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

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Supporting Information

ABSTRACT: The primary objective of this article is to gain fundamental insights into the dependences of component permeances $\Pi_i$ in microporous membranes on the operating conditions (upstream partial pressures, temperature, and feed composition). It is argued that the permeances $\Pi_i$ for unary systems and mixtures need to be compared on the basis of the adsorption potential $\pi A/RT$, a convenient and practical proxy for the spreading pressure $\pi$ that is calculable using the ideal adsorbed solution theory for mixture adsorption equilibrium. The use of $\pi A/RT$ as a yardstick serves to elucidate and rationalize a wide variety of published experimental $\Pi_i$ data on unary and mixture permeances in microporous membranes. For cage-type host structures such as SAPO-34, DDR, and ZIF-8, the $\Pi_i$ values are uniquely dictated by the magnitude of $\pi A/RT$, irrespective of the partner species in the mixture. For MFI membranes, the tardier species slows down the more mobile partners due to correlated molecular motion within the channels; the degree of correlation is also a function of $\pi A/RT$.

1. INTRODUCTION

Membrane technologies find applications in a variety of separation applications such as gas separations and water/ alcohol pervaporation.\textsuperscript{1,2} The permselective membrane layers often consist of microporous materials such as zeolites (aluminosilicates), metal–organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), or carbon molecular sieves.\textsuperscript{3–16} Experimental data on membrane permeation are most commonly presented in terms of the component permeances defined by

$$\Pi_i = \frac{N_i}{p_{i0} - p_{i\delta}}$$

where $N_i$ is the permeation flux and $p_{i0} - p_{i\delta}$ is the difference in the partial pressures at the upstream (subscript 0) and downstream (subscript $\delta$) faces of the membrane layer of thickness $\delta$. The permeance of any guest species is influenced by a variety of factors such as the connectivity and pore topology of the microporous host material, operating conditions (temperature, pressure, and feed mixture composition), and the choice of the partner species in the mixture. The pore landscapes of four important host materials CHA, DDR, ZIF-8, and MFI that have membrane applications are shown in Figure 1. CHA zeolite consists of cages of $316 \ \text{Å}^3$ volume, separated by 8-ring windows of $3.8 \ \text{Å} \times 4.2 \ \text{Å}$ size. DDR zeolite has cages of $278 \ \text{Å}^3$ volume, separated by 8-ring windows of $3.65 \ \text{Å} \times 4.37 \ \text{Å}$ size. ZIF-8 has an SOD (sodalite) topology, consisting of cages of $1168 \ \text{Å}^3$ volume, separated by $3.3 \ \text{Å}$ windows; the windows are flexible. MFI zeolite consists of a set of intersecting straight channels and zigzag (or sinusoidal) channels of $5.5 \ \text{Å}$ size.

Figure 2a,b presents experimental data for permeances of CO$_2$ and H$_2$ determined for unary and mixture permeation across the SAPO-34 membrane. SAPO-34 has the same structural topology as CHA zeolite. Compared at the same partial pressures, the H$_2$ permeance is significantly reduced due to the presence of partner species CO$_2$, CH$_4$, and N$_2$; the reduction is significantly higher with CO$_2$ as a partner. In sharp contrast, CO$_2$ permeance is only marginally influenced by the presence and choice of the partner species in the mixtures: CH$_4$, N$_2$, and H$_2$.

Figure 3a compares the experimental data on permeances of CO$_2$ and H$_2$ determined for unary and binary mixture permeation across an MFI membrane. The CO$_2$ and H$_2$ mixture permeances are both lower than the corresponding values for unary systems when compared at the same partial pressures in the upstream compartment. For H$_2$, the more mobile guest, the
lowering is by about 1 order of magnitude, while the permeance of the tardier CO$_2$ is lowered by a factor of about 2. The data based on unary permeation anticipates H$_2$-selective separation whereas the data for mixture permeation displays CO$_2$-selective separations.

Consider the experimental data for permeation of CH$_4$/C$_2$H$_6$ and CH$_4$/C$_3$H$_8$ mixtures across an MFI membrane at 303 K presented in Figure 3b. The two sets of experimental permeance data are plotted as functions of the mole fraction of the more mobile guest, CH$_4$, in the feed gas mixture in the upstream compartment. Increasing the proportion of the tardier component C$_2$H$_6$ in the CH$_4$/C$_2$H$_6$ feed mixture has the effect of progressively reducing the permeance of the more mobile CH$_4$ by up to an order of magnitude. The reduction of CH$_4$ permeance is significantly higher, by up to 2 orders of magnitude, for CH$_4$/C$_3$H$_8$ mixture permeation.

