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Highlighting the Influence of Thermodynamic Coupling on Kinetic Separations with Microporous Crystalline Materials

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ABSTRACT: The main focus of this article is on mixture separations that are driven by differences in intracrystalline diffusivities of guest molecules in microporous crystalline adsorbent materials. Such “kinetic” separations serve to over-ride, and reverse, the selectivities dictated by mixture adsorption equilibrium. The Maxwell–Stefan formulation for the description of intracrystalline fluxes shows that the flux of each species is coupled with that of the partner species. For n-component mixtures, the coupling is quantified by a n × n dimensional matrix of thermodynamic correction factors with elements \( \Gamma_{ij} \) these elements can be determined from the model used to describe the mixture adsorption equilibrium. If the thermodynamic coupling effects are essentially ignored, i.e., the \( \Gamma_{ij} \) is assumed to be equal to the Kronecker delta, the Maxwell–Stefan formulation degenerates to yield uncoupled flux relations. The significance of thermodynamic coupling is highlighted by detailed analysis of separations of five different mixtures: \( \text{N}_2/\text{CH}_4, \text{CO}_2/\text{C}_2\text{H}_6, \text{O}_2/\text{N}_2, \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \), and hexane isomers. In all cases, the productivity of the purified raffinate, containing the tardier species, is found to be significantly larger than that anticipated if the simplification \( \Gamma_{ij} = \delta_{ij} \) is assumed. The reason for the strong influence of \( \Gamma_{ij} \) on transient breakthroughs is traceable to the phenomenon of uphill intracrystalline diffusion of more mobile species. The major conclusion to emerge from this study is that modeling of kinetic separations needs to properly account for the thermodynamic coupling effects.

1. INTRODUCTION

Most commonly, the driver for mixture separations in fixed-bed adsorbers is the selectivity based on mixture adsorption equilibrium. Industrially important examples of such equilibrium-based separations include \( \text{H}_2 \) purification, production of purified oxygen, and separation of xylene isomers.\(^1\)\(^-\)\(^8\) However, there are practical instances of kinetic separations in which diffusional effects over-ride the influence of mixture adsorption equilibrium and are the prime driver for separations.\(^9\)\(^-\)\(^10\) examples include production of \( \text{N}_2 \) from air and removal of \( \text{N}_2 \) from natural gas.\(^2\)\(^-\)\(^4\)

In recent years, there has been substantial progress in the development of novel materials for industrially important separations\(^10\) that are primarily driven by diffusion selectivities and size exclusion. For industrially important separation of \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) mixtures, the pore dimensions of UTSA-280, an ultra-microporous molecular sieve \( \text{[Ca(C}_4\text{O}_4)(\text{H}_2\text{O})] \), are tuned to only allow \( \text{C}_2\text{H}_4 \) to enter the channels, resulting in almost total exclusion of the saturated alkane.\(^11\) Pimentel and Lively\(^12\) demonstrate the potential of ZIF-8/cellulose acetate fiber sorbents for the kinetic separation of \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) mixtures. Several other examples of kinetic separations are discussed in the review by Wang and Zhao.\(^13\)

For the design and development of pressure swing adsorption (PSA) technologies exploiting diffusion-selective separations, it is of vital importance to use mathematical models for transient uptakes and breakthroughs in fixed adsorbers that properly describe both mixture adsorption equilibrium and the intracrystalline diffusion characteristics.\(^14\) Commonly, the ideal adsorbed solution theory (IAST)\(^15\) is the appropriate model to describe mixture adsorption equilibrium.\(^9\) In the simple case of single-site Langmuir isotherms, with equal saturation capacities of guest species, the IAST degenerates to yield the mixed-gas Langmuir model

\[
\frac{q_i}{q_{i,\text{sat}}} = \frac{b_i p_i}{1 + \sum_{j=1}^{n} b_j p_j}; \quad i = 1, 2, \ldots, n
\]

In eq 1, \( p_i \) are the component partial pressures, \( q_i \) are the component loadings defined in terms of moles per kg of framework, \( q_{i,\text{sat}} \) are the saturation capacities, and \( b_i \) are Langmuir binding constants, with units of \( \text{Pa}^{-1} \).

