

Supporting Information

Molecular Simulation Investigation into the Performance of Cu-BTC Metal Organic Frameworks for Carbon Dioxide-Methane Separations

*Juan José Gutiérrez-Sevillano¹, Alejandro Caro-Pérez¹, David Dubbeldam², and
Sofía Calero^{1*}*

¹Department of Physical, Chemical, and Natural Systems. University Pablo de Olavide.
Ctra. Utrera km. 1. 41013 Seville, Spain.

²University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV, Amsterdam, The
Netherlands.

* E-mail: scalero@upo.es

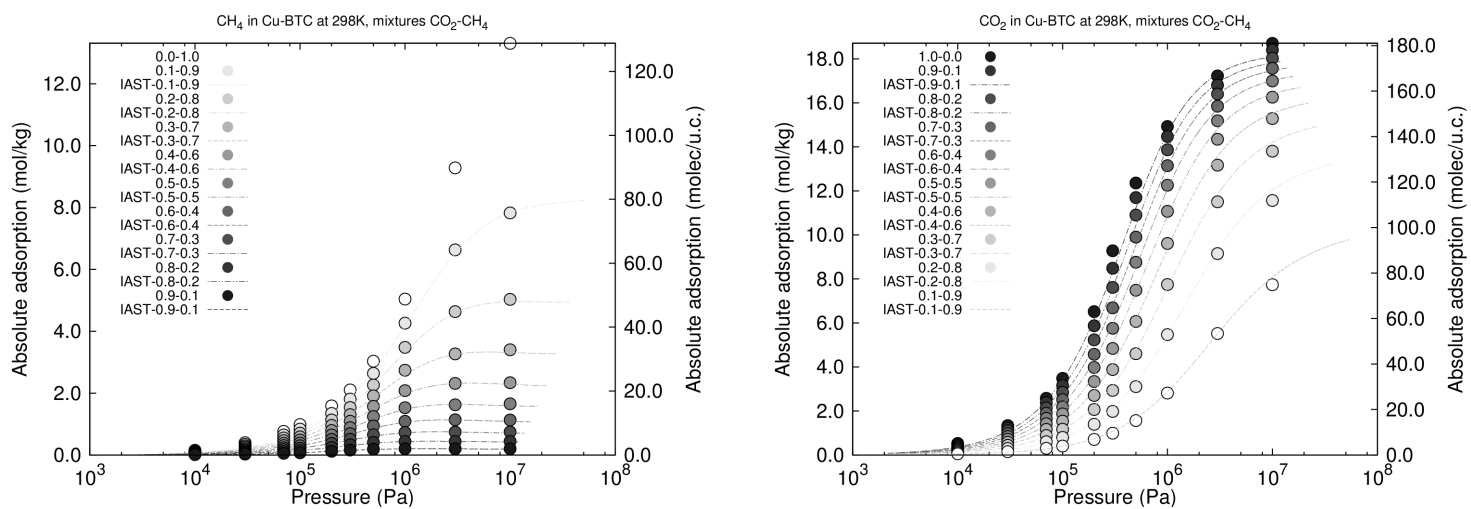


Figure 1S: Adsorption isotherms of methane (left) and carbon dioxide (right) obtained from GCMC (symbols) and from IAST (curves) for the different mixtures.