For 50:50 CH$_4$/n-C$_4$H$_{10}$ mixture permeation across an MFI membrane, the experimental data show that the reduction of CH$_4$ permeance due to the presence of the tardier partner n-C$_4$H$_{10}$ is considerably more significant at lower temperatures (see Figure 3c). As the temperature is increased, the component permeances become closer in values.

The experimental data for permeation of mixtures of n-hexane (nC6) and 2,2-dimethylbutane (22DBM) across an MFI membrane are remarkable in that the permeance of the tardier 22DBM is further reduced by more than 2 orders of magnitude by the presence of the more mobile nC6 partner (see Figure 4). The wide variety of characteristics of membrane permeances witnessed in Figures 2–4 is a reflection of a combination of mixture adsorption equilibrium and mixture diffusion. The mixture adsorption equilibrium dictates the component loadings.
within the membrane layer; the component loadings, in turn, affect the guest mobilities, and slowing-down, or correlation, effects that often influence mixture permeation.\textsuperscript{17–20} The primary objective of this article is to gain fundamental insights into the characteristics of unary and mixture permeances. Specifically, we aim to show that the fundamentally appropriate choice of the $x$ axes in Figures 2–4 is the spreading pressure $\pi$ calculated by use of the ideal adsorbed solution theory (IAST) of Myers and Prausnitz\textsuperscript{21} for mixture adsorption. We shall demonstrate that the spreading pressure not only is a reflection of mixture adsorption equilibrium but also dictates the loading dependence of the guest diffusivities and correlation effects.\textsuperscript{20}

2. METHODOLOGY FOR MODELING OF MIXTURE ADSORPTION AND DIFFUSION

2.1. IAST for Mixture Adsorption Equilibrium. Within microporous crystalline host materials, the guest constituent molecules exist entirely in the adsorbed phase. The Gibbs adsorption equation in differential form is\textsuperscript{22–24}

$$A\ d\pi = \sum_{i=1}^{n} q_i \ d\mu_i$$ \hspace{1cm} (2)

In eq 2, $A$ represents the surface area per kilogram of the framework, $q_i$ is the molar loading, $\mu_i$ is the molar chemical potential, and $\pi$ is the spreading pressure. At phase equilibrium, equating the component chemical potentials $\mu_i$ in the adsorbed phase and in the bulk gas phase mixture in the upstream membrane compartment, we write

![Figure 4.](image)

**Figure 4.** Experimental data of Gump et al.\textsuperscript{47} for unary and 50:50 nC6/22DMB mixture permeances across the MFI membrane M2 at 398 K.

![Figure 5.](image)

**Figure 5.** (a,b) Maxwell–Stefan diffusivity $D_i$ of CO$_2$ determined for MD simulation data\textsuperscript{20} for diffusion of a variety of equimolar ($q_1 = q_2$) CO$_2$/H$_2$, CO$_2$/CH$_4$, and CO$_2$/N$_2$ mixtures in MFI zeolite at 300 K plotted as a function of the (a) adsorption potential $\pi A/RT$ and (b) the occupancy $\theta$. Also shown in open symbols are the MD simulations of $D_i$ for unary CO$_2$ diffusion. (c) MD simulation data\textsuperscript{20} for degree of correlations $D_2/D_{12}$ for equimolar ($q_1 = q_2$) CO$_2$/H$_2$, CO$_2$/CH$_4$, CO$_2$/N$_2$, CH$_4$/C$_2$H$_6$, CH$_4$/C$_3$H$_8$, CH$_4$/n-C$_4$H$_{10}$, and CH$_4$/n-C$_6$H$_{14}$ mixtures in MFI zeolite at 300 K. (d) MD simulation data\textsuperscript{20} for degree of correlations $D_2/D_{12}$ for equimolar ($q_1 = q_2$) CO$_2$/H$_2$ mixtures in MFI, MgMOF-74, and LTA at 300 K.
\[
d\mu_i = RT \ln p_i 
\]  
\[
\rho \frac{d\mu_i}{dz} = \frac{x_i N_1 - x_i N_2}{D_{12}} + \frac{N_1}{D_1} 
\]

