Thermodynamic Insights into the Characteristics of Unary and Mixture Permeances in Microporous Membranes

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1 Preamble

The Supporting Information accompanying our article *Thermodynamic Insights into the Characteristics of Unary and Mixture Permeances in Microporous Membranes* provides (a) detailed derivation of the IAST calculation procedures for the spreading pressure, and its proxy $\frac{\pi A}{RT}$, using the unary adsorption isotherms, (b) structural details for zeolites considered and analyzed in this article, and (c) Unary isotherm parameter fits for all guest/host combinations considered in our article.
2 Thermodynamics of Mixture Adsorption in Micro-porous Materials

Within microporous crystalline materials, the guest molecules exist in the adsorbed phase, and the thermodynamics of mixture adsorption has an important bearing on the diffusion characteristics of guest molecules. For that reason, we provide below a brief summary of the Ideal Adsorbed Solution Theory (IAST) theory of Myers and Prausnitz.1

2.1 Brief outline of IAS theory

The Gibbs adsorption equation2 in differential form is

\[ d\pi = \sum_{i=1}^n q_id\mu_i \]  

(S1)

The quantity \( A \) is the surface area per kg of framework, with units of m\(^2\) per kg of the framework of the crystalline material; \( q_i \) is the molar loading of component \( i \) in the adsorbed phase with units moles per kg of framework; \( \mu_i \) is the molar chemical potential of component \( i \). The spreading pressure \( \pi \) has the same units as surface tension, i.e. N m\(^{-1}\).

The chemical potential of any component in the adsorbed phase, \( \mu_i \), equals that in the bulk fluid phase. If the partial fugacities in the bulk fluid phase are \( f_i \), we have

\[ d\mu_i = RTd \ln f_i \]  

(S2)

where \( R \) is the gas constant (\( = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \)).

Briefly, the basic equation of Ideal Adsorbed Solution Theory (IAST) theory of Myers and Prausnitz1 is the analogue of Raoult’s law for vapor-liquid equilibrium, i.e.

\[ f_i = P_i^0 x_i; \quad i = 1,2,...,n \]  

(S3)

where \( x_i \) is the mole fraction in the adsorbed phase
\[ x_i = \frac{q_i}{q_1 + q_2 + \ldots q_n} \]  

(S4)

and \( P_i^0 \) is the pressure for sorption of every component \( i \), which yields the same spreading pressure, \( \pi \) for each of the pure components, as that for the mixture:

\[ \frac{\pi A}{RT} = \int_0^{P_i^0} q_i^0(f) \, df = \int_0^{P_i^0} q_j^0(f) \, df = \int_0^{P_i^0} q_k^0(f) \, df = \ldots \]  

(S5)

where \( q_i^0(f) \) is the pure component adsorption isotherm. For \( n \)-component adsorption, there are \( n-1 \) independent equalities in Equations (S5). The units of \( \frac{\pi A}{RT} \), also called the adsorption potential, are \( \text{mol kg}^{-1} \). Each of the integrals in Equation (S5) can be evaluated analytically.

The unary isotherms may be described by say the dual-Langmuir-Freundlich model

\[ q_i^0(f) = q_{A,\text{sat}} \frac{b_A f_i^\text{vol}}{1 + b_A f_i^\text{vol}} + q_{B,\text{sat}} \frac{b_B f_i^\text{vol}}{1 + b_B f_i^\text{vol}} \]  

(S6)

For the dual-site Langmuir-Freundlich isotherm, the integration yields for component \( i \),

\[ \frac{\pi A}{RT} = \int_{f_i=0}^{P_i^0} q_i^0(f) \, df = \frac{q_{A,\text{sat}}}{V_A} \ln \left( 1 + b_A \left( P_i^0 \right)^{v_A} \right) + \frac{q_{B,\text{sat}}}{V_B} \ln \left( 1 + b_B \left( P_i^0 \right)^{v_B} \right) \]  

(S7)

Invoking equation (S3) to express the sorption pressures in terms of the partial fugacities and component mole fractions we obtain

\[ \frac{\pi A}{RT} = \int_{f_i=0}^{P_i^0} q_i^0(f) \, df = \frac{q_{A,\text{sat}}}{V_A} \ln \left( 1 + b_A \left( \frac{f_i}{x_i} \right)^{v_A} \right) + \frac{q_{B,\text{sat}}}{V_B} \ln \left( 1 + b_B \left( \frac{f_i}{x_i} \right)^{v_B} \right) \]  

(S8)

For a specified set of partial fugacities \( f_i \) in the bulk fluid phase, a total of \( n \) in number, the right hand side of equation (S8) is a function of the mole fraction in the adsorbed phase \( x_i \). For \( n \)-component adsorption, there are \( n-1 \) independent mole fractions \( x_i \) that are determined by solving the set of \( n-1 \) independent equalities in Equations (S5). These constraints may be solved using a suitable equation solver to determine the \( x_1, x_2, x_3, \ldots x_{n-1} \), and \( x_n = 1 - x_1 - x_2 - \ldots - x_{n-1} \). In all of the calculations
presented in this article, the set of \( n-1 \) non-linear equations were solved using the Given-Find solve block of MathCad 15.\(^4\) For a binary mixture, a simple root finder is required to solve a single non-linear equation.

From knowledge of the adsorbed phase mole fractions \( x_i \), the sorption pressures \( P_1^0, P_2^0, P_3^0, \ldots P_n^0 \) are then determined from

\[
P_i^0 = \frac{f_i}{x_i}; \quad i = 1, 2, \ldots n
\]  
(S9)

A key assumption of the IAST is that the enthalpies and surface areas of the adsorbed molecules do not change upon mixing. If the total mixture loading is \( q_t \), the area covered by the adsorbed mixture is \( \frac{A}{q_t} \) with units of \( m^2 \) (mol mixture)\(^{-1}\). Therefore, the assumption of no surface area change due to mixture adsorption translates as

\[
\frac{A}{q_t} = \frac{Ax_1}{q_1^0(P_1^0)} + \frac{Ax_2}{q_2^0(P_2^0)} + \cdots + \frac{Ax_n}{q_n^0(P_n^0)}; \quad \text{the total mixture loading is } q_t \text{ is calculated from}
\]

\[
q_t = q_1 + q_2 + \cdots + q_n = \frac{1}{\frac{x_1}{q_1^0(P_1^0)} + \frac{x_2}{q_2^0(P_2^0)} + \cdots + \frac{x_n}{q_n^0(P_n^0)}}
\]  
(S10)

in which \( q_1^0(P_1^0), q_2^0(P_2^0), \ldots q_n^0(P_n^0) \) are determined from the unary isotherm fits, using the sorption pressures for each component \( P_1^0, P_2^0, P_3^0, \ldots P_n^0 \) that are available from the solutions of Equations (S5), (S8), and (S9).

From knowledge of the adsorption potential, \( \frac{\pi A}{RT} \), the fractional occupancy for mixture adsorption is then calculated using

\[
\theta = 1 - \exp \left( -\frac{\pi A}{q_{sat,mix}RT} \right)
\]  
(S11)

For a binary mixture, the saturation capacity \( q_{sat,mix} \) is calculated from the saturation capacities of the constituent guests
Thermodynamics of Mixture Adsorption in Micro-porous Materials

\[ q_{\text{sat, mix}} = \frac{1}{x_1 \frac{q_1}{q_{1,\text{sat}}} + x_2 \frac{q_2}{q_{2,\text{sat}}}}; \quad q_{1,\text{sat}} = q_{1,A,\text{sat}} + q_{1,B,\text{sat}}; \quad q_{2,\text{sat}} = q_{2,A,\text{sat}} + q_{2,B,\text{sat}} \]  \hspace{1cm} (S12)

where

\[ x_1 = \frac{q_1}{q_1 + q_2}; \quad x_2 = \frac{q_2}{q_1 + q_2} \]  \hspace{1cm} (S13)

are the mole fractions in the adsorbed mixture. For equimolar mixtures, \( x_1 = x_2 = 0.5 \), equation (S13) simplifies to yield

\[ q_{\text{sat, mix}} = \frac{2}{\frac{1}{q_{1,\text{sat}}} + \frac{1}{q_{2,\text{sat}}}}. \]

The fundamental justification of Equation (S12) is provided by applying equation (S10) to pore saturation conditions.