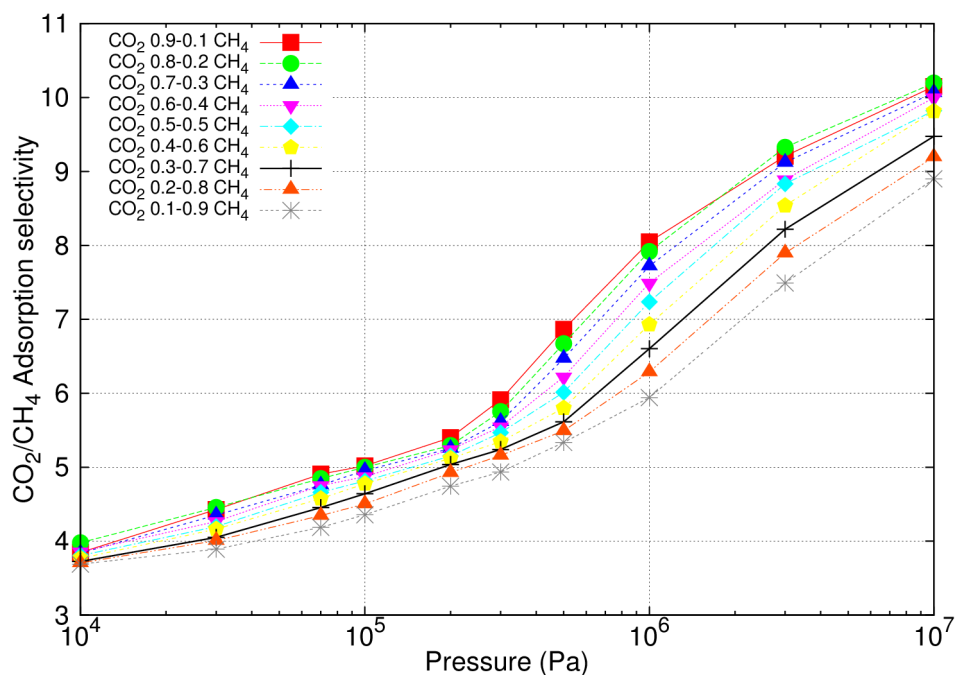


Figure 2S: Adsorption selectivity for the different mixtures of carbon dioxide and methane obtained from GCMC (symbols) and from IAST (curves).