The most practical approach to modeling n-component diffusion in porous materials is the Maxwell–Stefan (M–S) formulation that has its basis in irreversible thermodynamics. The M–S formulation relates the intracrystalline molar fluxes \( N_i \) to the chemical potential gradients

\[
-\rho \frac{q_i}{RT} \frac{\partial \mu_j}{\partial r} = \sum_{j=1}^{n} \frac{x_j N_i - x_i N_j}{D_{ij}} \frac{N_i}{D_j} \quad i = 1, 2, \ldots, n
\]

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In eq 2, $R$ is the gas constant, $T$ is the temperature, $\rho$ represents the framework density of the microporous crystalline material, $r$ is the radial distance coordinate, and the component loadings $q_i$ are defined in terms of moles per kg of framework. The $x_i$ in eq 2 are the component mole fractions of the adsorbed phase within the micropores

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

Characterize and quantify the interaction between species $i$ and pore walls. The advantage of using eq 2 is that the M–S diffusivity $D_i$ equals the corresponding diffusivity for a unary system, determined at the same pore occupancy. Furthermore, the M–S diffusivity $D_i$ for any species $i$ in a mixture remains invariant to the choice of the partner(s) species. $D_i$, defined in the first right member of eq 2, reflect how the facility for transport of species $i$ correlates with that of species $j$. The Onsager reciprocal relations demand the symmetry constraint

$$D_{ij} = D_{ji}$$

The magnitude of $D_i$ relative to that of $D_j$ determines the extent to which the flux of species $i$ is influenced by the driving force of species $j$. The degree of correlations, defined by $D_i/D_j$, is governed by a wide variety of factors such as pore size, channel topology, and connectivity. Generally speaking, the smaller the pore size and smaller the pore diameter, the stronger the correlations are undesirable for kinetic separations that seek to exploit the differences in the effective mobilities of the constituent species within the pores. Therefore, correlation effects are undesirable for kinetic separations that seek to exploit the differences in the mobilities. In practice, we aim to select materials for which $D_i/D_j \rightarrow \infty$ is a good approximation and the first right member of eq 2 can be ignored, resulting in

$$N_i = -\rho D_i \frac{dq_i}{dr}; \quad i = 1, 2, \ldots n$$

Examples of materials for which the flux expression 5 provides a good description of intracrystalline fluxes are cage-type structures such as CHA, DDR, ERI, LTA, and ZIF-8 that have narrow windows in the 3–4 Å size range. In such structures, the windows allow the intercage hopping of only one molecule at a time; consequently, the jumps are practically uncorrelated.

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

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

The thermodynamic correction factors $\Gamma_{ij}$ can be calculated by differentiating the model describing the mixture adsorption equilibrium, such as eq 1. Combining eqs 5 and 6, we get

$$N_i = -\rho D_i \sum_{j=1}^{n} \Gamma_{ij} \frac{\partial q_j}{\partial r}; \quad i = 1, 2, \ldots n$$

Finite magnitudes of the off-diagonal elements $\Gamma_{ij} (i \neq j)$ cause the flux of species $i$ to be also influenced by the gradient of the molar loading of species $j$. To appreciate the significance of such thermodynamic “coupling”, Figure 1 presents the calculations of the thermodynamic correction factors $\Gamma_{ij}$ for

![Figure 1. Calculations of the matrix of thermodynamic factors for 50:50 C3H6(1)/C3H8(2) mixture adsorption within the crystals of all-silica CHA at 353 K. Further details and input data are provided in Chapter 9 of the Supporting Information.](https://example.com/figure1.png)

Even though eq 8 is strictly valid at low pore occupancies, a large number of implementations of intracrystalline diffusion in models for fixed-bed adsorbers ignore the contribution of $\Gamma_{ij}$ see the comprehensive review of Shafeeyan et al. The primary objective of this article is to investigate and highlight the strong influence of thermodynamic coupling effects, engendered by $\Gamma_{ij} (i \neq j)$, on the effectiveness of kinetic separations. We aim to show that the use of the simpler uncoupled flux expression 8 often leads to significant errors in the prediction of recoveries and productivities of the purified raffinate during the adsorption cycle of PSA operations. To meet our objective, we investigate the kinetically driven separation of five different mixtures $N_2/CH_4, CO_2/CH_4, O_2/N_2, C_2H_2/C_2H_6$, and hexane isomers. In each case, we compare the separation effectiveness predicted by breakthrough simulations incorporating eqs 7 and 8.