Equation (S11) is the appropriate generalization of Equation (S25), derived in the following section for the mixed-gas Langmuir model. It is also to be noted that equation (15) of our earlier publication has a typographical error in the calculation of \( q_{\text{sat, mix}} \); the correct form is given by equation (S12).

\[ q^0(f) = q_{\text{sat}} \frac{bf}{1 + bf}; \quad \theta = \frac{bf}{1 + bf} \]  \hspace{1cm} (S14)

where we define the fractional occupancy of the adsorbate molecules, \( \theta = q^0(f)/q_{\text{sat}} \). The superscript 0 is used to emphasize that \( q^0(f) \) relates the pure component loading to the bulk fluid fugacity.

For unary adsorption, the adsorption potential for a 1-site Langmuir isotherm can be calculated analytically.
The objective is to determine the molar loadings, $q_1$, and $q_2$, in the adsorbed phase.

Performing the integration of Equation (S5) results in an expression relating the sorption pressures $P_i^0$ of the two species

$$\frac{\pi A}{RT} = q_{\text{sat}} \ln \left(1 + b_i P_i^0 \right) = q_{\text{sat}} \ln \left(1 + b_2 P_2^0 \right)$$

$$b_1 P_1^0 = b_2 P_2^0 = \exp \left( \frac{\pi A}{q_{\text{sat}} RT} \right) - 1$$

The adsorbed phase mole fractions of component 1, and component 2 are given by equation (S9)

$$x_1 = \frac{f_1}{P_1^0}; \quad x_2 = 1 - x_1 = \frac{f_2}{P_2^0}$$

Combining equations (S16), and (S17):

$$\exp \left( \frac{\pi A}{q_{\text{sat}} RT} \right) - 1 = b_1 \frac{f_1}{x_1} = b_2 \frac{f_2}{1-x_1}$$

$$\frac{\pi A}{q_{\text{sat}} RT} = \ln \left(1 + b_1 \frac{f_1}{x_1} \right) = \ln \left(1 + b_2 \frac{f_2}{x_2} \right)$$

The adsorbed phase mole fractions can be determined

$$\frac{x_1}{x_2} = \frac{q_1}{q_2} = \frac{b_1 f_1}{b_2 f_2}; \quad x_1 = \frac{q_1}{q_1 + q_2} = \frac{b_1 f_1}{b_1 f_1 + b_2 f_2}; \quad x_2 = \frac{q_2}{q_1 + q_2} = \frac{b_2 f_2}{b_1 f_1 + b_2 f_2}$$

Once $x_1$, and $x_2 = 1 - x_1$ are determined, the sorption pressures can be calculated:

$$P_1^0 = \frac{f_1}{x_1}; \quad P_2^0 = \frac{f_2}{x_2} = \frac{f_2}{1-x_1}$$

From equations (S16), (S19), and (S20) we get

$$b_1 P_1^0 = b_2 P_2^0 = \frac{b_1 f_1}{x_1} = \frac{b_2 f_2}{x_2} = b_1 f_1 + b_2 f_2$$

$$1 + b_1 P_1^0 = 1 + b_2 P_2^0 = 1 + b_1 f_1 + b_2 f_2$$

Combining equations (S18), and (S21) we get the following expression for the adsorption potential for the mixture
\[ \frac{\pi A}{RT} = q_{sat} \ln \left(1 + b_1 f_1 + b_2 f_2 \right) \] 

(S22)

The total amount adsorbed, \( q_t = q_1 + q_2 \) can be calculated from Equation (S10)

\[ q_t = q_1 + q_2 = q_{sat} \frac{b_1 P_1^0}{1 + b_1 P_1^0} = q_{sat} \frac{b_2 P_2^0}{1 + b_2 P_2^0} = q_{sat} \frac{b_1 f_1 + b_2 f_2}{1 + b_1 f_1 + b_2 f_2} \] 

(S23)

Combining equations (S19), and (S23) we obtain the following explicit expressions for the component loadings, and fractional occupancies

\[ \theta_1 = \frac{q_1}{q_{sat}} = \frac{b_1 f_1}{1 + b_1 f_1 + b_2 f_2}, \quad \theta_2 = \frac{q_2}{q_{sat}} = \frac{b_2 f_2}{1 + b_1 f_1 + b_2 f_2} \] 

(S24)

Equation (S24) is commonly referred to as the mixed-gas Langmuir model.

From equations (S16), (S23), and (S24) we derive the following expression for the total occupancy of the mixture

\[ \theta = \theta_1 + \theta_2 = \frac{q_t}{q_{sat}} = 1 - \exp \left( - \frac{\pi A}{q_{sat} RT} \right) = \frac{b_1 f_1 + b_2 f_2}{1 + b_1 f_1 + b_2 f_2} \] 

(S25)

For unary adsorption of component \( i \), say, \( f_i = P_i^0 \), the occupancy of component 1 is

\[ \theta_i = 1 - \exp \left( - \frac{\pi A}{q_{sat} RT} \right) = \frac{b_i f_i}{1 + b_i f_i} ; \quad \text{unary adsorption of species } i \] 

(S26)

From equations (S25), and (S26) we may also conclude the occupancy may be considered to be the appropriate proxy for the spreading pressure. The conclusion that we draw from the foregoing analysis is that the equalities of spreading pressures for unary adsorption of component 1, unary adsorption of component 2, and binary 1-2 mixture adsorption also implies the corresponding equalities of the corresponding occupancies for unary adsorption of component 1, unary adsorption of component 2, and binary 1-2 mixture adsorption.
3 Diffusion in Microporous Crystalline Materials

3.1 The Maxwell-Stefan (M-S) description of diffusion

Within micro-porous crystalline materials, such as zeolites, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs), the guest molecules exist in the adsorbed phase. The Maxwell-Stefan (M-S) equations for $n$-component diffusion in porous materials is applied in the following manner\textsuperscript{6-13}

$$-ho q_i \frac{\partial \mu_i}{\partial r} = \sum_{j=1}^{n} \frac{x_j N_i - x_i N_j}{D_j} + \frac{N_i}{D_i}; \quad i = 1, 2, \ldots, n$$ \hspace{1cm} (S27)

where $\rho$ is the framework density with units of kg m\textsuperscript{-3}, $q_i$ is the molar loading of adsorbate, and the adsorbed phase mole fractions are $x_i = q_i / q_t$ where $q_t$ is the total mixture loading $q_t = \sum_{i=1}^{n} q_i$. The fluxes $N_i$ in equations (S27) are defined in terms of the moles transported per m\textsuperscript{2} of the total surface of crystalline material.

An important, persuasive, argument for the use of the M-S formulation for mixture diffusion is that the M-S diffusivity $D_i$ in mixtures can be estimated using information on the loading dependence of the corresponding unary diffusivity values, provided the comparison is made at the same value of the adsorption potential, calculated from IAST using Equation (S5), or its proxy the occupancy, $\theta$, calculated using equations (S11), (S12), (S13). Essentially this implies that the M-S diffusivity $D_i$ can be estimated from experimental data on unary diffusion in the porous material.

The exchange coefficients $D_{ij}$, defined by the first right member equations (S27), are introduced to quantify the coupling between species diffusion. At the molecular level, the $D_{ij}$ reflect how the facility for transport of species $i$ correlates with that of species $j$.