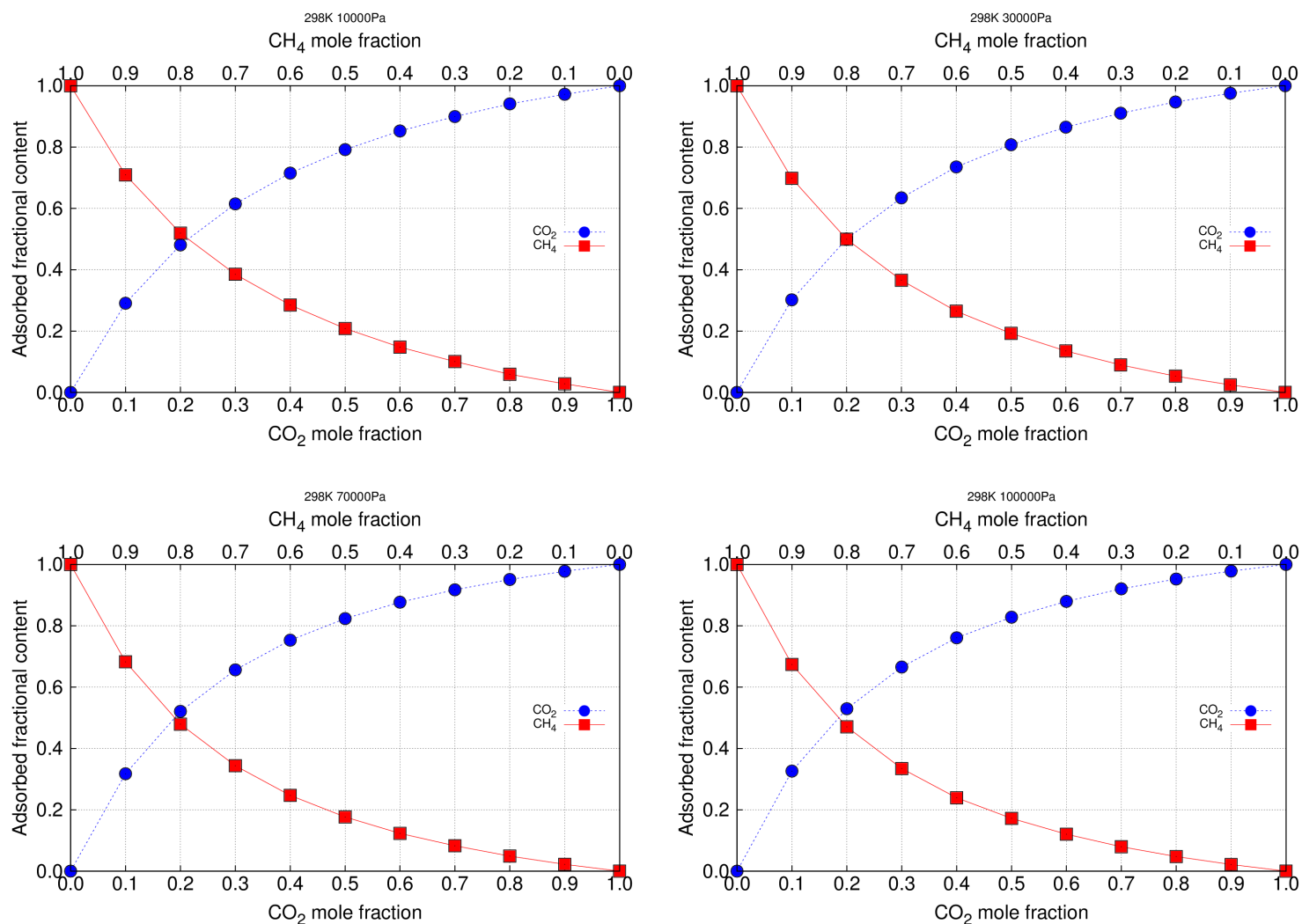


Figure 3S. Adsorbed fractional content of molecule against the same fraction in the external gas phase computed at 298 K and 10E4 Pa (top left), 3x10E4 Pa (top right), 7x10E4 Pa (bottom left), and 10E5Pa (bottom right)