The Supporting Information accompanying this publication provides (a) details of the methodology used for modeling of the transient breakthroughs in fixed-bed adsorbers, with incorporation of the IAST and the Maxwell–Stefan diffusion formulations, (b) input data on unary isotherms, and M–S diffusivities, for each of the five cases studies investigated, and (c) structural details of the zeolites and metal–organic frameworks (MOFs).
2. MODELING TRANSIENT UPTAKES AND BREAKTHROUGHS

For an $n$-component gas mixture flowing through a fixed-bed adsorber maintained under isothermal, isobaric conditions, the molar concentrations in the gas phase at any position and instance of time are obtained by solving the following set of partial differential equations for each of the species $i$ in the gas mixture:\cite{4,18,26}

\[
-D_{ax} \frac{\partial^2 c_i(t, z)}{\partial z^2} + \frac{\partial c_i(t, z)}{\partial t} + \frac{\partial (\nu(t, z) c_i(t, z))}{\partial z} + \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial q_i(t, z)}{\partial t} = 0; \quad i = 1, 2, \ldots n
\]  

In eq 9, $t$ is the time, $z$ is the distance along the adsorber, $\varepsilon$ is the bed voidage, $D_{ax}$ is the axial dispersion coefficient, $\nu$ is the interstitial gas velocity, and $q_i(t, z)$ is the spatially averaged molar loading within the crystallites of radius $r_e$ monitored at position $z$ and at time $t$. Ruthven et al.\cite{4} state, "when mass transfer resistance is significantly greater than axial dispersion, one may neglect the axial dispersion term and assume plug flow". The assumption of plug flow is appropriate for kinetically controlled separations and is invoked in all the simulation results presented in this article.

The radial distribution of molar loadings, $q_o$, is obtained from a solution of a set of differential equations describing the transient uptake within a spherical crystallite of radius $r_c$

\[
\rho \frac{\partial q_i(r, t)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \Gamma_i)
\]

The intracrystalline fluxes $\Gamma_i$, in turn, are related to the radial gradients in the molar loadings by eq 7. At any time $t$, the component loadings at the surface of the particle $q_i(r_c, t) = q_i^0$ is in equilibrium with the bulk phase gas mixture. The loadings $q_i^0$ are determined by the IAST or mixed-gas Langmuir model, as appropriate.\cite{30}

At any time $t$, during the transient approach to thermodynamic equilibrium, the spatial-averaged component loading within the crystallites of radius $r_c$ is calculated using

\[
\bar{q}_i(t) = \frac{3}{r_c^2} \int_0^{r_c} q_i(r, t) r^2 \, dr
\]

In all of the simulations reported in this article, the entire bed of crystalline particles is considered to be devoid of adsorbates at time $t = 0$, i.e., we have the initial condition

\[
t = 0; \quad q_i(0, z) = 0
\]

At time, $t = 0$, the inlet to the adsorber, $z = 0$, is subject to a step input of the feed gas mixture, with inlet partial pressures $p_{i0}$ and this step input is maintained till the end of the adsorption cycle when steady-state conditions are reached.

\[
t \geq 0; \quad p_i(0, t) = p_{i0}; \quad c_i(0, t) = c_{i0}
\]

Combination of the discretized partial differential equations along with the algebraic equations describing mixture adsorption equilibrium (IAST or mixed-gas Langmuir model) results in a set of differential–algebraic equations, which are solved using a sparse matrix solver based on the semi-implicit Runge–Kutta method;\cite{30} further numerical details are provided in the Supporting Information.