The Maxwell-Stefan diffusion formulation is consistent with the theory of irreversible thermodynamics. The Onsager Reciprocal Relations imply that the M-S pair diffusivities are symmetric.
3.2 Thermodynamic correction factors

At thermodynamic equilibrium, the chemical potential of component \( i \) in the bulk fluid mixture equals the chemical potential of that component in the adsorbed phase. For the bulk fluid phase mixture we have

\[
\frac{1}{RT} \frac{\partial \mu_i}{\partial r} = \frac{\partial \ln f_i}{\partial r} = \frac{1}{f_i} \frac{\partial f_i}{\partial r}; \quad i = 1, 2, \ldots n
\]  

(S29)

The chemical potential gradients \( \partial \mu_i / \partial r \) can be related to the gradients of the molar loadings, \( q_i \), by defining thermodynamic correction factors \( \Gamma_{ij} \)

\[
\frac{q_i}{RT} \frac{\partial \mu_i}{\partial r} = \sum_{j=1}^{n} \Gamma_{ij} \frac{\partial q_j}{\partial r}; \quad \Gamma_{ij} = \frac{q_i}{f_i} \frac{\partial f_i}{\partial q_j}; \quad i, j = 1, \ldots, n
\]  

(S30)

The thermodynamic correction factors \( \Gamma_{ij} \) can be calculated by differentiation of the model describing mixture adsorption equilibrium. Generally speaking, the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz\(^1\) is the preferred method for estimation of mixture adsorption equilibrium. In the special case in which the unary isotherms are described for every component with the 1-site Langmuir model with equal saturation capacities, the mixed-gas Langmuir model

\[
\frac{q_i}{q_{sat}} = \theta_i = \frac{b_i f_i}{1 + \sum_{i=1}^{n} b_i f_i}; \quad i = 1, 2, \ldots n
\]  

(S31)

Is derivable from the IAST. Analytic differentiation of equation (S31) yields

\[
\Gamma_{ij} = \delta_{ij} + \left( \theta_i \frac{\partial \theta_i}{\partial \theta_j} \right); \quad i, j = 1, 2 \ldots n
\]  

(S32)

where the fractional vacancy \( \theta_v \) is defined as

\[
\theta_v = 1 - \theta_i = 1 - \sum_{i=1}^{n} \theta_i
\]  

(S33)
The elements of the matrix of thermodynamic factors $\Gamma_{ij}$ can be calculated explicitly from information on the component loadings $q_i$ in the adsorbed phase; this is the persuasive advantage of the use of the mixed-gas Langmuir model. By contrast, the IAST does not allow the calculation of $\Gamma_{ij}$ explicitly from knowledge on the component loadings $q_i$ in the adsorbed phase; a numerical procedure is required.

### 3.3 M-S formulation for binary mixture diffusion

For binary mixture diffusion inside microporous crystalline materials the Maxwell-Stefan equations (S27) are written

$$
\begin{align*}
-\rho \frac{q_1}{RT} \frac{\partial \mu_1}{\partial r} &= \frac{x_1 N_i - x_1 N_2}{D_{12}} + \frac{N_1}{D_i} \\
-\rho \frac{q_2}{RT} \frac{\partial \mu_2}{\partial r} &= \frac{x_2 N_2 - x_2 N_1}{D_{12}} + \frac{N_2}{D_2}
\end{align*}
$$

(S34)

The first members on the right hand side of Equation (S34) are required to quantify slowing-down effects that characterize binary mixture diffusion.\textsuperscript{8, 9, 14} There is no experimental technique for direct determination of the exchange coefficients $D_{12}$, that quantify molecule-molecule interactions.

In two-dimensional matrix notation, equation (S30) take the form

$$
\begin{pmatrix}
\frac{q_1}{RT} \frac{\partial \mu_1}{\partial r} \\
\frac{q_2}{RT} \frac{\partial \mu_2}{\partial r}
\end{pmatrix} = [\Gamma]
\begin{pmatrix}
\frac{\partial q_1}{\partial r} \\
\frac{\partial q_2}{\partial r}
\end{pmatrix}
$$

(S35)

For the mixed-gas Langmuir model, equation (S31), we can derive simple analytic expressions for the four elements of the matrix of thermodynamic factors:\textsuperscript{15}

$$
\begin{bmatrix}
\Gamma_{11} & \Gamma_{12} \\
\Gamma_{21} & \Gamma_{22}
\end{bmatrix} = \frac{1}{1 - \theta_2 - \theta_1} \begin{bmatrix}
1 - \theta_2 & \theta_1 \\
\theta_2 & 1 - \theta_1
\end{bmatrix}
$$

(S36)

where the fractional occupancies, $\theta_i$, are defined by equation (S31).

Let us define the square matrix $[B]$
$[B] = \begin{bmatrix} \frac{1}{D_1} + \frac{x_2}{D_{12}} & -\frac{x_1}{D_{12}} \\ -\frac{x_2}{D_{12}} & \frac{1}{D_2} + \frac{x_1}{D_{12}} \end{bmatrix}$; \quad $[B]^{-1} = \frac{1}{1 + \frac{x_1 D_2}{D_{12}} + \frac{x_2 D_1}{D_{12}}} \begin{bmatrix} D_1 \left(1 + \frac{x_1 D_2}{D_{12}}\right) & \frac{x_1 D_2}{D_{12}} \\ \frac{x_2 D_1}{D_{12}} & D_2 \left(1 + \frac{x_2 D_1}{D_{12}}\right) \end{bmatrix}$ \quad (S37)

In proceeding further, it is convenient to define a 2x2 dimensional square matrix $[\Lambda]$:

$[\Lambda] = \begin{bmatrix} \frac{1}{D_1} + \frac{x_2}{D_{12}} & -\frac{x_1}{D_{12}} \\ -\frac{x_2}{D_{12}} & \frac{1}{D_2} + \frac{x_1}{D_{12}} \end{bmatrix}^{-1} = \frac{1}{1 + \frac{x_1 D_2}{D_{12}} + \frac{x_2 D_1}{D_{12}}} \begin{bmatrix} D_1 \left(1 + \frac{x_1 D_2}{D_{12}}\right) & \frac{x_1 D_2}{D_{12}} \\ \frac{x_2 D_1}{D_{12}} & D_2 \left(1 + \frac{x_2 D_1}{D_{12}}\right) \end{bmatrix}$ \quad (S38)

Equation (S34) can be re-cast into 2-dimensional matrix notation

$\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} = -\rho [\Lambda] \begin{bmatrix} \partial(q) \\ \partial(r) \end{bmatrix}$.

\begin{align*}
\begin{pmatrix} N_1 \\ N_2 \end{pmatrix} &= -\rho \begin{bmatrix} D_1 \left(1 + \frac{x_1 D_2}{D_{12}}\right) & \frac{x_1 D_2}{D_{12}} \\ \frac{x_2 D_1}{D_{12}} & D_2 \left(1 + \frac{x_2 D_1}{D_{12}}\right) \end{bmatrix} \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} \begin{bmatrix} \partial q_1 \\ \partial r \end{bmatrix} \\
\end{align*} \quad (S39)

The elements of $[B]$ can be obtained by inverting the matrix $[\Lambda]$:

$\begin{bmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{bmatrix} = \begin{bmatrix} \frac{1}{D_1} + \frac{x_2}{D_{12}} & -\frac{x_1}{D_{12}} \\ -\frac{x_2}{D_{12}} & \frac{1}{D_2} + \frac{x_1}{D_{12}} \end{bmatrix} = [\Lambda]^{-1}$ \quad (S40)

### 3.4 Negligible correlations scenario for M-S diffusivities

For values of $D_1 / D_{12} \to 0$, and $D_2 / D_{12} \to 0$, the contribution of the first right member of M-S Equation (S34) can be ignored and correlations can be considered to be of negligible importance; we derive
Equation (S41) is valid, as a first approximation, for diffusion in cage-type zeolites with 8-ring windows (CHA, LTA, DDR, ERI) and ZIF-8. When correlation effects are negligible, the diffusional coupling effects are solely traceable to mixture adsorption thermodynamics, embodied in the matrix $[\Gamma]$. 

\[
\begin{align*}
 \frac{D_1}{D_{1z}} &\rightarrow 0; \quad \frac{D_2}{D_{2z}} \rightarrow 0; \quad \begin{bmatrix}
 \Lambda_{11} & \Lambda_{12} \\
 \Lambda_{21} & \Lambda_{22}
 \end{bmatrix} \rightarrow \begin{bmatrix}
 D_1 & 0 \\
 0 & D_2
 \end{bmatrix} \\
 \begin{bmatrix}
 N_1 \\
 N_2
 \end{bmatrix} &=-\rho \begin{bmatrix}
 D_1 & 0 \\
 0 & D_2
 \end{bmatrix} \begin{bmatrix}
 \Gamma_{11} & \Gamma_{12} \\
 \Gamma_{21} & \Gamma_{22}
 \end{bmatrix} \begin{bmatrix}
 \frac{\partial q_1}{\partial r} \\
 \frac{\partial q_2}{\partial r}
 \end{bmatrix}
\end{align*}
\]
4 Quasi-Chemical Theory for Occupancy Dependence of Unary Diffusivity