Briefly, the basic equation of the IAST theory is the analogue of Raoult’s law for vapor—liquid equilibrium, that is

\[
p_i = P_i^0 x_i; \quad i = 1, 2, \ldots, n
\]

where \( x_i \) is the mole fraction in the adsorbed phase defined by

\[
x_i = q_i / q; \quad q_i = q_1 + q_2 + \ldots + q_n; \quad i = 1, 2, \ldots, n
\]

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:

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

In eq 6, \( q_i^0(f) \) is the pure component adsorption isotherm. Since the surface area \( A \) is not directly accessible from experimental data, the adsorption potential \( \pi A/RT \), with a unit of mole per kilogram, serves as a convenient and practical proxy for the spreading pressure, \( \pi \). For the simple case of a binary mixture in which each isotherm is described by the single-site Langmuir model with equal saturation capacities for each constituent

\[
q_i^0(f) = q_{sat1} \left( 1 + b_f f \right) \quad i = 1, 2
\]

the following explicit expression can be derived

\[
\frac{\pi A}{RT} = q_{sat} \ln(1 + b_f p_1 + b_f p_2)
\]

For the more general case in which the saturation capacities of the constituents are unequal, the entire set of equations must be solved numerically. The unary isotherm data for all guest/host combinations analyzed in this article, along with the numerical details for determination of \( \pi A/RT \), are provided in the Supporting Information.

2.2. Maxwell—Stefan Description of Mixture Diffusion.

The Maxwell—Stefan (M—S) approach is the most convenient and practical formulation that relates the molar permeation fluxes to the gradients of the molar chemical potential of the guest constituents. For binary mixtures, the M—S equations are

\[
\begin{align*}
-\rho \frac{d\mu_1}{dz} &= \frac{x_1 N_1 - x_1 N_2}{D_{12}} + \frac{N_1}{D_1} \\
-\rho \frac{d\mu_2}{dz} &= \frac{x_2 N_2 - x_2 N_1}{D_{12}} + \frac{N_2}{D_2}
\end{align*}
\]

where \( \rho \) represents the framework density of the microporous crystalline material. The \( D_1 \) and \( D_2 \) characterize the guest—wall interactions. The exchange coefficient \( D_{12} \) reflects how the facility for transport of species \( i \) correlates with that of species \( j \). The ratios \( D_1/D_{12} \) and \( D_2/D_{12} \) quantify the degrees of correlation. The magnitude of \( D_i \), relative to that of \( D_{12} \), determines the extent to which the flux of species \( i \) is influenced by the chemical potential gradient of species \( 2 \). The larger is the degree of correlation, \( D_1/D_{12} \), the stronger is the influence of diffusional “coupling.”

The persuasive advantage of using the M—S formulation is that the M—S diffusivities \( D_i \) can be identified with the corresponding diffusivities for unary systems provided that the values are determined at the same adsorption potential \( \pi A/RT \); this has been established in earlier work with the aid of molecular dynamics (MD) simulations for a vast number of mixture diffusion in several zeolites and MOFs. As illustrated, Figure 5a compares the M—S diffusivity \( D_1 \) of CO2 for MD simulation data for diffusion of equimolar \( (q_1 = q_2) \) CO2/H2, CO2/CH4, and CO2/N2 mixtures in MFI zeolite with the corresponding unary diffusivity. Compared at the same value of \( \pi A/RT \), the M—S diffusivities \( D_i \) have practically the same value, confirming that the adsorption potential is the correct yardstick to compare diffusivities. To rationalize the lowering of the M—S diffusivity with increasing values of \( \pi A/RT \), we plot in Figure 5b the diffusivity data as a function of the fractional occupancy \( \theta \) determined from

\[
\theta = 1 - \exp(-\pi A/q_{sat}RT)
\]

For a binary mixture, the saturation capacity \( q_{sat} \) is defined as follows

\[
\frac{1}{q_{sat}} = \frac{x_1}{q_{1,sat}} + \frac{x_2}{q_{2,sat}}
\]