Validation of the simulation methodology for transient uptakes and breakthroughs by comparison with published experimental works is available in earlier works.\cite{18,29,31–34} As an illustration, Figure 2 presents the experimental data of Jolimaitre et al.\cite{35} for transient breakthrough of a ternary mixture of 2-methylbutane (2MB), 2-methylpentane (2MP), and 2,2-dimethylbutane (22DMB) at 473 K in a fixed bed packed with MFI zeolite that has a topology consisting of a set of intersecting straight channels and zig-zag channels approximately 5.5 Å in size. Branched alkanes are located preferentially at the channel intersections. The hierarchy of adsorption strengths is 2MP $>$ 22DMB $>$ 2MB, whereas the diffusion hierarchy is 2MB $>$ 2MP $\approx$ 22DMB. Due to the diffusional penalty, 22DMB breaks through earlier than the more mobile 2MB. The experimental breakthroughs are quantitatively captured by simulations that adopt the flux expressions including $\Gamma_{iy}$. If the assumption $\Gamma_{iy} = \delta_{iy}$ is invoked, the agreement is significantly worse. Similar good agreement of the breakthrough simulations based on eq 7 is obtained for the complete set of seven experimental runs, with different entering feed mixture compositions, using the same set of isotherm and diffusivity parameters;\cite{35} further details are provided in Chapter 10 of the Supporting Information.

Figure 2. Transient breakthrough experiments of run 20 of Jolimaitre et al.\cite{35} for 2MB/2MP/22DMB ternary mixtures at 473 K.\cite{18} The continuous solid lines are simulations based on eq 7. The dashed lines are the simulations based on eq 8. Further details and input data are provided in Chapter 10 of the Supporting Information.
In a classic paper published in 1958, Habgood reported experimental data on transient uptake of \( \text{N}_2/(1)/\text{CH}_4(2) \) mixtures in crystallites of LTA-4A zeolite at 194 K. The data measured with partial pressures (a) \( p_1 = 50.9 \text{kPa}, p_2 = 49.1 \text{kPa} \) and (b) \( p_1 = 10 \text{kPa}, p_2 = 90 \text{kPa} \) are shown in Figure 3a,b. The nitrogen molecule has a “pencil-like” shape with dimensions of 4.4 Å × 3.3 Å; it can hop length-wise across the narrow 4.1 Å 8-ring windows of LTA-4A.41 The methane molecule is spherical with dimensions of 3.7 Å; it is much more severely constrained and has a diffusivity that is 22 times lower than that of \( \text{N}_2 \).29,42 The adsorption strength of \( \text{CH}_4 \) is higher than that of \( \text{N}_2 \) by a factor 2.2. During the early stages of the transient uptake process, the pores of LTA-4A are significantly richer in the more mobile \( \text{N}_2 \). With increasing time, the nitrogen contained within the pores is progressively displaced by the more strongly adsorbed, tardier \( \text{CH}_4 \) molecules.39 The net result is an overshoot in the \( \text{N}_2 \) uptake in both experimental uptake campaigns. The continuous solid lines in Figure 3a,b are uptake simulations based on eq 7; these simulations successfully capture the overshoot in the uptake of the more mobile \( \text{N}_2 \). The dashed lines are the simulations based on eq 8, ignoring thermodynamic coupling, i.e., \( \Gamma_\gamma = \delta_\gamma \); in this scenario, no \( \text{N}_2 \) overshoot is experienced. The attainment of supraequilibrium loadings of \( \text{N}_2 \) during the early transience signals the phenomena of uphill diffusion, which can be exploited to achieve kinetic separations in fixed-bed adsorption devices.7,20,29

Figure 3c shows the transient breakthrough simulations for \( \text{CO}_2/\text{CH}_4 \) mixtures through fixed-bed adsorber packed with LTA-4A crystals operating at 194 K and total pressure \( p_t = 100 \text{kPa} \).29 The \( \alpha \)-axis is the dimensionless time, \( \tau = tL/\nu \), obtained by dividing the actual time, \( t \), by the characteristic time, \( L/\nu \), where \( L \) is the length of the adsorber.5,6,30 The continuous solid lines are simulations based on eq 7; the dashed lines are simulations based on eq 8. For the target purity of \( \text{CH}_4 \) is 96%, corresponding to prescribed pipeline specification, we can determine the moles of 96% + pure \( \text{CH}_4 \) produced. Expressed per kg of LTA-4A zeolite in the packed bed, the respective productivities are 0.09 and 0.002 mol kg\(^{-1}\). Ignoring the thermodynamic coupling effects severely underestimates the separation performance by a factor of about 50. \( \text{N}_2/\text{CH}_4 \) separations with LTA-4A zeolite are effective only at low temperatures, and other materials such as Ba-ETS-4 and clinoptilolites are more suitable for kinetic separations at ambient conditions.3,36−38 The experimental data of Majumdar et al. show overshoots in \( \text{N}_2 \) loading, confirming the manifestation of uphill diffusion and thermodynamic coupling effects.18,29