The simplest model to describe this occupancy dependence is

\[ D_i = D_i(0)(1 - \theta) = D_i(0)\theta_r \]  \hspace{1cm} (S42)

where \( D_i(0) \) is the M-S diffusivity at “zero-loading”, and \( \theta_r = (1 - \theta) \) is the fractional vacancy, determined from Equation (S11), where the saturation capacity is determined from the unary isotherm fits. Equation (S42) is essentially based on a simple hopping model in which a molecule can jump from one adsorption site to an adjacent one, provided it is not already occupied. The loading dependence portrayed in equation (S42) has been termed the “strong confinement” scenario by Krishna and Baur.\(^{15}\)

For the specific case of a binary mixture, the hopping of molecules from one site to another on a 2D lattice is depicted in Figure S1. Using a simple lattice model, the M-S diffusivity in the limit of vanishingly small occupancies, \( D_i(0) = \frac{1}{\xi} \nu_i(0)\lambda^2 \), where \( \xi = 4 \) is the coordination number of the 2D array of lattice sites, \( \lambda \) is the jump distance on the square lattice, and \( \nu_i(0) \) is the jump frequency at vanishingly small occupancy.\(^{23}\)

More generally, molecule-molecule interactions serve to influence the jump frequencies by a factor that depends on the energy of interaction, \( w \). For repulsive interactions, \( w > 0 \), whereas for attractive interactions, \( w < 0 \). Using the quasi-chemical approach of Reed and Ehrlich\(^{24}\) to quantify such interactions, the following expression is obtained for the occupancy dependence of the M-S diffusivities

\[ D_i = D_i(0) \left( \frac{1 + \beta_i}{2(1 - \theta_i)} \right)^{-\xi} \left( 1 + \frac{\beta_i(1 + 2\theta_i)}{2(1 - \theta_i)} \phi \right)^{\xi-1} \]  \hspace{1cm} (S43)

where the following dimensionless parameters are defined
\[ \beta_i = \sqrt{1 - 4 \theta \left(1 - \theta \right) \left(1 - 1/\phi \right)}; \quad \phi = \exp(w/RT) \] (S44)

In the limiting case of negligible molecule-molecule interactions, \( w = 0, \phi = 1, \beta_i = 1 \) equations (S43), and (S44) degenerate to yield Equation (S42).
4.1 List of Figures for Quasi-Chemical Theory for Occupancy Dependence of Unary Diffusivity

Exchange coefficient quantifying correlations

\[
- \frac{d\mu_1}{dz} = -RT \frac{d\ln p_1}{dz} = \frac{RT}{D_{12}} \theta_2(u_1 - u_2) + \frac{RT}{D_{1V}} \theta_V(u_1 - u_V) \\
- \frac{d\mu_2}{dz} = -RT \frac{d\ln p_2}{dz} = \frac{RT}{D_{12}} \theta_1(u_2 - u_1) + \frac{RT}{D_{2V}} \theta_V(u_2 - u_V)
\]

Figure S1. The Maxwell- Stefan description of hopping of molecules on a 2D surface.
5 SAPO-34 membrane permeation

SAPO-34 has the same structural topology as CHA zeolite, consisting of cages of volume 316 Å³, separated by 3.8 Å × 4.2 Å 8-ring windows; the pore landscape and structural details are provided in Figure S2, and Figure S3. 27-30

For adsorption in SAPO-34, the model based on statistical thermodynamics described in Chapter 3 of Ruthven² is particularly relevant and useful

\[
q_i = \frac{q_{i,\text{sat}}}{\Omega_i} \left[ 1 + b_i f_i \sum_{m=2}^{\Omega_i} \frac{(b_i f_i)^m}{(m-1)!} \right]^{\Omega_i - 1} \left[ 1 + \frac{m}{\Omega_i + 1} \right]^{-1}
\]

(S45)

In Equation (S45) \( q_i \) represents the loading in mol kg\(^{-1}\), \( q_{i,\text{sat}} \) is the saturation loading in mol kg\(^{-1}\), and \( \Omega_i \) is maximum capacity expressed in molecules per cage. Based on the atomic composition of SAPO-34 used in our experiments of Li et al.,31 \((\text{Si}_{0.061}\text{Al}_{0.483}\text{P}_{0.455})\text{O}_2\), we calculate \( q_{i,\text{sat}} = 1.369 \Omega_i \).

The unary isotherms fit parameters are provided in Table S1.

The mixture adsorption equilibrium was determined using the IAST.

Experimental data of Li et al.31-33 for component permeances for CO\(_2\)/CH\(_4\), CO\(_2\)/H\(_2\), CO\(_2\)/N\(_2\), CH\(_4\)/H\(_2\), CH\(_4\)/N\(_2\), CH\(_4\)/Ar, and N\(_2\)/H\(_2\) mixtures in SAPO-34 membrane at 295 K are compared to unary permeation data in Figure S4, Figure S5, Figure S6, Figure S7, Figure S8, Figure S9, Figure S10. The permeance data are plotted as function of (a) upstream partial pressures, \( p_{i0} \), (b) adsorption potential \( \frac{\pi A}{RT} \) and (c) occupancy \( \theta \) at the upstream face of the membrane.

Experimental data of Li et al.31-33 for permeances of CO\(_2\), CH\(_4\), N\(_2\), and H\(_2\) determined for unary and equimolar binary mixture permeation across SAPO-34 membrane at 295 K are presented in Figure S11.
and Figure S12. The data are plotted, respectively, as function of the adsorption potential $\pi A/RT$ and occupancy $\theta$ at the upstream face of the membrane.

From the experimental data on the component permeances, the transport coefficients $\rho D_i/\delta$ can be backed-out; details of the backing-out procedure are provided in Li et al.31-33. Figure S13 presents plots of the transport coefficients $\rho D_i/\delta$, with units kg m$^{-2}$ s$^{-1}$, of CO$_2$, CH$_4$, N$_2$, and H$_2$ determined for unary and equimolar binary mixture permeation across SAPO-34 membrane at 295 K. The data are plotted as function of the occupancy $\theta$ at the upstream face of the membrane. The continuous solid lines are the Reed-Ehrlich$^{24}$ model calculations that quantifies the occupancy dependence of the transport coefficients.

The continuous solid lines in Figure S13 are fits of the experimental data on transport coefficients by fitting the sets of parameters: $\rho D_i(0)/\delta$, and $\phi=\phi_0 \exp(-a\theta)$. For all four guest molecules in SAPO-34, equations (S43), and (S44) degenerate provide good descriptions of the occupancy dependence.
5.1 List of Tables for SAPO-34 membrane permeation

Table S1. Pure component isotherm fit data for guest species in SAPO-34, as tabulated in Li et al. 31

| Molecule | $b_i$       | $\Omega_i$ | $q_{i,\text{sat}}$ |
|----------|-------------|------------|-------------------|
| CO$_2$   | 7.67×10$^{-5}$ | 6          | 8.2               |
| CH$_4$   | 5.87×10$^{-6}$  | 6          | 8.2               |
| N$_2$    | 1.26×10$^{-6}$  | 6          | 8.2               |
| H$_2$    | 2.84×10$^{-7}$  | 9          | 12.3              |
| O$_2$    | 1.2×10$^{-6}$   | 6          | 8.2               |
| CO       | 2.31×10$^{-6}$  | 6          | 8.2               |
| Ar       | 1.26×10$^{-6}$  | 6          | 8.2               |

$b_i$ is expressed in Pa$^{-1}$, $\Omega_i$ in molecules per cage, $q_{i,\text{sat}}$ in mol kg$^{-1}$. 
5.2 List of Figures for SAPO-34 membrane permeation

**CHA landscape**

There are 6 cages per unit cell. The volume of one CHA cage is 316.4 Å³, slightly larger than that of a single cage of DDR (278 Å³), but significantly lower than FAU (766 Å³).

