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Using the spreading pressure to inter-relate the characteristics of unary, binary and ternary mixture permeation across microporous membranes

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A B S T R A C T

The primary objective of this article is to investigate the possibility of inter-relating the characteristics of unary, binary, and ternary mixtures across microporous zeolite membranes. Towards this end, we performed Configurational-Bias Monte Carlo (CBMC) simulations of mixture adsorption equilibrium, and Molecular Dynamics (MD) simulations of guest diffusivities in unary (CO$_2$, CH$_4$, N$_2$, and H$_2$), binary (CO$_2$/CH$_4$, CO$_2$/N$_2$, CH$_4$/N$_2$, CO$_2$/H$_2$), and ternary (CO$_2$/CH$_4$/N$_2$, CO$_2$/CH$_4$/H$_2$, CO$_2$/N$_2$/H$_2$) mixtures in four zeolites: CHA, DDR, MPI, and FAU. The combined CBMC and MD data are used to obtain fundamental insights into the adsorption, diffusion, and permeation characteristics of the variety of guest/host combinations. Application of the Myers-Prausnitz theory shows that the adsorption selectivity for the $i$-$j$ pair, $S_{ad,ij}$, in ternary mixtures has practically the same value as for the binary $i$-$j$ mixture, provided the comparison is made at the same spreading pressure, $\pi$, that is calculable on the basis of the data on the unary isotherms of the constituent guests. For the mixtures investigated, departures from thermodynamic ideality do not cause deviations from the uniqueness of the $S_{ad,ij}$ vs $\Phi$ dependence because the ratios of the activity coefficients $\gamma_i/\gamma_j$ also appear to uniquely depend on $\Phi$.

The surface potential $\Phi$ is also the thermodynamically correct metric to describe the loading dependence of diffusivities. Compared at the same $\Phi$, the diffusion selectivity for the $i$-$j$ pair, $S_{diff,ij}$, in ternary mixtures has practically the same value as for the binary $i$-$j$ mixture. Consequently, the permeation selectivity, $S_{perm,ij} = S_{ad,ij} \times S_{diff,ij}$ is also uniquely dependent on $\Phi$. When compared at the same $\Phi$, the component permeabilities, $\Pi_i$, for CO$_2$, CH$_4$, and N$_2$ are found to be independent of the partners in the binary and ternary mixtures investigated and have practically the same values for the corresponding unary permeabilities.

1. Introduction

Membrane technologies find applications for separation a variety of gaseous mixtures, such as CO$_2$/CH$_4$, CO$_2$/N$_2$, CO$_2$/H$_2$, and CH$_4$/N$_2$ [1–6]. The perm-selective membrane layers often consist of crystalline microporous materials such as zeolites (alumino-silicates) [7–18] metal-organic frameworks (MOFs) [19], or zeolitic imidazolate frameworks (ZIFs) [20–22].

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

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

where $N_i$ is the permeation flux and $\Delta f_i = f_i - f_u$ is the difference in the partial fugacities between the upstream $(f_i)$ and downstream $(f_u)$ faces of the membrane layer of thickness $\delta$. For the $i$-$j$ pair in $n$-component mixtures, the membrane permeation selectivity, $S_{perm,ij}$, is defined as the ratio of the component permeabilities

$$S_{perm,ij} = \frac{N_i/\Delta f_i}{N_j/\Delta f_j} = \frac{\Pi_i}{\Pi_j}$$

In previous works [23,24], we had established the benefits of using the spreading pressure, $\pi$, defined by the Gibbs adsorption equation [25], to characterize the component permeabilities. These studies showed that the component permeabilities $\Pi_i$ for binary mixture permeation are relatable to the corresponding unary permeabilities, provided the comparisons are made at the same values of $\pi$. The primary objective of the

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The present communication is to extend the previous analyses to include ternary mixtures. Using a fundamental thermodynamic analysis of adsorption and diffusion of mixtures of guest molecules in microporous materials, we aim to show that the permeation characteristics of n-component mixtures, with \( n = 1, 2 \) or 3, are relatable to one another provided the comparisons at the same value of \( \pi \). The secondary objective is to demonstrate that the conclusions drawn in this work are not significantly altered by departures from thermodynamic idealities in mixture adsorption.