3.2. Separation of \( \text{CO}_2/\text{C}_2\text{H}_6 \) Mixtures. The separation of \( \text{CO}_2/\text{C}_2\text{H}_6 \) mixtures is relevant in the context of natural gas processing. Current technologies for \( \text{CO}_2/\text{C}_2\text{H}_6 \) separations use extractive distillation because of \( \text{CO}_2/\text{C}_2\text{H}_6 \) azeotrope formation.46 Another alternative is to combine distillation technology with membrane separations; for this purpose, cross-linked poly(ethylene oxide) membranes have demonstrated to have good separation potential.45−47

Figure 4a–c shows the experimental data of Binder et al. and Lauerer et al. for spatial-averaged transient uptake of (a) 1:1, (b) 2:1, and (c) 3:1 \( \text{CO}_2/\text{C}_2\text{H}_6 \) gas mixtures within the crystals of DDR zeolite at 298 K.9 The DDR zeolite consists of cages of 277.8 Å\(^3\) volume separated by 3.65 Å 8-ring windows.41,50 Both guest molecules, \( \text{CO}_2 \) and \( \text{C}_2\text{H}_6 \), jump length-wise across the 8-ring windows of the DDR zeolite.51

The cross-sectional dimension of \( \text{CO}_2 \) is smaller than that of \( \text{C}_2\text{H}_6 \) and therefore, the intracrystalline M−S diffusivity of \( \text{CO}_2 \) is significantly higher than that of \( \text{C}_2\text{H}_6 \); by about 2−3 orders of magnitude; for further details, see Chapter 7 of the Supporting Information.

The Maxwell−Stefan flux expression including thermodynamic coupling quantitatively captures the overshoots in \( \text{CO}_2 \) loadings with good accuracy for all three experiments.29 If
thermodynamic coupling effects are ignored and the assumption $\Gamma_{ij} = \delta_{ij}$ is invoked, no overshoots in CO$_2$ uptake are experienced, and the simulations show poor agreement with experiments during the early transience.\(^2^9\)

Figure 4d shows the transient breakthrough simulations for 1:1 CO$_2$/C$_2$H$_6$ mixtures through fixed-bed adsorber packed with DDR crystals operating at 298 K and total pressure $p_t = 40$ kPa.\(^{2^9}\) Assuming that target purity of C$_2$H$_6$ is 90%, we can determine the moles of more than 90% pure C$_2$H$_6$ produced. The productivities of more than 90% pure C$_2$H$_6$ are 0.18 and 0.054 mol kg$^{-1}$, respectively, for the two scenarios in which thermodynamic coupling is accounted for, or ignored. Ignoring the thermodynamic coupling effects underestimates the separation performance by a factor of about three.

### 3.3. Separation of O$_2$/N$_2$ Mixtures.

For the production of purified N$_2$ from air, it is desirable to have an adsorbent that is selective to O$_2$, which constitutes 21% of the feed mixture; purified N$_2$ can be recovered as a raffinate during the initial transience of the adsorption cycle.\(^3,^{1^8,5^2}\) However, for most adsorbents, the mixture adsorption equilibrium is in favor of N$_2$, which has a higher quadrupole moment compared to O$_2$. Oxygen-selective separations are achieved with LTA-4A zeolite and carbon molecular sieve (CMS); in these materials, O$_2$ has higher diffusivity due to its smaller size.\(^3,^{5^3–5^6}\)

