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Using Molecular Simulations to Unravel the Benefits of Characterizing Mixture Permeation in Microporous Membranes in Terms of the Spreading Pressure

Rajamani Krishna* and Jasper M. van Baten

ABSTRACT: The separation performance of microporous crystalline materials in membrane constructs is dictated by a combination of mixture adsorption and intracrystalline diffusion characteristics; the permeation selectivity $S_{perm}$ is a product of the adsorption selectivity $S_{ads}$ and the diffusion selectivity, $S_{diff}$. The primary objective of this article is to gain fundamental insights into $S_{ads}$ and $S_{diff}$ by use of molecular simulations. We performed configurational-bias Monte Carlo (CBMC) simulations of mixture adsorption equilibrium and molecular dynamics (MD) simulations of guest self-diffusivities of a number of binary mixtures of light gaseous molecules (CO$_2$, CH$_4$, N$_2$, H$_2$, and C$_2$H$_6$) in a variety of microporous hosts of different pore dimensions and topologies. Irrespective of the bulk gas compositions and bulk gas fugacities, the adsorption selectivity, $S_{ads}$, is found to be uniquely determined by the adsorption potential, $\Phi$, a convenient and practical proxy for the spreading pressure $\pi$ that is calculable using the ideal adsorbed solution theory for mixture adsorption equilibrium. The adsorption potential $\Phi$ is also a proxy for the pore occupancy and is the thermodynamically appropriate yardstick to determine the loading and composition dependences of intracrystalline diffusivities and diffusion selectivities, $S_{diff}$. When compared at the same $\Phi$, the component permeabilities, $\Pi_i$ for CO$_2$, CH$_4$, and N$_2$, determinable from CBMC/MD data, are found to be independent of the partners in the various mixtures investigated and have practically the same values as the values for the corresponding unary permeabilities. In all investigated systems, the H$_2$ permeability in a mixture is significantly lower than the corresponding unary value. These reported results have important practical consequences in process development and are also useful for screening of materials for use as membrane devices.

1. INTRODUCTION

Membrane technologies find applications in a variety of separation applications such as gas separations and water/ alcohol pervaporation.$^{1-5}$ The perm-selective membrane layers often consist of crystalline microporous materials such as zeolites (alumino-silicates)$^{6-12}$ metal–organic frameworks (MOFs),$^{13,14}$ or zeolitic imidazolate frameworks (ZIFs).$^{15,16}$

For any given application, the separation performance of a microporous membrane is characterized by two metrics: permeability and permeation selectivity. The permeability of component $i$ is defined as follows

$$\Pi_i = \frac{N_i}{\Delta f / \delta}$$

(1)

where $N_i$ is the permeation flux and $\Delta f = f_i - f_\delta$ is the difference in the partial fugacities between the upstream ($f_i$) and downstream ($f_\delta$) faces of the membrane layer of thickness $\delta$. Often, the component permeances, defined by $N_i/\Delta f_i \equiv \Pi_i/\delta_i$, are more easily accessible from experiments because of uncertainties in the precise values of the membrane thickness, $\delta$. For binary mixtures, the membrane permeation selectivity, $S_{perm}$, is defined as the ratio of the component permeabilities

$$S_{perm} = \frac{\Pi_1}{\Pi_2}$$

(2)

Following Robeson,$^{17}$ it is a common practice to plot the experimental data on $S_{perm}$ as a function of $\Pi_i$ for evaluation of membrane materials; the best material would occupy the top right corner of such Robeson plots.$^{18-21}$

If the partial fugacities of the components at the downstream face are negligibly small in comparison with those at the upstream face, $\Delta f_i \approx f_\delta$, the component permeabilities may be estimated from

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\[ \Pi_i = \frac{\rho D_{i,\text{self}} q_i}{f_i} \]  

where \( \rho \) is the crystal framework density, \( q_i \) are the component loadings at the upstream face, and \( D_{i,\text{self}} \) are the component self-diffusivities that are readily accessible from either molecular dynamics (MD) simulations or experiments.\(^{19,20,22}\) Combining eqs 2 and 3, we can express the permeation selectivity \( S_{\text{perm}} \) as a product of the adsorption selectivity

\[ S_{\text{ads}} = \frac{q_1 / q_2}{f_1 / f_2} \]  

and diffusion selectivity

\[ S_{\text{diff}} = \frac{D_{1,\text{self}}}{D_{2,\text{self}}} \]  