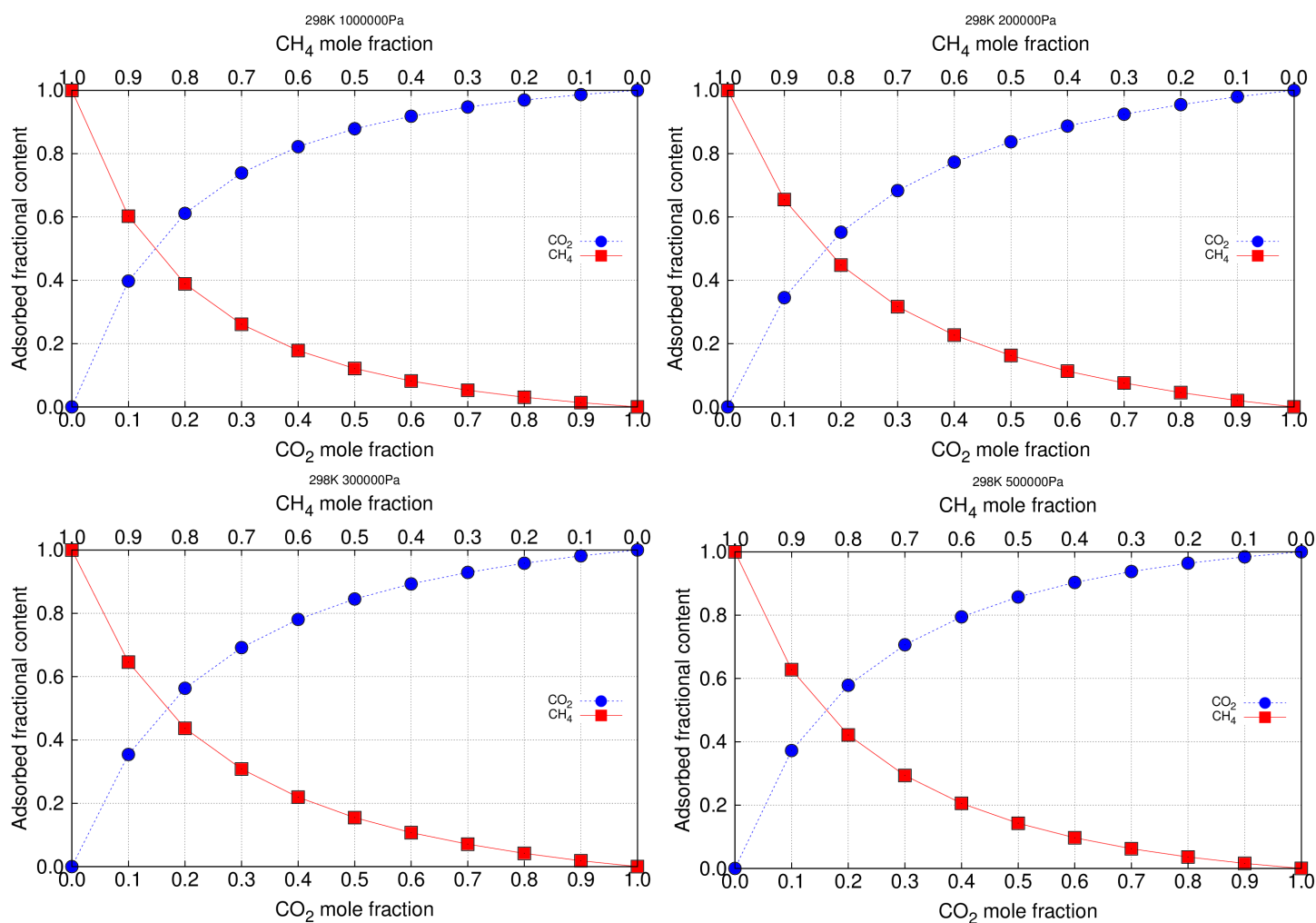


Figure 4S. Adsorbed fractional content of molecule against the same fraction in the external gas phase computed at 298 K and 2x10⁵ Pa (top left), 3x10⁵ Pa (top right), 5x10⁵ Pa (bottom left), and 10x10⁵ Pa (bottom right)

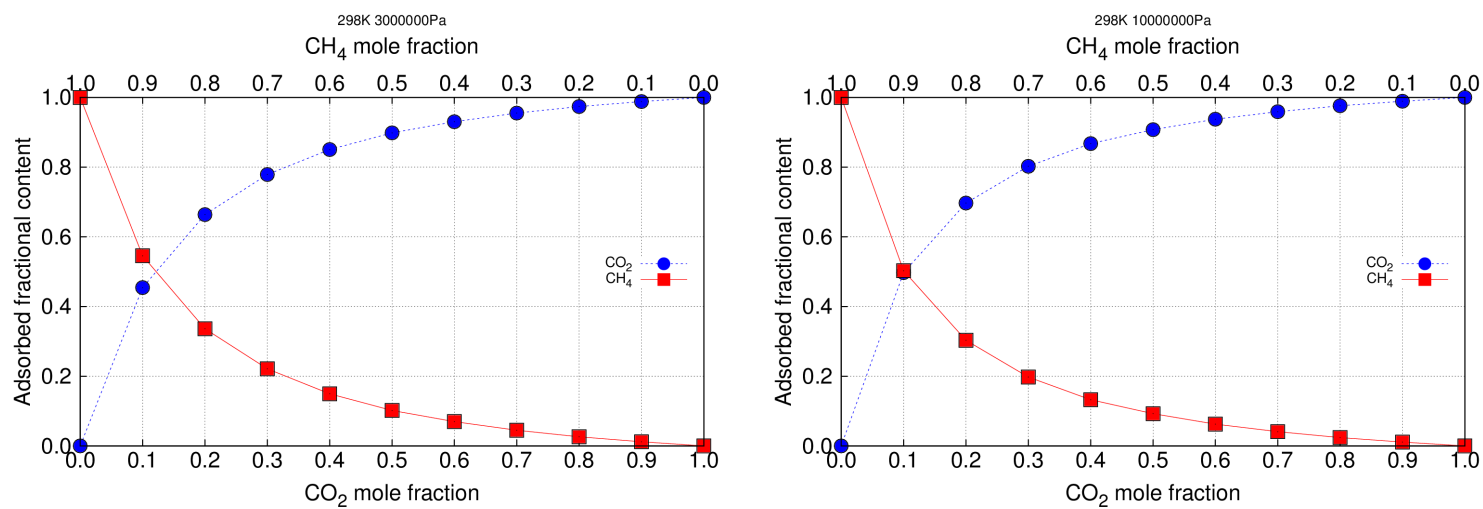


Figure 5S. Adsorbed fractional content of molecule against the same fraction in the external gas phase computed at 298 K and 3x10E6 Pa (left) and 10E7Pa (right)