**Snapshots showing location of CH₄ and CO₂**

Structural information from: C. Baerlocher, L.B. McCusker, Database of Zeolite Structures, International Zeolite Association, http://www.iza-structure.org/databases/

Figure S2. Pore landscape and structural details of all-silica CHA zeolite.
**CHA window and pore dimensions**

The window dimensions calculated using the van der Waals diameter of framework atoms = 2.7 Å are indicated above by the arrows.

| Parameter | CHA |
|-----------|-----|
| a /Å | 15.075 |
| b /Å | 23.907 |
| c /Å | 13.803 |
| Cell volume /Å³ | 4974.574 |
| Conversion factor for [molec/uc] to [mol per kg Framework] | 0.2312 |
| Conversion factor for [molec/uc] to [kmoi/m²] | 0.8747 |
| ρ [kg/m³] | 1444.1 |
| MIV unit cell [g/mol(framework)] | 4328.106 |
| Fractional pore volume | 0.382 |
| Open space /Å³/uc | 1898.4 |
| Pore volume /cm³/g | 0.264 |
| Surface area /m²/g | 758.0 |
| DeLaunay diameter /Å | 3.77 |

Figure S3. Pore landscape and structural details of all-silica CHA zeolite.
Figure S4. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for CO\textsubscript{2}/CH\textsubscript{4} mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{\text{up}}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S5. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for CO\textsubscript{2}/H\textsubscript{2} mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{i0}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S6. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for CO\textsubscript{2}/N\textsubscript{2} mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, \(p_{0}\), (b) adsorption potential \(\pi A/RT\) and (c) occupancy \(\theta\) at the upstream face of the membrane.
Figure S7. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for CH\textsubscript{4}/H\textsubscript{2} mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{\text{f0}}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S8. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for CH\textsubscript{4}/N\textsubscript{2} mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{0u}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S9. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for CH\textsubscript{4}/Ar mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{0a}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S10. Experimental data of Li et al.\textsuperscript{31-33} for component permeances for N\textsubscript{2}/H\textsubscript{2} mixtures in SAPO-34 membrane at 295 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, \(p_{i0}\), (b) adsorption potential \(\pi A/RT\) and (c) occupancy \(\theta\) at the upstream face of the membrane.
Figure S11. Experimental data of Li et al.\textsuperscript{31-33} for permeances of CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}, and H\textsubscript{2} determined for unary and equimolar binary mixture permeation across SAPO-34 membrane at 295 K. The data are plotted as function of the adsorption potential $\pi A/RT$ at the upstream face of the membrane.
Figure S12. Experimental data of Li et al.\textsuperscript{31-33} for permeances of CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}, and H\textsubscript{2} determined for unary and equimolar binary mixture permeation across SAPO-34 membrane at 295 K. The data are plotted as function of the occupancy $\theta$ at the upstream face of the membrane.
SAPO-34 membrane permeation

**SAPO - 34, 295 K; Component = CO$_2$**
$\rho D_\text{i}(0)/\delta = 5 \times 10^{-1}$
$\phi_\text{i} = \phi_\text{i}_0 \exp(-a_i \theta)$
$\phi_\text{i}_0 = 1.8; \ a_i = -0.1$

**SAPO - 34, 295 K; Component = N$_2$**
$\rho D_\text{i}(0)/\delta = 1.5 \times 10^{-2}$
$\phi_\text{i} = \phi_\text{i}_0 \exp(-a_i \theta)$
$\phi_\text{i}_0 = 1.2; \ a_i = -0.65$

**SAPO - 34, 295 K; Component = CH$_4$**
$\rho D_\text{i}(0)/\delta = 3.5 \times 10^{-4}$
$\phi_\text{i} = \phi_\text{i}_0 \exp(-a_i \theta)$
$\phi_\text{i}_0 = 2.1; \ a_i = -0.3$

**SAPO - 34, 295 K; Component = H$_2$**
$\rho D_\text{i}(0)/\delta = 0.27$
$\phi_\text{i} = \phi_\text{i}_0 \exp(-a_i \theta)$
$\phi_\text{i}_0 = 1.2; \ a_i = 0.0$

Figure S13. Experimental data of Li et al.$^{31-33}$ for transport coefficients $\rho D_\text{i}/\delta$ of CO$_2$, CH$_4$, N$_2$, and H$_2$ determined for unary and equimolar binary mixture permeation across SAPO-34 membrane at 295 K. The data are plotted as function of the occupancy $\theta$ at the upstream face of the membrane. The continuous solid lines are the Reed-Ehrlich model calculations, equations (S43), and (S44), with the parameters as indicated alongside the corresponding Figures.
6 DDR membrane permeation

DDR consists of cages of 277.8 Å³ volume, separated by 3.65 Å × 4.37 Å 8-ring windows; the pore landscapes and structural details are provided in Figure S14, and Figure S15. The guest molecules jump one-at-a-time across the narrow 8-ring windows.

CBMC simulations of the unary isotherm data for CO₂, CH₄, and N₂ for a variety of temperatures were fitted with a 3-site Langmuir model in previous work; see Figure S16, and Figure S17.₁⁹ The 3-site Langmuir parameters are provided in Table S2. The CBMC simulations are in very good agreement with the experimental data of Himeno et al.,₃⁴-₃⁶ see comparisons in Figure S16.

Experimental data of Van den Bergh et al.₃⁷, ₃₈ for component permeances for 50/50 CO₂/CH₄, and 50/50 N₂/CH₄ mixtures in DDR membrane at 303 K are compared to unary permeation data in Figure S18, and Figure S19. The permeance data are plotted as function of (a) upstream partial pressures, \( p_{i0} \), (b) adsorption potential \( \pi A/RT \) and (c) occupancy \( \theta \) at the upstream face of the membrane.

Figure S20 presents a comparison of CH₄ component permeances for 50/50 CO₂/CH₄ and 50/50 N₂/CH₄ binary mixture permeation across DDR membrane at 303 K, compared to unary permeance. The data are plotted as function of the adsorption potential \( \pi A/RT \) and occupancy \( \theta \) at the upstream face of the membrane.

Figure S21 presents experimental data of Himeno et al.₃⁵ for component permeances for 50/50 CO₂/CH₄ binary mixture permeation across DDR membrane at 298 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, \( p_{i0} \), (b) adsorption potential \( \pi A/RT \) and (c) occupancy \( \theta \) at the upstream face of the membrane.

When compared at the same adsorption potential, or occupancy, the component permeances are the same for mixtures as for unary systems.
6.1 List of Tables for DDR membrane permeation

Table S2. Temperature dependent 3-site Langmuir parameters for CO₂, CH₄, and N₂ in DDR. The fits are those reported in the Supplementary Material accompanying Krishna and van Baten.¹⁹

\[ q = \frac{q_{\text{sat},A} b_A f}{1 + b_A f} + \frac{q_{\text{sat},B} b_B f}{1 + b_B f} + \frac{q_{\text{sat},C} b_C f}{1 + b_C f} \]

For CO₂: \( b_A = 7.8 \times 10^{-11} \exp\left(\frac{3400}{T}\right); \) \( q_{\text{sat},A} = 3.0 \text{ mol/kg}; \)

\( b_B = 2 \times 10^{-13} \exp\left(\frac{3800}{T}\right); \) \( q_{\text{sat},B} = 1.0 \text{ mol/kg}; \) \( b_C = 1.9 \times 10^{-14} \exp\left(\frac{3450}{T}\right); \) \( q_{\text{sat},C} = 0.6 \text{ mol/kg} \)

For CH₄: \( b_A = 2.39 \times 10^{-9} \exp\left(\frac{2200}{T}\right); \) \( q_{\text{sat},A} = 1.6 \text{ mol/kg}; \)

\( b_B = 1.24 \times 10^{-11} \exp\left(\frac{2200}{T}\right); \) \( q_{\text{sat},B} = 1.6 \text{ mol/kg}; \) \( b_C = 1.27 \times 10^{-12} \exp\left(\frac{1000}{T}\right); \) \( q_{\text{sat},C} = 1.0 \text{ mol/kg} \)

For N₂: \( b_A = 1.57 \times 10^{-9} \exp\left(\frac{1650}{T}\right); \) \( q_{\text{sat},A} = 1.8 \text{ mol/kg}; \)

\( b_B = 4.5 \times 10^{-11} \exp\left(\frac{1650}{T}\right); \) \( q_{\text{sat},B} = 1.8 \text{ mol/kg}; \) \( b_C = 3 \times 10^{-13} \exp\left(\frac{1650}{T}\right); \) \( q_{\text{sat},C} = 1.8 \text{ mol/kg} \)
6.2 List of Figures for DDR membrane permeation

Figure S14. Pore landscape of all-silica DDR zeolite.
**DDR window and pore dimensions**