Simulations of transient uptake of O$_2$/N$_2$ mixture in LTA-4A zeolite at 298 K and total pressure of 600 kPa, display an overshoot in the O$_2$ uptake (see Figure 5a). The overshoot in the O$_2$ loading disappears with the simplification $\Gamma_{ij} = \delta_{ij}$. The experimental data of Chen et al.\(^5^5\) for transient O$_2$/N$_2$ uptake in CMS also show an overshoot in the O$_2$ uptake, confirming the occurrence of uphill diffusion and attainment of superequilibrium O$_2$ loadings for a short time span.\(^2^0,2^9\)

Figure 5b presents transient breakthrough simulations for a fixed-bed operating at 298 K and total pressure of 600 kPa. For an assumed target purity of more than 95% N$_2$, we can determine the moles of more than 95% pure N$_2$ produced; expressed per kg of LTA-4A zeolite in the packed bed, the productivities are 0.066 and 0.036 mol kg$^{-1}$ for the respective models including and ignoring thermodynamic coupling influences. Ignoring thermodynamic coupling effects underestimates the separation performance by a factor of 50%.

### 3.4. Separation of C$_3$H$_6$/C$_3$H$_8$ Mixtures.

Cryogenic distillation of C$_3$H$_6$/C$_3$H$_8$ mixtures is the currently used technology for making polymer-grade propene with more than 99.5% purity. Propane of more than 90% purity is used for
bind with M\textsuperscript{2+} of M\textsubscript{2}(dobdc), with side-on attachment and industries with about 150 and tallest distillation columns used in the petrochemical Consequently, the distillation columns are some of the largest each other: propene (226 K) and propane (231.3 K). alternative for C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separations because of its expected kPa. (b) Transient breakthrough characteristics of O\textsubscript{2}/N\textsubscript{2} mixture in LTA-4A zeolite at 298 K and total pressure of 600 kPa. The partial pressures of the components in the bulk gas phase are p\textsubscript{1} = 126 kPa and p\textsubscript{2} = 474 kPa. The dashed lines are simulations based oneq 8. Further details and input data are provided in Chapter 8 of the Supporting Information. The recovery of high-purity C\textsubscript{3}H\textsubscript{6} product in the final vacuum blowdown step is expected to be enhanced if C\textsubscript{3}H\textsubscript{8} is (almost) excluded from the pores during the high-pressure adsorption cycle. Near-total exclusion of C\textsubscript{3}H\textsubscript{8} is achievable by kinetically based separations using cage-type zeolites with 8-ring windows.\textsuperscript{51} Due to the smaller cross section of the propene molecule (the dimensions are provided by Chng et al.\textsuperscript{61}), kinetic separations selective to propene are possible using all-silica CHA zeolite that consists of cages of volume 316 Å\textsuperscript{3} and separated by 3.8 Å 8-ring windows.\textsuperscript{8,57,69–71}

Using the input data on isotherms and diffusivities provided by Khalighi et al.\textsuperscript{57} we first examine the influence of thermodynamic coupling on transient uptake within a single spherical crystallite of CHA zeolite, initially devoid of guest molecules, exposed to a bulk 50:50 C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixture at 100 kPa and T = 353 K. For the uptake simulations using eq 7, the approach to thermodynamic equilibrium (see Figure 6a).\textsuperscript{20,29} The more mobile C\textsubscript{3}H\textsubscript{6} exhibits a pronounced overshoot in its approach to thermodynamic equilibrium (see Figure 6a).\textsuperscript{20,29}

If thermodynamic coupling is ignored, no C\textsubscript{3}H\textsubscript{6} overshoot is detected. We should expect the transient overshoot phenomena, and uphill diffusion, to have a beneficial effect on the transient breakthrough characteristics in fixed beds.\textsuperscript{77} Figure 6b shows the simulations for transient breakthrough of 50:50 C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixtures in a fixed bed adsorber packed with crystals of all-silica CHA at 353 K and operating at a total pressure of 100 kPa. The simulations clearly show that more than 90% pure C\textsubscript{3}H\textsubscript{8} can be collected during the earlier stages of transience. If thermodynamic coupling effects are ignored and simplified eq 8 are invoked, the time interval during which more than 90% pure C\textsubscript{3}H\textsubscript{8} can be recovered is reduced by about an order of magnitude. Expressed per kg of CHA zeolite in the packed bed, the respective productivities of more than 90% pure C\textsubscript{3}H\textsubscript{8} are 0.62 and 0.06 mol kg\textsuperscript{−1} s\textsuperscript{−1}, a reduction by a factor of about 10 due to neglect of thermodynamic coupling.