The detailed derivation of eq \( S \), starting with the Maxwell–Stefan diffusion formulation,\(^{23,24}\) is available in earlier works.\(^{19,25}\) For any guest/host combination, published data from MD simulations and experiments show that the diffusivities \( D_{i,\text{self}} \) are strongly dependent on the component loadings \( q_i \).\(^{23,24,26,27}\) The component loadings, in turn, are strongly dependent on the total fugacity, fluid phase fugacity \( f_i = f_{i1} + f_{i2} \) and gas mixture composition, \( y_i = f_{i1} / f_t \)

As an illustration, Figure 1a,b presents data on \( S_{\text{ads}} \) obtained from configurational-bias Monte Carlo (CBMC) simulations of \( \text{CO}_2(1)/\text{CH}_4(2) \) mixtures in CHA zeolite at 300 K. In the (a) bulk gas-phase, mole fractions are maintained at \( y_1 = 0.5 \) or \( y_1 = 0.15 \) and \( S_{\text{ads}} \) is plotted as a function of the bulk gas mixture fugacity, \( f_t = f_{11} + f_{12} = 10^8 \) Pa, and \( S_{\text{ads}} \) is plotted as a function of the bulk gas mole fraction of \( \text{CO}_2, y_1 \). Figures 1c,d MD simulations of the diffusion selectivities, \( S_{\text{diff}} \), obtained from four different campaigns, plotted as a function of the (c) total load, \( q_t = q_{1t} + q_{2t} \) and (d) mole fraction of \( \text{CO}_2 \) in the adsorbed phase, \( x_1 = q_{1t} / q_t \). All simulation details and input data are provided in the Supporting Information accompanying this publication.

Figure 1. (a,b) CBMC simulations of the adsorption selectivity, \( S_{\text{ads}} \), for \( \text{CO}_2(1)/\text{CH}_4(2) \) mixtures in CHA zeolite at 300 K. In the (a) bulk gas-phase, mole fractions are maintained at \( y_1 = 0.5 \) or \( y_1 = 0.15 \) and \( S_{\text{ads}} \) is plotted as a function of the bulk gas mixture fugacity, \( f_t = f_{11} + f_{12} = 10^8 \) Pa, and \( S_{\text{ads}} \) is plotted as a function of the bulk gas mole fraction of \( \text{CO}_2, y_1 \). (c,d) MD simulations of the diffusion selectivities, \( S_{\text{diff}} \), obtained from four different campaigns, plotted as a function of the (c) total load, \( q_t = q_{1t} + q_{2t} \) and (d) mole fraction of \( \text{CO}_2 \) in the adsorbed phase, \( x_1 = q_{1t} / q_t \). All simulation details and input data are provided in the Supporting Information accompanying this publication.
increasing proportion of CO$_2$ in the adsorbed phase; see Figure 1d.

On the basis of eqs 3−5 and 7 along with the set of CBMC and MD data on $S_{\text{ads}}$ and $S_{\text{diff}}$ in Figure 1, we would conclude that the permeation selectivity $S_{\text{perm}}$ = $S_{\text{ads}}$× $S_{\text{perm}}$ (7)

exhibits a complex dependence of both $f_1 = f_1 + f_2$ and $y_1$ at the upstream face. As a corollary to the composition dependences, we would be prompted to conclude that $S_{\text{perm}}$ cannot be estimated on the basis of the data on the permeabilities of the unary guest species. As illustration, Figure 2 presents experimental data$^{6−8}$ for permeances of (a) CO$_2$, (b) CH$_4$, (c) H$_2$, and (d) N$_2$ determined for unary and equimolar binary mixture permeation across the SAPO-34 membrane at 295 K. The permeances are plotted as function of the partial pressures $p_i^0$ at the upstream face of the membrane. All calculation details and input data are provided in the Supporting Information accompanying this publication.