The window dimensions calculated using the van der Waals diameter of framework atoms = 2.7 Å are indicated above by the arrows.

| Property                                      | DDR    |
|-----------------------------------------------|--------|
| 4.37 Å                                        |        |
| 3.65 Å                                        |        |

Figure S15. Structural details of all-silica DDR zeolite.
Figure S16. Comparison of CBMC simulated isotherms\textsuperscript{19} for CO$_2$, CH$_4$ and N$_2$ with experimental data of Himeno et al.\textsuperscript{34-36} Also shown by the continuous solid lines are the 3-site Langmuir fits of the isotherms using the parameters specified in Table S2.
Figure S17. Comparison of CBMC simulated isotherms\textsuperscript{19} for CO$_2$, CH$_4$, N$_2$ and Ar with 3-site Langmuir fits of the isotherms using the parameters specified in Table S2.
Figure S18. Experimental data of Van den Bergh et al.\textsuperscript{37, 38} for component permeances for 50/50 CO\(_2/\)CH\(_4\) binary mixture permeation across DDR membrane at 303 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, \(p_\text{up}\); (b) adsorption potential \(\pi A/RT\) and (c) occupancy \(\theta\) at the upstream face of the membrane.
Figure S19. Experimental data of Van den Bergh et al.\textsuperscript{37, 38} for component permeances for 50/50 N\textsubscript{2}/CH\textsubscript{4} binary mixture permeation across DDR membrane at 303 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{i0}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S20. Comparison of CH₄ component permeances for 50/50 CO₂/CH₄ and 50/50 N₂/CH₄ binary mixture permeation across DDR membrane at 303 K, compared to unary permeance. The data are plotted as function of the adsorption potential $\pi A/RT$ and occupancy $\theta$ at the upstream face of the membrane.
Figure S21. Experimental data of Himeno et al.,\textsuperscript{35} scanned from Figures 6, 10, and 11 of their paper, for component permeances for 50/50 CO\textsubscript{2}/CH\textsubscript{4} binary mixture permeation across DDR membrane at 298 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, \(p_{\text{in}}\), (b) adsorption potential \(\pi A/RT\) and (c) occupancy \(\theta\) at the upstream face of the membrane.
7 ZIF-8 membrane permeation

ZIF-8 has a cage-window SOD (sodalite) topology (see pore landscapes in Figure S22, and Figure S23). The crystallographic size of the windows of ZIF-8 are 3.3 Å, but the windows are flexible. The separation of C₂H₄/C₂H₆, and C₃H₆/C₃H₈ mixtures using ZIF-8 membranes is primarily based on differences in the diffusivities of the alkenes and alkanes; such differences arise due to subtle differences in bond lengths and bond angles. The ratio of the diffusivity of C₃H₆ propene to that of C₃H₈ in ZIF-8 has a value of 125 based on the uptake data of Li et al. A further confirmation of the subtle influence of bond lengths and bond angles on diffusivities of alkenes and alkanes is provided by Ruthven and Reyes who report diffusion selectivity values for C₃H₆/C₃H₈ mixtures in excess of 1000 for CHA and DDR zeolites.

The adsorption selectivities for C₂H₄/C₂H₆, and C₃H₆/C₃H₈ mixtures using ZIF-8 favor the saturated alkane; this implies that adsorption and diffusion do not proceed hand in hand. The diffusion selectivities over-ride the adsorption selectivities, yielding permeation selectivities in favor of the unsaturated alkene. From the unary isotherm data in Table S4, the ratio of single-site Langmuir parameters $b_2/b_1$ for C₃H₆/C₃H₈ is 1.08 at 308 K.

Figure S24 presents the experimental data of Bux et al. for component permeances for 50/50 C₂H₄/C₂H₆ binary mixture permeation across ZIF-8 membrane at 298 K, compared to unary permeances. The data are plotted as function (a) upstream partial pressures, $p_{i0}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.

Figure S25 presents the experimental data Liu et al. of permeances for 50/50 C₃H₆/C₃H₈ mixtures in ZIF-8 membrane at 308 K, compared to unary permeances. The data are plotted as function of (a) upstream partial pressures, $p_{i0}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
7.1 List of Tables for ZIF-8 membrane permeation

Table S3. 1-site Langmuir-Freundlich parameters for ethene and ethane in ZIF-8. The $T$-dependent parameters are obtained by fitting the combined sets of pure component isotherm data of Böhme et al. determined for a variety of temperatures in the range 273 K to 408 K.

$$q = q_{\text{sat}} \frac{bp^\nu}{1 + bp^\nu}, \quad b_T = b_0 \exp\left(\frac{E}{RT}\right)$$

|          | $q_{\text{sat}}$ mol kg$^{-1}$ | $b_0$ Pa$^{-\nu}$ | $E$ kJ mol$^{-1}$ | $\nu$ dimensionless |
|----------|---------------------------------|-------------------|-------------------|---------------------|
| ethene   | 12                              | 9.37×10$^{-11}$   | 21.5              | 1.08                |
| ethane   | 12                              | 8.55×10$^{-11}$   | 23.2              | 1.08                |
Table S4. 1-site Langmuir parameters for propene and propane in ZIF-8. The $T$-dependent parameters are obtained by fitting the combined sets of pure component isotherm data of Li et al. and Böhme et al. determined for a variety of temperatures in the range 273 K to 408 K.

\[ q = q_{\text{sat}} \frac{b_p}{1 + b_p}; \quad b_p = b_0 \exp \left( \frac{E}{RT} \right) \]

|       | $q_{\text{sat}}$ mol kg$^{-1}$ | $b_0$ Pa$^{-1}$ | $E$ kJ mol$^{-1}$ |
|-------|--------------------------------|----------------|-----------------|
| propene | 5.2                           | $4.57 \times 10^{-11}$ | 33.9           |
| propane | 5.2                           | $1.39 \times 10^{-10}$ | 31.3           |
7.2 List of Figures for ZIF-8 membrane permeation

**ZIF-8** pore landscapes

There are 2 cages per unit cell. The volume of one ZIF-8 cage is 1168 Å³, significantly larger than that of a single cage of DDR (278 Å³), or FAU (785 Å³).

Figure S22. Pore landscape and structural details of ZIF-8.
ZIF-8 dimensions

This plot of surface area versus pore dimension is determined using a combination of the DeLaunay triangulation method for pore dimension determination, and the procedure of Düren for determination of the surface area.

| Property                          | ZIF-8       |
|----------------------------------|-------------|
| a /Å                             | 16.991      |
| b /Å                             | 16.991      |
| c /Å                             | 16.991      |
| Cell volume / Å³                 | 4905.201    |
| conversion factor for [molec/uc] to [mol per kg Framework] | 0.3663     |
| conversion factor for [molec/uc] to [kmol/m³]      | 0.7106      |
| ρ (kg/m³)                        | 924.253     |
| MW unit cell [g/mol(framework)]  | 2730.182    |
| ϕ, fractional pore volume        | 0.476       |
| open space / Å³/uc               | 2337.0      |
| Pore volume / cm³/g              | 0.515       |
| Surface area /m²/g               | 1164.7      |
| DeLaunay diameter /Å             | 3.26        |

Figure S23. Pore landscape and structural details of ZIF-8.
Figure S24. Experimental data of Bux et al.\textsuperscript{41} for component permeances for 50/50 C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} binary mixture permeation across ZIF-8 membrane at 308 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_i$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane. The isotherm data are provided in Table S3.
Figure S25. Experimental data of Liu et al.\textsuperscript{42} for component permeances for 50/50 C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} binary mixture permeation across ZIF-8 membrane at 308 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{i0}$, (b) adsorption potential $\frac{\pi A}{RT}$ and (c) occupancy $\theta$ at the upstream face of the membrane. The isotherm data are provided in Table S4.
8 MFI zeolite membrane permeation

8.1 MFI structural details

MFI zeolite (also called silicalite-1) has a topology consisting of a set of intersecting straight
channels, and zig-zag (or sinusoidal) channels of approximately 5.5 Å size. The pore landscapes and
structural details are provided in Figure S26, and Figure S27.

