. Bux, H., Chmelik, C., Krishna, R. & Caro, J. *J. Membr. Sci.* **369**, 284–289 (2011).
3. Pan, Y., Li, T., Lestari, G. & Lai, Z. *J. Membr. Sci.* **390–391**, 93–98 (2012).
4. Vanduyfhuys, L. *et al. J. Comput. Chem.* **36**, 1015–1027 (2015).
5. Vanduyfhuys, L. *et al. J. Comput. Chem.* **39**, 999–1011 (2018).
6. Allinger, N. L., Yuh, Y. H. & Lii, J. H. 1. *J. Am. Chem. Soc.* **111**, 8551–8566 (1989).
7. Ferrenberg, A. M. & Swendsen, R. H. *Comput. Phys.* **3**, 101–104 (1989).
7. ThermoLIB, https://molmod.ugent.be/software/thermolib.