The primary objective of this article is to gain more fundamental insights into the characteristics of $\Pi_i$ and $S_{\text{perm}}$ in ordered crystalline microporous materials so as to enable their estimations using more easily accessible data inputs on unary adsorption isotherms and unary diffusivities. In particular, we aim to demonstrate the benefits of using the spreading pressure $\pi$, as the thermodynamically correct parameter to quantify the extent of pore occupancy; the $\pi$ is calculable using the ideal adsorbed solution theory (IAST) of Myers and Prausnitz.$^{28}$ We shall establish that data on permeabilities of unary guests may indeed be gainfully employed for prediction of mixture permeation, provided the comparisons are made at the same values of the spreading pressure $\pi$.

The desired objectives are met by detailed analysis of CBMC and MD data on adsorption and diffusion of light gaseous molecules (CO$_2$, CH$_4$, N$_2$, H$_2$, and C$_2$H$_6$) and their binary mixtures (CO$_2$/CH$_4$, CO$_2$/N$_2$, CO$_2$/H$_2$, CH$_4$/H$_2$, and CH$_4$/C$_2$H$_6$) in a variety of porous crystalline hosts. The host materials are carefully chosen to represent four different pore...
topologies: (i) intersecting channels \([\text{MFI} \approx 5.5 \text{ Å}]\), (ii) cages separated by narrow \((\approx 3.3 - 3.8 \text{ Å})\) windows \((\text{CHA, DDR, ZIF-8})\), and (iii) cavities separated by large \((\approx 7.4 \text{ Å})\) windows \((\text{FAU, NaY, NaX})\), (iv) one-dimensional channels \([\text{MgMOF-74} \approx 11 \text{ Å}], \text{and meso-porous BTP-COF}^{30} \approx 34 \text{ Å}]\). The Supporting Information accompanying this publication provides (a) detailed structural information on all host materials, (b) CBMC and MD simulation methodologies, (c) CBMC data on unary isotherms and isotherm fits, and (d) CBMC and MD data on adsorption, diffusion, and permeation of variety of mixtures. The entire CBMC and MD data sets are summarized in Figures S9—S55 of the Supporting Information.

2. RESULTS AND DISCUSSION

2.1. Spreading Pressure and Its Proxy. Within microporous crystalline host materials, the guest constituent molecules exist entirely in the adsorbed phase. The Gibbs adsorption equation in differential form is as follows\(^{31-33}\)

\[
A \, d\sigma = \sum_{i=1}^{n} q_i \, d\mu_i
\]  

In eq 8, \(A\) represents the surface area per kg of 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

\[
d\mu_i = RT \, d\ln f_i\]  

The basic equation of IAST of Myers and Prausnitz\(^{28}\) is the analogue of Raoult’s law for vapor—liquid equilibrium that is

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

where \(P_i^0\) 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 binary mixture

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

In eq 11, \(q_i^0(f)\) is the pure component adsorption isotherm. For general background to the various forms of analytic expressions to model the unary isotherms in different host materials, the reader is referred to the published literature.\(^{34-38}\) For all of the guest/host combinations considered
in this article, the unary isotherms, determined from CBMC, are accurately described by the dual-Langmuir−Freundlich model
\[ q(f) = q_{\text{sat}}^A \frac{b_A f^\nu_A}{1 + b_A f^\nu_A} + q_{\text{sat}}^B \frac{b_B f^\nu_B}{1 + b_B f^\nu_B} \]
\[ \left( \begin{array}{c} \nu_A \\ \nu_B \end{array} \right) \]
(12)
Each of the integrals in eq 11 can be evaluated analytically
\[ \frac{\pi A}{RT} = \int_{0}^{P_i} \frac{q_i(f)}{f} \, df \]
\[ = \frac{q_{\text{sat}}^A}{\nu_A} \ln(1 + b_A(P_i)^{\nu_A}) + \frac{q_{\text{sat}}^B}{\nu_B} \ln(1 + b_B(P_i)^{\nu_B}) \]
\[ \left( \begin{array}{c} \nu_A \\ \nu_B \end{array} \right) \]
(13)
Because the surface area \( A \) is not directly accessible from experimental data, the adsorption potential \( \pi A/RT \equiv \Phi \)
with the units mol kg\(^{-1}\), serves as a convenient and practical proxy for the spreading pressure \( \pi \). For binary mixture adsorption, each of the equalities on the right hand side of eq 11 must be satisfied. These constraints may be solved using a suitable equation solver, to yield the set of values of \( P_1^0 \) and \( P_2^0 \), both of which satisfy eq 11.

