Supplementary Material for PCCP

Supplementary Information for:

The Osmotic Framework Adsorbed Solution Theory: Predicting Mixture Coadsorption in Flexible Nanoporous Materials

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A. Resolution of the IAST equations in the low-pressure limit

The main IAST equation describing the coadsorption of two fluids for which pure-component adsorption follows Langmuir isotherms is Eq. 17. Although it is analytical, its solution has no expression in closed form. In the low-pressure limit, however, it is possible to obtain an analytical solution to this equation as a power series in P. We derive here the expressions of the selectivity, α, and the total quantity of adsorbed fluids, N_{tot}, in the low-pressure limit to the second order in P.

Eq. 17 can be rewritten in a more symmetric form:

$$N_{\text{B}} \ln\left(1 + \frac{K_{\text{B}}}{N_{\text{B}}} \times P_{\text{B}}^*\right) = N_{\text{C}} \ln\left(1 + \frac{K_{\text{C}}}{N_{\text{C}}} \times \frac{P(1-y_{\text{B}})P_{\text{B}}^*}{P_{\text{B}}^* - P y_{\text{B}}}\right) \tag{S1}$$

We develop P_{B}^* as a power series in P, $P_{\text{B}}^* = \sum_i a_i P^i$. Substituting this series in Eq. S1 and developping the logarithms to the second power in P yields the following values for the a_i's:

$$\begin{cases} a_0 = 0 \\ a_1 = \dfrac{K_{\text{C}} y_{\text{C}} + K_{\text{B}} y_{\text{B}}}{K_{\text{B}}} \\ a_2 = -\dfrac{K_{\text{C}} y_{\text{C}} (N_{\text{B}} - N_{\text{C}})(K_{\text{C}} y_{\text{C}} + K_{\text{B}} y_{\text{B}})}{2 K_{\text{B}} N_{\text{B}} N_{\text{C}}} \end{cases} \tag{S2}$$

From there, we can express the molar fraction of B, $x_{\text{B}} = P y_{\text{B}}/P_{\text{B}}^*$, the fraction of C, $x_{\text{C}} = 1 - x_{\text{B}}$, the selectivity, $\alpha = (x_{\text{B}}/x_{\text{C}})/(y_{\text{B}}/y_{\text{C}})$, and the total adsorbed quantity, $N_{\text{tot}}^{-1} = x_{\text{B}}/N_{\text{B}}^*(P_{\text{B}}^*) + x_{\text{C}}/N_{\text{C}}^*(P_{\text{C}}^*)$. Of particular interest are the expression of the selectivity:

$$\alpha(P) = \frac{K_{\text{B}}}{K_{\text{C}}} + \frac{K_{\text{B}}}{K_{\text{C}}} \times \frac{(N_{\text{B}} - N_{\text{C}})(K_{\text{C}} y_{\text{C}} + K_{\text{B}} y_{\text{B}})}{2 N_{\text{B}} N_{\text{C}}} P + O(P^2) \tag{S3}$$

and that of N_{tot}:

$$N_{\text{tot}}(P) = (K_{\text{C}} y_{\text{C}} + K_{\text{B}} y_{\text{B}})\, P - \frac{(K_{\text{C}} y_{\text{C}} + K_{\text{B}} y_{\text{B}})(K_{\text{B}} N_{\text{C}} y_{\text{B}} + K_{\text{C}} N_{\text{B}} y_{\text{C}})}{N_{\text{B}} N_{\text{C}}} P^2 + O(P^3) \tag{S4}$$

B. High-pressure asymptotic expressions of the IAST solutions

In this section, we propose asymptotic expressions for the IAST selectivity α and total adsorbed quantity of fluid N_{tot} in the high-pressure limit. To do so, we will first find an asymptotic expression for P_{B}^* from Eq. S1:

$$N_{\text{B}} \ln\left(1 + \frac{K_{\text{B}}}{N_{\text{B}}} \times P_{\text{B}}^*\right) = N_{\text{C}} \ln\left(1 + \frac{K_{\text{C}}}{N_{\text{C}}} \times \frac{P(1-y_{\text{B}})P_{\text{B}}^*}{P_{\text{B}}^* - Py_{\text{B}}}\right) \tag{S1}$$

The solution P_{B}^* lies in the range $Py_{\text{B}} < P_{\text{B}}^* < \infty$, and therefore goes to infinity when P does. We rewrite Eq. S1 by setting $P_{\text{B}}^* = \omega P y_{\text{B}}$ (where $\omega > 1$):

$$N_{\text{B}} \ln\left(1 + \frac{K_{\text{B}} y_{\text{B}}}{N_{\text{B}}} \times P\omega\right) = N_{\text{C}} \ln\left(1 + \frac{K_{\text{C}} y_{\text{C}}}{N_{\text{C}}} \times P\frac{\omega}{\omega - 1}\right) \tag{S5}$$

To make things easier, we set $\Xi = K_{\text{C}} y_{\text{C}}/N_{\text{C}}$, $\Psi = K_{\text{B}} y_{\text{B}}/N_{\text{B}}$ and $\lambda = N_{\text{B}}/N_{\text{C}}$. Eq. S5 can then be written as:

$$\Xi P \frac{\omega}{\omega - 1} = (1 + \Psi P\omega)^{\lambda} - 1 \tag{S6}$$

Assuming that $\lambda > 1$ (i.e. $N_{\text{B}} > N_{\text{C}}$; otherwise, the role of B and C are permuted), the first two terms in the asymptotic expansion in P of the solution are:

$$\omega(P) = 1 + \frac{\Xi}{\Psi^{\lambda}} \times \frac{1}{P^{\lambda-1}} + O\left(\frac{1}{P^{\lambda}}\right) \tag{S7}$$

which gives the following expression for P_{B}^*:

$$P_{\text{B}}^*(P) = Py_{\text{B}} + P^{2-\frac{N_{\text{B}}}{N_{\text{C}}}} y_{\text{B}} \left(\frac{K_{\text{C}} y_{\text{C}}}{N_{\text{C}}}\right)\left(\frac{K_{\text{B}} y_{\text{B}}}{N_{\text{B}}}\right)^{-\frac{N_{\text{B}}}{N_{\text{C}}}} + O\left(P^{1-\frac{N_{\text{B}}}{N_{\text{C}}}}\right) \tag{S8}$$