8.2 CO₂/H₂ permeation at 296 K, and 273 K

For analysis of the CO₂/H₂ permeation data of Sandström et al., measured at 296 K the required
isotherm parameters are specified in Table S5. The isotherms are fitted with the single-site Langmuir
model with equal saturation capacities for either species, equation (S14). The analysis of the
experimental permeation data is summarized in Figure S28.

The experimental data are amenable to modeling using the Maxwell-Stefan equations:

\[
\frac{-\rho q_1}{RT} \frac{d\mu_1}{dz} = \frac{x_1N_1 - x_1N_2}{D_{12}} + \frac{N_1}{D_1};
\]

\[
\frac{-\rho q_2}{RT} \frac{d\mu_2}{dz} = \frac{x_1N_2 - x_2N_1}{D_{12}} + \frac{N_2}{D_2}
\]

where \( \rho \) represents the framework density of the microporous crystalline material. For steady state
permeation across a microporous membrane of thickness \( \delta \) (see schematic in Figure S29), the M-S
equations can be solved using the simple linearization technique described in earlier work to yield

\[
\begin{pmatrix}
N_1 \\
N_2
\end{pmatrix} = \frac{D}{\delta} [\Lambda] [\Gamma]
\begin{pmatrix}
q_{10} - q_{1\delta} \\
q_{20} - q_{2\delta}
\end{pmatrix};
\]

\[
[\Lambda] = \frac{1}{1 + \frac{x_1D_2}{D_{12}} + \frac{x_2D_1}{D_{12}}} \begin{pmatrix}
D_1 \left(1 + \frac{x_1D_2}{D_{12}}\right) & \frac{x_1D_1D_2}{D_{12}} \\
\frac{x_2D_1D_2}{D_{12}} & D_2 \left(1 + \frac{x_2D_1}{D_{12}}\right)
\end{pmatrix}
\]

\[
[\Gamma] = \frac{1}{1 - \theta_1 - \theta_2} \begin{pmatrix}
1 - \theta_2 & \theta_1 \\
\theta_2 & 1 - \theta_1
\end{pmatrix}
\]
A simple approach is to assume that the two-dimensional square matrices $[\Lambda]$ and $[\Gamma]$ are independent of loadings in the membrane, and evaluated at conditions corresponding to the upstream face of the membrane that is in equilibrium with the feed mixture in the upstream compartment. The component loadings $q_{10}$, $q_{20}$, adsorbed phase mole fractions, $x_1$, $x_2$, and the fractional occupancies $\theta_1$, $\theta_2$, can be evaluated using the mixed-gas Langmuir model Equation (S24). The model calculations are shown by the continuous solid lines in Figure S30. The zero-loading M-S diffusivities are fitted from unary permeance data: $\rho D_1(0)/\delta = 3.2$, and $\rho D_2(0)/\delta = 100$ kg m$^{-2}$ s$^{-1}$. The degree of correlations is taken to increase linearly with occupancy $\theta$: $D_z/D_{12} = b_1\theta = b_2(\theta_1 + \theta_2)$. The H$_2$ permeance is significantly influenced by correlation effects, as is evidenced in Figure S30 for calculations taking $D_z/D_{12} = 1.0\theta$, $3.0\theta$, and $10.0\theta$; the choice $D_z/D_{12} = 10.0\theta$ affords the best match with experimental data of Sandström et al.$^{45}$

For analysis of the experimental CO$_2$/H$_2$ permeation data of Sjöberg et al.$^{46}$ measured at 273 K the required isotherm parameters are also specified in Table S5. The analysis of the permeation data is summarized in Figure S31. The continuous solid lines in Figure S31 are the M-S model calculations using precisely the same model parameters as used in the analysis of the experimental data of Sandström et al.$^{45}$ $\rho D_1(0)/\delta = 3.2$, $\rho D_2(0)/\delta = 100$ kg m$^{-2}$ s$^{-1}$, and $D_z/D_{12} = 10.0\theta$. The only essential difference in the calculations presented in Figure S30 and Figure S31 are that use of two different single-site Langmuir parameters for the 296 K, and 273 K, respectively.

### 8.3 CH$_4$/C$_2$H$_6$, and CH$_4$/C$_3$H$_8$ permeation at 303 K

For analysis of the CH$_4$/C$_2$H$_6$, and CH$_4$/C$_3$H$_8$ permeation data at 303 K of van de Graaf et al.$^{47}$ the required isotherm parameters are specified in Table S6. The analysis of the permeation data are summarized in Figure S32, and Figure S33.
8.4 CH₄/n-C₄H₁₀ permeation at various temperatures

For analysis of the experimental data of Vroon et al.⁴⁸ for CH₄/n-C₄H₁₀ permeation the required unary isotherm fit parameters are provided in Table S7. The analysis of the permeation data is summarized in Figure S34.

8.5 nC₆/22DMB permeation at 398 K

For analysis of the experimental data of Gump et al.⁴⁹ for nC₆/22DMB permeation data at 398 K, the required unary isotherm fit parameters are provided in Table S8. The unary isotherm fits are based on CBMC simulation data presented in Figure S35. The analysis of the permeation data is summarized in Figure S36.
8.6 List of Tables for MFI zeolite membrane permeation

Table S5. Langmuir parameter fits for CO$_2$ and H$_2$ in MFI (silicalite-1) zeolite. The CO$_2$ isotherm fits are based on CBMC simulation data at three different temperatures, 200 K, 253 K, and 300 K. The H$_2$ fits are based on CBMC simulation data at 300 K, combined with experimental data of Golden and Sircar$^{50}$ at 305.15 K, and 353.25 K. The $T$-dependent isotherm fits from the sets of data were interpolated, or extrapolated, to 273 K and 296 K. The single-site Langmuir parameters at these two temperatures are provided below.

$T = 273$ K:

|          | $q = \frac{q_{sat}bp}{1+bp}$ | $q_{sat}$ | $b$     |
|----------|-----------------------------|----------|---------|
|          | mol kg$^{-1}$               |          | Pa$^{-1}$|
| CO$_2$   | 3.7                         | 1.447×10$^{-5}$ |
| H$_2$    | 3.7                         | 7.70×10$^{-8}$ |

$T = 296$ K:

|          | $q = \frac{q_{sat}bp}{1+bp}$ | $q_{sat}$ | $b$ |
|----------|-----------------------------|----------|-----|
|          | mol kg$^{-1}$               |          | Pa$^{-1}$|
| CO$_2$   | 3.7                         | 5.94×10$^{-6}$ |
| H$_2$    | 3.7                         | 5.50×10$^{-8}$ |
Table S6. Dual-site Langmuir-Freundlich parameters for CH₄, C₂H₆, and C₃H₈ molecules in MFI at 303 K. The isotherm parameters were obtained by fitting to CBMC simulated isotherms as reported in earlier work.⁵ To convert saturation loadings from molecules uc⁻¹ to mol kg⁻¹, multiply by 0.173367.

|       | Site A |          |          | Site B |          |          |
|-------|--------|----------|----------|--------|----------|----------|
|       | Θₐ,ₛₐₜ | bₐ       | νₐ       | Θₐ,ₛₜ | bₐ       | νₐ       |
|       | molecules uc⁻¹ | Pa⁻ν | dimensionless | molecules uc⁻¹ | Pa⁻ν | dimensionless |
| CH₄   | 7      | 5.00E⁻⁰⁹ | 1        | 16     | 3.10E⁻⁰⁶ | 1        |
| C₂H₆  | 3.3    | 4.08E⁻⁰⁷ | 1        | 13     | 7.74E⁻⁰⁵ | 1        |
| C₃H₈  | 1.4    | 3.35E⁻⁰⁴ | 0.67     | 10.7   | 6.34E⁻⁰⁴ | 1.06     |
Table S7. Dual-site Langmuir-Freundlich parameters for CH$_4$, and n-C$_4$H$_{10}$ molecules in MFI at various temperatures $T$. CBMC simulations of unary isotherms at various temperatures were fitted with

$$q = q_{A,sat} \frac{b_A P^{v_A}}{1 + b_A P^{v_A}} + q_{B,sat} \frac{b_B P^{v_B}}{1 + b_B P^{v_B}}.$$  The $b$ parameters for each site are temperature-dependent

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \quad b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right).$$  The parameters are provided in the Table below. To convert saturation loadings from molecules uc$^{-1}$ to mol kg$^{-1}$, multiply by 0.173367.