In view of eq 10, we rewrite 4 as the ratio of the sorption pressures
\[ S_{\text{ads}} = \frac{x_1 f_1}{x_2 f_2} = \frac{P_2^0}{P_1^0} \]
(14)

Applying the restriction specified by eq 11, it follows that \( S_{\text{ads}} \) is uniquely determined by the adsorption potential \( \Phi \); this represents a significant simplification.

A further physical interpretation of \( \Phi \) becomes transparent if we consider the simple scenario in which each isotherm is described by the single-site Langmuir model with equal saturation capacities for each constituent
\[ q_i(f) = q_{\text{sat}} \frac{b_i f_i}{1 + b_i f_i} \]
\[ \left( \begin{array}{c} i \\ 1, 2 \end{array} \right) \]
(15)
The following explicit expression can be derived (see Supporting Information for details)
\[ \Phi = q_{\text{sat}} \ln(1 + b_1 f_1 + b_2 f_2) \]
(16)
The fractional occupancy, \( \theta \), is related to the adsorption potential
\[ \theta \equiv \frac{q_1}{q_{\text{sat}}} = 1 - \exp \left( - \frac{\Phi}{q_{\text{sat}}} \right) \]
(17)

Figure 4. CBMC/MD simulations of the permeabilities, \( \Pi_i \) of (a) \( \text{CO}_2 \), (b) \( \text{CH}_4 \), (c) \( \text{H}_2 \), and (d) \( \text{N}_2 \) in different equimolar \( (q_1 = q_2) \) binary mixtures in CHA zeolite at 300 K, plotted as a function of the adsorption potential, \( \Phi \). Also plotted (using open symbols) are the corresponding values of the unary permeabilities. All simulation details and input data are provided in the Supporting Information accompanying this publication.
Typically for separation of gaseous mixtures considered in this article, values of \( \Phi \approx 30 - 40 \text{ mol kg}^{-1} \) correspond to pore saturation conditions, \( \theta \approx 1 \). Equation 17 implies that \( \Phi \) may also be interpreted as a proxy for the pore occupancy. Consequently, \( \Phi \) is also the thermodynamically appropriate parameter to describe the loading dependence of diffusivities in microporous materials, as has been established in earlier publications.\(^\text{27,44}\) Further background on the wide variety of loading dependences of guest molecules in nanoporous materials is available in the published literature.\(^\text{45 - 49}\) The presence of surface barriers has also been demonstrated to have a significant influence of the guest diffusivities.\(^\text{50 - 54}\)

Armed with these physical insights, let us revisit the set of CBMC and MD data presented in Figure 1.

2.2. Binary Mixture Permeation in Microporous Materials. In Figure 3a, we plot the data for three different CBMC campaigns for mixture adsorption (as presented in Figure 1a,b), in terms of \( S_{\text{ads}} \) versus \( \Phi \). All data sets fall on a unique curve, confirming that \( S_{\text{ads}} \) is indeed uniquely determined by \( \Phi \).

In Figure 3b, MD simulations of the self-diffusivities, \( D_{\text{self}} \) in equimolar \( (q_1 = q_2) \) binary \( \text{CO}_2/\text{CH}_4 \) mixtures in CHA are plotted as a function of \( \Phi \). These self-diffusivities are nearly equal to the corresponding values for the unary guests, when compared at the same \( \Phi \) value. This result suggests that \( \Phi \) also uniquely determines the diffusion selectivities. As verification, Figure 3c demonstrates that the four different MD campaigns (cf. Figure 1c,d) for \( S_{\text{diff}} \) coincide to yield a unique dependence on \( \Phi \). For the same four MD campaigns, the product of \( S_{\text{diff}} \) with the corresponding values of \( S_{\text{ads}} \) are plotted in Figure 3d to conclude that \( S_{\text{perm}} \) is also uniquely related to \( \Phi \).

