

Supporting Information for:
Evaluating mixture adsorption models using molecular
simulation

Joseph A. Swisher, Li-Chiang Lin, Jihan Kim, Berend Smit

Dept. of Chemical and Biomolecular Engineering
University of California, Berkeley, CA 94720

Materials Sciences Division
Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Parameters for the dual-site Langmuir model

Tables S1-S4 give parameters for the dual-site Langmuir isotherm for the pure components adsorbing in the materials considered in this study. All fitting was performed with the R statistical package [1].

Table S1: Dual-site Langmuir isotherm parameters for PCOD8286959.

	b_1 Pa^{-1}	m_1 $mol\ kg^{-1}$	b_2 Pa^{-1}	m_2 $mol\ kg^{-1}$
CO ₂	5.439×10^{-3}	0.4229	5.342×10^{-7}	8.811
N ₂	3.894×10^{-7}	0.4229	4.548×10^{-8}	7.298

Table S2: Dual-site Langmuir isotherm parameters for PCOD8200029.

	b_1 Pa^{-1}	m_1 $mol\ kg^{-1}$	b_2 Pa^{-1}	m_2 $mol\ kg^{-1}$
CO ₂	4.924×10^{-4}	1.510	5.226×10^{-7}	0.7354
N ₂	3.837×10^{-7}	1.510	9.083×10^{-8}	0.7564

Table S3: Dual-site Langmuir isotherm parameters for MOR.

	b_1 Pa^{-1}	m_1 $mol\ kg^{-1}$	b_2 Pa^{-1}	m_2 $mol\ kg^{-1}$
CO ₂	4.490×10^{-4}	4.165	1.203×10^{-6}	13.39
C ₃ H ₈	3.322×10^{-4}	3.005	1.603×10^{-8}	4.993

Table S4: Dual-site Langmuir isotherm parameters for NaX.

	b_1 Pa^{-1}	m_1 $mol\ kg^{-1}$	b_2 Pa^{-1}	m_2 $mol\ kg^{-1}$
CO ₂	2.576×10^{-4}	4.687	8.122×10^{-7}	1.994
N ₂	2.827×10^{-7}	4.687	5.468×10^{-9}	3.055

Force field for N₂ in aluminosilicate zeolites

The Lennard-Jones epsilon parameters for N₂ interacting in sodium-containing aluminosilicate zeolites was scaled from the parameters of the interaction between the carbon of CO₂ and zeolite sodium and oxygen atoms taken from the force field of García-Sánchez et al. [2]. The scaling was performed by taking the ratio of polarizabilities for atomic carbon and nitrogen. N₂-N₂ interactions and partial atomic charges were taken from the force field of García-Pérez et al. [3]. Sigmas were computed using Lorentz-Berthelot mixing rules with Na⁺ and zeolite oxygen parameters from Calero et al. [4] and Talu and Myers [5]. The resulting predictions of this model compare well with recent experimental data (see Fig. S1).

Table S5: Lennard-Jones parameters for sodium and zeolite oxygen interactions with the atoms of N₂ molecules.

Interaction	σ Å	ϵ/k_B K
O _{zeolite} -N	3.062	28.23
Na ⁺ -N	2.74	291.6

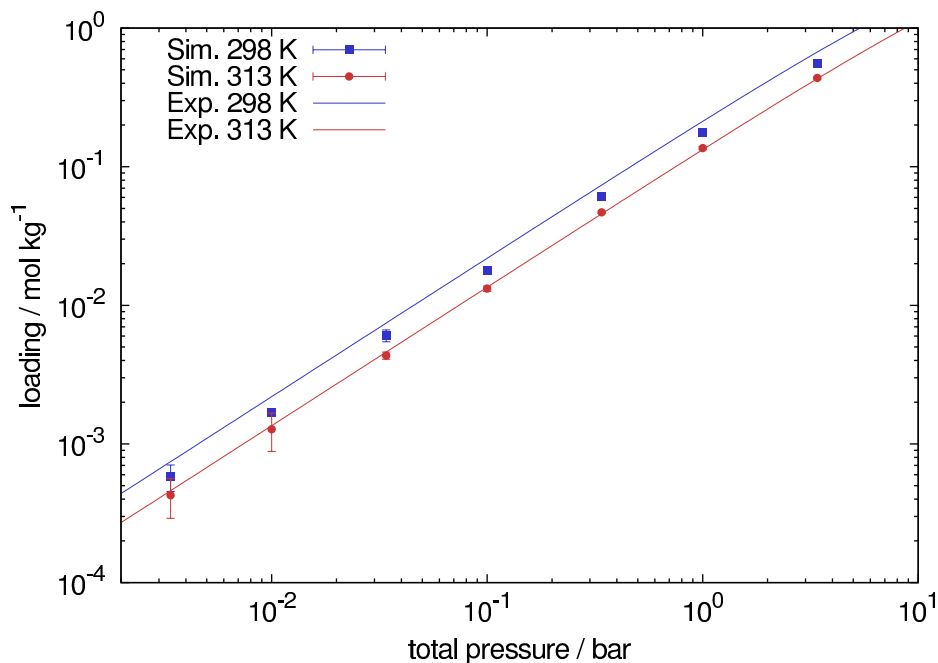


Figure S1: Comparison of GCMC-predicted and experimental isotherms for N₂ adsorption in NaX using the force field in S5. Experimental data are the single-site Langmuir fits reported in Bae et al.[6]