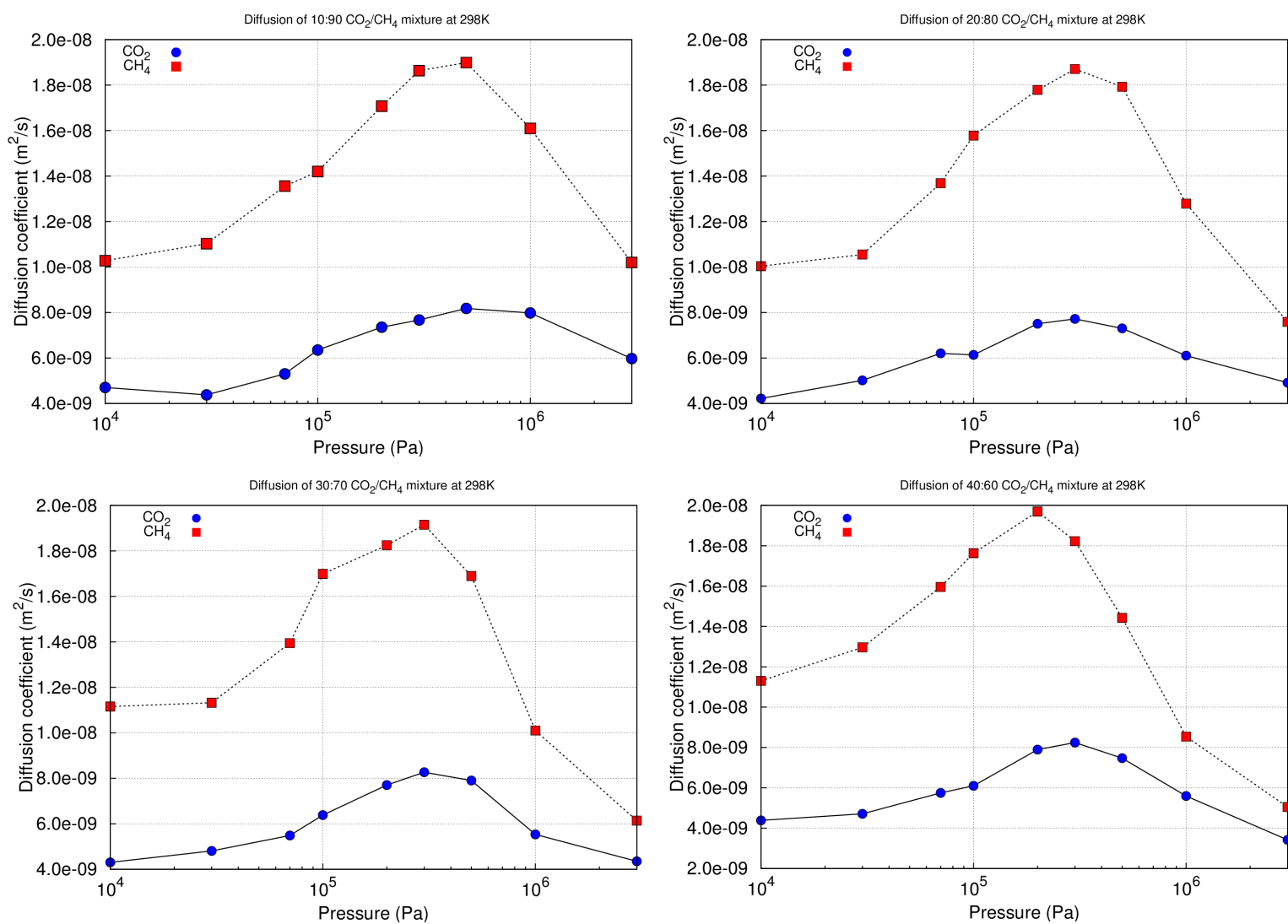


Figure 6S. Diffusion coefficients computed as a function of pressure in Cu-BTC for the 10:90 mixture of carbon dioxide and methane (top left), 20:80 mixture of carbon dioxide and methane (top right), 30:70 mixture of carbon dioxide and methane (bottom left), and 40:60 mixture of carbon dioxide and methane (bottom right).