To meet the objective set for this article, we undertake molecular simulations of both mixture adsorption and intra-crystalline diffusion in CHA, DDR, MFI, and FAU zeolites, each in the all-silica form (i.e. Si/Al \( \rightarrow \infty \)). The pore landscapes of these four materials, commonly used as perm-selective membranes, are shown in Fig. 1. CHA zeolite consists of cages of volume 316 Å\(^3\), separated by 8-ring windows of 3.8 Å \( \times \) 4.2 Å size. DDR zeolite has cages of 278 Å\(^3\) volume, separated by 8-ring windows of 3.65 Å \( \times \) 4.37 Å size. MFI zeolite consists of a set of intersecting straight channels, and zig-zag (or sinusoidal) channels of 5.5 Å size. FAU zeolite has cages of 786 Å\(^3\) volume, separated by 7.4 Å 12-ring windows. FAU is commonly used in cation-exchanged form called NaX or 13X; per unit cell of NaX zeolite we have 106 Si, 86 Al, 86 Na\(^+\) with Si/Al = 1.23.

We undertake Configurational-Bias Monte Carlo (CBMC) simulations for adsorption of light gaseous unary guests (CO\(_2\), CH\(_4\), N\(_2\), H\(_2\)), binary (CO\(_2\)/CH\(_4\), CO\(_2\)/N\(_2\), CH\(_4\)/N\(_2\), CO\(_2\)/H\(_2\)) mixtures, ternary (CO\(_2\)/CH\(_4\)/N\(_2\), CO\(_2\)/CH\(_4\)/H\(_2\), CO\(_2\)/N\(_2\)/H\(_2\)), and quaternary (CO\(_2\)/CH\(_4\)/N\(_2\)/H\(_2\)) mixtures. Molecular Dynamics (MD) simulations are also undertaken to determine the self-diffusivities, \( D_{\text{self}} \), of each guest species in corresponding unary, binary and ternary mixtures. For MFI and FAU, additional simulations on adsorption and diffusion of CH\(_4\)/C\(_2\)H\(_6\)/C\(_3\)H\(_8\) mixtures, along with the constituent binary mixtures were also investigated. To specifically investigate the influence of thermodynamic non-idealities adsorption simulations for NaX zeolite were conducted for CO\(_2\)/CH\(_4\)/N\(_2\), and CO\(_2\)/CH\(_4\)/C\(_3\)H\(_8\) mixtures. The CBMC and MD simulation methodologies are detailed in the Supplementary Material accompanying this publication.

2. Thermodynamics of mixture adsorption

The Gibbs adsorption equation [25] relates \( x \) to the molar chemical potential, \( \mu_i \), and the component molar loading, \( q_i \), in the adsorbed phase as follows

\[
Ad\pi = \sum_{i=1}^{n} q_i d\mu_i \tag{3}
\]

where \( A \) represents the surface area per kg of framework. At phase equilibrium, equating the component chemical potentials, \( \mu_i \), in adsorbed phase and in the bulk gas phase mixture in the upstream membrane compartment, we write

\[
d\mu_i = RTd \ln f_i \tag{4}
\]
Fig. 2. (a, b) CBMC simulations of CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} adsorption selectivities, S\textsubscript{ads}, in (a) MFI, (b) FAU zeolites at 300 K, plotted as function of the surface potential, Φ. The pair selectivities are determined from CBMC data for binary, ternary, and quaternary mixtures. The dashed lines are IAST estimates of S\textsubscript{ads}. All calculation details and input data are provided in the Supplementary Material accompanying this publication.

Using the analogy with vapor/liquid equilibrium, Myers and Prausnitz [26] write the following expression relating the partial fugacities in the bulk gas mixture

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

(5)

to the mole fractions, \( x_i \), in the adsorbed phase mixture

\[ x_i = \frac{q_i}{q_1 + q_2 + ... + q_n} \quad i = 1, 2, ..., n \]  

(6)

In eq (5), \( P_i^0 \) 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 \( n \)-component mixture:

\[ \frac{\pi \Lambda}{RT} = \int_0^{P_i^0} \frac{d f_i}{f} = \int_0^{P_j^0} \frac{d f_j}{f} = \int_0^{P_2^0} \frac{d f_2}{f} \]  