Using the other IAST equations, we can calculate from this expression of P_{B}^* all other quantities, including the selectivity:

$$\alpha \sim (Py_{\text{B}})^{\frac{N_{\text{B}}}{N_{\text{C}}}-1} \left(\frac{N_{\text{C}}}{K_{\text{C}}}\right)\left(\frac{K_{\text{B}}}{N_{\text{B}}}\right)^{\frac{N_{\text{B}}}{N_{\text{C}}}} \tag{S9}$$

and the total adsorbed quantity of fluid:

$$N_{\text{tot}} = N_{\text{B}} - N_{\text{B}} \left(\frac{K_{\text{C}} y_{\text{C}}}{N_{\text{C}}}\right)\left(\frac{K_{\text{B}} y_{\text{B}}}{N_{\text{B}}}\right)^{-\frac{N_{\text{B}}}{N_{\text{C}}}} \left(1 + \frac{N_{\text{B}}}{N_{\text{C}}}\right) P^{1-\frac{N_{\text{B}}}{N_{\text{C}}}} + O\left(P^{-\frac{N_{\text{B}}}{N_{\text{C}}}}\right) \tag{S10}$$

C. Analytical expression of the gate-opening pressure

We establish an approximate analytical expression for the gate-opening pressure upon adsorption of a mixture of fluids, as a function of the composition of the mixture, relating it to the gate-opening pressures for its individual components. This requires the knowledge of an approximate expression for $N_{\text{tot}}(P, \mathbf{y})$, the total quantity of adsorbed fluid in the open structure. The most straightforward way to proceed is to use the second-order power series of $N_{\text{tot}}(P)$ derived above (Eq. S4). However, the domain of validity of this approximation is usually rather small,[†]. Moreover, the analytic calculation is thus rather convoluted. To avoid both these issues, and because the total adsorption isotherms $N_{\text{tot}}(P)$ for the mixture as a function of pressure clearly look like Langmuir isotherms, we use a Langmuir equation to describe them:

$$N_{\text{tot}}(P, \mathbf{y}) = \frac{K(\mathbf{y})P}{1 + \frac{K(\mathbf{y})P}{N(\mathbf{y})}} \tag{S11}$$

[†]The domain of validity of the second-order approximation is smaller than the radius of convergence of the power series itself, which corresponds to $P = \min_i (N_i/K_i)$, where index i runs over all the components of the mixture.

with parameters $K(\mathbf{y})$ and $N(\mathbf{y})$ that depend on the mixture composition and are adjusted to reproduce the second-order low-pressure behavior of Eq. S4. This yields:

$$\begin{cases} K(\mathbf{y}) = K_B y_B + K_C y_C \\ N(\mathbf{y}) = \dfrac{K_C y_C + K_B y_B}{\frac{K_C y_C}{N_C} + \frac{K_B y_B}{N_B}} \end{cases} \tag{S12}$$

With this approximate form for N_{tot}, we can establish the value of the gate-opening pressure upon adsorption of the mixture. The difference in osmotic potential between the close phase and the open phase of the material is:

$$\begin{aligned} \Delta\Omega_{\mathrm{os}} &= \Delta F_{\mathrm{host}} - RT \int_0^P \frac{N_{\mathrm{tot}}(p)}{p}\,\mathrm{d}p \\ &= \Delta F_{\mathrm{host}} - N(\mathbf{y})RT \ln\left(1 + \frac{K(\mathbf{y})P}{N(\mathbf{y})}\right) \end{aligned} \tag{S13}$$

The gate-opening pressure P_{gate} is such that $\Delta\Omega_{\mathrm{os}}(P_{\mathrm{gate}}) = 0$, which means that

$$P_{\mathrm{gate}}(\mathbf{y}) = \frac{N(\mathbf{y})}{K(\mathbf{y})}\left[\exp\left(\frac{\Delta F_{\mathrm{host}}}{N(\mathbf{y})RT}\right) - 1\right] \tag{S14}$$

In the approximation we use here, where the gate-opening happens before the plateau of the isotherm is reached, we have $\Delta F \ll N_i RT$ and thus, the gate-opening pressure is

$$P_{\mathrm{gate}}(\mathbf{y}) \simeq \frac{\Delta F_{\mathrm{host}}}{K(\mathbf{y})RT} \tag{S15}$$

By substituting the expression of $K(\mathbf{y})$ from Eq. S12 and identifying the gate-opening pressures for the adsorption of the pure components B and C, we get the analytical expression:

$$\frac{1}{P_{\mathrm{gate}}(\mathbf{y})} = \frac{y_B}{P_{\mathrm{gate,B}}} + \frac{y_C}{P_{\mathrm{gate,C}}} \tag{S16}$$

Finally, it can be demonstrated straightforwardly but quite tediously that this approximate expression is also valid for mixtures involving more than two components:

$$\frac{1}{P_{\mathrm{gate}}(\mathbf{y})} = \sum_i \frac{y_i}{P_{\mathrm{gate},i}} \tag{S17}$$