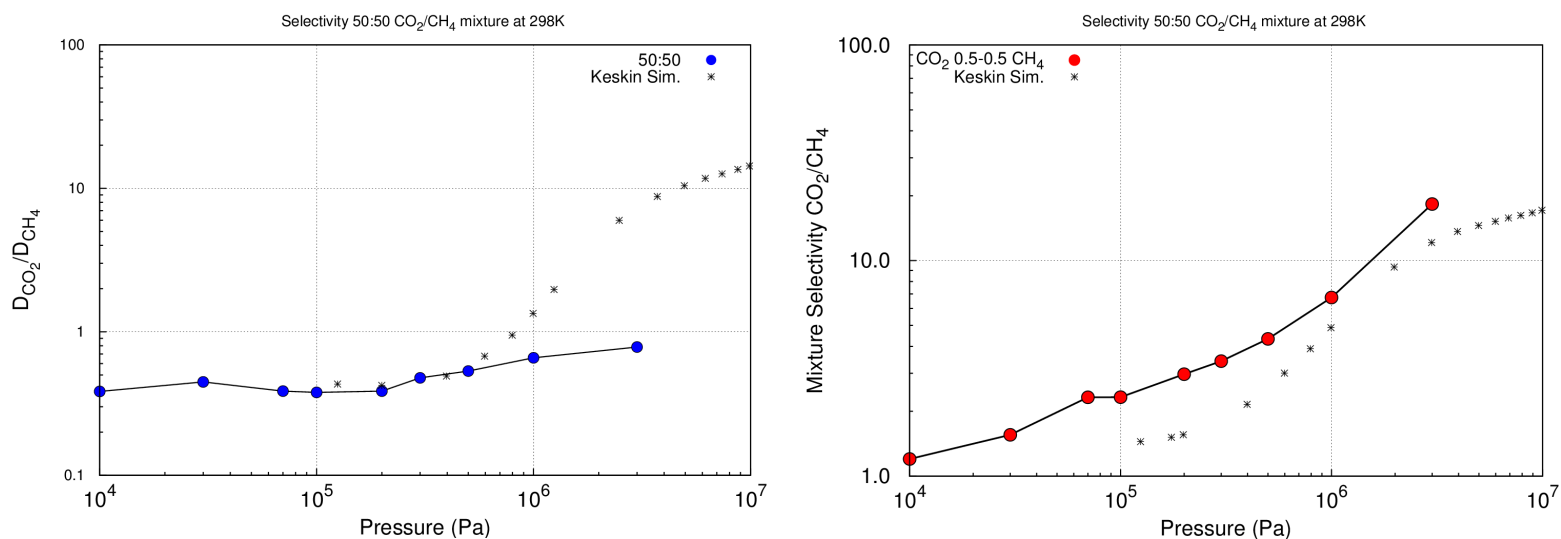


Figure 7S. Comparison between Diffusion selectivity (left) and Mixture selectivity (right) of this work and previous Keskin et al. results.¹

Ideal Adsorption Solution Theory

The (IAST) is analogous to Raoult's law for vapour-liquid equilibrium, i.e:

$$P_i = P_i^0(\pi_i)x_i$$

Where x_i and π_i are the molar fraction and spreading pressure of component i in the adsorbed phase, respectively. At the adsorption equilibrium, the reduced spreading pressures must be the same for each component and the mixture:

$$\pi_i^* = \frac{\pi_i}{RT} = \int_0^{P_i^0} \frac{n_i^0(P)}{P} dP \quad i = 1, 2, 3, \dots, N$$

$$\pi_1^* = \pi_2^* = \dots = \pi_N^* = \pi^*$$

The function $n_i^0(P)$ is the pure component equilibrium capacity and P_i^0 is the pure component hypothetical pressure which yields the same spreading pressure as that of the mixture.

By assuming ideal mixing at constant π and T , the total amount adsorbed, n_t , is:

$$\frac{1}{n_t} = \sum_{i=1}^N \left[\frac{x_i}{n_i^0(P_i^0)} \right]$$

With the constraint:

$$\sum_{i=1}^N x_i = 1$$

Since the equations are nonlinear and the integrals of π_i^* cannot be solved analytically for most of the pure component isotherm equations, the classical IAST needs iterative integration processes.

(1) Keskin, S.; Liu, J. C.; Johnson, J. K.; Sholl, D. S. *Microporous and Mesoporous Materials* **2009**, *125*, 101.