Increasing the fractional occupancy lowers the values of \( D_i \) because the channels of MFI become increasingly crowded; indeed, \( D_i \to 0 \) as \( \theta \to 1 \) for all guest species. For binary mixtures in which the unary isotherms are described by eq 7, eqs 10 and 11 are simplified to yield

\[
\theta = \frac{q_{sat}}{q_{1,sat}} = \frac{b_1 p_1 + b_2 p_2}{1 + b_1 p_1 + b_2 p_2}
\]

The simplest model to describe the occupancy dependence is indicated by the dashed line in Figure 5b

\[
D_i = D_i(0)(1 - \theta)
\]

where \( D_i(0) \) is the M—S diffusivity at “zero loading”. Equation 13 is essentially based on a simple hopping model in which a molecule can jump from one adsorption site to an adjacent one, provided that it is not already occupied. Using a simple two-dimensional square lattice model, the M—S diffusivity in the limit of vanishingly small occupancies is \( D_i(0) = \frac{1}{4} \nu(0)^2 \), where \( \nu(0) \) is the jump frequency in the square lattice, and \( \nu(0) \) is the jump frequency at a vanishingly small occupancy. 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, \( w < 0 \). The quasichemical approach of Reed and Ehrlich can be used to quantify such interactions.

The implication of the plots in Figure 5a,b is that \( \pi A/RT \) and \( \theta \) are the appropriate thermodynamic measures of the loadings within the pores of microporous materials.

MD simulation data for several mixture/host combinations also show that the degree of correlation increases with pore occupancy, practically linearly, as illustrated in Figure 5c for binary mixtures in MFI zeolite. For CO2/CH4 mixtures, the
degrees of correlation for MFI, MgMOF-74, and LTA are compared in Figure 5d. For LTA with narrow windows separating adjacent cages, the degree of correlation is significantly lower than those for MFI and MgMOF-74.

From the LAST and M–S theories, it emerges that the adsorption potential \( \pi A/RT \) not only encapsulates mixture adsorption equilibrium but also serves as the proper measure of the loading dependence of the M–S diffusivities \( D_1 \) and \( D_2 \) and the degree of correlation \( D_1/D_2 \). We should therefore expect \( \pi A/RT \) to be the correct yardstick to compare component permeances for unary and mixture permeation in Figures 2–4.

3. RESULTS AND DISCUSSION

3.1. Permeation across SAPO-34, DDR, and ZIF-8 Membranes. Figure 6 presents plots of the component permeances for \( \text{CO}_2 \) and \( \text{H}_2 \) determined for unary and equimolar binary mixture permeation across the SAPO-34 membrane at 295 K, plotted as a function of \( \pi A/RT \) calculated at the upstream face of the membrane, in equilibrium with the feed mixture in the upstream compartment. The \( \text{CO}_2 \) and \( \text{H}_2 \) permeances appear to be uniquely dependent on the adsorption potential and are independent of the partner species. The reasons for this simple and convenient finding are threefold: (i) the mixture adsorption equilibrium between the feed mixture and the upstream face of the membrane is properly quantified by the choice of \( \pi A/RT \) as the adsorption potential, (ii) the loading dependence of the diffusivities is also described by \( \pi A/RT \), and (iii) the correlation effects are of negligible importance in SAPO-34 because the guest molecules jump one at a time across the narrow windows, resulting in \( D_1/D_2 \to 0 \) as evidenced by MD data.

In Figure 7a–c, the experimental data on component permeances for 50:50 \( \text{CO}_2/\text{CH}_4 \) and 50:50 \( \text{N}_2/\text{CH}_4 \) mixture permeation across a DDR membrane are plotted as a function of \( \pi A/RT \).
the adsorption potential at the upstream face of the membrane. The intercage hopping of guest molecules is uncorrelated, and there are no slowing-down effects experienced by the more mobile partner species. The component permeances in the mixture have the same values as those in the corresponding unary systems. The CH₄ permeance is independent of the choice of CO₂ or N₂ as a partner in the mixture (see Figure 7c).

Experimental data for component permeances for 50:50 C₂H₆/C₃H₈ binary mixture permeation across the ZIF-8 membrane at 308 K have practically the same magnitudes as the corresponding unary permeances when compared at the same πA/RT at the upstream face of the membrane (see Figure 8). The explanation is precisely analogous to that for SAPO-34 and DDR membranes.