Analogous sets of CBMC and MD data for adsorption and diffusion of \( \text{CO}_2/\text{H}_2, \text{CO}_2/\text{N}_2, \text{CH}_4/\text{H}_2, \text{CH}_4/\text{N}_2, \) and \( \text{H}_2/\text{N}_2 \) mixtures in CHA were gathered (see Figures S23 and S24) and used to examine the permeabilities of \( \text{CO}_2, \text{CH}_4, \text{H}_2, \) and \( \text{N}_2 \) in the presence of different partners with the values of unary permeabilities; see Figure 4. When inspected at the same \( \Phi \), the component permeabilities for \( \text{CO}_2, \text{CH}_4, \) and \( \text{N}_2 \) are found to be independent of the partners in the mixtures and have practically the same values as the values for the corresponding unary permeabilities. This represents an important result of practical consequences in membrane process development. For \( \text{H}_2 \) that has a very high mobility but extremely poor adsorption strength; the unary permeability is significantly higher than that in the different mixtures. The lowering in the permeabilities of \( \text{H}_2 \) in the different mixtures is attributable to mixture adsorption that

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c05269)
favors the different partners CO₂, CH₄, and N₂ to a significant extent. The more strongly adsorbed partner species also have the effect of retarding the intercage hopping of H₂ molecules.55

Results entirely analogous to those presented in Figure 4 are obtained for all other microporous materials investigated with different pore sizes and topologies. As illustration, Figures 5 and 6 present the CBMC/MD data for permeabilities of the four different guests within the intersecting channel structures of MFI and 1D channels of MgMOF-74. The data for other host materials are presented in Figures S26–S55. In all cases, the unary permeabilities for CO₂, CH₄, and N₂ are practically the same as the values in different binary mixtures, when compared at the same Φ. For H₂, the permeabilities in the mixtures are significantly lower than the unary values.

Experimental verification that the data such as these illustrated in Figures 4, 5, and 6 are available for a wide variety of guest/host combinations; see earlier work.44 For CO₂/H₂ permeation in MFI, for example, a fundamental re-analysis of the experimental data of Sandström et al.¹⁰ provides confirmation that the permeability of H₂ in mixtures with CO₂ is significantly lowered by about an order of magnitude below the value for unary H₂ permeation. For permeation of various mixtures across the SAPO-34 membrane, the same set of experimental data in Figure 2, is plotted in Figure 7 as functions of Φ, determined at the upstream membrane face. With use of Φ as the yardstick, the component permeances of each of the four guests are found to be practically independent of partner species, in consonance with the data in Figure 4. The comparisons between the plots in Figures 2 and 7 accentuate the advantages of the use of Φ as yardsticks for comparison of unary permeances with those in various mixtures.

Published MD data for mixture diffusion have shown that the occurrence of molecular clustering, because of say hydrogen bonding, causes the component diffusivities in mixtures to deviate significantly from the values for the corresponding unaries.²⁵,²⁶,⁴³,⁵⁶–⁶²

2.3. Screening of Microporous Materials in Membrane Applications. Having established the benefits of using Φ, a practical proxy for spreading pressure, as a convenient tool for relating component permeabilities in binary mixtures to unary permeabilities, we turn to the process of screening membrane materials for any specific separation applications. Consider CO₂/CH₄ mixture separations that is of relevance in purification of natural gas, which can contain up to 92% CO₂ impurity at its source.⁶³,⁶⁴ Removal of CO₂, which is most...
commonly accomplished using amines, is conducted at pressures ranging to about 2 MPa. CBMC simulations were carried out for equimolar $f_1 = f_2$ CO$_2$/CH$_4$ mixtures in different host materials. The values of the adsorption selectivities, $S_{ads}$, are plotted in Figure 8a as function of $\Phi$. The highest values of $S_{ads}$ are realized with cation-exchanged zeolites (NaX and NaY) and MgMOF-74 with exposed Mg$^{2+}$ cation sites, resulting in strong binding of CO$_2$ molecules to cations. Significantly lower $S_{ads}$ values are realized with all-silica zeolites. Remarkably, the hierarchy of diffusion selectivities is essentially the reverse of the hierarchy of $S_{ads}$; see MD simulation data for $S_{diff}$ versus $\Phi$ in Figure 8b. The highest diffusion selectivities are obtained with DDR, CHA, and ZIF-8 that consist of cages separated by narrow ($\approx 3.3\sim3.8$ Å) windows. In such structures, CO$_2$ jumps length-wise across the windows as evidenced in video animations. The smaller cross-sectional dimension (cf. Figure 8c) of CO$_2$ (3.1 Å) compared to CH$_4$ (3.7 Å) accounts for the significantly higher $S_{diff}$ in favor of CO$_2$.