It must be remarked that the model used by Khalighi et al.\textsuperscript{57} takes due account of thermodynamic coupling effects, whereas more simplified approach using the linear driving force approximation is adopted by Da Silva and Rodrigues\textsuperscript{61} for modeling kinetic separations of C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixtures using LTA-4A zeolite.

Cadiau et al.\textsuperscript{72} report the synthesis of NbOFFIVE-1-Ni (also named KAUST-7), a customized MOF for C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separations that belongs to the class of SIFSIX materials,\textsuperscript{73} using pyrazine as the organic linker. The (SiF\textsubscript{6})\textsuperscript{2−} pillars in the cage are replaced with somewhat bulkier (NbOF\textsubscript{5})\textsuperscript{2−} pillars. This causes tilting of the pyrazine molecule on the linker, effectively reducing the aperture opening from 0.50 nm [with

![Figure 5. (a) Transient uptake of O\textsubscript{2}/N\textsubscript{2} mixture in LTA-4A zeolite at 298 K and total pressure of 600 kPa. The partial pressures of the components in the bulk gas phase are p\textsubscript{1} = 126 kPa and p\textsubscript{2} = 474 kPa. (b) Transient breakthrough characteristics of O\textsubscript{2}/N\textsubscript{2} mixture in a fixed-bed adsorber packed with LTA-4A operating at a total pressure of 600 kPa and 298 K. The partial pressures of the components in the bulk gas phase at the inlet are p\textsubscript{1} = 126 kPa and p\textsubscript{2} = 474 kPa. The continuous solid lines are simulations based on eq 7. The dashed lines are simulations based on eq 8. Further details and input data are provided in Chapter 8 of the Supporting Information.](image)
(SiF₆)₂ pillars] to 0.30 nm. The small aperture permits ingress of the smaller C₃H₆ molecules but practically excludes C₃H₈ on the basis of subtle differences in bond lengths, bond angles, and molecular conformations. Figure 7 presents a comparison of the percentage C₃H₈ in the outlet gas leaving fixed-bed adsorbers packed with KAUST-7 and CHA zeolite. Both simulations are based on eq 7. Further details and input data are provided in Chapter 9 of the Supporting Information.

3.5. Separation of Mixtures of Hexane Isomers. An important step in the production of high-octane gasoline is the separation of hexane isomers, n-hexane (nC₆), 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (22DMB), and 2,3-dimethylbutane (23DMB). The values of the Research Octane Number (RON) increases with the degree of branching: nC₆ = 30, 2MP = 74.5, 3MP = 75.5, 22DMB = 94, and 23DMB = 105. Due to their higher RON values, di-branched isomers are preferred products for inclusion in the high-octane gasoline pool. Separations using MFI zeolite have some unique characteristics; these features arise from the preferential location of the mono- and di-branched isomers at the channel intersections, whereas the linear nC₆ can locate anywhere within the channel network. Consequently, both adsorption and diffusion act synergistically.

The transient uptake of nC₆/2MP mixtures in MFI crystals, exposed to an equimolar gas-phase mixture at constant total pressure (=2.6 Pa) have been reported by Titze et al. (see Figure 8a). The transient equilibration of nC₆ displays a pronounced overshoot, achieving supraequilibrium loadings during transient equilibration. The origin of the nC₆ overshoot is traceable to the contribution of finite off-diagonal elements of Γᵢⱼ; if the assumption Γᵢⱼ = δᵢⱼ is invoked, the overshoot disappears.