(7)

In eq (7), \( q_i^0(f) \) is the pure component adsorption isotherm. Since the surface area \( A \) is not directly accessible from experimental data, the surface potential \( \pi \Lambda/RT \equiv \Phi \), with the units \( \text{mol kg}^{-1} \), serves as a convenient and practical proxy for the spreading pressure \( \pi \) [23,24,27, 28]. From eq (7), it is evident that the value of \( \Phi \) depends on partial fugacities \( f_i \) of each of the guests, along with the unary isotherms; the isotherms reflect the specific guest/host interactions. In view of eq (5), we may express the adsorption selectivity for the \( i-j \) pair in \( n \)-component mixtures as follows

\[ S_{ads.ij} = \frac{q_i/q_j}{f_i/f_j} = \frac{x_i/f_i}{x_j/f_j} = \frac{P_{ij}^0}{P_{ji}^0} \]  

(8)

In the Ideal Adsorbed Solution Theory (IAST), we further assume that the activity coefficients of each of the components in the mixture are equal to unity, leading the following simplification

\[ \gamma_i = \gamma_j = 1 \quad S_{ads.ij} = \frac{P_{ij}^0}{P_{ji}^0} \quad i, j = 1, 2, ..., n \]  

(9)

The applicability of eq (9) mandates: (i) all of the adsorption sites within the microporous material are equally accessible to each of the guest molecules, implying a homogeneous distribution of guest adsorbates within the pore landscape, (ii) there are no preferential locations of any guest species in the pore landscape, and (iii) there is no molecular clustering as a result of say hydrogen bonding between guest molecules as is the case for water/alcohol mixtures [29–32].

Applying the restriction specified by eq (7), it follows that \( S_{ads.ij} \) is uniquely determined by the surface potential \( \Phi \). It is important to note that eq (9) is valid irrespective of the total number of components in the mixture. The presence of component 3 in the ternary mixture influences the adsorption selectivity \( S_{ads.12} = P_{2i}/P_{1i}^0 \) for the 1–2 pair, only via the values of the sorption pressures \( P_j^0 \) which must satisfy eq (7) to yield the same value of surface potential \( \Phi \) for each of the individual components in the mixture. A further point that requires to be underscored is that the calculation of the surface potential \( \Phi \) does not mandate that \( \gamma_i = 1 \).

In Fig. 2a and b, the CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/N\textsubscript{2} adsorption selectivities in MFI and FAU zeolites determined from CBMC simulations data for binary mixtures are compared with the values determined for CO\textsubscript{2}/CH\textsubscript{4}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4}/N\textsubscript{2}/H\textsubscript{2} mixtures. The CBMC data for each binary pair on \( S_{ads} \) displays a unique dependence on the surface potential \( \Phi \), as anticipated from the application of eq (7), and (9). Also, the CBMC data
Fig. 3. (a, b) CBMC simulations of CO$_2$/CH$_4$, CO$_2$/H$_2$, CO$_2$/N$_2$, and CH$_4$/N$_2$ adsorption selectivities, S$_{ads}$, in (a) CHA, and (b) DDR zeolites at 300 K, plotted as function of the surface potential, $\Phi$. The pair selectivities are determined from CBMC data for binary, ternary, and quaternary mixtures. The dashed lines are IAST estimates of S$_{ads}$. (c, d) CBMC simulations of the ratio of activity coefficients of ratio of activity coefficients of CO$_2$ and CH$_4$, $\gamma_1/\gamma_2$, in (c) CHA, and (d) DDR zeolites, as function of the surface potential $\Phi$. All calculation details and input data are provided in the Supplementary Material accompanying this publication.
are in excellent agreement with the IAST estimates, determined from dual-Langmuir-Freundlich fits of the unary isotherms; see details in the Supplementary Material.