3.2. Permeation across an MFI Membrane. Correlation or slowing-down effects are of significant importance for guest diffusion in MFI zeolite, as has been established by MD simulations¹⁻²⁻²⁰ (see data on degrees of correlation in Figure 5c,d). Consequently, the permeance of more mobile partners should be expected to be lowered due to correlated jumps with the tardier partner species within the pores. Figure 9a,b compares the component permeances of 50:50 CO₂/H₂ feed mixtures in the MFI membrane with the corresponding values for the unary species. Also shown by continuous solid lines are the estimations using the M–S model.¹⁹ In the model calculations, the occupancy dependence of each guest is assumed to follow eq 13 wherein the zero-loading diffusivities are fitted from the unary permeance data: ρD₁(0)/δ = 3.2 and ρD₂(0)/δ = 100 kg m⁻² s⁻¹. The degree of correlation is taken to increase linearly with occupancy θ. The H₂ permeance is significantly influenced by correlation effects, as evidenced in Figure 9b with calculations for D₂/D₁₂ = 1.0θ, 3.0θ, and 10.0θ; the choice D₂/D₁₂ = 10.0θ affords the best match with experimental data and is also in accordance with the MD data in Figure 5d.

Figure 10a,b compares the permeances for (a) CH₄/C₂H₆ and (b) CH₄/C₃H₈ mixtures in MFI with the corresponding values for unary systems as a function of πA/RT. For both mixtures, the permeances of the more strongly adsorbed but tardier components in the two mixtures, C₂H₆ and C₃H₈, are practically the same as the unary values. The permeance of the more mobile CH₄ is reduced significantly below the unary values due to two separate reasons: (i) the M–S diffusivity of CH₄ reduces with increasing values of πA/RT and (ii) the CH₄ mobility in the intersecting channel structures is strongly correlated with those of the tardier partners C₂H₆ and C₃H₈. The correlation effects increase with increasing values of πA/RT, as evidenced in the MD simulation data in Figure 5c. It is also noteworthy that the degree of correlations for CH₄/C₂H₆ mixtures is higher than that for CH₄/C₃H₈; this rationalizes the stronger reduction in the CH₄ permeance due to partnership with C₃H₈.

The influence of the operating temperature for CH₄/n-C₄H₁₀ mixture permeation across the MFI membrane (cf. Figure 3d) is simply elucidated by plotting the permeances as a function of πA/RT, calculated at the upstream face of the membrane (see Figure 10c). The permeance of the tardier, more strongly adsorbed n-C₄H₁₀ is practically the same as the corresponding values for unary diffusion. The permeance of the more mobile, poorly adsorbed CH₄ is reduced significantly below the unary values due to reduction in the M–S diffusivity of CH₄ with increased pore occupancy and the increasing influence of correlations, as evidenced in the MD simulation data in Figure 5c.
The explanation of the nC6/22DMB mixture permeation data in Figure 4 requires insights into entropy effects in mixture adsorption,\textsuperscript{33−37} gained from configurational-bias Monte Carlo (CBMC) simulations\textsuperscript{36,37} for nC6/22DMB mixture adsorption. The linear nC6 molecule can locate along both the straight channels and zigzag channels, whereas the more compact but bulkier dibranched isomer 22DMB can locate only at the intersections (see computational snapshots in Figure 11a). Per unit cell of MFI, there are only four intersection sites, and therefore, the saturation capacity of 22DMB is restricted to four molecules per unit cell. On the other hand, the saturation capacity for nC6 is eight molecules per unit cell. CBMC simulations for nC6/22DMB mixture adsorption show that, for bulk phase partial pressure \( p_i = 1 \) kPa, the 22DMB loading

Figure 10. Experimental data of van de Graaf et al.\textsuperscript{45} for component permeances of (a) CH\(_4\)/C\(_2\)H\(_6\) and (b) CH\(_4\)/C\(_3\)H\(_8\) mixtures in MFI membrane at 303 K. (c) Experimental data of Vroon et al.\textsuperscript{46} for 50:50 CH\(_4\)/n-C\(_4\)H\(_10\) mixture permeation across the MFI membrane at a total pressure of 100 kPa and varying temperatures. The x axes in panels (a), (b), and (c) represent the adsorption potential, corresponding to the conditions at the upstream face of the membrane.