Figure 8a,b also shows that the diffusion selectivities in host materials with larger characteristic pore dimensions (FAU, NaY, NaX; MgMOF-74, and BTP-COF) in which the guest molecules are less strongly constrained, the $S_{diff}$ favors CH$_4$ that has the larger kinetic diameter. This apparent paradox is accentuated by the comparison of the data for FAU, NaY, and NaX; these three materials have the same pore size and topology consisting of cavities ($\approx 11$ Å) separated by 12-ring windows ($\approx 7.4$ Å) but display the $S_{diff}$ hierarchy FAU > NaY > NaX. Clearly, the $S_{diff}$ is determined by factors other than pore size and degree of guest confinement. The observed hierarchy of $S_{diff}$ values can be rationalized on the basis of the stronger binding strength of CO$_2$. Figure 8d plots the CBMC simulation data on isosteric heats of adsorption, $Q_{st}$, a measure of the binding energy of CO$_2$, as function of $\Phi$. The hierarchy of $Q_{st}$ is NaX > NaY $\approx$ MgMOF-74 > MFI $\approx$ FAU $\approx$ BTP-COF is precisely the reverse of the hierarchy of $S_{diff}$ found in Figure 8b. Stronger binding of CO$_2$ implies higher degree of “stickiness” and, consequently, lower mobility.

Figure 9a,b compares the values of the permeation selectivity $S_{perm} = S_{ads} \times S_{perm}$ and CO$_2$ permeabilities $\Pi_1$ in different materials. The hierarchies of these two important metrics governing membrane separations are not precisely the reverse of each other, suggesting that there is room for optimizing the choice of material. For specific choice of upstream operating conditions, $f_1 = f_2 = f_3 = 10^6$ Pa, Figure 9c shows the Robeson plot of $S_{perm}$ versus $\Pi_1$. The highest $S_{perm}$ values in excess of 100 are obtained with zeolites with 8-ring windows DDR and CHA, for which $S_{ads}$ and $S_{diff}$ complement each other. For DDR and CHA, there is experimental
evidence that such high permeation selectivities can be realized in practice.\textsuperscript{6–8,11,55,71–73} For MFI, the $S_{\text{perm}}$ value of 2.3 is in agreement with the experiment.\textsuperscript{6} The stronger CO$_2$ binding achievable using NaY, NaX, and MgMOF-74 does not guarantee high permeation selectivities. There is considerable scope for development of novel materials that would lead to a performance at the top right corner of the Robeson plot, using mixed-matrix membranes that attempt to profit from both adsorption and diffusion characteristics of the constituent materials.\textsuperscript{4,18}

Analogous Robeson plots constructed by CBMC/MD data for CO$_2$/N$_2$ and CO$_2$/H$_2$ separations are shown in Figures S57–S58.

### 3. CONCLUSIONS

The adsorption and diffusion characteristics of a variety of mixtures (CO$_2$/CH$_4$, CO$_2$/N$_2$, CO$_2$/H$_2$, CH$_4$/H$_2$, and CH$_4$/C$_2$H$_6$) in a variety of microporous hosts (CHA, DDR, ZIF-8, BTP-COF, MgMOF-74, FAU, NaY, NaX, and MFI) were investigated using CBMC and MD simulations. The following major conclusions emerge from a detailed analysis of the obtained results.

1. The adsorption potential, $\Phi$, a proxy for the spreading pressure and calculable from the IAST, is a proper yardstick to compare data on adsorption, diffusion, and permeation in microporous materials.

2. For adsorption of binary mixtures of light gaseous constituents (CO$_2$, CH$_4$, N$_2$, H$_2$, and C$_2$H$_6$), the adsorption selectivity $S_{\text{ads}}$ is uniquely determined by the adsorption potential, $\Phi$, irrespective of mixture composition and total fugacity, $f_t$.