Fig. 3a and b plots the selectivities for $\text{CO}_2/\text{CH}_4$, $\text{CO}_2/N_2$, $\text{CO}_2/H_2$, and $\text{CH}_4/N_2$ pairs in CHA, and DDR zeolites determined from CBMC data for adsorption of binary, ternary and quaternary mixtures of a variety of compositions. Each of the individual pair selectivities displays a unique dependence on $\Phi$, irrespective of the number of components in the mixture. The IAST calculations (indicated by dashed lines in Fig. 3a and b) shows small deviations from the CBMC simulated data due to non-idealities caused by preferential perching of $\text{CO}_2$ at the window regions of CHA and DDR; detailed explanations are provided in our earlier works [29–32]. For further elucidation of the influence of thermodynamic non-idealities, the ratio of the activity coefficient of $\text{CO}_2$ to that of $\text{CH}_4$ is plotted in Fig. 3c and d as a function of the surface potential $\Phi$. Other examples demonstrating that the ratios of activity coefficients are uniquely determined by $\Phi$ are presented in Figs. S92–S113 of the Supplementary Material.

3. Mixture diffusion and permeation

As derived in detail in Chapter 3 of the Supplementary Material, the fractional pore occupancy, $\theta$, is related to the surface potential by

$$\theta = 1 - \exp \left( - \frac{\Phi}{q_{\text{sat,mix}}} \right) \tag{10}$$

For adsorption of $\text{CO}_2/\text{CH}_4$ mixtures in cation-exchanged NaX zeolite, the thermodynamic non-idealities are much stronger due to the congregation of $\text{CO}_2$ molecules around the Na$^+$ cations [29–33]; this causes an inhomogeneous distribution of adsorbates in the pore space, violating the IAST mandate of homogeneous distribution [31,33]. Fig. 4a shows CBMC simulations of the $\text{CO}_2/\text{CH}_4$ adsorption selectivity, $S_{\text{ads}}$, for binary and ternary mixture adsorption in NaX zeolite. Despite the large deviations from the IAST estimates (shown by the dashed line), the $S_{\text{ads}}$ vs $\Phi$ relationship is practically the same for both binary and ternary mixtures. Fig. 4b confirms that the ratio of the activity coefficient of $\text{CO}_2$ to that of $\text{CH}_4$ is uniquely dependent on surface potential $\Phi$. Other examples demonstrating that the ratios of activity coefficients are uniquely determined by $\Phi$ are presented in Figs. S92–S113 of the Supplementary Material.
where \( q_{\text{sat,mix}} \) is the saturation capacity for mixture adsorption. Eq (10) 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 [23,24,34]. In all of the simulation data presented in this work, the values of the surface potential \( \Phi \) range from about \( 10^{-3} \) to 40 mol kg\(^{-1} \); values of \( \Phi \approx 40 \) mol kg\(^{-1} \) correspond to pore saturation conditions, \( \theta \approx 1 \); see the \( \theta \) vs \( \Phi \) calculations for CHA, DDR, MFI, and FAU presented in Fig. S4 of the Supplementary Material.

Fig. 5a plots the data for \( \mathrm{H}_2/\mathrm{CO}_2 \) diffusion selectivities defined by

\[
S_{\text{diff,ij}} = \frac{D_{\text{self,ij}}}{D_{\text{self,i}}}
\]

that were determined from MD simulations for both binary (\( \mathrm{CO}_2/\mathrm{H}_2 \)) and ternary (\( \mathrm{CO}_2/\mathrm{N}_2/\mathrm{H}_2 \), and \( \mathrm{CO}_2/\mathrm{CH}_4/\mathrm{H}_2 \)) mixtures in CHA zeolite at 300 K, plotted as function of the surface potential \( \Phi \). The \( S_{\text{diff}} \) vs \( \Phi \) relation is unique for the three MD data sets.

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

\[
\Pi_i = \frac{\rho_{\text{down}} q_i}{f_i}
\]

In earlier work [35] we had used the Maxwell-Stefan diffusion formulation to establish the validity of the use of the component self-diffusivities in determining the \( S_{\text{diff,ij}} \) and \( \Pi_i \) in eq (11), and (12); further details are provided in Chapter 6 of the Supplementary Material.

