Supporting Information

Enhancing Gas Solubility in Nanopores: A Combined Study using Classical Density Functional Theory and Machine Learning

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Bulk density computational details:

The MBWR EOS takes the form:

$$F_{LJ}^{ex} = N\varepsilon_x \left(\sum_{k=1}^{8} a_k \rho^{*k} + \sum_{k=1}^{6} b_k G_k \right), \tag{1}$$

where F_{LJ}^{ex} is the excess free energy of the LJ system and $\rho^* = \rho \sigma_x^3$, $\sigma_x^3 = \sum_i \sum_j X_i X_j \sigma_{ij}^3$,

$\varepsilon_x = \dfrac{1}{\sigma_x^3} \sum_i \sum_j X_i X_j \varepsilon_{ij} \sigma_{ij}^3$. The detailed expression of a_k, b_k, G_k can be found in the original

paper[1]. The chemical potential of $i-$th component consist of two parts, i.e., the ideal part and

the excess part:

$$\mu_i = \mu_i^{id} + \mu_i^{ex}, \tag{2}$$

where $\mu_i^{id} = k_B T \ln \rho_i \Lambda_i^3$ is the ideal chemical potential of $i-$th component, the excess part reads:

$$\mu_i^{ex} = \frac{dF_{LJ}^{ex}}{d\rho_i}. \tag{3}$$

After liquid and gas system reach phase equilibrium, the chemical potential of $i-$th

component should simultaneously equal to its counterparts in gas phase:

$$\mu_i^L = \mu_i^G. \tag{4}$$

The MBWR EOS also gives the relationship between the pressure and the density:

$$P^* = \rho^* T^* + \sum_{k=1}^{8} a_k \rho^{*(k+1)} + F \sum_{k=1}^{6} b_k \rho^{*(2k+1)}, \tag{5}$$

where $P^* = P\sigma_x^3 / \varepsilon_x$, $F = \exp(-\gamma \rho^{*2})$, $\gamma = 3$.

In our calculation, an iterative algorithm was adopted. We first set the initial guess of mole

fraction of solvent in liquid and gas phase as x_1 and y_1. The density of solvent and solute could

be obtained by Eq.(5) under a specific thermodynamic condition. By combining Eq.(1) and

Eq.(3), we can get the chemical potential of solvent and solute in both liquid and gas phase, i.e. $\mu_1^L, \mu_2^L, \mu_1^G, \mu_2^G$. The differential equation of Eq. (3) is solved by difference method. If one of the values $\left|(\mu_1^L - \mu_1^G)/\mu_1^L\right|$ and $\left|(\mu_2^L - \mu_2^G)/\mu_2^L\right|$ is larger than the threshold, i.e., 10^{-4}, then change the mole fraction until the iteration approach convergence.
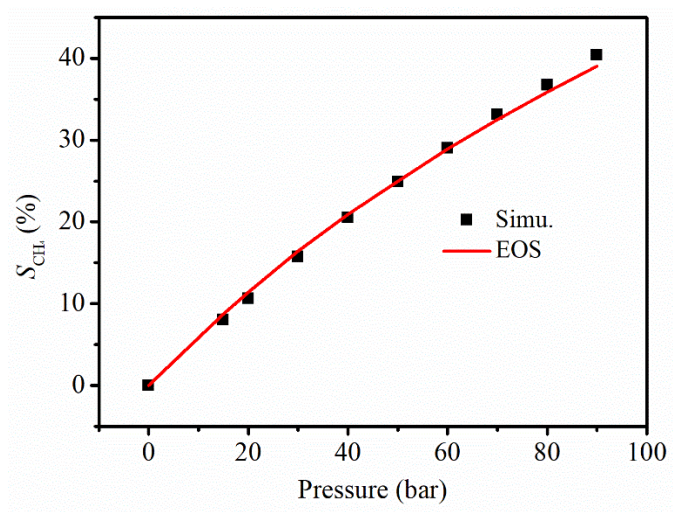

Figure S1. Bulk solubility of methane in benzene at 323 K. Symbols are simulation results, while solid line presents MBWR prediction.

Figure S1 presents the predicted solubility of methane in bulk benzene. The MBWR prediction (red solid line) agrees well with the simulation results[2] (black squares), demonstrating that the MBWR calculation on bulk solubility is highly reliable.

References:

1. Johnson, J. K., Zollweg, J. A. & Gubbins, K. E. The Lennard-Jones equation of state revisited. *Molecular Physics*, **1993,** 78 (3), 591-618.

2. Hu, Y., Huang, L., Zhao, S., Liu, H. & Gubbins, K. E. Effect of confinement in nano-porous materials on the solubility of a supercritical gas. *Molecular Physics*, **2016,** 114 (22), 3294-3306.