|       | Site A |       | Site B |       |       |       |
|-------|--------|-------|--------|-------|-------|-------|
|       | $q_{A,sat}$ molecule uc$^{-1}$ | $b_{A0}$ Pa$^{-v_A}$ | $E_A$ kJ mol$^{-1}$ | $V_A$ dimensionless | $q_{B,sat}$ molecule uc$^{-1}$ | $b_{B0}$ Pa$^{-v_B}$ | $E_B$ kJ mol$^{-1}$ | $V_B$ dimensionless |
| CH$_4$ | 7      | 9.52E-08 | 10     | 0.6   | 16    | 5.51E-10 | 21     | 1     |
| nC$_4$H$_{10}$ | 2.5    | 6.6E-09  | 35     | 10.64 | 7.4   | 3.98E-15 | 70     | 1.35  |
Table S8. Dual-site Langmuir-Freundlich parameters for nC6, and 22DMB molecules in MFI at 398 K. The isotherm parameters were obtained by fitting to CBMC simulated isotherms as reported in earlier work.\textsuperscript{5} To convert saturation loadings from molecules uc\textsuperscript{-1} to mol kg\textsuperscript{-1}, multiply by 0.173367.

|       | Site A                                      | Site B                                      |
|-------|---------------------------------------------|---------------------------------------------|
|       | $\Theta_{\text{A,sat}}$ molecules uc\textsuperscript{-1} | $\Theta_{\text{B,sat}}$ molecules uc\textsuperscript{-1} |
|       | $b_\Lambda$ Pa$^{-\nu}$ | $b_\Lambda$ Pa$^{-\nu}$ | $\nu_\Lambda$ dimensionless | $\nu_\Lambda$ dimensionless |
| nC6   | 4                                           | 3.7                                         | 1.24E-03                 | 1.104E-04                 | 1 |
| 22DMB | 4                                           | 1.24E-03                                   | 1 |
Figure S26. Structural details and pore landscape for MFI zeolite.
MFI pore dimensions

10 ring channel of MFI viewed along [100]

5.4 Å

5.6 Å

10 ring channel of MFI viewed along [010]

5.4 Å

5.5 Å

Snapshot of CH₄ and C₂H₆

Snapshot of CH₄ and C₃H₈

Figure S27. Structural details and pore landscape for MFI zeolite.
Figure S28. Experimental data of Sandström et al.\textsuperscript{45} on component permeances for 50/50 CO\textsubscript{2}/H\textsubscript{2} binary mixture permeation across MFI membrane at 296 K, compared to unary permeation data. The data are plotted as function of (a) upstream partial pressures, $p_{\text{10}}$, (b) adsorption potential $\frac{\pi A}{RT}$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S29. Schematic showing binary mixture permeation across microporous membrane.
Figure S30. Experimental data of Sandström et al.\textsuperscript{45} on component permeances for 50/50 CO\textsubscript{2}/H\textsubscript{2} binary mixture permeation across MFI membrane at 296 K, compared with the M-S model calculations for various values of the degrees of correlation. The data are plotted as function of (a, b) adsorption potential $\pi A/RT$ and (c, d) occupancy $\theta$ at the upstream face of the membrane.
Figure S31. Experimental data of Sjöberg et al.\textsuperscript{46} on component permeances for 50/50 CO\textsubscript{2}/H\textsubscript{2} binary mixture permeation across MFI membrane at 273 K. The data are plotted as function of (a) upstream partial pressures, $p_{\text{in}}$, (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane. The continuous solid lines are the M-S model calculations.
Figure S32. Experimental data of van de Graaf et al.\textsuperscript{47} on component permeances for CH$_4$/C$_2$H$_6$ binary mixture permeation across MFI membrane at 303 K, and 101 kPa. The data are plotted as function of (a) upstream feed compositions and (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S33. Experimental data of van de Graaf et al.\textsuperscript{47} on component permeances for CH\textsubscript{4}/C\textsubscript{3}H\textsubscript{8} binary mixture permeation across MFI membrane at 303 K, and 101 kPa. The data are plotted as function of (a) upstream feed compositions and (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S34. Experimental data of Vroon et al.\textsuperscript{48} for unary and 50/50 CH\textsubscript{4}/n-C\textsubscript{4}H\textsubscript{10} component permeances across MFI membrane at 100 kPa, and various temperatures. The data are plotted as function of (a) temperature and (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
Figure S35. Configurational-Bias Monte Carlo (CBMC) simulations of unary and 50/50 nC6/22DMB mixture adsorption in MFI at 398 K. The data are plotted as function of upstream partial pressures, $p_{i0}$. 
Figure S36. Experimental data Gump et al.\textsuperscript{49} for unary and 50/50 nC6/22DMB mixture permeances across MFI membrane M2 at 398 K. The data are plotted as function of (a) upstream partial pressures, $p_{i0}$ and (b) adsorption potential $\pi A/RT$ and (c) occupancy $\theta$ at the upstream face of the membrane.
9 Nomenclature

Latin alphabet

$A$ surface area per kg of framework, m$^2$ kg$^{-1}$

$b_A$ dual-Langmuir-Freundlich constant for species $i$ at adsorption site A, Pa$^{-y_A}$

$b_B$ dual-Langmuir-Freundlich constant for species $i$ at adsorption site B, Pa$^{-y_B}$

$[B]$ Maxwell-Stefan matrix, m$^2$ s

$D_i$ Maxwell-Stefan diffusivity for molecule-wall interaction, m$^2$ s$^{-1}$

$D_i(0)$ M-S diffusivity at zero-loading, m$^2$ s$^{-1}$

$D_{ij}$ M-S exchange coefficient, m$^2$ s$^{-1}$

$D_{12}$ M-S exchange coefficient for binary mixture, m$^2$ s$^{-1}$

$f_i$ partial fugacity of species $i$, Pa

$f_t$ total fugacity of bulk fluid mixture, Pa

$n$ number of species in the mixture, dimensionless

$N_i$ molar flux of species $i$ with respect to framework, mol m$^{-2}$ s$^{-1}$

$p_i$ partial pressure of species $i$ in mixture, Pa

$p_t$ total system pressure, Pa

$P_i^0$ sorption pressure, Pa

$q_i$ component molar loading of species $i$, mol kg$^{-1}$

$q_{i,sat}$ molar loading of species $i$ at saturation, mol kg$^{-1}$

$q_t$ total molar loading in mixture, mol kg$^{-1}$

$R$ gas constant, 8.314 J mol$^{-1}$ K$^{-1}$

$T$ absolute temperature, K
Nomenclature

\[ w \] energy of interaction, J mol\(^{-1}\)

\[ x_i \] mole fraction of species \( i \) in adsorbed phase, dimensionless

\[ z \] distance coordinate, m

Greek alphabet

\[ \beta \] parameter defined in equation (S43), and (S44), dimensionless

\[ \Gamma_{ij} \] thermodynamic factors, dimensionless

\[ [\Gamma] \] matrix of thermodynamic factors, dimensionless

\[ \delta_{ij} \] Kronecker delta, dimensionless

\[ \varepsilon \] fractional pore volume of particle, dimensionless

\[ \zeta \] coordination number defined in equation Error! Reference source not found., dimensionless

\[ \lambda \] jump distance in lattice model, m

\[ [\Lambda] \] matrix of Maxwell-Stefan diffusivities, m\(^2\) s\(^{-1}\)

\[ \mu_i \] molar chemical potential of component \( i \), J mol\(^{-1}\)

\[ \pi \] spreading pressure, N m\(^{-1}\)

\[ \Pi_i \] permeance of species \( i \) for zeolite membrane, mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)

\[ \Theta_i \] loading of species \( i \), molecules per unit cell

\[ \Theta_{i,\text{sat}} \] saturation loading of species \( i \), molecules per unit cell

\[ \Theta_t \] total mixture loading, molecules per unit cage, or per unit cell

\[ \nu \] jump frequency, s\(^{-1}\)

\[ \nu \] exponent in dual-Langmuir-Freundlich isotherm, dimensionless

\[ \phi \] parameter defined in equation (S43), and (S44), dimensionless

\[ \rho \] framework density, kg m\(^{-3}\)
Nomenclature

Subscripts

1 referring to component 1
2 referring to component 2
i referring to component \( i \)
t referring to total mixture
sat referring to saturation conditions
10 References

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