Combining eqs ((2), (8), (11) and (12)) we conclude that the permeation selectivity is a product of the adsorption and diffusion selectivities

\[
S_{\text{perm,ij}} = S_{\text{ads,ij}} \times S_{\text{diff,ij}}
\]

Since we have already established that both \( S_{\text{ads,ij}} \) and \( S_{\text{diff,ij}} \) are uniquely determined by \( \Phi \) for both binary and ternary mixtures, we should expect \( S_{\text{perm,ij}} \) to exhibit the analogous unique dependence on the surface potential \( \Phi \). The \( \mathrm{CO}_2/\mathrm{H}_2 \) permeation selectivity calculations for CHA zeolite in Fig. 5b confirm this expectation. Precisely analogous results for \( S_{\text{diff,ij}} \) vs \( \Phi \), and \( S_{\text{perm,ij}} \) vs \( \Phi \) dependences are obtained for \( \mathrm{CO}_2/\mathrm{CH}_4 \), \( \mathrm{CO}_2/\mathrm{N}_2 \), and \( \mathrm{CO}_2/\mathrm{H}_2 \) pairs in the various hosts; see Figures S30-S36, S46-S49, S69-S76, and S82-S88.

Fig. 6 and Fig. 7 present data on the permeabilities, \( \Pi_i \), for \( \mathrm{CO}_2 \), CH\(_4\), N\(_2\) and H\(_2\) in CHA, and DDR zeolites, respectively, determined using eq (12) by combining CBMC and MD simulation data on mixture adsorption and diffusion data. Noteworthily, the \( \Pi_i \) for any component in binary and ternary mixtures in both CHA and DDR has practically the same values as the unary permeabilities when compared at the same values of surface potential \( \Phi \); the unary permeability of H\(_2\) is slightly higher than in mixtures. Analogous results for component permeabilities in MFI and FAU zeolites are presented in Figs. S78 and S90 of the of the Supplementary Material.

As validation of the CBMC/MD data in Figs. 6 and 8 presents a re-analysis of the experimental data of Li et al. [7--9] for permeances of (a) \( \mathrm{CO}_2 \), (b) CH\(_4\), (c) N\(_2\) and (d) H\(_2\), determined for unary, binary and ternary mixture permeation across SAPO-34 membrane at 295 K. Compared at the same \( \Phi \), the component permeances of each of the four guests is the same in binary and ternary mixtures. These data also suggest that the permeation selectivities in mixtures can be estimated to a reasonably fair accuracy on the basis of unary permeances, determined at the same surface potential \( \Phi \).

Confirmation of the data in Fig. 7 for DDR is available for binary \( \mathrm{CO}_2/\mathrm{CH}_4 \) and CH\(_4\)/N\(_2\) mixtures only; see the re-analysis of the published experimental data of Van den Bergh et al. [12,18] and Himeno et al. [17] presented in Figs. S52-S55 of the Supplementary Material.

![Fig. 5](image_url)

(a) MD simulations of the \( \mathrm{H}_2/\mathrm{CO}_2 \) diffusion selectivities, \( S_{\text{diff}} \), determined from binary (\( \mathrm{CO}_2/\mathrm{H}_2 \)) and ternary (\( \mathrm{CO}_2/\mathrm{N}_2/\mathrm{H}_2 \), and \( \mathrm{CO}_2/\mathrm{CH}_4/\mathrm{H}_2 \)) mixtures in CHA zeolite at 300 K, plotted as function of the surface potential \( \Phi \). (b) Plot of the \( \mathrm{CO}_2/\mathrm{H}_2 \) permeation selectivity \( S_{\text{perm}} \) as function of the surface potential \( \Phi \). All calculation details and input data are provided in the Supplementary Material accompanying this publication.
4. Conclusions

The adsorption and diffusion characteristics of binary (CO$_2$/CH$_4$, CO$_2$/N$_2$, CH$_4$/N$_2$, CH$_4$/H$_2$, CO$_2$/H$_2$), and ternary (CO$_2$/CH$_4$/N$_2$, CO$_2$/CH$_4$/H$_2$, CO$_2$/N$_2$/H$_2$) mixtures in four all-silica zeolites: CHA, DDR, MFI, and FAU were investigated using CBMC and MD simulations. The following major conclusions emerge.

(1) The adsorption selectivity $S_{ads}$ of the $i$-$j$ pair is uniquely determined by the surface potential, $\Phi$, irrespective of mixture composition and total fugacity, $f$. The presence of additional species does not influence $S_{ads}$, provided the comparison is made at the same $\Phi$.