Competitive isotherm models

When considering thousands of materials simultaneously, it is advantageous to have computationally the simplest model possible. In previous work on screening zeolites for carbon capture, competitive Langmuir isotherms were used, owing to the ease of computing the isotherm parameters using infinite dilution simulations [7]. Figure S2 compares the use of the segregated IAST model with the competitive DPL model for predicting the adsorption of a CO_2 and N_2 mixture in PCOD8286959 and PCOD8200029 (the segregated IAST data is reproduced from Figures 2 B and 4 B). In both materials there is excellent agreement among both models and the GCMC results. Only at the highest fugacities considered does the DPL [8] model differ significantly from the segregated IAST model. Due to the form of the model, competitive isotherms will always exhibit a constant loading for each component as fugacity continues to increase. This effect is most clearly seen in Figure 6 B, as discussed above. The most important aspects of this approach is not that the competition is modeled by integrating Equation 10, but the fact that each component is modeled as accessing all sites available to it and sites that correspond to the a fixed small volume have identical saturation loadings since this value is determined by the structure of the material.

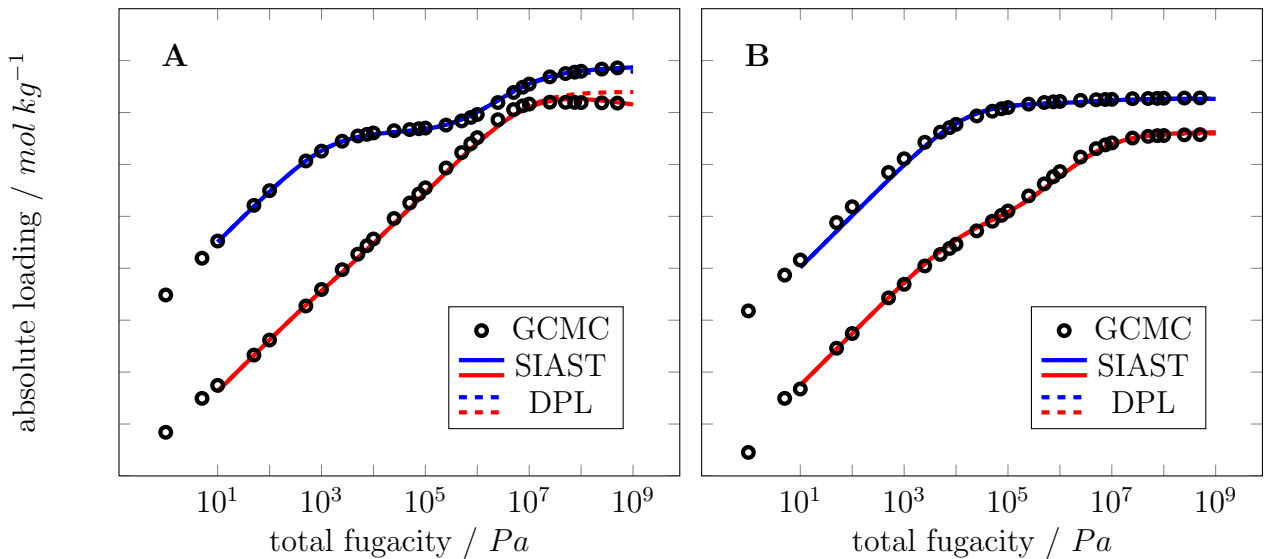


Figure S2: Comparison of GCMC, segregated IAST, and dual-process Langmuir model predictions of mixture isotherms for a 14% CO_2 (blue), 86% N_2 mixture at 300 K in (A) PCOD8286959 and (B) PCOD8200029. Symbols are GCMC results, solid lines represent the segregated IAST model, and the dashed line represents the DPL model.

Literature Cited

- [1] R Development Core Team. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria. 2011. ISBN 3-900051-07-0. URL <http://www.R-project.org/>
- [2] García-Sánchez A, Ania CO, Parra JB, Dubbeldam D, Vlugt TJH, Krishna R, Calero S. Transferable Force Field for Carbon Dioxide Adsorption in Zeolites. *J Phys Chem C*. 2009;113:8814–8820.
- [3] García-Pérez E, Parra J, Ania C, García-Sánchez A, van Baten J, Krishna R, Dubbeldam D, Calero S. A computational study of CO₂, N₂, and CH₄ adsorption in zeolites. *Adsorption*. 2007;13:469–476.
- [4] Calero S, Dubbeldam D, Krishna R, Smit B, Vlugt TJH, Denayer JFM, Martens JA, Maesen TLM. Understanding the Role of Sodium during Adsorption: A Force Field for Alkanes in Sodium-Exchanged Faujasites. *J Am Chem Soc*. 2004;126:11377–11386.
- [5] Talu O, Myers AL. Molecular simulation of adsorption: Gibbs dividing surface and comparison with experiment. *AIChE Journal*. 2001;47:1160–1168.
- [6] Bae TH, Hudson MR, Mason JA, Queen WL, Dutton JJ, Sumida K, Micklash KJ, Kaye SS, Brown CM, Long JR. Evaluation of Cation-Exchanged Zeolite Adsorbents for Post-Combustion Carbon Dioxide Capture. *Energy Environ Sci*. 2012;5:in press.
- [7] Lin LC, Berger AH, Martin RL, Kim J, Swisher JA, Jariwala K, Rycroft CH, Bhowm AS, Deem MW, Haranczyk M, Smit B. In silico screening of carbon-capture materials. *Nat Mater*. 2012;11:633–641.
- [8] Ritter JA, Bhadra SJ, Ebner AD. On the Use of the Dual-Process Langmuir Model for Correlating Unary Equilibria and Predicting Mixed-Gas Adsorption Equilibria. *Langmuir*. 2011;27:4700–4712.