1st Fickian Law to predict gas selectivity of a nanoporous membrane

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The separation of short chain olefin/paraffin pairs like ethylene/ethane and propylene/propane is a hot topic in chemical industry. The common technology is cryogenic distillation, but adsorption and especially membrane permeation processes would be much more energy-efficient. However, the existing polymers do not allow the fabrication of powerful membranes for the olefin/paraffin separation.

Since the olefin molecules ethylene and propylene are slightly smaller than the corresponding paraffins, molecular sieve membranes with a pore size exact between the olefin and paraffin molecules could be applied. At first sight, MOFs are the disruptive material that could allow the construction of such molecular sieve membranes. However, MOFs show the effect of framework flexibility with no sharp molecular sieving effect. Therefore, theoretical calculations predicting the membrane selectivity turned out as difficult.

The poster will discuss the applicability of the 1st Fickian Law to predict gas separation through a MOF membrane based on independent experimental data. The flux density of component A is described by

$$j_A = -D_{TA}\,\frac{\partial c}{\partial x} \qquad (1)$$

with j_A as the flux density in mol of A per time and area, D_{TA} is the transport diffusivity of A, and $\partial c/\partial x$ is the concentration gradient of component A across the membrane. As a rough estimate, we substitute the concentration gradient for the concentration difference over the membrane divided by the thickness of the membrane. Further, due to the presence of vacuum or a sweep gas on the permeate side of the membrane, the concentration of A at the desorption side of the membrane is considered zero.

Thus, the selectivity of the membrane is the ratio of the fluxes A and B acc. to (1),

$$\alpha_{A,B} = \frac{j_A}{j_B} = \frac{D_{TA}}{D_{TB}}\frac{c_A}{c_B} \qquad (2)$$

To predict the selectivity of a membrane, we need independent data for the transport diffusivities D_{TA} and D_{TB} as well as adsorption data c_A and c_B. Infrared microscopy is an excellent novel method to determine transport diffusivities [1]. The following table shows that the MOF membrane of structure type ZIF-8 should be very promising in propylene/propane separation but not suitable for the ethylene/ethane separation. Experimental permeation studies at room temperature on supported ZIF-8 membranes have exactly found this prediction.

	Ethylene	**Ethane**	**Propylene**	**Propane**
D_T from ref. [2] in m^2/s c at 1 bar in mmol/g	$4\cdot10^{-11}$ 1.5 from [3]	$1\cdot10^{-11}$ 2.3 from [3]	$2\cdot10^{-13}$ 4.2 from [4]	$4\cdot10^{-16}$ 4.5 from [4]
Predicted selectivity acc. (2)	2.6		470	
Measured selectivity	2.4 from [5]		> 200 from [6]	

References

[1] J. Kärger, T. Binder, C. Chmelik, et al.: *Microimaging of transient guest profiles to monitor mass transfer in nanoporous materials*. Nature Mater. **13**, 333–343 (2014). https://doi.org/10.1038/nmat3917

[2] C. Chmelik, J. Kärger: *The predictive power of classical transition state theory revealed in diffusion studies with MOF ZIF-8*. Micropor. Mesopor. Mater. **225**, 128–132 (2016). https://doi.org/10.1016/j.micro meso.2015.11.051

[3] P. Krokidas, M. Castier, I.G. Economou: *Computational study of ZIF-8 and ZIF-67 performance for separation of gas mixtures*. J. Phys. Chem. C **121**, 17999–18011 (2017). https://doi.org/10.1021/acs.jpcc.7b05700

[4] D. Liu, X. Maa, H. Xi, Y.S. Lin: *Gas transport properties and propylene/propane separation characteristics of ZIF-8 membranes*. J. Membr. Sci. **451**, 85-93 (2014). https://doi.org/10.1016/j.memsci.2013.09.029

[5] H. Bux, C. Chmelik, R. Krishna, J. Caro: *Ethene/ethane separation by the MOF membrane ZIF-8: Molecular correlation of permeation, adsorption, diffusion*. J. Membr. Sci. **369,** 284-289 (2011). https://doi.org/10.1016/j.memsci.2010.12.001

[6] S. Park, K.Y. Chob, H.K. Jeong: *Enhancing the propylene/propane separation performances of ZIF-8 membranes by postsynthetic surface polymerization*. J. Mater. Chem. A, in press (2022). https://doi.org/10.1039/D1TA09096H