(2) For the mixtures investigated, ratios of the activity coefficients $\gamma_i / \gamma_j$ also appear to uniquely depend on $\Phi$. Consequently, departures from thermodynamic idealities do not cause significant deviations from the uniqueness of the $S_{ads}$ vs $\Phi$ dependence.

(3) The surface potential $\Phi$ also represents the thermodynamically correct metric to describe the loading dependence of diffusivities. Compared at the same $\Phi$, the diffusion selectivity, $S_{diff}$, in ternary mixtures has practically the same value as for the corresponding binary $i$-$j$ mixture.

(4) When compared at the same $\Phi$, the component permeabilities, $\Pi$, for CO$_2$, CH$_4$, and N$_2$ in binary and ternary mixtures investigated are found to be largely independent of the partners and have practically the same as the values for the corresponding unary permeabilities.

CRediT authorship contribution statement

Rajamani Krishna: Conceptualization, Data curation, Investigation, Validation, Methodology, Writing. Jasper van Baten: Molecular simulations, including code development.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Fig. 7. CBMC/MD simulations of the permeabilities, $\Pi_i$, of (a) CO$_2$, (b) CH$_4$, (c) N$_2$ and (d) H$_2$ in different equimolar binary ($q_1 = q_2$) (CO$_2$/CH$_4$, CO$_2$/N$_2$, CO$_2$/H$_2$, CH$_4$/N$_2$) and equimolar ($q_1 = q_2 = q_3$) ternary (CO$_2$/CH$_4$/N$_2$, CO$_2$/CH$_4$/H$_2$, CO$_2$/N$_2$/H$_2$) mixtures in DDR zeolite at 300 K, plotted as a function of the surface potential $\Phi$. Also plotted are the corresponding values of the unary permeabilities.
Fig. 8. Re-analysis of the experimental data of Li et al. [7-9] for permeances of (a) CO$_2$, (b) CH$_4$, (c) N$_2$ and (d) H$_2$, determined for equimolar binary and ternary mixture permeation across SAPO-34 membrane at 295 K, compared with unary permeance, when plotted as function of the surface potential $\Phi$ at the upstream face of the membrane. All calculation details and input data are provided in the Supplementary Material accompanying this publication.
Nomenclature

Latin alphabet

- \( A \) surface area per kg of framework, \( \text{m}^2 \text{kg}^{-1} \)
- \( D_{\text{self}} \) self-diffusivity of species \( i \), \( \text{m}^2 \text{s}^{-1} \)
- \( f_i \) partial fugacity of species \( i \), Pa
- \( f_t \) total fugacity of bulk gas mixture, Pa
- \( N_i \) permeation flux of species \( i \) with respect to membrane, \( \text{mol m}^{-2} \text{s}^{-1} \)
- \( p_i \) partial pressure of species \( i \), Pa
- \( P_i \) total pressure, Pa
- \( q_i \) component molar loading of species \( i \), mol kg\(^{-1} \)
- \( q_{i,\text{sat}} \) molar loading of species \( i \) at saturation, mol kg\(^{-1} \)
- \( R \) 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

Greek alphabet

- \( \delta \) thickness of membrane, m
- \( \gamma_i \) activity coefficient of component \( i \) in adsorbed phase, dimensionless
- \( \mu_i \) molar chemical potential of component \( i \), J mol\(^{-1} \)
- \( \Pi \) spreading pressure, N m\(^{-1} \)
- \( \theta \) fractional occupancy, dimensionless
- \( \Pi_i \) membrane permeability of species \( i \), \( \text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1} \)
- \( \rho \) crystal framework density, \( \text{kg m}^{-3} \)
- \( \Phi \) surface potential, mol kg\(^{-1} \)

Subscripts

- \( 0 \) referring to upstream side of membrane
- \( i \) referring to component \( i \)
- \( t \) referring to total mixture
- \( \text{sat} \) referring to saturation conditions
- \( \delta \) referring to downstream side of membrane

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2021.120049.

References


R. Krishna, J.M. Van Baten, Using molecular simulations to unravel the benefits of characterizing mixture permeation in microporous membranes in terms of the spreading pressure, ACS Omega 5 (2020) 32769–32780, https://doi.org/10.1021/acsomega.0c05269.