3. The adsorption potential $\Phi$ also serves as the thermodynamically appropriate proxy to represent the pore occupancy. As a consequence, the diffusion selectivity $S_{\text{diff}}$ is also uniquely dependent on $\Phi$.

4. When compared at the same $\Phi$, the component permeabilities, $\Pi_i$ for CO$_2$, CH$_4$, and N$_2$, determinable from CBMC/MD data using eq 3, are found to be largely independent of the partners in the various mixtures investigated and have practically the same values as the values for the corresponding unary permeabilities. This simple result, verified in a number of experimental investigations,\textsuperscript{44} has important consequences for membrane process development.

5. In all investigated mixtures, the permeability of H$_2$ falls significantly below the values of the unary permeabilities.

6. As exemplified in Figure 8 for CO$_2$/CH$_4$ separation, the hierarchy of $S_{\text{ads}}$ versus $\Phi$ data are found to be precisely
opposite to the hierarchy of $S_{\text{diff}}$ versus $\Phi$ data. This underscores the fact that adsorption and diffusion do not go hand-in-hand. In host materials wherein the guests are not too strongly confined (FAU, NaY, NaX, MFI, MgMOF-74, BTP-COF), stronger binding of CO$_2$ results in lower mobility.

(7) The insights gained in this investigation assist in the choice of the appropriate membrane material for a specified separation, appropriately balancing adsorption selectivity with diffusion selectivity.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05269.

Detailed structural information on all host materials, CBMC and MD simulation methodologies, CBMC data on unary isotherms and isotherm fits, and CBMC and MD data on adsorption, diffusion, and permeation of variety of mixtures (PDF)

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Notes

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**NOMENCLATURE**

Latin alphabet

- $A$ = surface area per kg of framework, m$^2$ kg$^{-1}$
- $b$ = dual-Langmuir–Freundlich constant, Pa$^{-\nu}$
- $D_{\text{self}}$ = self-diffusivity of species $i$, m$^2$ s$^{-1}$
- $f_i$ = partial fugacity of species $i$, Pa
- $f_i$ = total fugacity of bulk fluid mixture, Pa
- $N_i$ = molar flux of species $i$ with respect to framework, mol m$^{-2}$ s$^{-1}$
- $P^*$ = sorption pressure, Pa
- $q_i$ = component molar loading of species $i$, mol kg$^{-1}$
- $q_i$ = molar loading of species $i$ at saturation, mol kg$^{-1}$
- $Q_{\text{st}}$ = isosteric heat of adsorption, J mol$^{-1}$
- $R$ = gas constant, 8.314 J mol$^{-1}$ K$^{-1}$
- $S_{\text{ads}}$ = adsorption selectivity, dimensionless
- $S_{\text{diff}}$ = diffusion selectivity, dimensionless
- $S_{\text{perm}}$ = permeation selectivity, dimensionless
- $T$ = absolute temperature, K
- $x_i$ = mole fraction of species $i$ in adsorbed phase, dimensionless
- $y_i$ = mole fraction of species $i$ in bulk gas phase, dimensionless

Figure 9. Comparison of (a) permeation selectivity, $S_{\text{perm}}$, and (b) CO$_2$ permeability, $\Pi_i$, for CO$_2$(1)/CH$_4$(2) mixtures in different microporous materials; the x-axis represents the adsorption potential, $\Phi$. (c) Robeson plot of $S_{\text{perm}}$ versus $\Pi_i$ data at $f_i = f_1 + f_2 = 10^6$ Pa and 300 K. All calculation details and input data are provided in the Supporting Information accompanying this publication.

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Greek alphabet

\[ \delta = \text{thickness of membrane, m} \]

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

\[ \pi = \text{spreading pressure, N m}^{-1} \]

\[ \theta = \text{fractional occupancy, dimensionless} \]

\[ \nu = \text{exponent in dual-Langmuir–Freundlich isotherm, dimensionless} \]

\[ \Pi_i = \text{membrane permeability of species } i, \text{ m mol m}^{-2} \text{ s}^{-1} \]

\[ \rho = \text{framework density, kg m}^{-3} \]

\[ \Phi = \text{adsorption potential, mol kg}^{-1} \]

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

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