The explanation of the nC6/22DMB mixture permeation data in Figure 4 requires insights into entropy effects in mixture adsorption,\textsuperscript{33−37} gained from configurational-bias Monte Carlo (CBMC) simulations\textsuperscript{36,37} for nC6/22DMB mixture adsorption. The linear nC6 molecule can locate along both the straight channels and zigzag channels, whereas the more compact but bulkier dibranched isomer 22DMB can locate only at the intersections (see computational snapshots in Figure 11a). Per unit cell of MFI, there are only four intersection sites, and therefore, the saturation capacity of 22DMB is restricted to four molecules per unit cell. On the other hand, the saturation capacity for nC6 is eight molecules per unit cell. CBMC simulations for nC6/22DMB mixture adsorption show that, for bulk phase partial pressure \( p_i = 1 \) kPa, the 22DMB loading

Figure 11. (a) Computational snapshots showing the location of nC6 and 22DMB within the intersecting channels of MFI zeolite. (b) Configurational-bias Monte Carlo simulations of nC6/22DMB mixture adsorption in MFI at 398 K. Also shown in the right y axis is the adsorption potential \( \pi_A/RT \). (c) Experimental data of Gump et al.\textsuperscript{47} for component permeances for nC6/22DMB mixture in MFI membrane M2 at 398 K plotted as a function of the adsorption potential \( \pi_A/RT \) at the upstream face of the membrane.
reaches a maximum value at an adsorption potential $\pi A/RT$ of 1.2 mol kg$^{-1}$ (see Figure 11b). For $p_i > 1$ kPa and $\pi A/RT > 1.2$ mol kg$^{-1}$, the increase of bulk phase partial pressures results in the decrease in the 22DMB loading, engendered by entropy effects that can be elucidated by invoking the entropy maximization principle of Boltzmann $S = k_B \ln(W)$.[33,39] The experimental permeance data for 50:50 $n$C6/22DMB mixtures were obtained under conditions corresponding to $\pi A/RT > 1.2$ mol kg$^{-1}$ (cf. Figure 11c), and the sharp reduction in 22DMB permeance below the unary permeance values is entirely ascribable to configurational entropy effects that cause 22DMB loading at the upstream to decrease despite the increase in the bulk phase partial pressures. Unusually, both adsorption and diffusion act in synergy to suppress 22DMB permeation; this synergy is also observed for transient uptake of hexane isomers in MFI zeolite.60

4. CONCLUSIONS

The following major conclusions emerge from our investigations.

1. The adsorption potential, $\pi A/RT$, calculable from the IAST, is the proper yardstick to compare permeances in mixtures with the corresponding data for unary systems.

2. The adsorption potential quantifies the thermodynamic equilibrium between the fluid mixture in the upstream compartment and the adsorbed phase in the upstream face of the membrane. The IAST prescribes that the adsorption potential $\pi A/RT$, a practical proxy for the spreading pressure $\pi$, be equal for each of the pure constituents and the mixture (see eq 6).

3. The same parameter $\pi A/RT$ also dictates the variation of the Maxwell–Stefan diffusivities, $D_1$ and $D_2$ and the degree of correlations $D_{12}/D_{11}$ with pore occupancy (see Figure 5). The degree of correlations depends on the guest/host combination.

4. For cage-type zeolite structures such as SAPO-34, DDR, and ZIF-8, the intercage hopping of guest molecules is practically uncorrelated. Therefore, the component permeances in such structures are uniquely dictated by the magnitude of $\pi A/RT$, irrespective of the partner species in the mixture.

5. In topologies such as MFI, correlation effects cause the permeance of the more mobile, less strongly adsorbed component to be lowered due to correlations with the tardier, more strongly adsorbed partners; the extent of lowering also correlates with $\pi A/RT$.

6. Also highlighted in this article is the permeation of $n$C6/22DMB mixtures in the MFI membrane; here, configurational entropy effects cause a significant lowering in the permeance of the tardier dibranched isomer.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00907.

Detailed derivation of the IAST calculation procedures for the spreading pressure and the adsorption potential using the unary adsorption isotherms, structural details for host materials considered and analyzed in this article, and unary isotherm parameter fits for all guest/host combinations considered in our article (PDF)

## REFERENCES