Uphill diffusion of nC₆ is beneficial to the hexane isomer separations in fixed beds because the desired raffinate phase will be richer in the branched isomers that have high octane numbers. To confirm this expectation, transient breakthrough simulations were performed for a 5-component nC₆/2MP/3MP/22DMB/23DMB mixture. The transient variations of the RON values of the gas mixture exiting the adsorber are plotted in Figure 8b. Assuming that the target RON value of the raffinate is 92+ RON, we can determine the number of moles of 92+ RON product that can be recovered during the initial transience. The 92+ RON productivity is lowered to a value of 0.28 mol kg⁻¹ for invoking the simplification Γᵢⱼ = δᵢⱼ.
approaches may lead to severely pessimistic estimates of the effectiveness of kinetic separations.

Thermodynamic coupling effects should also be expected to have strong influences on the selectivity and conversion of diffusion-limited zeolite-catalyzed reactions carried out in fixed-bed reactors; this aspect deserves further investigation.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03480.

Calculation procedure for mixture adsorption equilibrium, along with derivations of the mixed-gas Langmuir model, summary of the Maxwell—Stefan theory of diffusion in microporous materials, methodology adopted for numerical solutions to transient uptake within single crystalline particle, methodology used for transient breakthroughs in fixed-bed adsorbers, and simulation details and input data on unary isotherms, and Maxwell—Stefan diffusivities are provided for each of the five case studies (PDF).

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**NOMENCLATURE**

**Latin Alphabet**

- $b_i$: Langmuir binding constant, Pa$^{-1}$
- $c_i$: molar concentration of species $i$, mol m$^{-3}$
- $c_{i0}$: molar concentration of species $i$ in fluid mixture at inlet, mol m$^{-3}$
- $D_{ij}$: axial dispersion coefficient, m$^2$ s$^{-1}$
- $D_M$: Maxwell—Stefan diffusivity for molecule—wall interaction, m$^2$ s$^{-1}$
- $D_{ij, M}$: $M$—$S$ exchange coefficient for $n$-component mixture, m$^2$ s$^{-1}$
- $n$: number of species in the mixture, dimensionless
- $L$: length of packed-bed adsorber, m
- $N_i$: 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
- $q_i$: component molar loading of species $i$, mol kg$^{-1}$
- $q_i^*$: molar loading of species $i$ at saturation, mol kg$^{-1}$
- $q_{tot}$: total molar loading in mixture, mol kg$^{-1}$
- $q_i(t)$: spatial-averaged component uptake of species $i$, mol kg$^{-1}$
- $r$: radial direction coordinate, m
- $r_c$: radius of crystallite, m
- $R$: gas constant, 8.314 J mol$^{-1}$ K$^{-1}$

Figure 8. (a) Experimental data of Titze et al.81 for the transient uptake of nC6/2MP mixtures in MFI zeolite at 298 K.29 (b) RON of product gas mixture leaving fixed-bed adsorber packed with MFI operating at a total pressure of 100 kPa and 433 K; the feed is a 5-component nC6/2MP/3MP/22DMB/23DMB mixture with partial pressure of 20 kPa for each component. The continuous solid lines are simulations based on eq 7. The dashed lines are simulations based on eq 8. Further details and input data are provided in Chapter 10 of the Supporting Information, which also contains the rationale for ignoring correlation effects.

**4. CONCLUSIONS**

The major conclusion that emerges from our investigation of kinetic separations of five different mixtures is the need for proper modeling of the intracrystalline diffusion, which takes proper account of thermodynamic coupling influences. The off-diagonal elements $\Gamma_{ij}$ ($i \neq j$) engender overshoots in the loading of the more mobile partner species during transient uptakes within a microporous particle. Such overshoots, signifying uphill diffusion, are beneficial, resulting in increasing productivity of the tardier component that is recovered in purified form as raffinate during the high-pressure adsorption cycle of PSA operations.

Although the inclusion of thermodynamic coupling influences for kinetic separations in adsorbers is properly recognized by Ruthven, Farooq, and others, there are several other published works that adopt much simpler approaches employing eq 8; the simulations presented in this article demonstrate that such simplified
Greek Alphabet

\[ \Gamma \] thermodynamic factors, dimensionless
\[ \delta_0 \] Kronecker delta, dimensionless
\[ \varepsilon \] voidage of packed bed, dimensionless
\[ \mu_i \] molar chemical potential, J mol\(^{-1}\)
\[ \rho \] framework density, kg m\(^{-3}\)
\[ r \] time, dimensionless

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